Phosphine-Based Flame Retardants for Polypropylene*

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Synopsis

Flame retardant formulations for polypropylene are described that comprise a heat-stable phosphonium bromide or phosphine oxide, containing cyanoethyl substituents, in combination with ammonium polyphosphate. At additive levels of (20–30)%, flame-retarded polypropylene, with an Underwriters' Laboratories UL 94 V-0 rating is obtained with little effect on thermal and mechanical properties of the polymer. A characteristic property of this flame retardant mixture is low smoke generation during burning. Mechanism studies indicate that the organophosphorus component alone acts as an inhibitor in the gas phase, whereas the ammonium polyphosphate alone acts in the condensed phase. The synergistic effect observed by the combination of these two components is due to the formation of a phosphorus-rich char which forms an insulating layer.

INTRODUCTION

The increased use of plastics in a variety of large volume applications has resulted in a growing awareness of flammability problems associated with these materials. Since polyolefins, and especially polypropylene, are involved in many applications covered by existing or proposed flammability regulations, the development of flame retardant systems for polypropylene has become an important area of research.

When ignited, polypropylene burns with a hot smoke-free flame without leaving a char residue. The burning is accompanied by dripping and flowing of the flaming polymer which represents a considerable hazard in itself. Therefore, a flame retardant should not only cause extinction of the burning polymer, but also prevent the flaming drip.

The most widely used flame retardant systems for polyolefins are mixtures of halogenated compounds with antimony oxide as a synergist.^{1,2} In the case of chlorine-containing compounds, the accepted mechanism assumes the formation of antimony oxychloride followed by endothermic reactions to form antimony trichloride. The volatile antimony trichloride then acts in the gas phase by inhibiting the exothermic oxidation reactions in the combustion zone of the flame.³ Typically, nondripping polyolefin formulations based on the chlorine-antimony system and having an Underwriters' Laboratories rating of UL 94 V-0 require combinations of chlorinated compounds and antimony oxide at a total concentration of 35% to 45% by weight.⁴

In this paper we report on the development of flame retardant formulations for polypropylene containing phosphine-based compounds such as phosphonium salts, phosphinic acids and phosphine oxides.

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EXPERIMENTAL

Materials

Hercules polypropylene, Profax 6401, was stabilized with 0.1% pentaerythrityl tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and 0.25% distearyl thiodipropionate. The ammonium polyphosphate was Phos-Chek P/30 by Monsanto; the remaining phosphorus-based compounds were research samples by American Cyanamid. Antimony oxide was by M & T Corporation and Dechlorane 515 was by Hooker Corporation.

Sample Preparation

The polypropylene was dry blended with the flame retardant, milled on a two-roll steam mill at 175°C and compression molded into $5 \times 0.5 \times 0.125$ in. $(127 \times 12.7 \times 3.8 \text{ mm})$ bars at 200°C. For the experiments depicted in Figures 5 and 6, the dry blend was laminated to glass fiber cloth. The finished samples had a thickness of 25 ± 2.5 mils (0.64 \pm 0.064 mm) and contained 25% glass fiber.

Test Methods

The flammability of the polypropylene samples was determined according to three different test methods:

ASTM D-635 is a method in which a polymer sample $(5 \times 0.5 \times 0.25 \text{ in.})$ is ignited in a horizontal position with a flame. The flame is removed after 30 sec and the sample is allowed to burn. If the flame extinguishes within the first four inches, the time of extinguishment and distance burned after removal of flame are reported. If the sample continues to burn beyond the 4-in. mark, the sample is considered free burning and the average burning rate is reported.

In Underwriters' Laboratories UL 94 a sample held in a vertical position is ignited at the bottom for 10 sec. The specimen is rated V-0 if the flame extinguishes within 5 sec (average of five determinations) after removal of the flame, and no dripping occurs that ignites cotton held under the sample. A V-1 classification is given to samples in which the flame is extinguished within 25 sec (average of five determinations) after removal of the flame, with no dripping. The specimen is classified V-2 if extinguishment occurs within 25 sec, but the dripping ignites the cotton.

ASTM D-2863 is also called the oxygen index method. In this test the specimen is also held in a vertical position but ignited at the top. The oxygen index (OI) is defined as the minimum percent oxygen in an atmosphere of oxygen and nitrogen which is needed to sustain the candlelike burning of the specimen. The OI is considered one of the most reproducible methods for measuring flammability but does not necessarily correlate with the ASTM D-635 and UL 94 tests.

To measure the temperature dependence of the OI, the combustion chimney of the flammability gauge was heated electrically; the temperature was determined by means of a mercury thermometer whose bulb was placed close to the sample.

Smoke generation during combustion was determined by two different methods, ASTM D-2843 and the NBS method.⁵

Temperature measurements within the burning polymer were carried out by means of a miniature chromel-alumel thermocouple with a 0.02 in. (0.5 mm) diameter (Omega), the temperature readout was via X-Y recorder. A hole was drilled into the polymer which allowed the thermocouple to be positioned at a defined location in the center of the sample. The sample was then placed in the OI gauge, ignited and the temperature-time curve recorded. Since the burning velocity for each sample had been determined independently, the temperature-time curves could be converted into temperature-distance plots in which the position of the thermocouple defines point zero on the abscissa.

RESULTS AND DISCUSSION

Phosphine Derivatives

The flame retardant potential of certain phosphine-based compounds for polyolefins was first recognized by Sherr et al.⁶ who found that compounds such as phosphine oxides, phosphinic acids, and phosphonium halides are sufficiently heat-stable to be processed into polyolefins and impart a high degree of flame retardancy to the polymer.^{7,8} Examples of phosphine oxides, phosphinic acids and phosphonium halides and their flame retardant effects in polyethylene are shown in Tables I–III.⁶ Among the three classes, the phosphonium halides appear to be the most effective flame retardants. Test results for two phosphonium bromides, both derivatives of *tris* (cyanoethyl)phosphine, are shown on Table IV. It is noteworthy that at 10%, both compounds cause flame extinguishment according to both ASTM and UL 94 laboratory tests. To provide the same degree of flame retardancy, commercial halogen compounds have to be used at concentrations of 15%. The flame retardant effect of phosphonium

	TABLE I Phosphine Oxides	
Preparation:	$R_3P \xrightarrow{[0]} R_3P = 0$	
Evaluation in polyethylene ^a		Percent concentration in polyethylene to pass
Compound	Melting point, °C	horizontal test ^b
$\left(Cl - Cl - CH_2 \right)_{a} P = 0$	185–188	15
$\left(\bigcirc \right)_{s} P = 0$	156-157	15
(HO ₂ CCH ₂ CH ₂) ₃ P==O	155-156	15
$\left(\left(\begin{array}{c} \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \left(\begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \left(\begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \left(\begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \left(\begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \left(\begin{array}{c} \\ \end{array} \right) \begin{array}{c} \\ \end{array} \right) \left(\end{array} \right) \left(\begin{array}{c} \\ \end{array} \right) \left(\end{array} \right) \left(\begin{array}{c} \\ \end{array} \right) \left(\end{array}$	105–107	10

^a Data taken from ref. 6.

^b Modified ASTM D-635.

TABLE II Phosphonic Acids and Phosphinic Acids

Preparation: (a) Phosphonic acids						
$\operatorname{RPH}_{2} + \operatorname{H}_{2}\operatorname{O}_{2} \longrightarrow \operatorname{RP(OH)}_{2}$						
$\begin{array}{ccc} & & & O \\ & & & \parallel \\ & & RCH_2Cl + P(OR')_1 & \longrightarrow RCH_2P(OR')_2 \end{array}$	$\operatorname{RCH}_{2}\operatorname{Cl} + \operatorname{P(OR')}_{3} \longrightarrow \operatorname{RCH}_{2}\operatorname{P(OR')}_{2} \xrightarrow{\operatorname{HCl}} \operatorname{RCH}_{2}\operatorname{P(OH)}_{2}$					
(b) Phosphinic acid						
$R_2PH + H_2O_2 \longrightarrow R_2POH$						
Evaluation in polyethylene ^a		Percent				
		concentration				
Compound	Melting point, °C	to pass horizontal test ^b				
Cl	Melting point, °C	to pass				
$\underbrace{\text{Compound}}_{\text{Cl}} \underbrace{\overset{\text{Cl}}{\substack{ \downarrow \\ \downarrow $	Melting point, °C 188–189	to pass				
		to pass horizontal test ^b				

^a Data taken from ref. 6.

^b Modified ASTM D-635.

bromides can be further enhanced by using them in combination with halogen compounds.⁹ Table V shows the flame retardancy of mixtures containing 5% of phosphonium bromide-I (PB-I), and 10% of different commercial halogen compounds. However, it should be noted that all these combinations give V-2 ratings according to the UL 94 test, indicating that flame extinguishment is accompanied by dripping.

Phosphonium Bromide-Ammonium Polyphosphate Mixtures

To obtain nondripping flame retardant formulations, a variety of inorganic compounds including metal oxides, carbonates and phosphates was tested in polypropylene in conjunction with mixtures of the phosphonium bromide PB-I and a halogenated hydrocarbon. The most effective inorganic compound was found to be ammonium polyphosphate (APP).¹⁰ The data in Table VI show that APP alone or in combination with a chlorinated paraffin is not an effective flame retardant for polypropylene. On the other hand, addition of APP to mixtures of phosphonium bromide PB-I and the halogen compound shows increased flame retardant activity. This increase in activity is also observed for combinations of APP and PB-I in the absence of the halogenated paraffin. This formulation gives fast extinguishment according to ASTM D-635, high OI, and

Preparation:	
$R_3P + R'X \rightarrow R_3R'\dot{P}\cdot X^-$	
$R_3P + X(CH_2)_n X \rightarrow R_3 \overset{+}{P}(CH_2)_n \overset{+}{P}R_3 \cdot 2X^-$	
Compound	Melting point, °C
$\begin{array}{ll} (\mathrm{NCCH}_{2}\mathrm{CH}_{2})_{3}\overset{1}{\mathrm{P}}\mathrm{CH}_{2}\mathrm{CH}_{2}\overset{1}{\mathrm{P}}(\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{CN})_{3}\cdot 2\mathrm{Br}^{-} & (\mathrm{I}) \\ (\mathrm{NCCH}_{2}\mathrm{CH}_{2})_{4}\overset{1}{\mathrm{P}}\cdot\mathrm{Br}^{-} & (\mathrm{II}) \end{array}$	301–302 276–280
$(NCCH_2CH_2)_2^{+}P \xrightarrow{P} (CH_2CH_2CN)_2 \cdot 2Br^{-} (III)$	312-315
$Cl \longrightarrow CH_2 \dot{P}(CH_2 CH_2 CN)_{s} \cdot Cl^- \qquad (IV)$	158-165
$\left(\left(\begin{array}{c} \end{array}\right)_{3}^{+} \operatorname{PCH}_{3}\operatorname{CH}_{3}\operatorname{P}\left(\left(\begin{array}{c} \\ \end{array}\right)_{3}^{+} 2\operatorname{Br}^{-} \right)_{3}^{+} 2\operatorname{Br}^{-} \right)$	297-308

TABLE I	II
Phosphonium H	Halides

TABLE IV			
Action of Phosphonium Bromides in Polypropylene			

			ASTM D-635/1971	UL 94	OI
$(NCCH_2CH_2)_3 \stackrel{1}{P}CH_2CH_2 \stackrel{1}{P}(CH_2CH_2CN)_3 \cdot 2Br^{-1}$	(I)	5%	FB ^a	FB	22.5
$(NCCH_2CH_2)_3 \stackrel{+}{P}CH_2CH_2 \stackrel{+}{P}(CH_2CH_2CN)_3 \cdot 2Br^{-1}$	(I)	10%	SE (0.5 in.)	V-2	23.0
$(\text{NCCH}_2\text{CH}_2)_4 \dot{\mathbf{P}} \cdot \mathbf{Br}^-$ (II)		10%	SE (0.75 in.)	V-2	22.8
Dechlorane ^b		15%	SE (2.0 in.)	V-2	22.6
Control (no additive)		•••	FB	FB	17.5

^a FB-free burning.

^b Hooker Chemicals and Plastics Corp.

TABLE V

Combinations of Phosphoni	um Bromide-I an	d Halogenated	l Compounds in	Polypropylene

5% PB-I +	ASTM D-635	
10% halogen compound	Distance burned (in.)	UL 94
Cloranª	1.5	V-2
Dechlorane 602 ^b	1.0	V-2
Chlorez 700 HMP ^c	0.5	V-2
Hexabromobenzene	0.5	V-2
Hexabromobiphenyl	1.0	V-2
Control	>4.0	FB

^a Reaction product of hexachlorocyclopentadiene and tetrahydrophthalic anhydride–UOP Chemical Co.

^b Chlorinated hydrocarbon-Hooker Chemicals and Plastics Corp.

^c Chlorinated paraffin-Dover Chemical Co.

only slow dripping is observed. Based on these results, a nondripping flame retardant formulation was developed by the additional incorporation of small amounts [(1-2)%] of various metal oxides acting as inert fillers. The results obtained with TiO₂, SiO₂, ZnO, and Sb₂O₃ are shown in Table VII; most suitable in terms of processing characteristics was titanium dioxide.

% PB-I	% Halogen compound ^b	% Ammonium polyphosphate	Oxygen index	ASTM D-635 in. Burnedª	Dripping
•••	•••	20	19.9	>4.0 ^c	Slow
•••	10	10	20.5	>4.0 ^c	Moderate
5	5	5	25.3	0.8	Moderate
5	• • •	10	27.5	0.7	Slow
10	•••	10	30.2	0.5	Slow

TABLE VI Phosphonium Bromide-I/Ammonium Polyphosphate Formulations

^a Sample size: $5 \times 0.5 \times 0.25$ in.

^b Chlorez 700 HMP.

^c Samples burned completely.

TABLE VII Effect of Metal Oxides on Flame Retardant Formulations

polyphosphate + metal oxide	UL 94 rating	Color of sample ^a
None	V-2	Off-white
1% SiO ₂	V-1	Off-white
2% SiO ₂	V-1	Off-white
1% TiO ₂	V-1	Off-white
2% TiO ₂	V-1	Off-white
2% ZnO	V-1	Yellow
2% Sb ₂ O ₃	V-1	Gray

* Sample: $5 \times 0.5 \times 0.25$ in.

As shown in Table VIII, replacement of the cyanoethyl groups in PB-I by either ethyl or phenyl groups changes the UL 94 rating from V-0 (nondripping) to V-2 (dripping). Thus it appears that the nondripping characteristic of this formulation is related to the presence of cyanoethyl groups in the phosphonium salt.

Phosphine Oxide-Ammonium Polyphosphate Mixtures

As in the case of phosphonium bromides, it was found that combinations of APP with phosphine oxides containing cyanoethyl groups also produce nondripping formulations.¹¹ Again, the nondripping properties appear to be related

TABLE VIII Effect of Structure on Phosphonium Bromide Activity			
10% ammonium polyphosphate 1% TiO ₂			
10% phosphonium bromide	UL 94 rating ^a		
$\overline{(\text{NCCH}_2\text{CH}_2)_3}^{\dagger}$ \overrightarrow{P} CH ₂ CH ₂ \overrightarrow{P} (CH ₂ CH ₂ CN) ₃ -2Br ⁻	V-1		
$(CH_3CH_2)_3 \dot{P}CH_2CH_2 \dot{P}(CH_2CH_3)_3 Br^-$	V-2		
() +PCH ₂ CH ₂ P + - - - - - - - - - - -	V-2		

^a Sample: $5 \times 0.5 \times 0.25$ in.

to the presence of cyanoethyl groups. As shown on Table IX, the flame retardant efficiency is reduced if the phosphine oxide contains phenyl substitutes.

The most effective compound is a durene substituted cyanoethyl phosphine oxide, phosphine oxide IV. An effective formulation is composed of 40% phosphine oxide IV, 56% APP, and 4% TiO₂. The UL 94 ratings for various concentrations of this flame retardant mixture in polypropylene are given in Table X.

10% ammonium polyphosphate, 1% TiO ₂ 10% phosphine oxide	UL 94 rating ^a	Polymer compatibility
$\left(\left(\begin{array}{c} \\ \end{array} \right) \right)_{2} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{0}{_{P}} \stackrel{(I)}{_{P}} \right)_{2} (I)$	Burning	Good
OO IIII (NCCH,CH,2h2PCH,CH2CCH2CH2CN); (II)	V-1/FB	Poor
$(\text{NCCH}_2\text{CH}_2)_2\text{PCH}_2 \longrightarrow CH_2\text{P}(\text{CH}_2\text{CH}_2\text{CN})_2 (\text{III})$	V-1	Good
$(\text{NCCH}_{2}CH_{2})_{2}PCH_{2} \xrightarrow{CH_{4}} CH_{4} \xrightarrow{CH_{4}} O \\ (H_{2}CH_{2}CH_{2})_{2}PCH_{2} \xrightarrow{CH_{4}} CH_{4} \xrightarrow{CH_{4}} O \\ CH_{4}CH_{4}P(CH_{2}CH_{2}CN)_{2} (IV)$	V-1	Good

TABLE IX Phosphine Oxide-Ammonium Polyphosphate Combinations

* Sample: $5 \times 0.5 \times 0.25$ in.

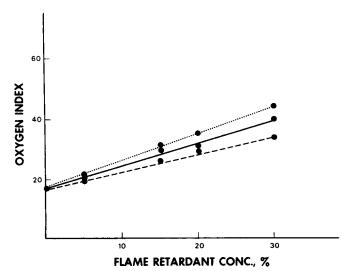


Fig. 1. Oxygen index measurements of polypropylene—flame retardant composition: phosphine oxide IV (40 parts), ammonium polyphosphate (56 parts), titanium dioxide (four parts). Specimen thickness:, $\frac{1}{4}$ in., --- $\frac{1}{6}$ in.

%	UL 94 ratings		
Flame retardant ^b	¹ / ₄ in.	1⁄ ₈ in.	1/ ₁₆ in.
5	Burning	Burning	Burning
15	V-1	V-2	V-2
20	V-0	V-1	V-2
30	V-0	V-0	V-2
45	V-0	V-0	V-0

TABLE X Effect of Specimen Thickness on UL 94 Rating^a

^a Additive composition: 40% phosphine oxide IV, 56% ammonium polyphosphate, 4% TiO₂. ^b Sample size: 5×0.5 in.

A pronounced effect of sample thickness on the flammability rating is apparent. For thicker sample specimens it is possible to achieve a nondripping V-1 rating with a 15% concentration of the above mixture.

The oxygen indices for these samples are shown on Figure 1. A linear increase with concentration is observed, up to 30% total flame retardant concentration.

Table XI shows the effect of this flame retardant combination on the mechanical and electrical properties of polypropylene. A decrease in percent elongation and an increase in flexular modulus is observed. Among the electrical properties, only the dissipation factor is affected.

Smoke Generation and Effect of Temperature on Flame Retardancy

Since smoke generation is an important hazard parameter in many fire situations, the effect of the system phosphine oxide IV, APP, and TiO₂ on smoke generation was tested according to ASTM D-2843 method. Polypropylene samples containing 30% of the flame retardant mixture (40% phosphine oxide IV, 56% APP, 4% TiO₂) were burned for four minutes and the time dependence of smoke formation was measured by the increase of light absorption across a light beam path. Figure 2 shows that both the control sample and the sample containing the phosphine oxide IV/APP/TiO₂ blend give a maximum light absorption of (35–37)% while, on the other hand, a conventional flame retarded polypropylene containing a mixture of a chlorinated compound and antimony oxide generates sufficient smoke within one minute to cause 100% light absorption.

		Polypropylene	
ASTM method	Property	Control	30% flame retardant ^a
D-638	Tensile strength at yield (psi)	4520	3450
D-638	Tensile elongation at yield (%)	6.2	3.9
D-790B	Flexural modulus (psi $\times 10^{-3}$)	204	325
D-648	Deflection temperature at 264 psi (°C)	58	69
D-150	Dielectric constant at 10 ⁶ Hz	2.20	2.74
D-150	Dissipation factor at 10 ⁶ Hz	0.0003	0.0216
D-149	Dielectric strength (V/mil)	414	401

TABLE XI Effect of Flame Retardant on Polymer Properties

^a 40% phosphine oxide IV, 56% ammonium polyphosphate, 4% TiO₂.

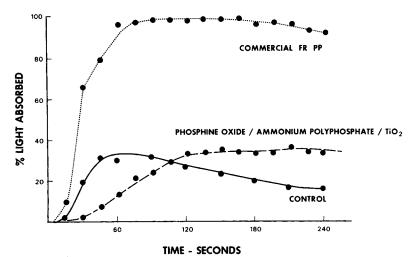


Fig. 2. Smoke density measurement of polypropylene samples (ASTM D-2843).

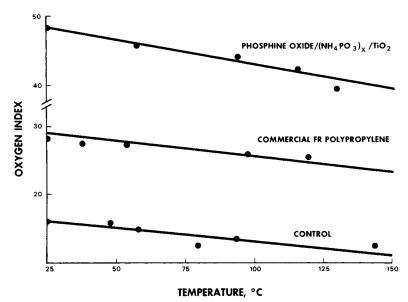


Fig. 3. Effect of temperature on oxygen index of polypropylene samples.

The smoke density under both smoldering and flaming conditions was also determined using the Aminco-NBS smoke chamber,⁵ since this smoke test is part of a proposed standard for aircraft interiors.¹² According to Table XII the phosphine oxide/APP is again superior to the conventional halogen–Sb₂O₃ system.

To further evaluate the practical usefulness of the phosphine oxide-APP system, its performance at elevated temperatures was studied. The results shown in Figure 3 indicate that the flame retardant system provides a controllable degree of flame retardancy up to about 150°C. Above this temperature reproducible measurements are difficult because of the softening of the polymer samples.

(AMINCO-NBS)					
Sample	Condition	Maximum specific optical density (D_m)	Specific optical density (D _s) at 4 min		
High-density PE (HDPE) control	Smoldering	532 ± 32	64 ± 25		
(Phillips)	Flaming	75 ± 32	48 ± 22		
HDPE + 30% phosphine oxide	Smoldering	80 ± 76	11 ± 1		
Blenda	Flaming	226 ± 21	88 ± 6		
Polypropylene control	Smoldering	510 ± 17	95 ± 6		
(Profax 6401)	Flaming	97 ± 12	40 ± 10		
Polypropylene + 30% phosphine	Smoldering	579 ± 149	227 ± 7		
Oxide blend ^a	Flaming	337 ± 141	157 ± 44		
Polypropylene + 30%	Smoldering	822	666		
Dechlorane 515 + 15% Sb_2O_3	Flaming	897	762		

TABLE XII
Smoke Density Measurements of Polypropylene Samples

^a Phosphine oxide blend: 40% phosphine oxide IV, 56% ammonium polyphosphate, 4% TiO₂.

Mechanism of Flame Retardant Action

In contrast to the conventional halogen-antimony oxide mixtures which are believed to function in the gaseous phase within the flame,³ the phosphorusnitrogen systems described in this paper appear to inhibit flammability in the condensed phase. The char which is observed during the burning of the flame retarded polypropylene acts first as an insulator to keep the condensed phase at lower temperatures, thus reducing production of volatile fuel, and second, as a barrier to prevent the volatile fuel from reaching the flame front. The assumption of a condensed phase mode of action can be tested experimentally by using nitrous oxide instead of oxygen to combust the flame retarded polymer. If the flame retardant action takes place in the condensed phase, the efficiency of the flame retardant should not depend on the nature of the oxidant. On the other hand, if gas phase inhibition is involved, the effectiveness of the flame retardant should change if the oxidant is changed.¹³ The data in Figure 4 show that both the oxygen indices and nitrous oxide indices increase linearly with the flame retardant concentration, the two plots having identical slopes. This result supports the assumption of a predominantly condensed phase mode of flame retardant action by the phosphine oxide-APP system.

The interaction between APP and phosphine oxide can be demonstrated by comparing the oxygen index (OI) versus concentration curves of the individual compounds, Figure 5, with the curve obtained for mixtures, Figure 6. One sees that in all cases the OI of the mixture exceeds the value calculated from the contributions of the individual components, the strongest enhancement being observed for a weight ratio of about 1. Based on these results, we have to assume the existence of a true synergism between APP and the phosphine oxide. Since, according to Figure 5, the efficiency of APP is maintained if the combustion is carried out in a N₂O atmosphere, one has to assume a condensed phase action for this component, while, on the other hand, the strong reduction of efficiency in N₂O for the phosphine oxide indicates a gas phase mechanism. As shown in Figure 6, the shapes of the efficiency curves for mixtures are similar in oxygen and N₂O, suggesting that the observed synergism of the two components of the

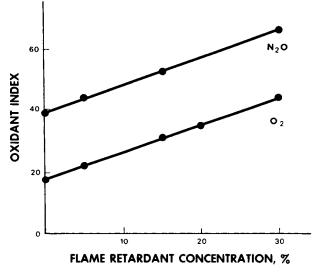


Fig. 4. Flame inhibition of polypropylene samples containing a mixture of: phosphine oxide IV (40 parts), ammonium polyphosphate (56 parts), titanium dioxide (four parts).

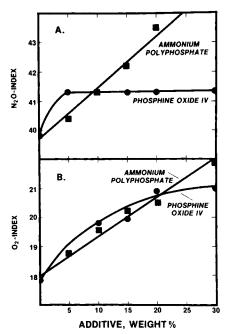


Fig. 5. Oxygen and N_2O index for phosphine oxide IV and ammonium polyphosphate in polypropylene.

flame retardant system can be accounted for by the char forming reactions in the condensed phase. The predominance of condensed phase action is further supported by the elemental analysis of the residual char which is obtained by combusting a PP sample containing 30% of a phosphine oxide-APP mixture in an oxygen-rich atmosphere. According to Table XIII, the phosphorus content of the char is almost as high as the phosphorus content of the original phosphine

AMMONIUM POLYPHOSPHATE, WEIGHT %

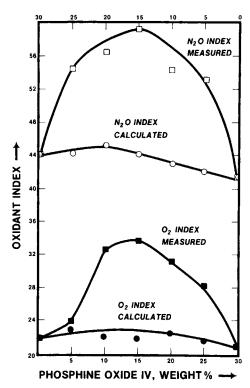


Fig. 6. Oxygen and N_2O index measurements for phosphine oxide IV-ammonium polyphosphate mixtures in polypropylene.

TABLE XIII

Comparison of the Elemental Compositions of the Ammonium Polyphosphate/Phosphine Oxide Flame Retardant and the Combustion Residue

Weight %	Flame retardant ^a	Char ^b
P	24.21	22.70
С	34.71	14.81
Н	5.50	2.91
Ν	12.52	3.23
0	23.65	56.35
(By Diff.)		

^a Composition: 40% phosphine oxide IV; 60% ammonium polyphosphate.

^b Flame retardant loading 30%.

oxide-APP mixture, indicating that very little volatilization of the phosphorus is taking place. On the other hand, the low nitrogen content of the char suggests that essentially all of the nitrogen is transformed into volatile products.

On the basis of these analytical results one may assume that the char residue consists of a network of polyphosphoric acid chains which may be crosslinked by carbon-containing fragments.

To demonstrate the insulation properties of the char formed during burning of this phosphorus-nitrogen system, an experiment was carried out in which the polymer temperature was measured in the vicinity of the flame front. The polymer sample was placed in the oxygen index apparatus and an oxygen atmosphere slightly above the oxygen index of the sample was maintained to allow a steady, candlelike burning after ignition. A thermocouple was placed in a fixed position near the center of sample and the temperature was recorded as a function of time. When the flame front reached the location of the thermocouple, the oxygen flow was cut off momentarily to extinguish the flame, and then turned on again with continued monitoring of temperature. Figure 7 shows the results obtained with a control and with two flame retardant polypropylene formulations. In the control sample, the temperature increased rapidly to a maximum of 540°C as the flame front reached the position of the thermocouple. When the flame was extinguished and oxygen was reintroduced, the temperature decreased rapidly to 50°C. In the phosphine oxide-APP containing sample, the temperature increased at a slower rate and a maximum temperature of only 250°C was recorded as the flame front reached the vicinity of the thermocouple. When the flame was extinguished and oxygen was again introduced, the temperature did not decrease rapidly but remained constant for some time. This temperature profile is explained on the basis of the insulation property of the char formed in this sample, minimizing combustion and pyrolysis in the bulk polymer core. An interesting result was obtained from a commercial halogenantimony oxide-based flame retardant polypropylene. This sample also showed a slow initial temperature rise, and a temperature of 225°C was recorded when the flame was extinguished. However, upon reintroduction of the oxygen, the temperature continued to rise to a maximum of 500°C. This latter temperature rise is due to continued combustion processes occurring on the surface of the polymer after flame extinguishment and is accompanied by the visible afterglow typical of such formulations.

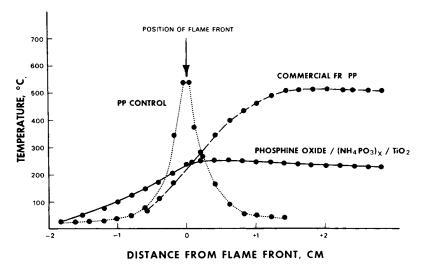


Fig. 7. Condensed phase temperature measurement of polypropylene samples.

CONCLUSIONS

In summary, it has been shown that mixtures of certain phosphine-based flame retardants with ammonium polyphosphate and small amounts of metal oxides provide flame retardancy for polypropylene in the absence of halogen. The practical advantages of this phosphorus-nitrogen flame retardant system over the conventional antimony oxide-halogen system are elimination of potential hazards caused by the liberation of corrosive hydrogen halides, lower smoke generation, absence of afterglow, and ease of processing.

On the basis of the evidence presented, it appears that the effectiveness of this system is due to solid or condensed phase inhibition attributed to char formation.

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