

## Thermal Oxidation of Thermoplastics

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### Synopsis

Commercial thermoplastics may be classified by the types of rate curves obtained on thermal oxidation. The rate of oxidation of an acrylonitrile-butadiene-styrene plastic is affected by sample thickness and appears to be diffusion-controlled. Pigmentation increases the reaction rate of this compound in all the cases studied because of the catalytic effect of the metals present. Carbon black adversely affects the oxidation rate of stabilized polypropylene. The acetal plastics decompose under oxidative conditions at 140°C. Of the thermoplastics examined, polytetrafluoroethylene, fluorinated ethylene-propylene copolymer, poly(vinylidene fluoride), poly(ethylene terephthalate), and polysulfone are the most resistant to thermal oxidation at 140°C.

### INTRODUCTION

The thermal oxidation of some plastic materials, notably the polyolefins, has been examined extensively.<sup>1</sup> Other thermoplastics, such as the rigid molding compounds, have not been studied as fully, since their structures are more complex and are not easily characterized. Commercial thermoplastic compounds were chosen for this evaluation. In many cases, these are not pure polymers, but contain both catalyst residues from polymerization and specific additives like stabilizers or lubricants. The oxidation rate curves obtained are therefore not truly representative of the resin structure alone, but do provide some insight into the behavior of the various commercial compounds during thermal oxidation.

The purpose of the work reported herein is to make an exploratory survey of some of the available commercial grade thermoplastics from the viewpoint of their thermal oxidation characteristics within the limitations discussed previously. It is hoped that eventually sufficient data will be obtained to determine whether, for practical purposes, a correlation exists between thermal aging processes at lower temperatures and this accelerated test. Such a correlation would clearly be valuable in predicting the service life of the various plastics in applications involving heat exposure.

### EXPERIMENTAL

Film specimens were prepared by compression molding of granules of the materials studied. The plastics were not milled, thus eliminating this heat treatment and its degradative effects. Duplicate samples 10 mils

thick, weighing 100 mg. were cut from the prepared films, except where noted.

A series of samples was made in a similar manner from several commercial pigmented grades of an ABS material. Since these compounds have an appreciable (4.6–9.6%) percentage of ash on ignition, a sample weight of each, sufficient to provide 100 mg. exclusive of the inorganic content, was used. This was done so that comparisons would be made on the same amount of polymer.

Thermal oxidation was carried out at 140°C. in a oven apparatus described previously.<sup>2</sup> A constant temperature bath<sup>3</sup> was used for long-term tests (>250 hr.) at 140°C. and for all experiments at 100°C.

### RESULTS AND DISCUSSION

Larsen et al.<sup>4</sup> oxidized a series of hydrocarbons and observed that plots of oxygen absorption versus time could be classified as shown in Figure 1: (a) linear, those which show no induction time but absorb oxygen at a relatively constant rate; (b) autoretardant, those which exhibit no induction period but absorb oxygen at a relatively rapid rate initially, followed by a slower, steady rate; (c) those which display autocatalytic behavior. (d) those which can be considered a combination of autocatalytic and autoretardant.

The last two types will be referred to as autocatalytic since reactions of this type usually become autoretardant in the later stages of oxidation.

The induction period is also illustrated in Figure 1 as that portion of the rate curve before autocatalysis begins. This period is determined by ex-

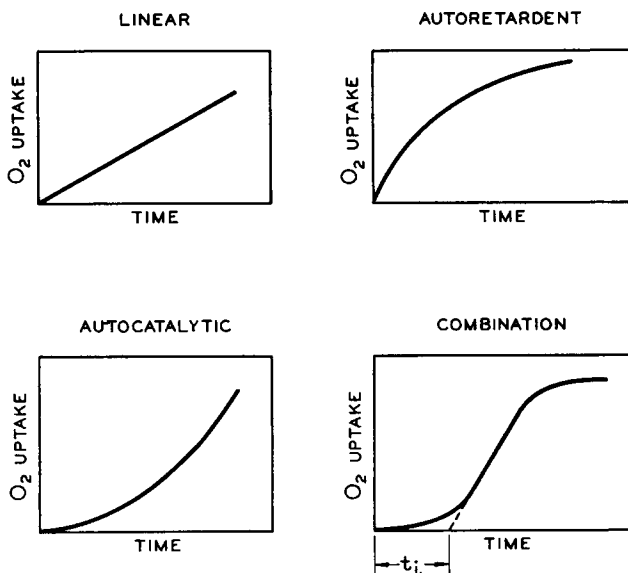


Fig. 1. Plots of oxygen uptake vs. time. Data of Larsen et al.<sup>4</sup>

trapolation of the tangent to the maximum rate portion of the curve back to the time axis and zero oxygen uptake.

It is realized that the data obtained are not absolute, since changes in the composition of these commercial thermoplastics can alter the type of rate curve. Therefore the classifications of Larsen et al. are used merely to group the materials studied for discussion.

### Linear Types

Figure 2 presents the curves for some of the materials which exhibit essentially a linear rate of reaction. The  $\alpha$ -methylstyrene-methyl methacrylate copolymer and the polycarbonate are quite stable. (The effect of temperature is shown by the fact that at 100°C., polycarbonate absorbs only a negligible volume of oxygen after 15,000 hr.) Polysulfone does not absorb any measurable amount of oxygen during a period of 1400 hr. at 140°C. Poly(vinylidene fluoride) is comparatively inert in oxygen at 140°C. Tests conducted on other fluorine-containing polymers show that neither polytetrafluoroethylene nor the fluorinated ethylene-propylene copolymer absorbs any oxygen in 2000 hr. at these conditions. In addi-

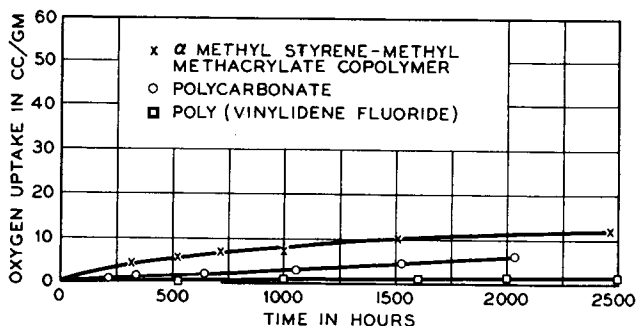


Fig. 2. Oxidation at 140°C.

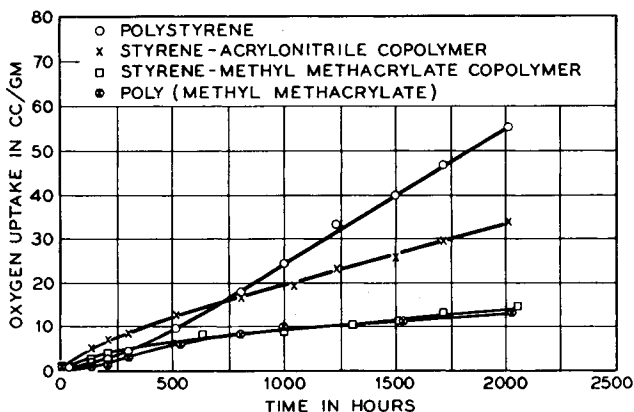


Fig. 3. Oxidation at 140°C.

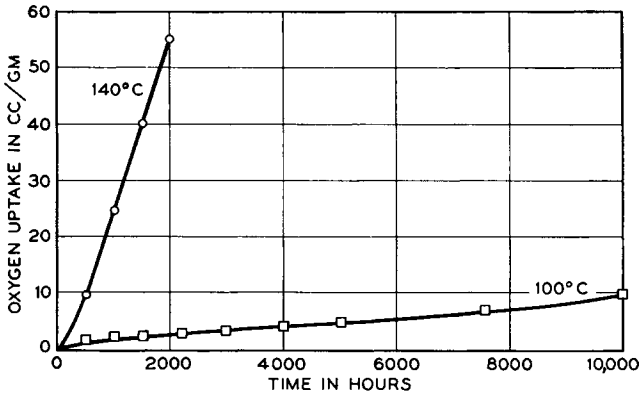


Fig. 4. Effect of temperature on oxidation of polystyrene.

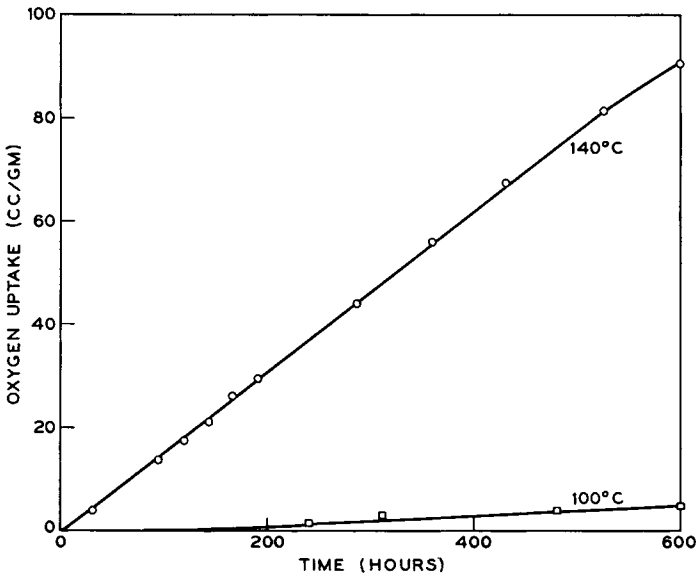


Fig. 5. Thermal oxidation of poly(phenylene oxide).

tion, poly(ethylene terephthalate) is as unreactive as the PTFE polymer and copolymer. The relative stability of the fluorocarbon polymers has been ascribed both to the high (94–120 kcal./mole) bond energy of the carbon–fluorine linkage and to the steric effect of the large, regularly arranged fluorine atoms along the carbon–carbon polymer backbone.<sup>5</sup>

The curves for other plastics which display linear behavior are depicted in Figure 3. The styrene–acrylonitrile copolymer absorbs an appreciable volume of oxygen under these conditions. Other polymers of this type, (which are not shown) react at approximately the same rate. The styrene–methyl methacrylate copolymer is as resistant to oxidation as poly(methyl

methacrylate), and both are comparable to the methacrylate copolymer shown in Figure 2. Although ordinary, atactic polystyrene oxidizes fairly readily at 140°C., Figure 4 shows that this reaction proceeds at a relatively slow rate at 100°C. Of the materials which have linear reaction rates, poly(phenylene oxide) reacts most readily (Fig. 5).

### Autoretardant Types

The nylons exhibit oxidation rate curves of the autoretardant type, i.e., those which have no induction period but absorb oxygen at a relatively rapid rate initially, followed by a slower steady rate. The data obtained on 10-mil nylon specimens are shown in Figure 6. Both the nylons 6 and 66 demonstrate essentially the same behavior.

Figure 7 illustrates the oxidative characteristics of 5-mil samples of various kinds of nylon. The 6 and 610 types react at approximately the same rate. The copolymers oxidize at a more rapid rate and absorb greater

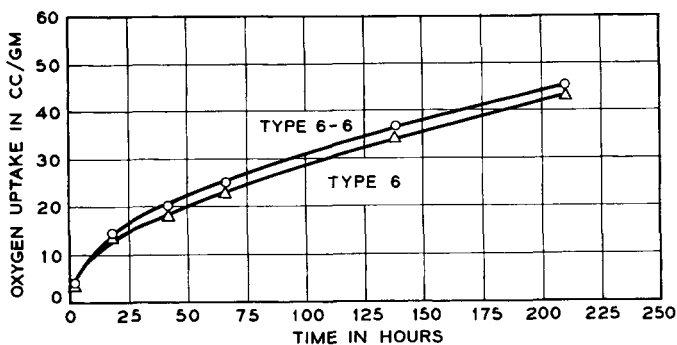


Fig. 6. Oxidation of nylon at 140°C.

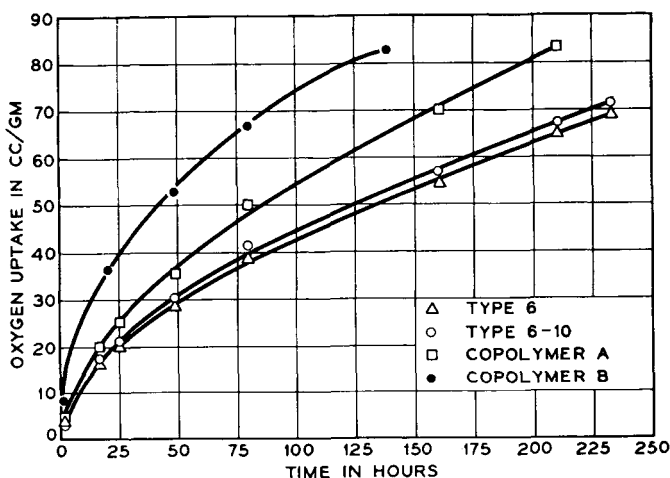


Fig. 7. Oxidation of 5-mil nylon specimens at 140°C.

final volumes of oxygen than the 6 and 610 types. No information is available on the exact composition of these copolymers although they are believed to be copolymers of 66 and 610 units. In any case, the copolymers are most likely less crystalline than the 6 and 610 types and thus more susceptible to oxidation. In their oxygen absorption studies, Mesrobian and Tobolsky<sup>6</sup> observed that nylon 66 was much less reactive than the 610 type. This behavior was attributed to the presence of more amide groups in nylon 66 per given number of carbon atoms in each repeating unit. The amide groups reportedly behave like chloride, cyanide, or phenyl groups to retard the rate of oxygen absorption, and hence nylon 610 reacts more rapidly. The greater abundance of available hydrogen in nylon 610 may also be responsible for its higher reactivity with oxygen.

All the materials studied were brittle after oxidation, but insufficient data are available to judge just what relationship exists between brittleness and the volume of oxygen absorbed for the various plastics.

### Autocatalytic Types

Several of the compositions tested displayed autocatalytic properties during oxidation. Some of these are represented in Figure 8, which includes three modified acrylic plastics. The ethylene-ethyl acrylate copolymer has a rate curve similar to that of polyethylene, as would be expected. Of the two rubber-modified acrylics in this graph, B appears to have a higher rubber content, and hence it oxidizes at a more rapid rate and takes up a larger volume of oxygen than A. This is presumably the result of the greater unsaturation present in sample B.

It is well known that polypropylene oxidizes autocatalytically. The behavior of stabilized unpigmented and pigmented samples is depicted in Figure 9. The natural composition shows no significant difference from

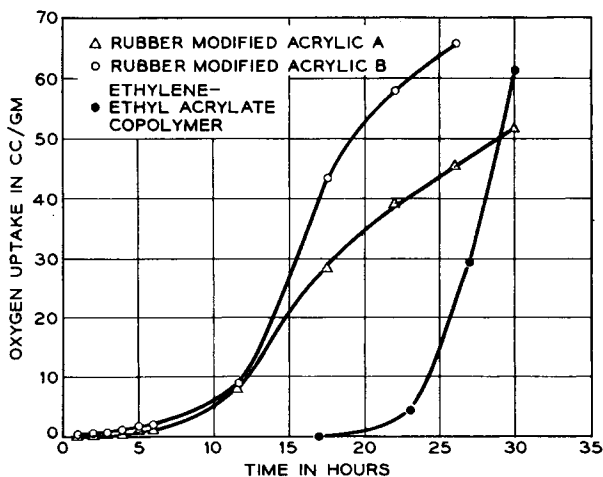


Fig. 8. Oxidation of modified acrylic plastics at 140°C.

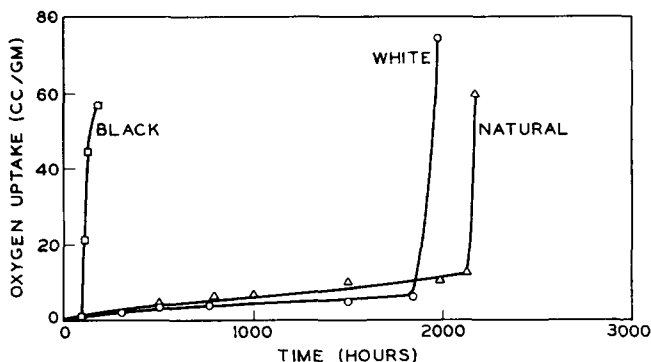


Fig. 9. Oxidation of polypropylene compound A at 140°C.

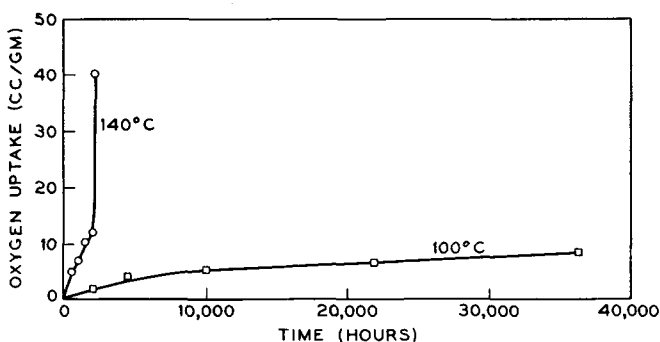


Fig. 10. Effect of temperature on oxidation of polypropylene compound A.

the white compound which contains titanium dioxide. Carbon black apparently has an adverse effect on the thermal stability of polypropylene containing antioxidant. This is further substantiated by the data in Table I. This phenomenon is most likely similar to the adverse effect of carbon black on amine and phenolic antioxidants in polyethylene found by Hawkins et al.<sup>7</sup> and attributed to absorption followed by direct oxidation of the antioxidant on the carbon black surface. The effect of temperature is illustrated in Figure 10. This particular compound is obviously quite stable at 100°C.

The oxidative characteristics at 140°C. of two acrylonitrile-butadiene-styrene (ABS) plastics are given in Figure 11. Both these plastics in their natural unpigmented form have an induction period; that of the compound B is longer than that of compound A. Comparison of Figure 11 with Figure 12 shows the effect of temperature. In the former, the most rapid changes occur within 200 hr. while in Figure 12, which shows the rate curves at 100°C., the rapid absorption of oxygen occurs between 1000 and 3000 hr. Here the S-shaped curves associated with autocatalytic behavior can be more clearly seen. It can reasonably be assumed that autocatalysis of these ABS plastics is due to the presence of butadiene in the molecule, since

TABLE I  
Oxidation of Polypropylenes at 140°C.

Compound	Color	$t_{10}$ , hr. <sup>a</sup>
A	Natural	1800
A	White	1850
A	Black	95
B	Natural	1300
B	Black	17
C	Natural	4500
C	Black	160
D	Natural	770
D	Black	150

<sup>a</sup> Time to absorption of 10 cc. of oxygen per gram of compound.

neither the polystyrene nor styrene-acrylonitrile compounds discussed previously exhibited an induction period but showed a relatively constant rate of oxygen absorption. This has recently been proven conclusively by Gesner.<sup>8</sup>

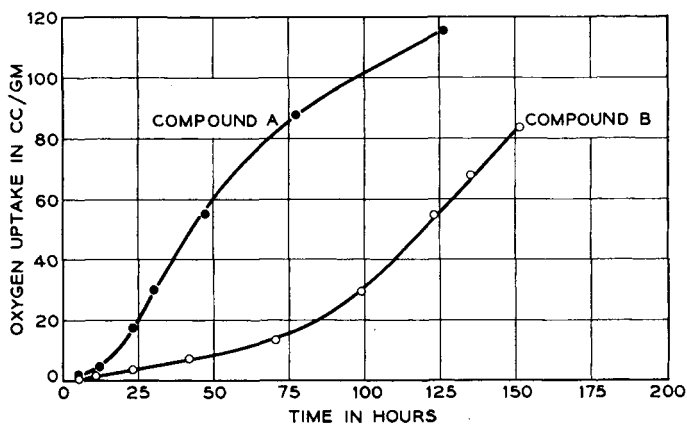


Fig. 11. Oxidation of acrylonitrile-butadiene-styrene plastics at 140°C.

The effect of sample thickness of compound A on the rate of oxygen absorption appears in Figure 13. The 6-mil specimen exhibits only a very slight induction time and then absorbs oxygen at a rapid rate. The 11.5- and 18.5-mil samples show little difference initially but differ in final volume of oxygen absorbed in the direction which would be expected. The curve for the 60-mil sample has a much lower slope than the other curves and continues at this rate for at least 1000 hr. The 60-mil sample was broken in half after oxidation and examined. Discoloration of the sample surface was observed but the color of the center portion was unchanged. It appears that the oxidation of thicker films of this ABS plastic is diffusion-controlled. This is partly in agreement with previous results on polypropylene,<sup>9</sup> but in the latter case the curves for the thicker samples were



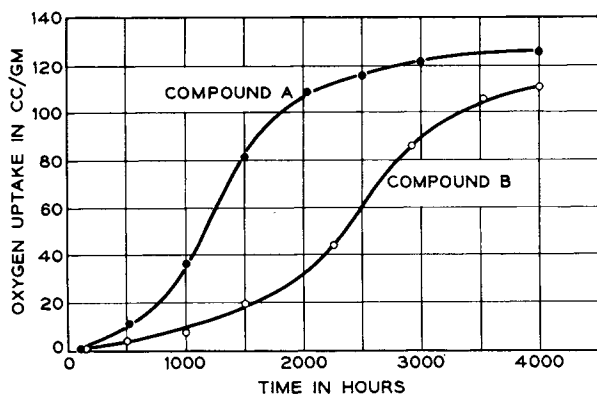


Fig. 12. Oxidation of acrylonitrile-butadiene-styrene plastics at 100°C.

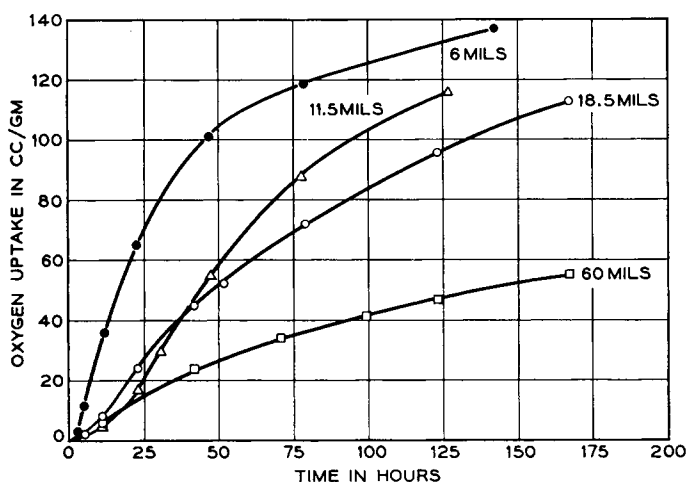


Fig. 13. Effect of thickness on oxidation of ABS compound A at 140°C.

displaced to the right along the time axis. This does not seem to be the case for this ABS plastic.

Figures 14 and 15 demonstrate the effect of pigmentation on the early portion of the rate curve for the ABS compound A at 140°C. In Figure 14, it can be seen that the beige, grey, and green oxidize readily. The turquoise is intermediate, and the red approaches the natural, which is the most stable. Figure 15 shows that the yellow and blue oxidize fairly rapidly, while the white and pink are intermediate. The natural material has again been included for comparison.

The induction periods and maximum slopes of these curves have been measured and compared with accelerated aging data<sup>10</sup> on the same batches of pigmented ABS plastic. These data were taken on molded stiffness strips 60 mil thick  $\times$   $\frac{1}{4}$  in. wide  $\times$  5 in. long. The test procedure (ASTM

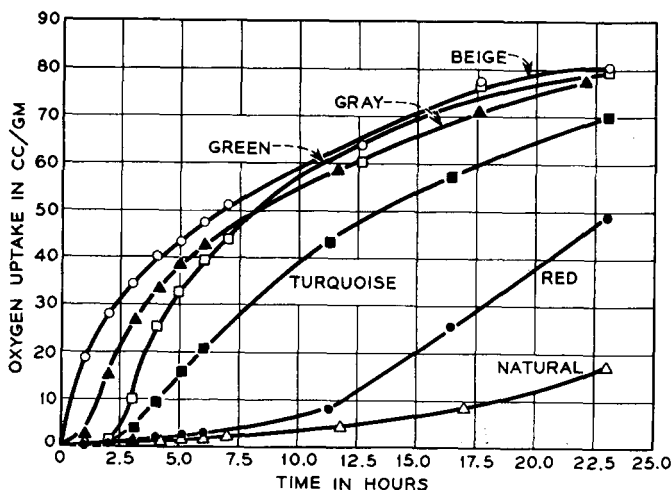


Fig. 14. Effect of pigments on oxidation of ABS compound A at 140°C.

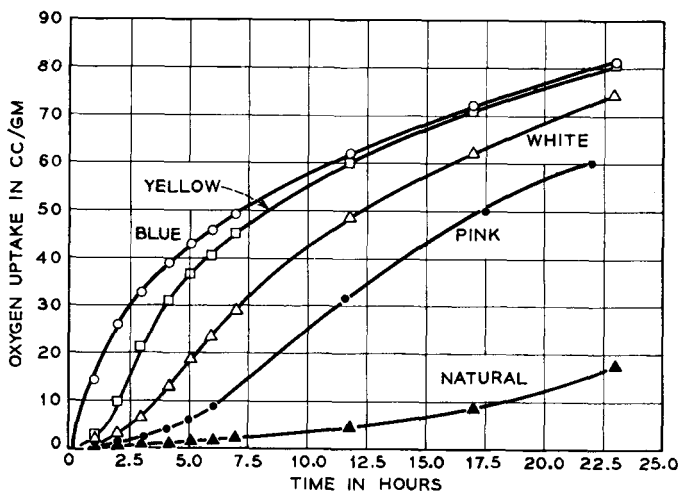


Fig. 15. Effect of pigments on oxidation of ABS compound A at 140°C.

D747) consists of bending a 1-in. section of a strip through 90° as a cantilever beam under a given load. Calculations are made to obtain an apparent modulus called the stiffness, and the angle at which the specimen breaks is also recorded. The angle at break serves as an indication of brittleness in the test piece, and the more brittle specimens have the lower values.

This comparison of induction periods and maximum slopes of the oxidation rate curves with angle at break values measured on heat-aged stiffness specimens is presented in Table II. The blue, beige, gray, and yellow formulations, which have very low induction times coupled with high slopes, show breakage after only 6 months aging at 82°C. The compositions with

induction periods of 2-4 hr. were severely embrittled within one year. The red and natural compounds were the most stable in both tests. Therefore, a fairly good correlation exists between the rating of these compounds by resistance to thermal oxidation at 140°C. and a rating by embrittlement as determined by this change in a mechanical property. These results also indicate that an accelerated test conducted at severe conditions of 140°C. in oxygen may, in some cases, be quite valuable in predicting results which require much longer periods of time at milder conditions.

TABLE II  
ABS Molding Compound A

Color	Oxidation in oxygen at 140°C.		Oxidation in air at 82°C., angle at break		
	$t_i$ , hr.	Max. slope	6 mo.	12 mo.	18 mo.
Blue	0	—	20	17	19
Beige	0	—	22	22	17
Gray	0.8	12.9	20	21	14
Yellow	1.2	12.0	19	16	19
Green	2.0	12.3	72	17	19
White	2.0	5.8	79	20	14
Turquoise	2.2	5.3	64	17	16
Pink	4.0	4.1	—	—	—
Red	9.5	3.6	77	84	44
Natural	12	1.6	76	67	66

The differences in behavior of the pigmented ABS molding compounds can possibly be attributed to the presence of metals and their effect on thermal oxidation. The compounds have been subjected to x-ray spectrochemical analysis. The metals which are present in higher amounts than those in the natural compound are listed in Table III. Stearates of all these metals were added to the natural ABS material, and samples were

TABLE III  
X-Ray Analysis of Pigmented ABS Plastics<sup>a</sup>

	Cop- per	Man- ganese	Co- balt	Iron	Cad- mium	Zinc	Chro- mium	Titan- ium	Cal- cium	Bar- ium
Blue			X	X		X	X	X	X	
Beige	X	X		X	X	X	X	X	X	
Gray			X	X	X	X	X	X	X	
Yellow	X	X		X	X	X	X	X	X	X
Green				X	X		X	X	X	X
White								X	X	
Turquoise							X	X	X	
Pink				X	X	X		X	X	X
Red		X		X	X			X	X	X

<sup>a</sup> Metals present in excess of those in the natural compounds.

TABLE IV  
Effect of Metallic Stearates on Thermal Oxidation of ABS Plastic at 140°C.

Additive <sup>a</sup>	Induction time, hr.
Control	2.8
Stearic acid	2.6
Ferrous stearate	0
Ferric stearate	0
Copper stearate	0.5
Manganese stearate	0.5
Cobalt stearate	0.5
Barium stearate	2.5
Chromium stearate	2.6
Cadmium stearate	2.8
Titanium tetrastearate	3.3
Calcium stearate	3.7

<sup>a</sup> 0.5% added.

oxidized to obtain the data in Table IV. Iron, copper, manganese, and cobalt obviously catalyze the thermal oxidation of this ABS plastic. Consideration of Table III shows that the blue, beige, gray, and yellow compounds have two or more of these deleterious metals present. This accounts for their relative instability on thermal oxidation.

Thermal oxidation experiments carried out on acetal plastics at 140°C., below the melting points of these compounds, show that both the homo-

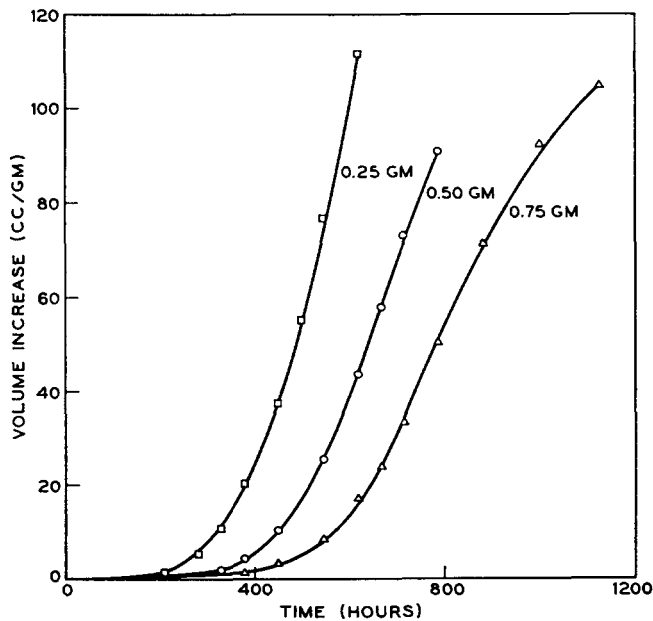


Fig. 16. Effect of molecular sieve concentration on thermal oxidation of acetal homopolymer at 140°C.

polymer and copolymer decompose. The oxygen absorption cannot be measured, but rather the volume increase as illustrated in Figure 16. It is apparent that the molecular sieve desiccant, which is a synthetic zeolite, has a significant effect on the reaction of the homopolymer with oxygen at 140°C. This desiccant is normally used in this test to absorb moisture and the oxides of carbon which are formed during the oxidation process. In the absence of desiccant, erratic changes in volume were observed, and a white deposit, most likely a formaldehyde polymer, was formed on the cooler portion of the reaction tube. In the presence of desiccant, no deposit was found, and the gas volume increased as shown in Figure 16; hence, the molecular sieves must absorb the decomposition product observed previously or the intermediate leading to it.

This method is not as well suited to the study of the thermal stability of acetal plastics as the measurement of weight loss. The thermal oxidation in air of the homopolymer and copolymer have been evaluated by using weight loss as a measure of stability. At temperatures in the range of 150–250°C. the homopolymer is more stable, while the reverse is true at lower temperatures. This behavior is dependent both on the structure of the two resins and on the particular antioxidant systems used. Berardinelli and co-workers, using a given combination of antioxidants, have recently shown that at high temperatures the copolymer is more stable than the homopolymer.<sup>11</sup> Kern et al.<sup>12,13</sup> have investigated the degradation of acetal polymers under various conditions and have discussed the mechanisms involved. Igarashi<sup>14</sup> has published results obtained by thermogravimetric analysis, and Kelleher and Jassie<sup>15</sup> have reported data obtained by infrared spectroscopy.

## CONCLUSIONS

A survey of the thermal oxidative characteristics of some commercially available thermoplastics has been presented. The oxidation data obtained are not necessarily representative of the polymer structure alone, since most of these commercial compounds contain specific additives. However, this accelerated test does give some insight into the thermal stability of the compositions studied. The oxidation rate curves seem to fall into three classes: (a) linear, those which have no induction time but absorb oxygen at a relatively constant rate, examples of materials of this type being poly(methyl methacrylate), polystyrene, and polycarbonate; (b) autoretardant, those which show no induction period, but absorb oxygen at a relatively rapid rate initially followed by a slower steady rate, a category including the nylons; (c) those which exhibit autocatalysis. The modified acrylics, acrylonitrile-butadiene-styrene, and polypropylene plastics display curves of this last type.

It was shown that sample thickness of an ABS plastic affects the oxidation rate curve and that rate of oxidation appears to be diffusion-controlled. The effect of pigmentation in reducing the resistance of this ABS compound toward thermal oxidation has been demonstrated. Pigmentation

increases the rate of reaction in all the cases studied because of the catalytic effect of the metals present. Carbon black adversely affects the oxidation rate of stabilized polypropylene. The acetal plastics decompose when subjected to oxidative conditions at 140°C.

Of the thermoplastics studied thus far, polytetrafluoroethylene, fluorinated ethylene-propylene copolymer, poly(vinylidene fluoride), poly(ethylene terephthalate), and polysulfone are the most resistant to thermal oxidation at 140°C.

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### Résumé

Les thermoplastiques commerciaux peuvent être plastifiés suivant le type de courbes de vitesse obtenu par oxydation thermique. La vitesse d'oxydation de plastiques à base d'acrylonitrile-butadiène-styrène est affectée par l'épaisseur de l'échantillon et peut être contrôlée par diffusion. La pigmentation augmente la vitesse de réaction de ce composé dans tous les cas étudiés par suite de l'effet catalytique des métaux présents. Par contre le noir de carbone diminue la vitesse d'oxydation du polypropylène stabilisé. Les plastiques acétaliques décomposent dans des conditions oxydantes à 140°C. De tous les thermoplastes examinés les plus résistants à l'oxydation thermique à 140°C sont le polytétrafluoroéthylène, les copolymères fluoroéthylène-propylène, le polyfluorure de vinylidène, le téréphthalate de polyéthylène et la polysulfone.

### Zusammenfassung

Kommerzielle Thermoplaste können nach dem Typus der bei der thermischen Oxydation erhaltenen Geschwindigkeitskurve eingeteilt werden. Die Oxydationsgeschwindigkeit eines Acrylnitril-Butadien-Styrol-Plastomeren wird durch die Probendicke beeinflusst und scheint diffusionskontrolliert zu sein. Eine Pigmentierung erhöht wegen der

katalytischen Wirkung der anwesenden Metalle die Reaktionsgeschwindigkeit dieser Verbindung in allen untersuchten Fällen. Russ beeinflusst die Oxydationsgeschwindigkeit von stabilisiertem Polypropylen ungünstig. Die Acetalplastomeren zersetzen sich unter oxydativen Bedingungen bei 140°C. Von den untersuchten Thermoplasten sind Polytetrafluoräthylen, ein fluoriertes Äthylen-Propylen-Kopolymeres, Poly(vinylidenfluorid), Poly(äthylenterephthalat) und Polysulfon gegen thermische Oxydation bei 140°C am beständigsten.

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