Flame-Retardant Thermoplastics. I. Polyethylene– Red Phosphorus*

EDWARD N. PETERS, *Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805*

Synopsis

Red phosphorus is a highly effective flame retardant for polyolefins. The low additive levels of red phosphorus in polyethylene make it an attractive route to nonhalogen flame-retardant systems. The mode of action of the red phosphorus has been investigated. Results indicate that the red phosphorus is effective both in the vapor and condensed phase. In the gas phase, PO species produced from the combustion of red phosphorus quench radical processes. In the condensed phase, the red phosphorus substantially lowers the heat of oxidation and traps radicals. This improved thermal stability results in a decrease in fuel production during burning.

INTRODUCTION

Conventional flame-retardant systems are known to be more effective in styrenics than in polyethylene. This is believed to be due in part to the different methods of decomposition of these polymers. Styrenics decompose in an orderly radical process to monomer. Halogen–antimony oxide systems are efficient in retarding these free radical processes. On the other hand, polyethylene degrades by a random chain scission mechanism.[1] Analysis of the volatile products indicates that the degradation of polyethylene proceeds preferentially via a series of intramolecular radical transfer steps.[2] Polymer flame dripping is a serious problem as these molecular weight degradation processes proceed. Halogen–antimony systems are much less effective in this situation. Indeed, additive levels twice as high as used in styrenics are often required to obtain similar flammability ratings in laboratory test specifications.

Elemental red phosphorus has been reported to be a flame retardant for several polymers.[3] This paper describes the use of red phosphorus in high-density polyethylene and the elucidation of its mode of action.

EXPERIMENTAL

The high-density polyethylene (HDPE) was from Union Carbide and had a melt index of 4. The red phosphorus was an amorphous powder from Mallinckrodt Chemical Works.

Thermogravimetric data were obtained on a Perkin-Elmer TGS-1 with a heating rate of 10°C/min. Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer DSC-2 with a heating rate of 10°C/min.

* It is not the intention of this report to correlate laboratory flame tests with large-scale fire behavior or even to imply that such a correlation may exist.

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Analysis of Combustion Gases

A sample of HDPE containing 8% red phosphorus was burned in a 26% oxygen atmosphere in an oxygen index apparatus, and the combustion gases were bubbled into water and analyzed for phosphorus species. Approximately 0.05% of the phosphorus remained in a residue after complete burning. Approximately 98% of the phosphorus was found via gravimetric analysis in the aqueous trap.[4]

Analysis for specific phosphorus-containing acids indicated that phosphoric acid was the major species, with trace amounts of phosphorus and hypophosphorus acids present.[5,6]

RESULTS AND DISCUSSION

Flammability Characteristics

The effect of red phosphorus on the flammability of HDPE was evaluated using the oxygen index (OI) method.[7] In the OI, or candle-type test, the polymer is burned downward in a vertical manner, and the minimum amount of oxygen necessary to support combustion is determined. The amount of red phosphorus was varied up to 12 wt %. The effect of red phosphorus on the OI of polyethylene is listed in Table I. A significant increase with increasing phosphorus concentration is noted up to 8 wt. %. This increase is characteristic of an effective flame retardant for polyethylene.

Red phosphorus at greater than 8 wt. % decreases the OI slightly. This is in line with a report that high levels of red phosphorus in polyethylene renders the resin more flammable.[8]

The dependence of OI on the phosphorus concentration (up to 8%) may be linearized by plotting the data from Table I versus the wt. % red phosphorus, as shown in Figure 1. The slope of this line is decribed by

$$OI = 0.186 + 0.00950[P] \tag{1}$$

In poly(ethylene terephthalate), it has been reported that there is a square-root dependence on the concentration of red phosphorus.[9]

In the Underwriter's Laboratory Bulletin 94, vertical flame test, polyethylene with 8% red phosphorus is rated V-0 at a 125-mil thickness.

It has been reported that certain organic nitrogen compounds are necessary additives to polyethylene–red phosphorus blends to achieve flame retardancy.[10]

TABLE I
Effect of Red Phosphorus on the Oxygen Index of Polyethylene

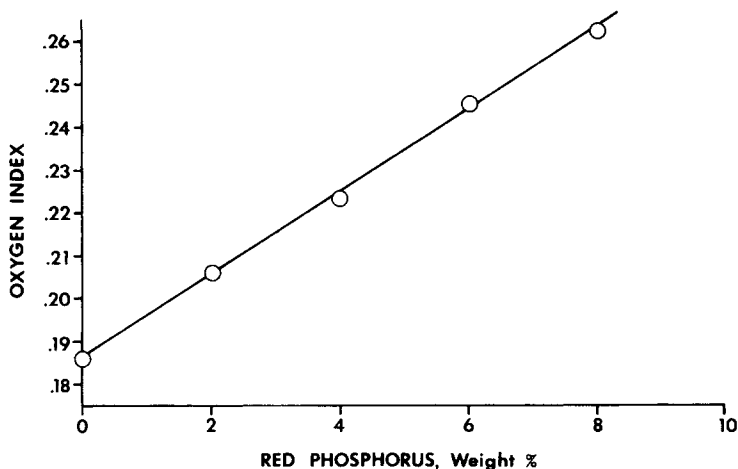| Red phosphorus, wt. %	OI
0	0.186
2	0.206
4	0.223
6	0.245
8	0.262
10	0.247
12	0.217

Fig. 1. Oxygen index versus red phosphorus concentration.

This difference in the flame-retarding effect of red phosphorus on polyethylene and the results reported here is probably due to differences in dripping during burning.

Mechanical Properties

The use of red phosphorus in polyethylene gives the lowest additive level for flame-retarding polyethylene. With halogen–antimony oxide systems, high additive levels (~29–30%) are required for comparable flammability ratings. High additive levels in HDPE have an adverse effect on physical properties. However, HDPE with 8% red phosphorus has properties equivalent to those of the base resin. The data for injection-molded samples appear in Table II.

Mechanism in the Gas Phase

Under actual fire conditions, the red phosphorus is oxidized to predominantly phosphoric acid derivatives and is eventually transported to the gas phase as phosphorus oxides. These phosphoric acid derivatives can act in the gas and condensed phases in flame-retarding polyethylene. In one experiment, the combustion gases from HDPE–red phosphorus were trapped in water and shown to consist of predominantly phosphoric acid with traces of phosphorus acid

TABLE II
Mechanical Properties of High-Density Polyethylene

Additive	Young's modulus, psi	Tensile strength, psi	Yield elongation, %	Elongation at break, %	Notched Izod impact, ft lb/in.^{3}
None	126,000	3500	40	600	1.5
8% Red phosphorus	110,000	2900	20	681	1.4

(0.03%) and hypophosphorus acid (0.02%):

$$\left[\begin{array}{c} P \\ P \diagup | \diagdown P \\ P \end{array} \right] \xrightarrow[\Delta]{O_2} H_3PO_4 + H_3PO_3 + H_3PO_2$$
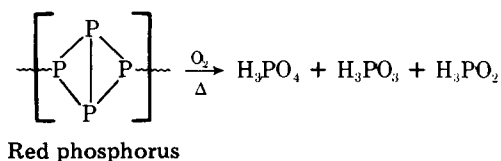
Red phosphorus

These phosphorus-containing acids result from the hydrolysis of phosphorus oxides.[11] Over 99% of the phosphorus is converted to volatile species during burning.

From the pioneering work of Fenimore and Jones,[12] the efficiency of a flame retardant which operates in the gas phase should be sensitive toward the nature of the oxidant, since the reactions that take place in the gas phase with oxygen would be different if the oxidant is changed to nitrous oxide. On the other hand, the efficiency of a flame retardant acting in the condensed phase should not be dependent on the nature of the oxidant.

For example, Granzow and Cannelongo[9] have reported that the flame-retardant effectiveness of red phosphorus in poly(ethylene terephthalate) is reduced if the sample is burned in a N_2O atmosphere. Thus these workers concluded that part of the flame retardancy imparted by red phosphorus involves gas-phase inhibition.

The N_2O index was determined for polyethylene containing up to 12 wt. % red phosphorus. The results are listed in Table III.

The N_2O index of pure polyethylene is 0.448, compared to an OI of 0.186. The higher N_2O index is explained in terms of the lower oxidant effectiveness of N_2O compared to oxygen. The N_2O index increases with increasing phosphorus concentration up to 10 wt. %.

However, it should be noted that the effect is smaller than in the case of the OI. The linearity between the N_2O index and the red phosphorus concentration is shown in Fig. 2. Equation (2) shows the linear dependence of the N_2O index on the concentration of red phosphorus:

$$N_2O \text{ index} = 0.448 + 0.00463[P] \qquad (2)$$

The slope in eq. (2) is about half the slope in eq. (1). This shows that the increase in the OI by a given concentration of red phosphorus is twice as high as

TABLE III
Effect of Red Phosphorus on the N_2O Index of Polyethylene

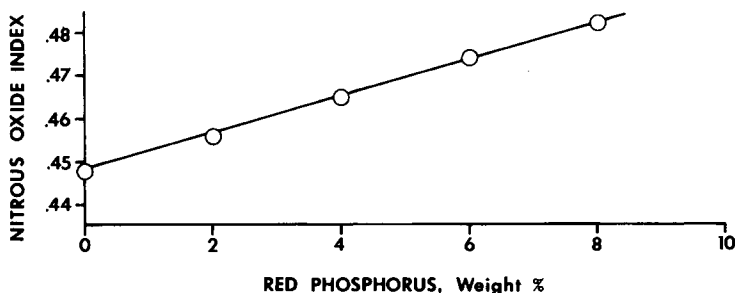| Red phosphorus, wt. %	N_2O index
0	0.448
2	0.456
4	0.465
6	0.474
8	0.482
10	0.488
12	0.462

Fig. 2. Nitrous oxide index versus red phosphorus concentration.

the corresponding increase in the N_2O index. This reduced effectiveness of samples burning in a N_2O environment indicates that a gas-phase mechanism contributes in part to the flame retardation of polyethylene by red phosphorus.

Hastie and McBee[13] have studied the mechanism of phosphorus containing flame retardants and found phosphorus monoxide to be the most significant phosphorus-containing species present in the flame. Moreover, the presence of such species results in a dramatic reduction in flame strength. For example, a concentration of several hundred ppm phosphorus monoxide in the flame is sufficient to markedly reduce the radical population and concomitantly the burning velocity or flame strength. Thus it was concluded that the observed degree of flame retardancy imparted by phosphorus substrates can be adequately accounted for by a vapor-phase mode of flame inhibition.

Mechanism in the Condensed Phase

Degradation of a polymer in the presence of an oxygen environment leads to simultaneous oxidative and pyrolytic reactions. The incorporation of red phosphorus into polyethylene increases the thermooxidative stability of the base resin. For example, thermogravimetric analysis (TGA) of HDPE with 8% red phosphorus at 400°C in air exhibited a 6% weight loss; on the other hand, the base resin showed a weight loss of $\sim$70%. The data are shown in Fig. 3.

This increase in thermo-oxidative stability is further exemplified by the heats of oxidation as determined by DSC. HDPE has a heat of oxidation of 527 cal/g. The incorporation of 6% red phosphorus lowers the heat of oxidation by a factor greater than four to 120 cal/g.

The TGA in nitrogen is shown in Fig. 4. At 440°C, polyethylene exhibited a weight loss of 70% compared to 8% weight loss for a sample containing 8% red phosphorus. Moreover, the onset of weight loss occurs at 100°C higher temperature. Similar effects have been reported in poly(ethylene terephthalate).[14]

This outstanding ability of red phosphorus to stabilize polyethylene is further demonstrated by gel-permeation chromatography results. Table IV contains molecular weight data on samples that have been heat aged in nitrogen at 400°C for 20 min. This data is shown graphically in Figs. 5 and 6.

Clearly no significant changes in molecular weight after heat aging are noted in the sample containing red phosphorus. On the other hand, without red phosphorus the molecular weight is reduced by approximately 50% after heat aging.
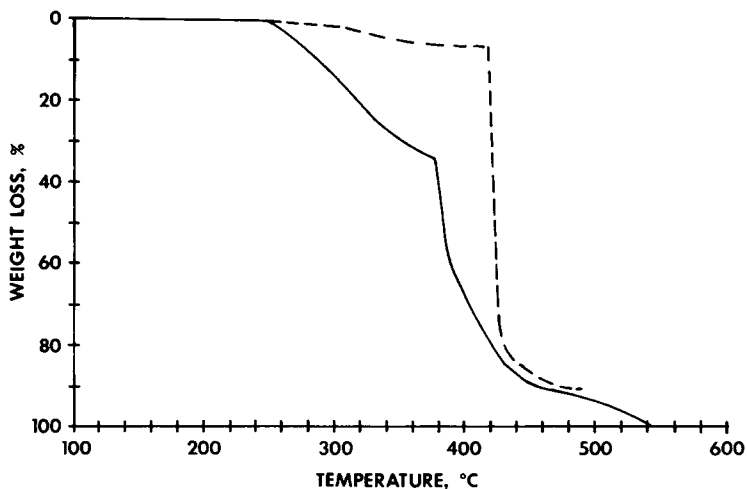
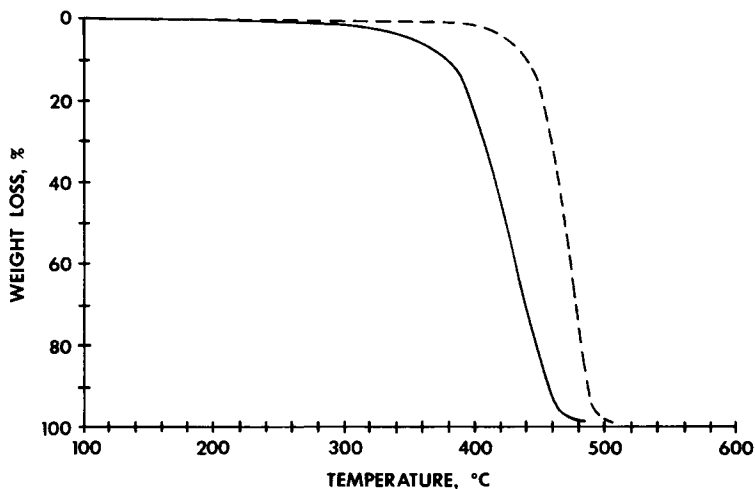Fig. 3. Thermogravimetric analysis in air.   (—) HDPE; (- - -) HDPE + 8% Red P.

Fig. 4. Thermogravimetric analysis in nitrogen.   (—) HDPE; (- - -) HDPE + 8% Red P.

TABLE IV
Effect of Heat Aging on Molecular Weight

	Unaged HDPE	Heat aged in nitrogen 20 min at 400°C	
		HDPE	HDPE with 6% red P
$\overline{M}_w \times 10^3$	85.2	45.7	77.7
$\overline{M}_n \times 10^3$	18.0	12.7	19.1

The TGA results in air suggest that the red phosphorus increases the thermo-oxidative stability of the base resin by scavenging oxygen at the surface of the polymer and thus retarding oxidative degradation processes.   This is not unlikely, since red phosphorus is known to react slowly with oxygen at ambient temperatures and more rapidly at elevated temperatures.

The outstanding stability in nitrogen indicates that red phosphorus retards the pyrolytic degradative processes.   Polyethylene degrades by a random
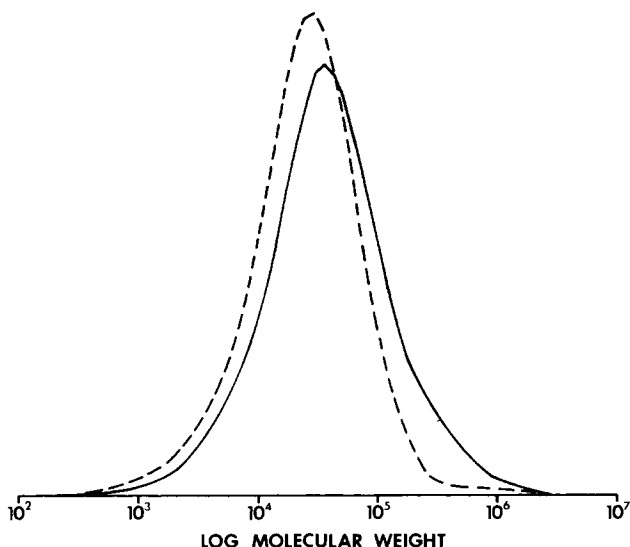
Fig. 5. Gel-permeation chromatography of HDPE: (—) HDPE; (- - -) HDPE heat aged.
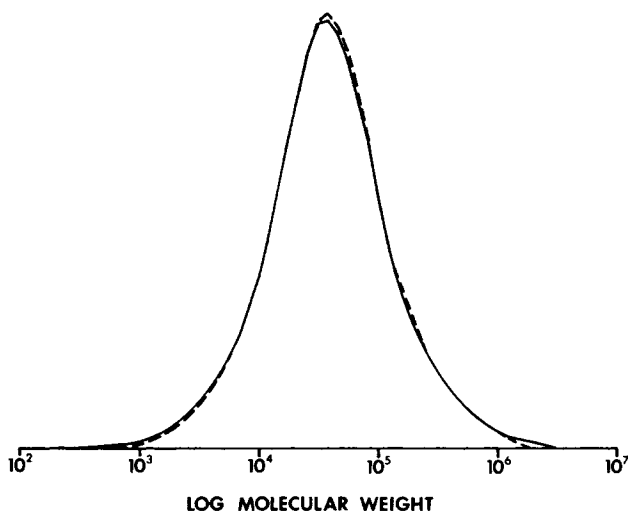

Fig. 6. Gel-permeation chromatography of HDPE and HDPE–red phosphorus: (—) HDPE; (- - -) HDPE + 6% Red P heat aged.

homolytic scission which produces radicals that undergo radical chain processes. Red phosphorus is known to react readily with free radical sources; thus the red phosphorus must quench polymer radicals and prevent free radical chain degradative processes. This should lead to the formation of carbon–phosphorus bonds.

It has been reported that alkyl phosphorus compounds produce P-H-containing species from thermal reactions at 300–450°C in nitrogen.[15,16] Phosphine was detected during the pyrolysis of a polyethylene–red phosphorus sample in nitrogen at 400°C. Presumably this is the product of the thermolysis of carbon–phosphorus bonds which resulted from the trapping of polymer radicals by red phosphorus.

Brauman[17] has reported that the mode of action of inorganic phosphate flame retardants in hydrocarbon polymers is in the formation of residual phosphoric acids which accumulate during burning, as a protective coating that physically limits fuel volatilization and oxygen access. Similarly the red phosphorus in HDPE undergoes oxidation to phosphoric acid derivatives during burning; in addition, the TGA and GPC results reported here indicate the operation of beneficial polyethylene–red phosphorus interactions at high temperatures. These combined actions of red phosphorus in the condensed phase result in a decrease in the generation of fuel.

CONCLUSION

Elemental red phosphorus is an effective flame retardant for polyethylene which operates in the vapor and condensed phases. In the gas·phase, PO species produced from the combustion of red phosphorus quench radicals. In the condensed phase, the red phosphorus substantially lowers the heat of oxidation; forms phosphoric acid derivatives which act as heat sinks and retard the production of combustible products; and traps radicals, which results in improved thermal stability. The overall effect in the condensed phase is to reduce the rates of both the pyrolytic and the thermo-oxidative degradation, thereby decreasing the production of volatile species which are a source of fuel for the fire.

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