

## The Effect of Red Phosphorus on the Flammability of Poly(ethylene Terephthalate)

A. GRANZOW and J. F. CANNELONGO, *Chemical Research Division, American Cyanamid Company, Bound Brook, New Jersey 08805*

### Synopsis

Addition of red phosphorus in concentrations of about 4% to poly(ethylene terephthalate) (PET) reduces the flammability of that polymer. The rates of flame propagation and the ignitability are reduced, while the oxygen index (O.I.) is increased. The surface temperature of burning PET amounts to  $T_S \approx 380^\circ\text{C}$ ; addition of 4% red phosphorus raises this value to  $T_S \approx 450^\circ\text{C}$ . An increase of the environmental temperature  $T_E$  enhances the flammability of PET and PET + phosphorus samples; the O.I. decreases and the rate of flame propagation increases with temperature. The flame-retardant effectiveness of red phosphorus is reduced if the sample is burned in a  $\text{N}_2\text{O}$  atmosphere. This indicates that part of the flame retardancy imparted by phosphorus involves gas-phase inhibition. The major flame-retardant action does, however, occur in the condensed phase, since the rate of pyrolysis of PET is affected by the presence of red phosphorus.

### INTRODUCTION

A large variety of phosphorus compounds has been reported as being useful in reducing the flammability of different polymeric materials.<sup>1,2</sup> The selection of a phosphorus compound for use in a particular polymer is usually limited by the thermal stability which is required to prevent the additive from decomposing at the processing temperature of that polymer. A second important factor in the choice of the additive is its physical compatibility with the polymer.

In order to separate the effect of phosphorus on the flammability of the polymer system from the contribution by the nonphosphorus part of the additive molecule, it is desirable to establish a reference point to which the effectiveness of practically useful flame retardants may be compared. Since red phosphorus consists only of the flame-retardant element, it would obviously be ideally suited to serve as the standard substance to which phosphorus-based flame retardants should be compared.

For obvious reasons, e.g., color and slow autoxidation, the practical use of red phosphorus as a flame retardant is severely limited, although there have been scattered reports in the literature concerning the application of red phosphorus as a flame-retardant additive for a variety of polymers. Among the polymers claimed to be flame retarded by red phosphorus are nylon,<sup>3</sup> cellulose,<sup>4</sup> poly(ethylene terephthalate) (PET),<sup>5</sup> and polyurethane foam.<sup>6</sup> We have studied the effect of red phosphorus on the burning characteristics of poly(ethylene terephthalate) samples since, to our knowledge, no systematic

investigation of the burning behavior of any polymer in the presence of red phosphorus has yet been reported.

## EXPERIMENTAL

### Materials

Amorphous red phosphorus (Fisher Scientific Company) was used after removing phosphine impurities by repeated washing with alcohol and ether. The purified red phosphorus was stored in vacuo over  $P_2O_5$ . Poly(ethylene terephthalate) with an inherent viscosity of 0.75 was obtained in pellet form. The pellets were cooled with Dry Ice and micromilled. Hercules polypropylene, Profax 6401, stabilized with 0.1% Irganox 1010 (pentaerythrityl tetrakis[3(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate]) and 0.2% STDP (3,3'-distearyl thiodipropionate), and Cosden Oil polystyrene, impact grade 825 TV, were used.

### Sample Preparation

The micromilled poly(ethylene terephthalate) was preconditioned by drying at 80°C in vacuo, dry blended with red phosphorus, melted under a nitrogen atmosphere at 290°C, and laminated to glass fiber cloth. The finished samples had a thickness of  $25 \pm 2.5$  mils and contained 25% glass fiber. The polypropylene and impact polystyrene were dry blended with red phosphorus, milled on a two-roll steam mill, and compression molded into  $\frac{1}{8}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$  5 in. bars.

**CAUTION:** Extreme caution should be exercised when processing phosphorus-containing samples in order to prevent overheating. Phosphorus burns should be treated immediately with a solution of  $CuSO_4$ .

### Combustion of the Samples

The samples were burned in vertical position in a GE flammability gauge. The atmosphere in the combustion chamber was an adjustable mixture of either  $N_2$  and  $O_2$  or of  $N_2$  and  $N_2O$ . The samples were ignited at the top using a microflame torch as the ignition source. Burning rates were determined by measuring the time required for the flame front to travel over a fixed distance. The environmental temperature of the sample was varied by electrically heating the combustion chamber; the sample temperature was determined by means of a mercury thermometer whose Hg bulb was placed close to the sample. The temperature at the surface of the burning polymer was monitored by means of a miniature Chromel-Alumel thermocouple (Omega), which was imbedded within the sample. The thermocouple readout was via a digital voltmeter.

### TGA Analysis

The TGA experiments were performed on a Perkin-Elmer TGS-1, which incorporates a Cahn RG electrobalance. The sample size was 5 mg; the inert gas atmosphere was maintained by a stream of 30 ml/min of purified argon.

## RESULTS AND DISCUSSION

## Effect of Red Phosphorus on the Ignitability, Flame Propagation Rate, and Extinction of PET

Important parameters to assess the fire hazard of a material are its rate of flame propagation, its ignitability, and the ease of extinction. In this section, the effect of red phosphorus on these flammability parameters is described.

The flame propagation rate for the standard PET samples increases linearly with the oxygen content of the atmosphere. In the presence of red phosphorus, the dependence on the oxygen concentration is likewise linear, although the slope is steeper in this case. Representative results are depicted in Figure 1; the slopes of the straight lines are  $0.578 \text{ cm sec}^{-1}/[\text{O}_2]$  for pure PET and  $1.17 \text{ cm sec}^{-1}/[\text{O}_2]$  for PET + 2% red phosphorus. A further increase of the phosphorus content has only a slight effect on the slope. It should be noted that the rate for the phosphorus-containing PET sample becomes greater than the rate for pure PET if  $[\text{O}_2] > 0.265$ . However, since under normal burning conditions the oxygen concentration is always below this value, addition of red phosphorus decreases the flame propagation rate for all practical purposes and, hence, reduces the fire hazard.

Extrapolation of the Figure 1 plots to zero propagation rates yields the limiting oxygen content of the atmosphere which is necessary for the sample to be ignited. This limit is 0.171 for pure PET and is increased to 0.218 by the addition of 2% red phosphorus, indicating that the addition of phosphorus makes PET more difficult to ignite. The extrapolated ignition limits are, however, experimentally not accessible, since at low oxygen concentrations, stable burning conditions with constant flame propagation rates cannot be maintained. In the region of unstable burning, which is indicated by the bro-

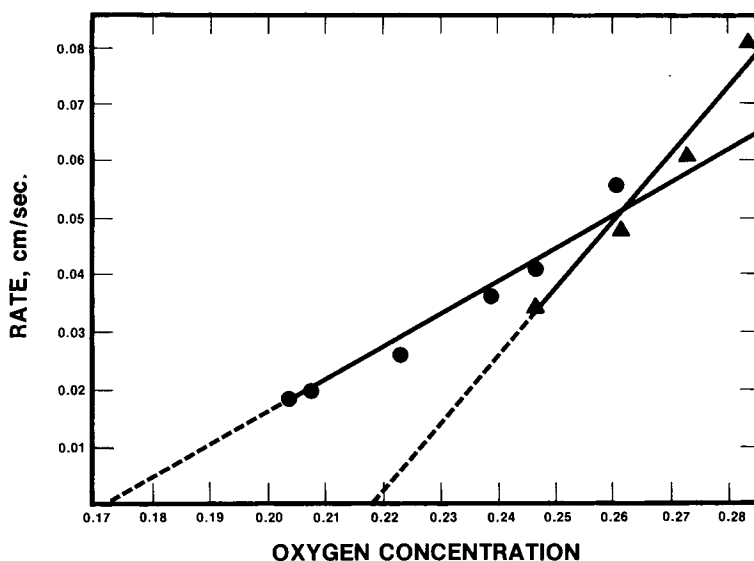


Fig. 1. Flame propagation rates as a function of oxygen partial pressure: (●) PET; (▲) PET + 2% red phosphorus.

TABLE I  
Self-Quenching Times, for PET and PET + Phosphorus Samples<sup>a</sup>

PET		PET + 2% P		PET + 4% P	
[O <sub>2</sub> ]	<i>t<sub>Q</sub></i> , sec	[O <sub>2</sub> ]	<i>t<sub>Q</sub></i> , sec	[O <sub>2</sub> ]	<i>t<sub>Q</sub></i> , sec
0.201	27	0.241	28	0.265	23
0.196	16	0.238	17	0.262	15.5
0.187	11.5	0.231	11	0.260	10
0.181	6.5	0.228	8	0.250	8
0.173	4.5	0.226	7	0.248	6.5
				0.238	5

<sup>a</sup> Ignition time 5 sec.

ken section of the Figure 1 plot, one observes after removal of the ignition source a steady decrease of the flame speed and subsequent extinction of the flame. The time interval between removal of the ignition source and extinction of the flame has been termed "self-quenching time"  $t_Q$ . Representative results are listed in Table I. One recognizes that the self-quenching times increase about exponentially with the O<sub>2</sub> concentration. The transition from unstable to stable burning conditions should correspond to  $t_Q \rightarrow \infty$ ; experimentally it is found that self-quenching times of more than 30 sec are difficult to reproduce. Therefore, a flame that continues to burn for more than about 30 sec after removal of the ignition source appears to have attained stable burning conditions.

The oxygen concentration at which transition from unstable to stable burning is taking place is identical with the oxygen index O.I. The effect of red phosphorus on the O.I. of PET is listed in Table II. A significant increase with increasing phosphorus concentration is noted. Red phosphorus thus increases the ease of extinction of burning PET and, therefore, has a beneficial effect also on this flammability parameter.

The dependence of O.I. on the phosphorus concentration may be linearized by plotting the data from Table II in the coordinates O.I. versus [%P]<sup>1/2</sup>, as shown in Figure 2. This transformed curve is then described by

$$\text{O.I.} = 0.204 + 0.0357 \times [\%P]^{1/2}. \quad (1)$$

We would like to point out that in the concentration range considered, the shape of the O.I.-versus per cent phosphorus curve cannot be accounted for by a simple leveling off of the effectiveness at high phosphorus concentrations. We therefore have to assume that the square-root dependence in eq. (1) reflects some physical reality.

TABLE II  
Effect of Red Phosphorus on the O.I. of PET

Red phosphorus, wt-%	O.I.
0.00	0.204
1.00	0.236
2.00	0.251
4.00	0.276
8.00	0.303

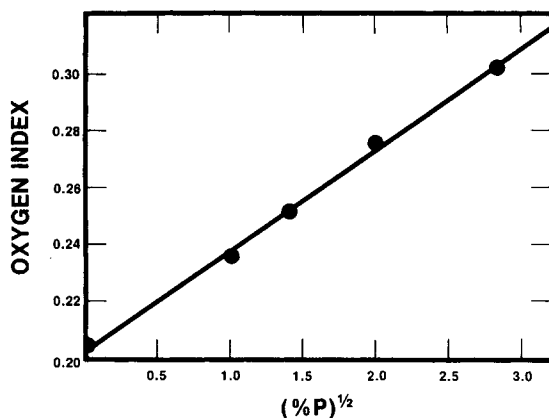


Fig. 2. Plot of oxygen index vs. square root of phosphorus concentration.

### The Effect of Temperature

The temperature at the surface of the burning PET sample can be measured by means of a miniature thermocouple which is imbedded in the polymer. To arrive at a meaningful value for the surface temperature, it is important to use very small thermocouples with low heat capacities. The requirement appears to be fulfilled for thermocouple diameters smaller than 0.02 in., since below this value the temperature readings were found to be independent of thermocouple size. Owing to the small thickness of the PET samples, the polymer melts uniformly across the sample diameter during

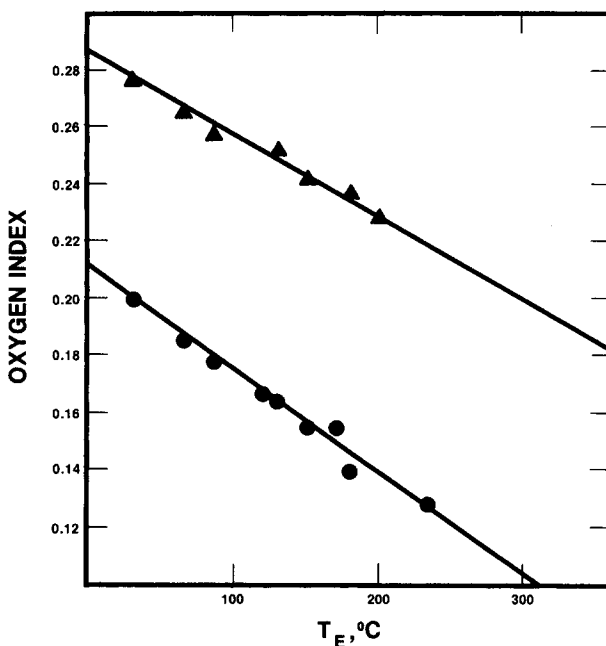


Fig. 3. Temperature dependence of oxygen index for PET (●) and PET + 4% red phosphorus (▲).

TABLE III  
Effect of Temperature on the  
Flame Propagation Rates for PET and PET + Red Phosphorus

$T_E$ , °Ca	Flame propagation rate, cm/sec <sup>b</sup>			
	PET	PET + 1% P	PET + 4% P	PET + 8% P
25	0.082	0.088	0.068	no burn
70	0.096	0.094	0.086	no burn
115	0.122	0.119	0.096	0.086
175	0.158	0.143	0.111	0.106
215	0.222	0.227	0.161	0.151

<sup>a</sup> Environmental temperature.

<sup>b</sup> Oxygen partial pressure, 0.30 atm.

burning. The temperature recorded in the molten PET layer that is closest to the flame is considered as the surface temperature. Care was taken that the thermocouple did not touch the supporting glass fiber cloth and that its tip was always entirely immersed in the pyrolyzing polymer while taking the temperature reading. Using this technique, surface temperatures of  $T_S = 380^\circ \pm 5^\circ\text{C}$  and  $T_S = 450^\circ \pm 10^\circ\text{C}$  were recorded for PET and PET + 4% red phosphorus, respectively. The partial pressure of oxygen amounted to 0.30 in these experiments. The surface temperature of burning PET is, therefore, apparently increased by the addition of red phosphorus.

During burning of the PET, the sample temperature has to be raised from the temperature of the environment  $T_E$  to the temperature which is established at the surface below the flame,  $T_S$ . Consequently, one should expect that an increase of  $T_E$  enhances the flammability of the sample, i.e., the oxygen index should decrease with increasing  $T_E$ . This is indeed the case, as is shown in Figure 3. The slopes of the straight lines are about the same for PET and PET + 4% P and have a value of  $\Delta(\text{O.I.})/\Delta T = -3.4 \times 10^{-4}$ . At temperatures  $>230^\circ$ , the PET begins to soften and an accurate determination of the O.I. becomes impossible.

A change of  $T_E$  should also affect the flame propagation rates. Representative results for pure PET and PET containing different amounts of red phosphorus are listed in Table III for different temperatures at a constant oxygen partial pressure of 0.30. One recognizes that, at low temperatures and low phosphorus concentrations, the flame propagation rates of phosphorus-containing samples are higher than for pure PET. This is explained by the fact that the oxygen concentration in these experiments is beyond the crossing point of Figure 1. For higher temperatures, the rates decrease in each line of Table III if the phosphorus content of the sample is increased and  $T_E$  is kept constant. On the other hand, if the composition of the sample is kept constant, the rates increase with increasing  $T_E$  for all columns of Table III.

The effect of temperature on the flame propagation rates cannot be accommodated by an Arrhenius-type relationship since the enhancement of the burning rate with temperature does not depend on a chemical activation energy but is rather governed by the difference between the surface temperature of the burning polymer and the temperature of the environment. This follows from the flame spread model originally derived by Magee and McAle-

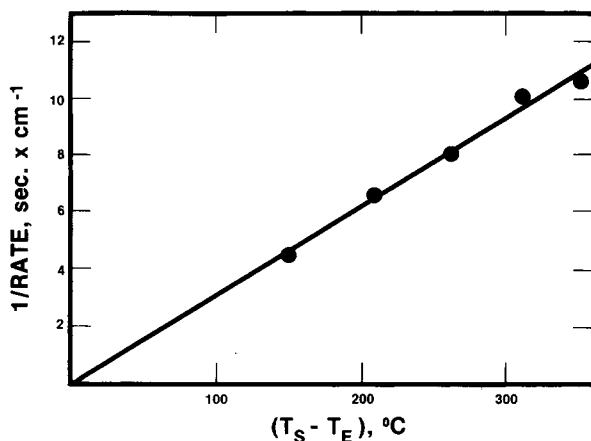


Fig. 4. Plot of reciprocal burning rates of PET vs. difference between surface and environmental temperatures; oxygen partial pressure, 0.30.

vy.<sup>7</sup> In this model, the rate of heat release by the exothermic oxidation of the volatile pyrolysis products is compared to the heat flux which is required for the endothermic pyrolysis to proceed at a rate that is sufficient to supply the fuel required to maintain a stable flame. Balancing the heat flux from the gas phase reaction with the heat flux required for the condensed phase pyrolysis yields the characteristic surface temperature  $T_S$  of the burning polymer, which remains constant until the entire sample has been consumed. The greater the difference between  $T_S$  and the environmental temperature  $T_E$ , the slower will be the rate of flame spread.

In the case of the thermally thin fuel bed which is expected to hold for our sample configuration, this flame spread model predicts an inversely proportional relationship between the rate of flame spread and the term  $(T_S - T_E)$ . A plot of the reciprocal rate of the flame spread versus  $(T_S - T_E)$  for pure PET is shown in Figure 4, assuming a value of  $T_S = 380^\circ\text{C}$ . The intercept of this plot should yield the flame propagation rate for  $T_E = T_S$ . As expected, this intercept is rather small, corresponding to a very high rate of flame propagation if the temperature of the environment approaches the temperature at the surface of the burning polymer.

Since a higher value of  $T_S$  requires a higher heat flux from the gas phase to the pyrolyzing polymer in order to achieve stable burning conditions, a higher characteristic surface temperature should make ignition more difficult, lower the rate of flame propagation, increase the O.I., and thus reduce the flammability. Due to these considerations, the lower flame propagation rates for the phosphorus-containing samples, as well as their higher oxygen indices, can be readily reconciled with the higher surface temperatures that are encountered in the case of the phosphorus-containing samples. For PET + 4% phosphorus, where  $T_S = 450^\circ\text{C}$  was measured, a plot of the reciprocal rates versus  $T_S - T_E$  is again linear. However, owing to the higher error in the measurement of  $T_S$ , the fit is not quite as good as in the case of pure PET. Nevertheless, it is obvious that the relationship between the reciprocal rate and the term  $T_S - T_E$  is still linear, as seen from the unity slope of the dilogarithmic plot depicted in Figure 5.

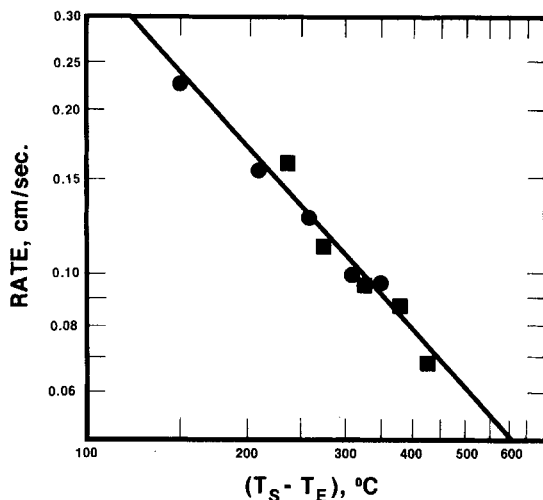


Fig. 5. Dilogarithmic plot of flame propagation rates vs. difference between PET (●) and PET + 4% red phosphorus (■).

### Effect of the Oxidant and the Mechanism of Flame Retardation

A flame retardant may either act in the condensed phase by altering the rate and/or the pathway of the pyrolytic decomposition of the polymer or, in the gas phase, by scavenging carrier species which are required to propagate the chain reactions that occur during the oxidation of volatile pyrolysis products in the flame. Since the flame chemistry, and hence the combustion mechanism, should depend on the nature of the oxidant, it is not likely that a flame retardant which acts in the gas phase with oxygen as the oxidant would also be effective if the oxidant is changed to nitrous oxide. On the other hand, a condensed-phase mechanism of flame retardation should work regardless of the nature of the oxidant but should be dependent on the nature of the polymer, provided that the decomposition of the polymer under burning conditions is predominantly pyrolytic rather than thermo-oxidative. According to the results of TGA experiments carried out in both  $\text{O}_2$  and Ar atmospheres, this assumption of a primarily pyrolytic mechanism has been shown to be true in the case of PET.<sup>8</sup> It therefore appears to be admissible to use the effectiveness of a flame retardant in an atmosphere containing  $\text{N}_2\text{O}$

TABLE IV  
Effect of Red Phosphorus on the  $\text{N}_2\text{O}$  Index of PET

Red phosphorus, wt-%	$\text{N}_2\text{O}$ Index
0.00	0.464
1.00	0.479
2.00	0.487
3.00	0.493
4.00	0.499



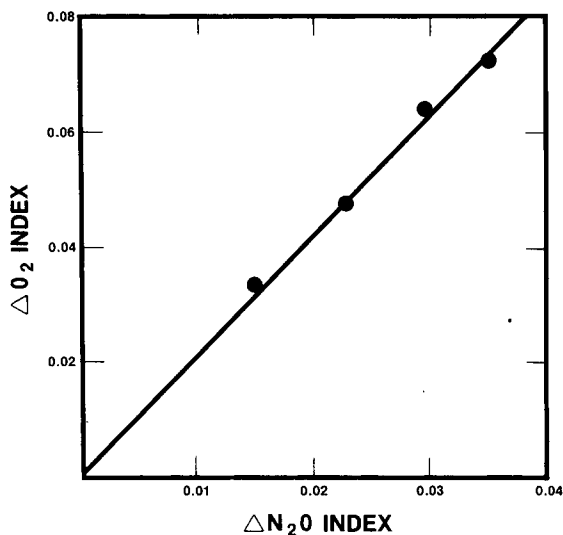


Fig. 6. Plot of increase of O<sub>2</sub> index vs. increase of N<sub>2</sub>O index for different phosphorus concentrations.

instead of O<sub>2</sub> as a criterion to discriminate between a gas phase and condensed-phase mechanism of flame retardation.<sup>9</sup>

The N<sub>2</sub>O index of PET as a function of the amount of red phosphorus added is tabulated in Table IV. One sees that the N<sub>2</sub>O index of pure PET is 0.464, as compared to an O.I. of 0.204; the higher value of the N<sub>2</sub>O index is readily explained in terms of the lower oxidant effectiveness of N<sub>2</sub>O as compared to O<sub>2</sub>. The results of Table IV show that addition of red phosphorus increases the N<sub>2</sub>O index, although the effect is smaller than in the case of the O<sub>2</sub> index. The concentration dependence of the N<sub>2</sub>O index can be accommodated by eq. (2), which shows the same square-root dependence on the phosphorus concentration as eq. (1):

$$\text{N}_2\text{O Index} = 0.464 + 0.0164 \times [\%P]^{1/2} \quad (2)$$

Plotting the increase of the oxygen index versus the increase of the nitrous oxide index at equal phosphorus concentrations according to Figure 6 yields a straight line with a slope  $\approx 2$ . This shows that the increase of the oxygen index achieved by a given phosphorus concentration is twice as high as the corresponding increase of the N<sub>2</sub>O index. This reduced effectiveness of red phosphorus for burning in a N<sub>2</sub>O-containing atmosphere indicates that a gas-phase mechanism may contribute to the flame-retardant action of red phosphorus.

Obviously red phosphorus, which itself is a polymeric material, cannot be volatilized without prior decomposition into smaller fragments. Consequently, the vapor phase over solid red phosphorus consists of P<sub>4</sub> which, at  $T \sim 800^\circ\text{C}$ , starts to dissociate into P<sub>2</sub> molecules.<sup>10</sup> The temperature dependence of the vapor pressure over red amorphous phosphorus between 320° and 500°C is reported to obey the equation

$$\log p = -4296/T + 6.404$$

where  $p$  is measured in atm.<sup>11</sup> For a temperature of  $\sim 400^\circ\text{C}$ , which is encountered at the surface of burning PET, one calculates a vapor pressure of about 1 atm, showing that pure red phosphorus would sublime with formation of  $\text{P}_4$  moieties at this temperature. This is supported by our own TGA measurements of the volatilization of red phosphorus. The TGA curve in Figure 7 shows that the weight loss becomes significant at  $T \sim 450^\circ\text{C}$ . Even at the comparatively low concentrations of red phosphorus in our experiments, a considerable vapor pressure of  $\text{P}_4$  should, therefore, be established over the surface of the burning P. More direct evidence for phosphorus species entering the gas phase can be derived from the characteristic greenish

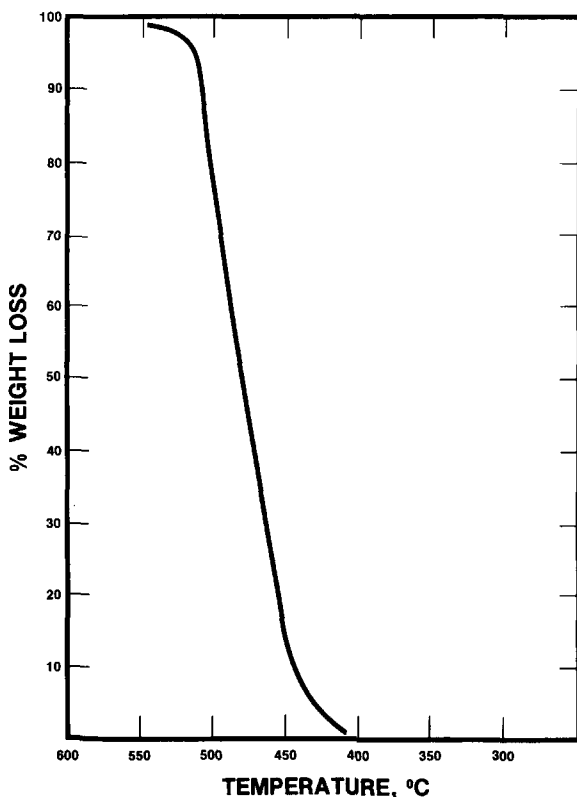


Fig. 7. Dynamic TGA curve for red phosphorus. Atmosphere, Ar; heating rate,  $10^\circ\text{C}/\text{min}$ .

yellow flame of burning PET + phosphorus samples, which is due to the emission by phosphorus species in the region of 500 to 600 nm.

The mere fact that under burning conditions phosphorus species are able to enter the gas phase is obviously insufficient evidence for a gas-phase inhibition. However, gas-phase inhibition of a hydrogen-air flame by phosphorus compounds has been reported.<sup>12</sup> Quantitative measurements of the quenching effectiveness in the gas phase show that phosphorus in compounds such as  $\text{PCl}_3$  inhibits the flame speed of a hydrogen-air flame more efficiently than halogens, with phosphorus being about 10 times as effective an inhibitor as bromine.<sup>13</sup>

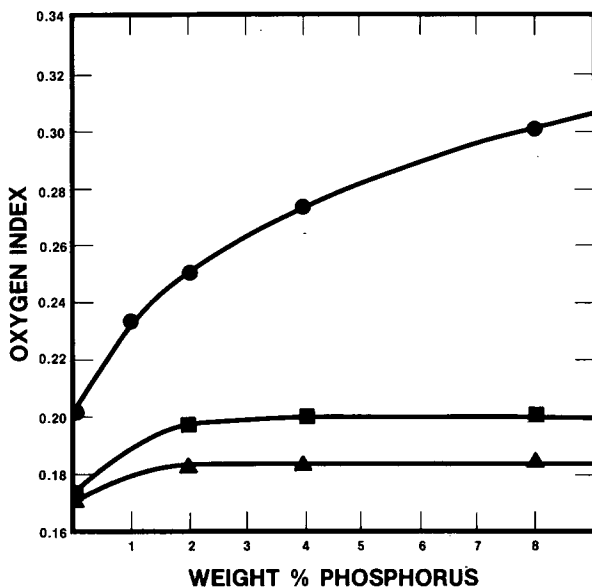


Fig. 8. Plot of oxygen index vs. concentration of red phosphorus: (●) PET; (■) polypropylene; (▲) impact polystyrene.

These considerations show conclusively that, under burning conditions, phosphorus species are indeed able to enter the gas phase and to interact to a certain extent with the chain carriers of the oxygen–hydrocarbon reaction.

According to the mechanistic criteria put forward by Fenimore and Jones,<sup>14</sup> the efficiency of a pure gas-phase flame retardant should be rather insensitive toward a change of the polymer matrix, since the reactions that take place in the diffusion flame above the surface of the burning polymer are assumed to occur independently from the condensed-phase pyrolysis. On the other hand, the efficiency of a flame retardant acting by condensed phase mechanisms should strongly depend on the nature of the polymer.

Thus, in order to test the possibility of a condensed phase action by red phosphorus in PET, its flame-retardant efficiency was also determined in both polypropylene and impact polystyrene. The effect of red phosphorus on the O.I. of these polymers as compared to the effect on the O.I. of PET is depicted in Figure 8. One recognizes that the efficiency is much higher in the case of PET. This strong influence of the nature of the polymer on the flame-retardant performance of phosphorus is indicative of a major contribution of a condensed-phase inhibition. This is corroborated by the fact that the small residual effect in polypropylene disappears if the samples are burned with nitrous oxide as the oxidant. The nitrous oxide index of 0.43 for polypropylene remains unchanged in the presence of red phosphorus. This indicates that the superior performance in PE is due to a condensed-phase inhibition by phosphorus.

Supporting evidence for this assumption is obtained from the comparison of isothermal TGA curves of pure PET and phosphorus-containing PET. Representative weight loss curves, plotted in the coordinates rate of weight loss versus per cent weight loss, are depicted in Figure 9. The appearance of

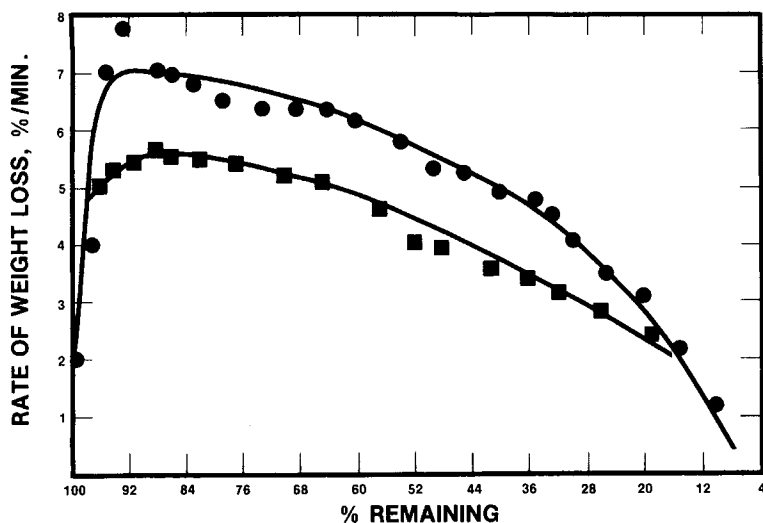


Fig. 9. Isothermal TGA curves for PET (●) and PET + 2% red phosphorus (■). Temperature, 402°C; atmosphere, Ar.

maxima in the rate of weight loss curves at about 15% conversion is indicative for a degradation by random scission, although the theoretical treatment predicts a maximum rate at about 25% conversion.<sup>15</sup> Since the position of the maximum is the same in the presence of phosphorus, one may assume that the general nature of the pyrolytic processes remains unchanged, although their rates are affected by the presence of phosphorus. This is corroborated by the results of GC analysis which indicate no change in the composition of the gaseous pyrolysis products in the presence of phosphorus. As in the case of pure PET,<sup>16</sup> the major constituent of the gas phase is acetaldehyde if the pyrolysis temperature amounts to 400°C.<sup>17</sup>

The isothermal temperature of 400°C for the Figure 9 experiments was selected in order to simulate the conditions at the surface of the burning polymer. Although the pyrolysis was carried out in an inert gas atmosphere, it is apparent that both the maximum rate of gas evolution and the total amount of gaseous products, given by the area under the curves, are reduced in the presence of red phosphorus. These results lead to the conclusion that under simulated burning conditions, phosphorus species are capable of affecting the condensed-phase reactions that lead to the generation of combustible volatiles and, thus, produce a flame-retardant effect. It is important that the inhibition by elemental phosphorus does not require the presence of oxygen in the atmosphere.

The primary step in the thermal decomposition of PET is assumed to involve a scission of the ester linkage by way of a concerted cyclic mechanism<sup>18</sup>; it is difficult to visualize how this reaction step could be inhibited by external scavengers. However, while this initial step does not involve any radical species, it is very likely that the subsequent pyrolysis reactions that lead to the formation of low molecular combustibles occur via a radical chain reaction. Carriers of this chain reaction may then be assumed to be susceptible to scavenging by phosphorus moieties such as P<sub>4</sub> or P<sub>2</sub>. Phosphorus species

are expected to be especially efficient scavengers for oxygen-containing intermediates owing to the strength of the PO bond. This may explain the fact that elemental phosphorus is a highly efficient flame retardant for oxygen-containing polymers such as PET, nylon, and cellulose, while its efficiency in oxygen-free polymers such as polyolefins is much lower.

As shown by this discussion, it is not necessary to invoke the formation of an insulating char layer and/or a dehydrating action by phosphorus pentoxide in order to account for the flame-retardant properties of elementary phosphorus in PET, although there is no doubt that this type of flame-retardant action is important for other systems such as polyolefins that are flame retarded by phosphine oxides.<sup>19</sup>

The authors thank Dr. W. B. Hardy for drawing their attention to the flame-retardant properties of elemental phosphorus and Dr. C. Savides for many helpful discussions. The TGA experiments were carried out by Dr. A. Wilson.

### References

1. J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Interscience, New York, 1970, pp. 29-67.
2. H. Vogel, *Flammfestmachen von Kunststoffen*, Dr. Alfred Huethig Verlag, Heidelberg, 1966, pp. 102-153.
3. O. Kaiser and A. Cadus, Ger. Offen. 1,965,635 (Oct. 8, 1970).
4. L. Vollbracht, Ger. Offen. 1,944,056 (Mar. 19, 1970).
5. H. Kraus, W. Herwig, and H. Cherdron, Ger. Offen. 2,143,348 (Sept. 28, 1971).
6. H. Piechota, *Kunststoffrundschau*, 12(4), 191 (1965).
7. R. S. Magee and R. F. McAlevy, *J. Fire & Flammability*, 2, 271 (1971).
8. A. Granzow and A. Wilson, to be reported.
9. C. P. Fenimore and F. J. Martin, Mechanism of Pyrolysis, Oxidation and Burning of Organic Materials, NBS Special Publication No. 357, Washington, D.C., 1972, p. 159.
10. A. Stock, G. E. Gibson, and E. Stamm, *Ber.*, 45, 3527 (1912).
11. J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. I, Interscience, New York, 1958, p. 117.
12. G. Lask and H. G. Wagner, *Eighth Symposium on Combustion*, Williams and Wilkins, Baltimore, 1962, p. 432.
13. J. W. Hastie, *J. Res. Nat. Bur. Stand.*, 77A, 733 (1973).
14. C. P. Fenimore and G. W. Jones, *Combust. Flame*, 8, 133 (1964).
15. S. Simha and L. A. Wall, *J. Phys. Chem.*, 56, 707 (1952).
16. E. P. Goodings, in Soc. Chem. Ind., *Monograph No. 13*, London, 1961, pp. 211-228.
17. D. L. Zabel and A. Granzow, unpublished results.
18. P. D. Ritchie, in Soc. Chem. Ind., *Monograph No. 13*, London, 1961, pp. 107-131.
19. C. Savides, A. Granzow, and J. F. Cannelongo, SPE RETEC, *Polyolefins*, Houston, March 1975.

Received April 17, 1975

Revised June 17, 1975