

Intumescent Flame-Retardant System of Phosphates and 5,5,5',5',5'',5''-Hexamethyltris(1,3,2-dioxaphosphorinanemethan)amine 2,2',2''-Trioxide for Polyolefins

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SYNOPSIS

A new halogen-free intumescent flame-retardant system was developed using melamine phosphates and 5,5,5',5',5'',5''-hexamethyltris(1,3,2-dioxaphosphorinanemethan)amine 2,2',2''-trioxide (XPM-1000, Monsanto Co.). This intumescent system, optimally at a weight ratio of about 1 : 2, showed effective flame retardancy by oxygen index (OI) and UL 94 tests in ethylene-vinyl acetate (EVA) and polyolefin formulations. At a constant loading and a constant weight ratio of phosphate/XPM-1000, the flame-retardant effectiveness was influenced by the phosphates in the order of melamine pyrophosphate > melamine phosphate \approx dimelamine phosphate > melamine amyl phosphate. The rate of char formation, as measured under flaming conditions, appeared to correlate better than did the char yield to the observed flame-retardant effectiveness of the different phosphate/XPM-1000 combinations and to the different ratios of phosphate/XPM-1000. A test procedure was developed to measure the char-forming rate which proved to be well correlated with flame retardancy. The possible composition of intumescent char was suggested based on infrared, XPS, and elemental analysis. The presence of polycondensed phosphorus acids with some P—NH— bonds appears likely. Such phosphorus–nitrogen species may help explain the observed synergism, since their formation could reduce the volatility of the phosphorus acids and enable them to better protect the char. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In an exploratory project to find halogen-free flame-retardant systems for polyolefins, particularly for wire and cable insulation, one of the approaches was to explore intumescent systems. The term intumescent refers to foamed char formed during the fire exposure of a polymer formulation containing an intumescent additive system. Typically, such a system contains three main additive ingredients, namely, a char former (carbonific, typically a pentaerythritol), a blowing agent (spumific, typically

melamine), and an acidic catalyst (typically ammonium polyphosphate) to induce carbonization of the char former. The chemistry and mechanism of intumescent flame-retardant systems has been studied and described by a number of research groups.¹⁻⁹ The catalyst and char formers tend to be hydrophilic materials, or in the case of ammonium polyphosphate, hydrolyzable materials,¹⁰ which pose problems for electrical insulation applications. We decided to take advantage of a newly available phosphonate ester, which has a high percentage of phosphorus, good thermal and hydrolytic stability, and, thus, predictably good electrical properties.

The present study led us to effective intumescent flame-retardant systems using phosphates and 5,5,5',5',5'',5''-hexamethyltris(1,3,2-dioxaphosphori-

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nanemethan)amine 2,2',2''-trioxide (XPM-1000).¹¹ Several commercially available phosphate flame retardants were used as co-additives in this research, including melamine pyrophosphate (MPP), melamine phosphate (MP), dimelamine phosphate (DMP), and melamine amyl phosphate (MAP). These phosphates have very low water solubility and low moisture absorption at both room temperature and 100°C.^{2,12,13} Their utility in flame-retarding plastics and coatings has been reviewed.¹²⁻¹⁴ The phosphonate XPM-1000 is a substantially water-insoluble product recently introduced on a developmental basis by Monsanto Co., and its use in flame-retardant polyurethane formulations has been advocated. The use of XPM-1000 in polyolefins or olefin copolymers seems not to have been reported. We found that the combination of a phosphate and XPM-1000 provides effective flame retardancy, i.e., V-0 ratings by the UL 94 test for ethylene-vinyl acetate copolymer and other polyolefins. Examples of synergistic combinations of certain phosphonate esters with melamine pyrophosphate have been reported in patents for applications in polybutylene terephthalate but not apparently in polyolefins.^{15,16}

The present study of the factors affecting the oxygen index (OI) and UL 94 results observed with the different phosphate combinations and phosphate/phosphonate ratios leads us to propose that the char-forming rate may be more important than the char yield in affecting the flame-retardancy results. We also suggest some possible components of the char produced during the combustion.

EXPERIMENTAL

Materials

The ethylene-vinyl acetate copolymer (ELVAX 460, 17.5–18.5 wt % vinylacetate content, DuPont), low-density polyethylene (PETROTHENE NA-951, Quantum Chemical), polypropylene (PROFAX 6523, MF = 4, Himont), polypropylene (injection grade, MF = 15, Showa Denko), melamine pyrophosphate (AEROGUARD MPP, American Cyanamid, now Cytec), melamine phosphate (AMGARD NH, Albright & Wilson), dimelamine phosphate (AMGARD ND, Albright & Wilson), melamine amyl phosphate (COBRAGUARD, Synthetic Products Co.), bispentaerythrityl phosphate carbonate (Akzo), 5,5',5'',5''-hexamethyltris(1,3,2-dioxaphosphorinanemethan)amine 2,2',-2''-trioxide (XPM-1000, Monsanto developmental

product), pentaerythrityl spirobis(phenylphosphonate) (PESBPP, Akzo laboratory sample), mono/diphenyl ester of phosphoric acid (PPA, Calgene Chemical), melamine (superfine grade, Melamine Chemicals, Inc.), and dipentaerythritol (DIPE, Aqualon Co.) were used as received.

Polymer Sample Preparation

The ethylene-vinyl acetate copolymer (EVA) or low-density polyethylene (LDPE) and other ingredients were mixed in a Brabender Plasticorder (Brabender Co.) at 120°C for 10 min, followed by molding at 120°C in a Carver press for 5 min. To prepare polypropylene formulations, 200°C was used for mixing and molding. The resulting sample plate was cut into test specimens of specific sizes required for ASTM D-2863 and UL 94 tests.

Testing

The oxygen index (OI) was determined by ASTM D-2863 using a Stanton Redcroft FTA Flammability Unit (Tarlin Scientific). The UL 94 vertical burning test was done by the standard procedure developed by Underwriter Laboratories. The thicknesses of the sample for the UL 94 test were $\frac{1}{8}$ in. (3.2 mm) and $\frac{1}{16}$ in. (1.6 mm).

The TGA measurements were done using a DuPont 951 thermogravimetric analyzer at a heating rate of 20°C/min and in 1% oxygen in nitrogen with a flow rate of 50 mL/min. The FTIR spectra were run on a Perkin-Elmer 1600 FTIR at the resolution of 2 cm⁻¹. Optical microscopy was performed with a Nikon Optiphot microscope and a high-intensity fiber optic illuminator (FIBER-LITE 3100, Dolan-Jenner Industries, Inc.).

X-ray photoelectron spectroscopy (XPS) was performed on an XSAM 800 surface analysis system (Kratos Analytical Inc.). Specimens of the char or the model compounds were bonded with the EVA copolymer and compressed to a reasonably flat surface. The samples were then analyzed using MgK α radiation. Data acquisition and processing were done using the DS 800 software. The background was subtracted prior to quantification and the weak signals were smoothed with the Savitsky Golay algorithm prior to curve fitting. Peak shifting caused by char buildup in the non-conducting specimens was compensated for by using the Cls peak from the EVA as the standard binding energy (285.1 eV). Since all the specimens had this peak, this method ensured the accuracy of the relative peak positions of the

Table I Flame Retardancy of EVA/MPP/XPM-1000 Formulations

Formulation	MPP (phr ^a)	XPM-1000 (phr)	P Wt % in Formulation	OI	UL 94 Rating	
					$\frac{1}{8}$ in.	$\frac{1}{16}$ in.
1	0	90	8.7	23.4	Burning	
2	30	60	8.1	28.9	V0	V0
3	45	45	7.8	26.1	V0	V-2
4	60	30	7.5	27.7	V-2	V-2
5	118	0	7.8	25.7	Burning	
6	10	50	6.7	25.8	V-2	V-2
7	15	45	6.5	26.5	V0	V-2
8	20	40	6.4	27.5	V0	V0
9	23.3	36.7	6.3	26.3	V0	V-2
10	26.7	33.3	6.2	25.0	Burning	

All formulations contain 100 phr of EVA.

^a phr, parts per hundred resin.

various samples. Elemental analysis were done at Galbraith Laboratory (Knoxville, TN).

Combustion Analysis for Char-forming Rate and Char Yield

The combustion analysis was conducted with an FTA flammability unit used to measure the OI at the oxygen concentration of 0.3–5.0% above OI. A specimen measuring 12 × 6.5 × 3 mm was mounted on a needle and inserted into the specimen after the needle was slightly heated over a flame. The needle was fixed vertically on the sample holder of the flammability unit. A wire gauze (with a diameter of about 50 mm) was placed beneath the specimen, with a distance of about 15 mm between the lowest edge of the specimen and the gauze. The specimen and char were carefully weighed before and after burning. The specimen was ignited by an electrically heated resistance wire. The time from the ignition to the completion of burning or extinguishing was recorded. An oxygen concentration of 3 units (i.e., 3.0%) above OI was used as the standard concentration in most experiments, this choice having been validated in the following section.

Calculation of Char Yield and Char-forming Rate

Char yield (CY) (%) = (char weight/weight of burned specimen) × 100, weight of burned specimen = total weight of the specimen – weight of unburned specimen. Char forming rate (CFR) (mg/min) = [char weight/time(sec)] × 60.

RESULTS AND DISCUSSION

Synergistic Flame Retardancy by Melamine Pyrophosphate and XPM-1000

A combination of melamine pyrophosphate (MPP) and XPM-1000 was employed to flame-retard the normally flammable EVA copolymer. The total loadings of MPP and XPM-1000 were 90 phr (or 47.4 wt %) and 60 phr (or 37.5 wt %) at the beginning of the investigation, while the loading could be varied as needed for various levels of flame retardancy of EVA or other polymers. MPP and XPM-1000 were mixed into EVA using a Brabender Plasticorder, followed by molding on a Carver press and cutting into test samples. This process gave highly uniform test samples, indicating good mixing of flame retardants and polymer.

The flame retardancy of EVA/MPP/XPM-1000 formulations was evaluated in terms of the limiting oxygen index (OI) and UL 94 vertical burning test with the usual rating order of V-0 > V-1 > V-2, and results were listed in Table I. Some important conclusions may be obtained from the table:

1. Combinations of MPP and XPM-1000 were more effective flame retardants than were either MPP or XPM-1000 at the same loading. At a weight ratio of MPP/XPM-1000 from 1 : 5 to 2 : 1, the combination of MPP/XPM-1000 provided satisfactory flame retardancy for EVA, while MPP or XPM-1000 alone did not. Different degrees of flame retardancy were obtained by varying the ratio

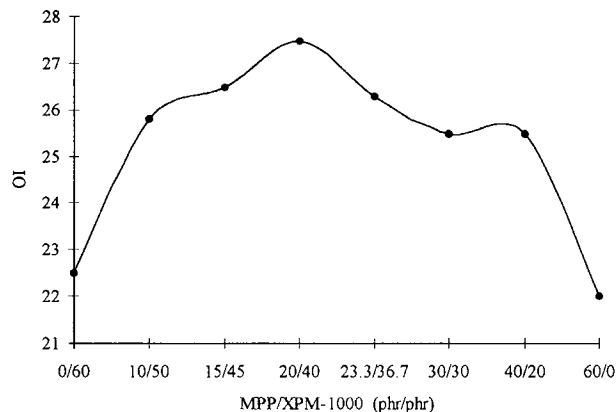


Figure 1 OI as a function of ratio of MPP and XPM-1000 at 60 phr total loading.

of MPP/XPM-1000. The ratio of MPP/XPM-1000 for the best flame retardancy as measured by OI or UL 94 was about 1 : 2. This result can be seen from Figure 1, which showed the OI as a function of the MPP/XPM-1000 ratio at a total loading of 60 phr.

2. The combination of MPP/XPM-1000 produced intumescent char during the burning test, which effectively reduced the flammability of EVA. Either MPP or XPM-1000 alone did not give intumescent char, but gave substantially unfoamed char.

Figure 1 shows clearly the synergism of MPP/XPM-1000 combination in raising the OI. The "head-and-shoulders" shape of the curve might indicate the complex burning behavior of EVA/MPP/XPM-1000 formulations. We did not try to draw a smooth curve with a single maximum through the data points, which would not be consistent with our estimate of the error limits of the OI readings (less than 1%). We believe that the "head-and-shoulders"

curve is not an unusual one for the synergism between various flame retardants.

Table II shows the effect of the total loading of MPP and XPM-1000 on the flammability of EVA. At the weight ratio of 1 : 2 of MPP/XPM-1000, the total loading needed to attain a UL 94 V-0 rating at $\frac{1}{8}$ in. thickness was 32.4 wt %, and for a V-0 rating at $\frac{1}{16}$ in. thickness, 37.5 wt %. Also, the OI increased linearly with the increase of the loading (Fig. 2).

Table III compares the flame retardancy of some other polyolefins containing MPP/XPM-1000, which shows that the potential application of MPP/XPM-1000 combinations extends beyond EVA. The synergistic flame retardancy provided by the combination of MPP and XPM-1000 is evident and significant, since neither MPP nor XPM-1000 alone could act as an effective flame retardant in the EVA formulations. To explore flame-retardant systems based on such combinations, we decided to further investigate the flame retardancy of some other phosphates in combination with XPM-1000.

Flame-retardant Action of Various Phosphates with XPM-1000

The same methodologies applied in studying EVA/MPP/XPM-1000 formulations was used to evaluate the combination of melamine phosphate (MP) and XPM-1000. Results in Table IV indicated that this combination also provided effective flame retardancy for the EVA copolymer. Like MPP/XPM-1000, the flame retardancy depended on the weight ratio of MP/XPM-1000, and the best ratio was about 7 : 11. Formulations of EVA/MP/XPM-1000 produced intumescent char upon burning.

Under the same processing conditions, three other phosphates—dimelamine phosphate (DMP), bis-pentaerythryl phosphate carbonate (BPEPC), and

Table II Effect of Total Loading of MPP/XPM-1000 on the Flammability of EVA

MPP (phr)	XPM-1000 (phr)	Total Loading (Wt %)	OI	UL 94 Rating	
				$\frac{1}{8}$ in.	$\frac{1}{16}$ in.
0	0	0	18.4	Burning	
15	30	31.0	25.5	V-2	V-2
16	32	32.4	25.9	V0	V-2
20	40	37.5	27.5	V0	V0
30	60	47.4	28.9	V0	V0

All formulations contain 100 phr of EVA.

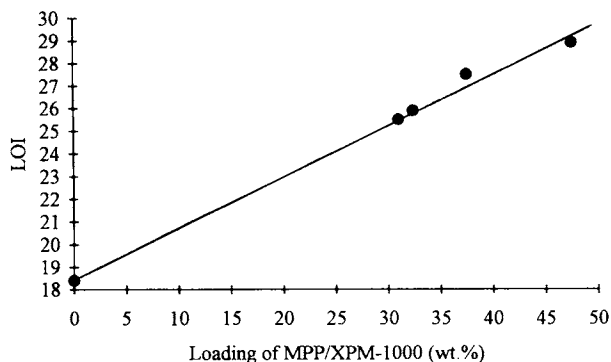


Figure 2 The relationship between the total loading and OI.

melamine amyl phosphate (MAP)—were substituted for MP to evaluate their flame-retardant effect in EVA (Table V). All combinations of XPM-1000 and these phosphates generated intumescent char during the combustion.

Summarizing data from Tables I, IV, and V, we found that at the constant loading and weight ratio the effectiveness of the flame retardancy (in terms of OI and UL 94 ratings) provided by the combinations of phosphates and XPM-1000 was influenced by the phosphate in the order of MPP > MP \approx DMP > BPEPC > MAP.

In these systems containing MPP or other phosphates and XPM-1000, we hypothesize that MPP is functioning as the acid catalyst and also as the source of the blowing agent (melamine) and that XPM-1000 is functioning as the principal char former. MPP may undergo thermal decomposition to release water, ammonia, and melamine,^{9,12,13} while XPM-1000 is a new compound and its chemistry in combustion or thermal decomposition has not yet been reported.

A number of experiments were conducted to examine the roles of MPP and XPM-1000 in the system (Table VI). The replacement of MPP by dipen-

taerythritol (DIPE) resulted in complete loss of the flame retardancy and no intumescent char, indicating that MPP is necessary in this intumescent system and is not mainly a char former. Moreover, the partial replacement of XPM-1000 by DIPE somewhat reduced the flame retardancy, as compared with Formulation 4 in Table I. Table VI also shows that a combination of MPP/pentaerythrityl spirobis(phenylphosphonate) offered satisfactory flame retardancy for EVA and generated intumescent char. By contrast, a combination of MPP and the mono/diphenyl ester of phosphoric acid (PPA), which is high in phosphorus but which is not a good char former, was not an effective flame-retardant combination.

The unfavorable flame retardant result from the replacement of MPP by DIPE is consistent with the proposal that MPP serves as a catalyst and source of blowing agent in the intumescent MPP/XPM-1000 system. DIPE is a known char former in an intumescent system of DIPE and ammonium polyphosphate (APP) in which APP is the catalyst for char formation and the donor of ammonia gas as the blowing agent.⁵ In our control experiments, we found that MPP/DIPE produced intumescent char upon burning, but MPP, DIPE, or XPM-1000 alone did not. Therefore, the combination of DIPE/XPM-1000 should have produced intumescent char if XPM-1000 were the char-forming catalyst and the source of the blowing agent. In fact, DIPE/XPM-1000 failed to produce intumescent char. Thus, we may rule out the possible functioning of XPM-1000 as a principal char-forming catalyst and as a source of the gas for blowing the foamed char. The failure to maintain flame retardancy after partial replacement of XPM-1000 by DIPE (Formulation 21 in Table VI) suggests that DIPE may even somewhat interfere with the char-producing interaction between MPP and XPM-1000 during the combustion. PESBPP has been claimed to be a char former,^{15,16}

Table III Flame Retardancy of Polyolefins Containing MPP/XPM-1000

Polymer (100 phr)	MPP (phr)	XPM-1000 (phr)	OI	UL 94 Rating $\frac{1}{8}$ in.
EVA	20	40	27.5	V0
LDPE ^a	20	40	26.9	V0
PP (MF 4) ^b	16	32	28.4	V0
PP (MF 15) ^c	16	32	27.5	V-2

^a LDPE, low-density polyethylene (PETROTHENE NA 951).

^b PP, polypropylene [PROFAX 6523, MF (melt flow) = 4].

^c PP, polypropylene (injection grade, MF = 15).

and MPP/PESBPP was found to be an effective intumescent system for EVA, more evidence of the assigned role of the MPP as a catalyst and blowing agent for the char-forming component.

Consistent with these results, we suggest that in the combination of MPP/XPM-1000 MPP mainly provides the char-forming catalyst and source of the blowing agent, and the XPM-1000 mainly serves as the char former. We do not rule out a minor catalyst role of the phosphorus in the XPM-1000.

Investigation of Char Composition and Morphology

We have concluded that under the burning condition the combination of phosphate/XPM-1000 generated intumescent char which effectively flame retards EVA and other polyolefins. Further investigation was conducted on the char composition and morphology to understand how they may relate to the observed flame retardancy of the EVA formulations. In these studies, char was prepared by burning the corresponding EVA/MPP/XPM-1000 formulation at an oxygen concentration of 3 units (i.e., 3%) above the OI.

Char (Burning Residue) Composition

Elemental analysis was employed to determine the content of carbon, hydrogen, nitrogen, total phosphorus, and extractable phosphate in the char. Table VII lists experimental data for individual chars from Formulations 6–10 in Table I. Phosphate (PO_4^{3-}) in the char was detected and measured by extraction with water at room temperature and determination by the standard phosphomolybdate colorimetric method; the content of phosphate or phosphoric acid is expressed in terms of the phosphorus element percentage in the char in Table VII. By calculation,

Table V Effect of Phosphates on the Flammability of EVA

Formulation	Phosphate	OI	UL 94 Rating	
			$\frac{1}{8}$ in.	$\frac{1}{16}$ in.
17	DMP	26.0	V0	V-2
18	BPEPC	25.3	V-2	V-2
19	MAP	24.2	V-2	Burning

All formulations contain 100 phr of EVA, 40 phr of XPM-1000, and 20 phr of phosphate.

we then estimated the possible composition of the chars (Table VIII). The calculated oxygen contents are considered high and rather unreliable because of possible carbon-bound oxygen and adventitious water uptake.

Some observations could be made on the basis of this investigation of the char composition, as follows:

1. The surface of the char was acidic, and it was found to be pH 1–2 by pH paper.
2. IR spectra (Fig. 3) of chars obtained from two different formulations were similar to that of H_3PO_4 published by Scharf et al.¹⁷ but also show a band in the 1400 cm^{-1} vicinity which was recently attributed by Levchik et al. to P—N-bonded structures.¹⁸
3. The above two observations, plus the detection of PO_4^{3-} by colorimetry, were consistent with the presence of H_3PO_4 (or a polyphosphoric acid).
4. As indicated in Table VIII, H_3PO_4 (or a precursor capable of hydrolyzing readily to H_3PO_4) was the major phosphorus component of the char. The measured H_3PO_4 con-

Table IV Flame Retardancy of EVA/MP/XPM-1000 Formulations

Formulation	MP (phr ^b)	XPM-1000 (phr)	P Wt % in Formulation	OI	UL 94 Rating	
					$\frac{1}{8}$ in.	$\frac{1}{16}$ in.
11	15	45	6.5	26.0	V0	V-2
12	20	40	6.4	26.0	V0	V-2
13	23.3	36.7	6.3	27.5	V0	V-2
14	26.7	33.3	6.2	25.7	V-2	Burning
15	30	30	6.1	25.8	Burning	
16	40	20	5.8	26.3	V-2	V-2

All formulations contain 100 phr of EVA.

Table VI Flame Retardancy of EVA Containing Different Additives

Formulation	Additive 1 (phr)	Additive 2 (phr)	OI	UL 94 Rating	
				$\frac{1}{8}$ in.	$\frac{1}{16}$ in.
20	DIPE (20)	XPM-1000 (40)	22.6	Burning	
21	MPP (60)	XPM-1000 (10) and DIPE (20)	26.9	V-2	Burning
22	MPP (60)	PESBPP (30)	27.4	V0	V0
23	MPP (60)	PPA (30)	23.0	Burning	

All formulations contain 100 phr of EVA.

tent in the char increased with the increase of MPP/XPM-1000 weight ratio.

The presence of H_3PO_4 in char is explainable by MPP in the formulation, since MPP may produce H_3PO_4 upon burning. In addition to the presence of H_3PO_4 , we also looked for evidence for the possible presence of a phosphorus nitride, a phosphorus oxynitride, or other P—N bonded products in the char residue. It is known that phosphorus oxynitride, (PON)_x, is formed at temperatures above about 600°C by the thermal decomposition of various phosphorus- and nitrogen-containing compounds.^{19–21} Phosphorus oxynitride is itself non-flammable²² and has been described as a useful flame-retardant additive.^{23,24} However, we think that the presence of phosphorus oxynitride itself is unlikely in view of the phosphoric acid-like infrared spectrum and the presence of extractable phosphoric acid. Instead, a P—N species of some sort is quite likely. The high H_3PO_4 content of the char (Table VII) and the high computed O/P ratios (Table VIII) in the char suggests that more likely the char contains species having one P—N bond and several P—O bonds per phosphorus atom. Thus, the species in our char resemble the species described by Lang-

ley et al. in the char from cellulose flame retarded with various phosphorus–nitrogen combinations²⁵ as well as the char from ammonium polyphosphate in nylon 6.¹⁸ Phosphoramidic and phosphorimidic acids are quite hydrolyzable²⁶ and might be determined as H_3PO_4 itself in the usual analytical method, which entails extraction of the sample with water.

An X-ray photoelectron spectrum (XPS) run on the char was compared with those run on phosphorus oxynitride (provided by Profs. Vitola and Miller, Latvian Academy of Science, Riga, who have done extensive studies on such compounds²⁷) and on ammonium polyphosphate. The broad N1s peak from the char, with its deconvoluted components, is shown in Figure 4. The N1s peak from the char showed three components after deconvolution; the strongest component at 402.4 eV matches that observed for ammonium polyphosphate. The second component at 400.6 eV agrees with the assignment by Brow et al.²⁸ to the P—NH₂ species. The third peak, accounting for about 10% of the total N1s peak from the char, is at 399.6 eV, which agrees very well with the assignment of 399.8 eV to P—NH—P by Brow et al. No peak was seen at 397.9 eV, the position assigned by Miller and Vitola²⁷ to the P=N—P in phosphorus oxynitride; also, their

Table VII Elemental Analysis of Intumescent Char

Corresponding Formulation ^a	Elemental Content in Char (%)					
	C	H	N	Total P	P in PO ₄ ³⁻	O by Difference ^b
6	20.82	5.36	1.60	22.15	16.34	50.07
7	23.74	6.16	1.94	23.47	17.22	44.69
8	21.85	5.80	2.43	23.44	18.32	46.48
9	10.89	3.81	2.43	23.24	20.16	59.63
10	11.47	3.93	2.60	23.76	20.96	58.24

^a For composition in these formulations, see Table I.

^b Calculated value.

Table VIII Calculated Char Composition Based on Data from Table VII

Corresponding Formulation	% P (as Non-PO ₄ ⁻³)	% O (as Non-PO ₄ ⁻³)	H ₃ PO ₄ %	P/N Molar Ratio	Computed PO _x N _y Structure
6	5.81	16.30	51.71	1.64	PO _{5.43} N _{0.61}
7	6.25	9.10	54.50	1.46	PO _{2.82} N _{0.69}
8	5.12	8.62	57.97	0.96	PO _{3.26} N _{1.05}
9	3.08	17.97	63.79	0.57	PO _{11.29} N _{1.74}
10	2.80	14.93	66.32	0.49	PO _{10.32} N _{2.05}

sample of phosphorus oxynitride showed a peak at 397.9 eV, which is far enough removed from 399.6 eV observed in the char to indicate that phosphorus oxynitride itself is not a principal P—N species in the char.

We noted in the infrared spectrum of the char a sharp band at about 1400 cm⁻¹, which was also reported by Levchik et al. in TGA residue from nylon-6 and ammonium polyphosphate and attributed by him to phosphorus oxynitride.¹⁸ We do not consider this band to be adequate evidence for phosphorus oxynitride, even though that substance does have a band (broad) at this position.²⁷ This band at 1400 cm⁻¹ might also result from non-phosphorus nitro-

gen-containing compounds. One of them might be the ammonium moiety (its deformation bands occur at 1390–1484 cm⁻¹ region²⁹), although survival of ammonium in his extensively heated sample seems rather unlikely. More likely compounds are melon and (most likely) melon which are formed by the thermal condensation polymerization of the melamine moiety of the MPP. We previously showed by means of infrared spectra that melon is generated by burning melamine-containing polyolefin formulations and that melon exhibits a strong 1400 cm⁻¹ band.³⁰ More XPS work will be needed to clarify the nitrogen-containing compounds having a 1400 cm⁻¹ band.

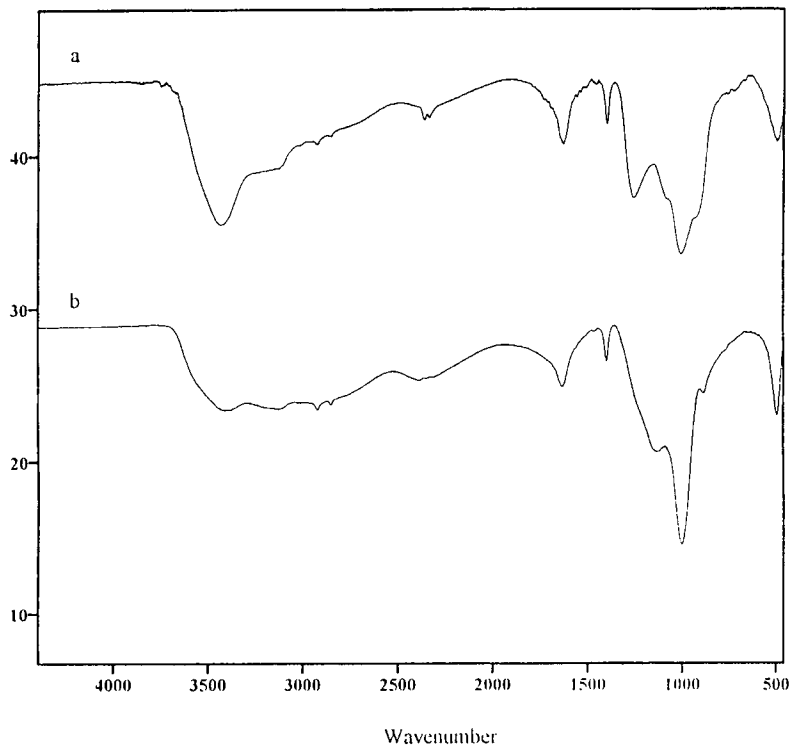


Figure 3 Infrared spectra (KBr) of (a) char from Formulation 8 and (b) char from Formulation 6.

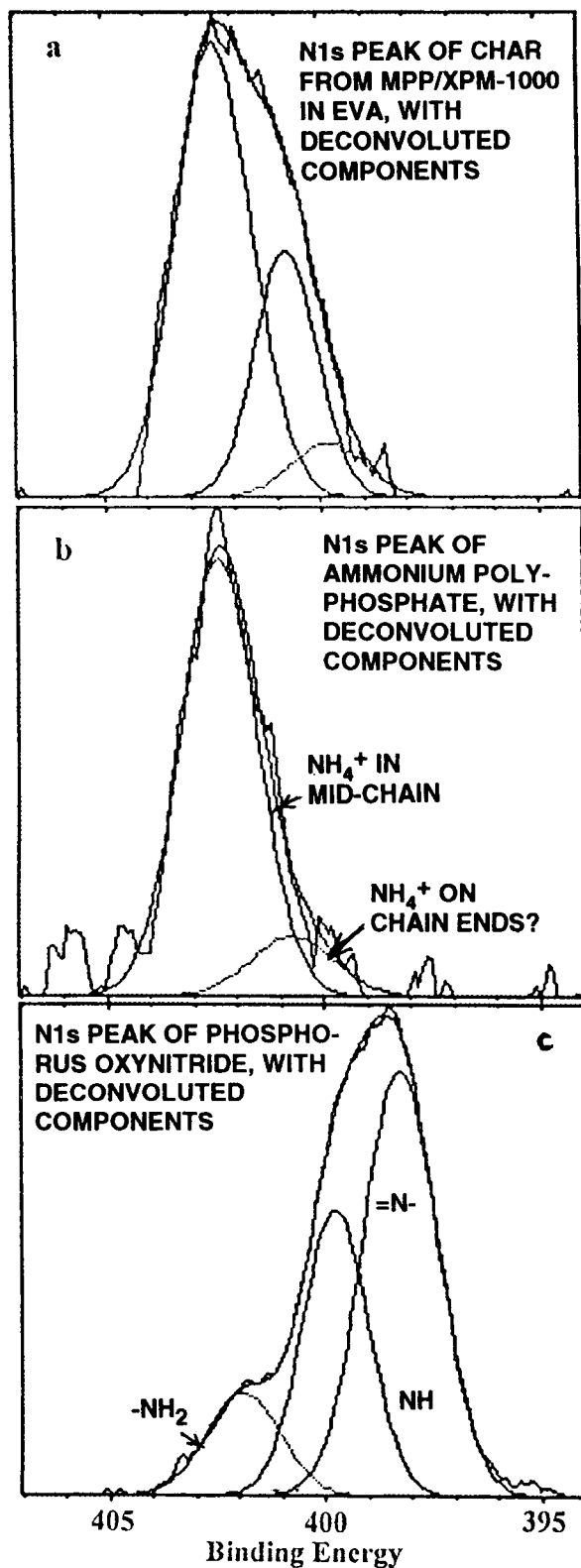


Figure 4 X-ray photoelectron spectra, N1s peaks: (a) from MPP/XPM-1000 in EVA; (b) from ammonium polyphosphate; (c) from phosphorus oxynitride.

Therefore, we suggest that char (or burning residue) from the EVA/MPP/XPM-1000 formulation contains a poly(phosphoric acid) as a major component, possibly an imidodiphosphoric acid or polycondensed version thereof. Such oxygenated P—N polyacids and partial nitrogen-containing salts thereof can have a glasslike character²⁸ and may account for the effective flame retardancy provided by MPP/XPM-1000. Similar oxygenated P—N species were found by char analyses in a study on phosphorus–nitrogen flame retardants in cellulose.²⁵ In the present case, the synergistic effect may be a combined result of the better retention of phosphorus [lower volatility of polyphosphorimide species than of poly(phosphoric acid) species], better barrier effect from the retained phosphorus, and faster rate of charring. All these features of phosphorus–nitrogen synergism have been observed in other flame-retardant systems as we have discussed in our recent reviews.^{31–34}

Char Morphology

The optical micrographs of char residues were taken under reflected light using a strong fiber-optic illuminator. These micrographs show a coherent outer layer (char surface) and a foamed inner layer, a combination believed to be a good barrier for both heat and mass flow; Figure 5(a) and (b) shows one of the chars from a formulation (no. 8) giving UL 94 V0 results.

Thermogravimetric Analysis (TGA) of the Intumescent Formulations

The TGA method was initially used in an effort to explain the OI values of the intumescent formulations, since the relationship between OI and TGA char yield was established (at least for polymers based on C, H, O, and N) by Van Krevelen³⁵ and we anticipated that the char yields in our system might also correlate to OI. This turned out not to be the case. All TGA experiments were carried out at a heating rate of 20°C/min and under 1% oxygen in nitrogen. This 1% O₂/99% N₂ atmosphere in TGA was used by Stuetz et al.³⁶ who found that the temperature required to reach a given thermooxidative decomposition rate under this atmosphere correlated well with the OI. Information on two important residues, R₅₂₀ and R_{final}, as measured by TGA, was studied in detail, although TGA also gave some other information. R₅₂₀ was the TGA residue observed at 520°C at which a major thermal decomposition was

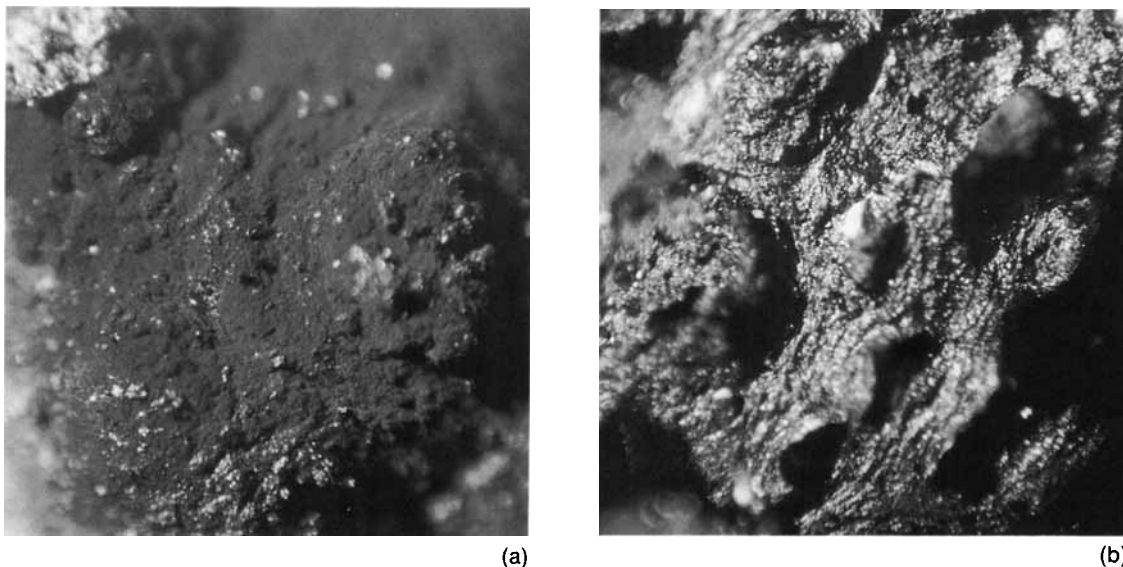


Figure 5 Optical micrographs of burning residue from Formulation 8: (a) outer layer surface; (b) inner layer. Magnification 40 \times .

just finished. Such major decomposition generated a temporary residue (or char) which persisted as a plateau in the TGA but then underwent further decomposition as the heating was continued. Thus, R_{520} was a temporary TGA residue at 520 $^{\circ}\text{C}$. R_{final} was the final residue at 700 $^{\circ}\text{C}$.

We observed that in EVA/MPP/XPM-1000 R_{520} or R_{final} seemed to have little relation to the weight ratio of MPP/XPM-1000 (Table IX). A similar situation was seen in EVA/MPP/XPM-1000/DIPE, EVA/MPP/PESBPP, and EVA/MPP/PPA (Formulations 21–23). At the constant ratio of MPP/XPM-1000, higher R_{520} more generally resulted in higher R_{final} , which might suggest that all temporary residues underwent similar thermal decomposition to the final residues.

It should be pointed out that the flame retardancy of the intumescent formulations was *not* well correlated with the residue yield. Van Krevelen's equation³⁵ relating the OI and TGA residue yield does not work well when applied to the phosphorus-containing systems of the present study; higher residue yield in our cases did not give higher OI and UL 94 ratings. As indicated in both Table I and Table IX, at MPP/XPM-1000 loading of 60 phr, the highest residue yield was observed in Formulation 10, but the best flame retardancy was with Formulation 8. Similarly, Formulation 22 had the best flame retardancy but not the highest residue yield.

Another unusual phenomenon in Tables I and IV was that the flame retardancy was not closely related

to the phosphorus content in the formulation. The highest phosphorus content did not lead to the highest OI and UL 94 ratings. A representative example was Formulation 1 which had the highest phosphorus content in the series of Formulations 1–4, but not the best flame retardancy.

It is often reported that the flame retardancy of a phosphorus-containing formulation is improved by increasing the phosphorus content. Our results are not wholly consistent with such a relationship, thus indicating that the phosphorus content may not be the only factor controlling the flame retardancy of our phosphorus-containing formulations.

The fact that neither the TGA residue yield nor the phosphorus content could explain the variation of the flame retardancy of the EVA formulations with different ratios of MPP/XPM-1000 or MP/XPM-1000 caused us to look more carefully for other factors governing the flame retardancy. The combustion behavior and rate of char formation were among these factors being considered in our next effort to explain the flame retardancy of intumescent formulations.

Attempts to Correlate Char Yield and Char Formation Rate of Intumescent Formulations to Flame-retardant Performance

Combustion experiments under controlled conditions were performed with a Stanton Redcroft FTA flammability unit used to measure the OI. We be-

Table IX TGA Residues of Intumescent Formulations

Formulation	R ₅₂₀ ^a (%)	R _{final} ^b (%)	Formulation	R ₅₂₀ ^a (%)	R _{final} ^b (%)
1	19.0	10.8	8	16.0	12.5
2	18.6	10.6	9	14.8	9.7
3	20.5	14.9	10	17.6	12.5
4	20.0	18.3	21	19.0	14.9
5	27.5	19.1	22	20.0	17.2
6	14.0	8.9	23	18.0	15.3
7	16.8	11.6			

For information on the formulations, see Tables I and VI.

^a R₅₂₀ = residue at temperature 520°C.

^b R_{final} = final residue.

lieved that both TGA and UL 94 test methods were not suitable for such studies because TGA even under an oxygen-enriched atmosphere does not represent a normal burning situation, while the UL 94 test does not result in steady-state burning; many of our formulations exhibited a V-0 rating in the UL 94 test, which means that they were self-extinguishing with a burning time of 10 s or less. Thus, the UL 94 method could not produce sufficient char for further study, and the char it does produce is not made under steady-state burning conditions.

We devised a simple combustion analysis method which seems capable of giving two interesting factors: char-forming rate (CFR) and char yield (CY) under more or less steady-state burning conditions, albeit at differing percent oxygen. The validity of this method rests on the surprising finding that the burning rate in the oxygen percent region up to about 3% above the OI was not much affected by percent oxygen. Whether this result is peculiar to just the present formulations or whether it has any further validity remains to be determined. The procedure

Table X Effect of Oxygen Concentration (%) on CFR and CY of Formulation 8

Oxygen %	Percentage (%) Above OI	CFR (mg/min)	CY (%)
27.8	0.3	38	22.3
28.5	1.0	38	20.0
29.5	2.0	38	18.9
30.5	3.0	38	17.4
31.5	4.0	34	15.2
32.5	5.0	36	16.5

For information on Formulation 8, see Table I.

of our combustion method to determine CFR and CY is detailed in the Experimental section.

Effect of Oxygen Concentration on the Char-forming Rate (CFR) and Char Yield (CY)

The combustion analysis was carried out at an oxygen concentration sufficient to support the complete burning. As a preliminary step to standardizing our combustion analysis method, the effect of oxygen concentration on the combustion was studied with Formulation 8 which has an OI of 27.5%, a V0 rating in UL 94 at both $\frac{1}{8}$ in. and $\frac{1}{16}$ in., and a TGA residue of 16.0%. Data in Table X showed that the char-forming rate (CFR) was not affected at the oxygen concentration from 27.8 to 30.5% (0.3–3.0% above the OI). The oxygen concentration of 31.5% reduced CFR. The char yield (CY) decreased with the increase of the oxygen concentration. Combustion at 27.8–31.5% oxygen was found to effectively convert the test specimen to char, leaving nearly no unburned sample. At a still higher oxygen concentration, 32.5%, the burning caused some drip of the molten specimen (nonflaming drip), which was considered likely to cause unreliable results for CFR and CY.

The results of CFR and CY were reproducible. The standard deviations of four runs at 30.5% oxygen were 1 mg/min for CFR and 0.7% for CY. Moreover, the specimen size from 200 to 300 mg did not seem to affect CFR and CY. Therefore, our method of combustion analysis appears to be suitable for its intended purpose. Because CFR was constant up to 30.5% oxygen (3% above the OI) and the combustion was complete, we chose an oxygen concentration of 3% above the OI for further studies on other formulations.

Table XI CFR and CY of Intumescent EVA Formulations

Formulation	CFR (mg/min)	CY (%)	Formulation	CFR (mg/min)	CY (%)
1	0	0	13	36	15.2
2	51	20.1	14	29	14.2
3	38	17.1	15	28	14.0
4	35	19.0	16	28	12.1
5	33	18.7	17	25	11.7
6	27	14.3	18	31	15.0
7	31	15.5	19	28	11.4
8	37	17.0	20	No char	
9	33	14.7	21	35	14.4
10	28	17.2	22	38	16.4
11	34	16.8	23	30	15.8
12	34	17.1			

For information on the formulations, see Tables I, IV, V, and VI.

Effect of Composition of Intumescent Formulations on CFR and CY

The method of combustion analysis described above was further applied to our intumescent formulations. All measurements were done at an oxygen concentration of 3% above the OI. Table XI summarizes the CFR and CY results from various intumescent formulations.

Formulations 1-5: No char could be collected for Formulation 1, since it did not form intumescent char or self-supported char. The total loading of MPP and XPM-1000 in this series was 90 phr (47.4 wt %) or above. The best flame-retardancy results were found with Formulation 2 (Table I) which also gave the highest CFR. Formulation 3 had the second best flame retardancy and second highest CFR. Formulation 5 had the highest loading of the flame-retardant additive (118 phr), but the lowest CFR, which might be the reason of its poor flame retardancy. CY values in the series were not conclusive and could not be used to explain the differences in flame retardancy.

Formulations 6-10: The total loading of MPP/XPM-1000 was 60 phr (37.5 wt %). The highest CFR was observed with Formulation 8 which also showed the best flame retardancy in the series (Table I). CFR seemed to be well correlated with the OI and UL 94 ratings of the formulations. Again, the highest CY did not necessarily result in the best flame retardancy.

Formulations 11-16: These formulations contained MP/XPM-1000 at a total loading of 60 phr. The first three formulations seemed to have almost the same CFR, and these formulations gave very

similar flame retardancy in terms of OI and UL 94 ratings (Table IV). Formulation 13 appeared to have slightly higher CFR and higher OI than those of the other formulations.

Formulations 17-19: The combination of XPM-1000 and different phosphates was used in this series. Formulation 17 had the best flame retardancy but the lowest CFR among the three formulations, which was an exception. Previously, we observed that at the same loading and the same ratio of the flame retardants the choice of the phosphate in the combination of phosphate/XPM-1000 affected the flame retardancy of EVA in the order of MPP > MP \approx DMP > BPEPC > MAP. This order appears to correlate well with the CFR (see Formulations 8, 12, 17, 18, and 19) with the exception of Formulation 17.

Formulations 20-23: Formulation 20 did not generate char during the burning. The CFR order was Formulation 22 > Formulation 21 > Formulation 23, which was exactly the same as their order in regard to flame retardancy (Table VI).

Figure 6 shows an almost linear relationship between CFR and the total loading (phr) of MPP and XPM-1000 at 1 : 2 ratio of MPP/XPM-1000 in EVA. Therefore, the flame retardancy of our intumescent formulations, characterized by OI and UL 94 ratings, correlated best with CFR. The flame retardancy was not correlated with either CY or TGA residue yield. CFR also may be used to explain the variation of the flame retardancy that resulted from different compositions of phosphate/XPM-1000 combinations. We believe that the faster the char is formed on the burning surface of a polymer sample during

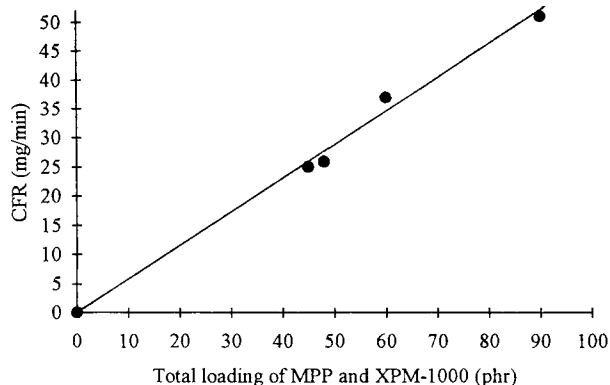


Figure 6 Effect of total loading (phr) of MPP and XPM-1000 on CFR. Weight ratio of MPP/XPM-1000 was 1 : 2.

the combustion of it the higher the likelihood that the fire propagation will be stopped and the better flame retardancy thus obtained. A low char yield leads to an insufficient amount of char. However, a coherent and effective char barrier may never be generated to cover the burning surface if the char formation is slow and cannot compete with the burning process. The slow char formation may result in continuous burning even if the final char yield is high. Thus, we suggest that the char-forming rate (CFR) is more important than is the char yield (either from the combustion analysis or TGA) in determining the flame retardancy of our intumescent formulations. We do not intend to imply that the char-forming rate (CFR) is necessarily a dominant variable in all char-forming polymers; indeed, from one published study on wood, it was found that the char-forming rate (measured under nonflaming conditions) was increased by some flame-retardant additives and decreased by others.³⁷ We suspect that in intumescent systems, where the char is the main defense against burning, an increase in char formation rate is likely to correlate with improved flame retardancy.

CONCLUSIONS

Our results provide a new example of synergism between two phosphorus-containing flame-retardant additives. These halogen-free intumescent flame-retardant formulations of polyolefins are based on a synergistic combination of a melamine phosphate and a cyclic phosphonate ester and may be useful in cable jacket and insulation applications. The formulations showed optimum flame retardancy by two

small-scale tests, namely, the oxygen index and the UL 94 vertical burning test, at a certain ratio of the two ingredients.

Some evidence was developed pointing to chemical interaction of the phosphorus and nitrogen components of the system to form a nonvolatile phosphorus acid (probably a polyphosphoric acid) with some P—N bonds. In the present study, the char-forming rate, as measured by a tentative method under flaming conditions, seemed to correlate better to flame retardancy than did the char yield, and we suggest that the char-forming rate may be an important factor in flame retardancy, deserving of further study.

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DISCLAIMER

The small-scale flammability tests performed in this research do not necessarily reflect the hazard of a real fire.

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