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STUDIES OF THE EFFECTS OF PHOSPHORUS–NITROGEN–BROMINE SYSTEMS ON THE COMBUSTION OF SOME THERMOPLASTIC POLYMERS

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Abstract—A study has been made of red phosphorus (P) (or phosphates) and nitrogen compounds as flame retardants/smoke suppressants for thermoplastic polymers [plasticized poly(vinyl chloride), polystyrene, high density polyethylene and poly(methyl methacrylate)], both on their own and in combination with a brominated flame retardant (decabromobiphenyl). The techniques used were limiting oxygen index, the Michigan smoke chamber, thermoanalysis and i.r. spectrometric analysis. The nitrogen compounds used serve as mild flame retardants but perhaps their most important effect is to decrease smoke formation from the polymers and in particular to nullify the large increase in smoke levels caused by the incorporation of P. In many systems, there is flame retardance and smoke suppression synergism, since the combination of P and nitrogen compounds decreases flammability and specific smoke formation to a greater extent than the additive effects of the individual materials. The nitrogen compounds appear to act by extending considerably the temperature range over which the system decomposes, and thus decreasing the average rate of production of volatiles. They also catalyse oxidation of P, which is the flame retardant mechanism for this material. The nitrogen compounds also break down to yield inert gases, which cause dilution of the gas mixture to outside the flammable range. All nitrogen compounds used, except benzotriazole, give large quantities of ammonia on decomposition; benzotriazole is the only nitrogen compound used which does not reduce flammability. In conclusion, it is considered that the disadvantages of P as a flame retardant outweigh its advantages for the systems studied.

INTRODUCTION

Red phosphorus (P) has been shown to be a potentially useful additive for decreasing the flammability of thermoplastic polymers. Some of the greatest success has been obtained with nitrogen-containing polymers. This material was first employed as an additive for polyurethanes [1] and also later for an acrylonitrile–butadiene–styrene (ABS) terpolymer [2]. Work has also been published describing its use in nylon systems [3], which is its most important commercial use [4]. More extensive work exists describing its application to polymers containing oxygen [5–11] and to styrenics [12–13]. It has further been stated that halogens can be beneficial in this respect [9, 14]. More recently, studies were made of the effects of P on the combustion of plasticized poly(vinyl chloride) (PVC) and of polystyrene (PS) [15]. This work involved the use of three additives, viz. P, a nitrogen-containing compound [melamine (MEL)] and a bromine-containing compound [decabromobiphenyl (DBB)]. It has shown that the simultaneous presence of nitrogen is necessary to ensure that any decrease in flammability is not accompanied by a large increase in the amount of smoke obscuration generated.

The present paper describes an extension of the work on plasticized PVC and PS, to include the effects of nitrogen compounds in addition to MEL and phosphorus esters as well as phosphorus in elemental form. Furthermore, studies have been made of the effects of these same additive systems on the combustion behaviour of two other polymers, viz. poly(methyl methacrylate) (PMMA) and high density polyethylene (HDPE), which normally give rise to relatively low levels of smoke obscuration.

EXPERIMENTAL PROCEDURES

The sources of most of the materials and the procedures used have already been described [15], but some further explanation will be given here.

Polymers

The plasticized PVC was prepared by mixing powdered resin (Corvic, donated by ICI) with di-2-ethylhexylphthalate (BDH) at a 40 phr level. Pelleted Carinex resin was the PS used (donated by Shell, U.K.). The PMMA was also provided by ICI (Diakon acrylic resin) and the HDPE (Solvay, HD Eltex B 4002) was supplied by Produits Chimiques Ugine Kuhlmann (PCUK).

Additives

Red P (Exolit 405, containing 98.6% P and a small amount of di-2-ethylhexylphthalate, donated by Hoechst U.K., Ltd), DBB (Adine 102, donated by PCUK), MEL (donated by ICI), urea (UR), guanidine carbonate (GC), barbituric acid (BA), benzotriazole (BT), triethyl phosphate (TEP) (all Aldrich products) and tritolyl phosphate (TTP, BDH).

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Table 1. Quantitative assessment of phosphorus–bromine–nitrogen

Polymer:	PVC	PVC	PVC	PVC	PVC	PVC	PS
Additives:	P/DBB/MEL	P/DBB/UR	P/DBB/GC	P/DBB/BA	P/DBB/BT	TEP/DBB/MEL	P/DBB/MEL
Coeff. order:	Cubic (F)	Cubic (F)	Cubic (F)	—	—	Quadratic	Cubic (F)
RMS difference:	0.77	0.83	0.89	—	—	0.41	0.49
Effect. coeff.							
P	−9	−14	−11	−12	−10	3	16
Br	25	28	25	—	—	26	27
N	10	4	22	18	6	10	8
Synerg. coeff.							
P–Br	−3	−24	15	—	—	−23	12
P–N	100	136	171	160	133	−24	168
Br–N	31	−105	−61	—	—	−24	−35
P–Br–N	1077	270	492	—	—	—	428

Coeff. order, order of best fit coefficients; cubic (F), full cubic; cubic (R), reduced cubic.
RMS difference, root mean square difference.
Effect. coeff., effectiveness coefficient.
Synerg. coeff., synergism coefficient.

Procedures

The flammability of the polymer systems was determined by measuring ease of extinction via the limiting oxygen index (LOI) using Stanton–Redcroft equipment, designed to meet ASTM D2863 test requirements.

Smoke obscuration was measured by means of a Michigan-type dynamic chamber, as described earlier [16]. This consists of employing the same candles of polymers used for the LOI test and igniting them, for 20 sec, at an oxygen concentration 1% higher than that of the LOI of the system (or in air, if the LOI is < 19.9) and leaving them to burn for 3 min. A smoke chamber (dimensions: 62 × 122 × 61 cm), containing a light source and a photocell (with a horizontal light obscuration path of 122 cm, measuring the transmitted light, T%), was installed above the exhaust of the LOI unit and the smoke was drawn through it and into a vent above it. The instrument constant [$V/(LA)$: the smoke chamber volume divided by the product of light path length and exposed polymer sample area] was determined, by calibration, to be 1891. The specific optical density at minimum transmission is reported, calculated as the product of $\{2 - \log_{10}(T\%)\}$ and the instrument constant. This technique measures the maximum smoke obscuration resulting from complete sample destruction, and no attempt was made to compensate for lower flammability of samples.

It is important to state that both of these techniques have been found to be seriously flawed with respect to their predictability in terms of full scale fire hazard, particularly because they cannot assess the effects of the large heat fluxes associated with real fires. They cannot, thus, be used to compare the fire performance of systems based on different polymers. Both techniques however, are very useful as screening tools to compare the effects of additives on the fire response characteristics of systems based on a specific individual polymer; they are used in this work in such a way.

Simultaneous thermoanalytical measurements (STA: TGA + DTA + DTG) were made using a Mettler Thermoanalyser II thermobalance, at a carrier flow rate of 60 cm^3/min, as described earlier [17].

In addition to the above techniques, the gaseous combustion products of some polymer-additive systems were analysed by i.r. spectrometry. A ceramic boat containing *ca* 1 g of sample was placed in a silica tube, which was heated at a rate of *ca* 6 deg/min in a horizontal tube furnace capable of reaching temperatures of up to 1000 K. The gaseous products were swept continuously through an i.r. gas cell, fitted with NaCl windows, by means of air or N_2 flowing at 100 cm^3/min. Spectra were recorded every 5 min, using a Perkin–Elmer Model 257 grating spectrometer.

Calculations

As in previous work [16, 18], the flammability and smoke density for polymer systems containing several additives are represented in the form of triangular diagrams. These were constructed by fitting the values of the LOI and maximum smoke density (D_s) determined for the systems concerned by a polynomial function of the composition coordinates. For quantitative assessment of the effects of additives on flammability and smoke formation, the same fitting program yields the "effectiveness coefficients" and "synergism coefficients", a concept introduced by Baldry [19]. These coefficients are calculated from the coefficients of the least squares fitting and represent the average contribution to the LOI or the D_s of the system of each additive or combination of additives over a specific composition range. Thus, for a single additive i, present in weight fraction x_i, the change in LOI (or in D_s) due to that additive is $k_i x_i$ (where k_i, the effectiveness coefficient of additive i, may be positive or negative depending on the type of effect resulting from the additive). Improved flame retardance results from higher LOI values and positive k_i values. Lower emission of smoke results from lower D_s values and negative k_i values.

For two additives, i and j, present in weight fractions x_i and x_j, respectively, the change in LOI (or in D_s) due to synergism is $k_{ij} x_i x_j$, where k_{ij} is the synergism coefficient for the interaction of additives i and j. If the additives are synergists as flame retardants (FR), their synergism coefficients will be positive for LOI; if they are synergists as smoke suppressants, their synergism coefficients will be negative for D_s. If the synergism coefficients have the opposite signs, that is an example of antagonism.

The dimensions of the effectiveness and synergism coefficients are given by those of the magnitudes measured, both of which are non-dimensional in this case. Thus, effectiveness coefficients will have units of LOI (or D_s)/(weight fraction) and synergism coefficients units of LOI (or D_s)/[(weight fraction) squared].

In all binary and ternary additive systems used, the maximum loadings were the same for each additive, at 30 wt%, so that only equilateral triangles are used to express the results. For ease of interpretation and comparison of one triangular diagram with another, the intervals of the contour lines in all diagrams are the same, namely 0.5 LOI units for flammability plots and 200 D_s units for smoke obscuration plots.

RESULTS

Flammability and smoke formation

As explained in the preceding section, the flammability and smoke obscuration results are represented in the form of triangular diagrams. For each system, between 35 and 45 compositions were studied, spread over the ranges bounded by the vertices. For all binary additive systems, the vertices corresponded to 100 wt% of polymer substrate and additive systems on the flammability of some thermoplastic polymers

PS	PS	PS	PS	PS	PMMA	PMMA	HDPE	HDPE
P/DBB/UR	P/DBB/GC	P/DBB/BA	P/DBB/BT	TTP/DBB/MEL	P/DBB/MEL	P/DBB/BT	P/DBB/MEL	P/DBB/BT
Cubic (F)	Quartic	—	—	Quadratic	Cubic (R)	—	Cubic (F)	—
0.54	0.63	—	—	0.43	0.44	—	0.51	—
Effect. coeff.								
16	15	18	11	20	20	14	5	3
26	27	—	—	26	11	—	17	—
7	10	8	8	12	14	8	11	5
Synerg. coeff.								
22	27	—	—	34	34	—	103	—
158	171	160	138	−59	93	178	157	222
3	49	—	—	−55	−11	—	−24	—
−488	209	—	—	—	823	—	−1060	—

70 wt% of substrate + 30 wt% of each additive. For the ternary additive systems, a constant total additive loading of 30 wt% was used, with each vertex representing 70 wt% of substrate + 30 wt% of one of the additives.

Tables 1 and 2 show the effectiveness coefficients and synergism coefficients respectively for the effects of various ternary combinations of additives on the flammability and smoke production tendency of all the polymers studied. Both the effectiveness and the synergism coefficients are tabulated on the basis of the key chemical element (viz. P, Br or N) contained in the additive. The effectiveness coefficients presented in these tables are those calculated for the individual additives within the combined additive system.

Plasticized PVC

It has already been shown [15] that red phosphorus, on its own, increases both the flammability (slightly) and the smoke production tendency of plasticized PVC but that, as the Br/P ratio increases, the LOI increases and the D_s decreases [15]. The following paragraphs will exemplify the use of the data in Tables 1 and 2, with one system.

The effectiveness coefficients for Br (as DBB) in the plasticized PVC/DBB/P/MEL system are 25 (for LOI) and 1580 (for D_s), corresponding to an LOI increase of 7.5 units and a D_s increase of 470 units the base compound. MEL itself has little effect on flammability (a coefficient of +10, similar in magnitude to that of P, but in an opposite direction), but counteracts the large detrimental effects of P on smoke release to return to the levels characteristic of plasticized PVC on its own (coefficient of −650). Significant synergism is observed between P and MEL, both in terms of improved flame retardance (+100; an increase in LOI of >2 units) and decreased smoke formation (−63,510; a decrease in D_s of *ca* 1430 units). In fact, all three additives show positive binary synergism in terms of both flammability and smoke formation (except for the mildly antagonistic P–Br system at −3). The ternary additive system is synergistic in flammability terms (coefficient of 1077) but antagonistic in smoke production tendency (coefficient of 238,890).

Figure 1 shows a triangular diagram for plasticized PVC containing (P + DBB + UR). The effectiveness coefficients of the individual components (for flammability) are quite similar to those found for the plasticized PVC/P/DBB/MEL system. In terms of synergism coefficients however there are some differences: although there is still good synergism between P and N (+136, corresponding to an increase in LOI of *ca* 3.1 units) and minor antagonism between P and Br, there is now antagonism between Br and N (DBB and urea; coefficient of −105, equivalent to 2.4 LOI units) and the ternary additive system has much less effective synergism.

GC is a better flame retardant for plasticized PVC, on its own, than either MEL or urea, and its effectiveness coefficient is comparable with that of DBB (22 vs 25). The P/DBB/GC additive system shows similar features to those of the two other systems just described, as regards the individual effects, the positive P–N synergism and the positive

Table 2. Quantitative assessment of the effects of phosphorus–bromine–nitrogen additive systems on smoke formation from some thermoplastic polymers

Polymer:	PVC		PS			PMMA	HDPE
Additive system:	P/DBB/MEL	TEP/DBB/MEL	P/DBB/MEL	P/DBB/UR	TTP/DBB/MEL	P/DBB/MEL	P/DBB/MEL
Coefficient order:	Full cubic	Full cubic	Quadratic	Red. cubic	Full cubic	Quadratic	Full cubic
RMS difference:	192	187	184	168	185	127	64
Effect. coeff.							
P	10,710	2600	3870	1920	−710	15,250	3040
Br	1580	2490	1520	1550	1890	1740	2030
N	−650	−760	−1130	−1940	−990	−50	−190
Synerg. coeff.							
P–Br	−45,970	44,640	−26,870	−11,320	−8880	−66,430	−5410
P–N	−63,510	−3950	19,340	14,460	7760	−55,390	−16,080
Br–N	−12,280	−21,030	1360	−3610	1570	1260	2920
P–Br–N	238,890	−277,170	—	−338,460	52,700	—	84,110

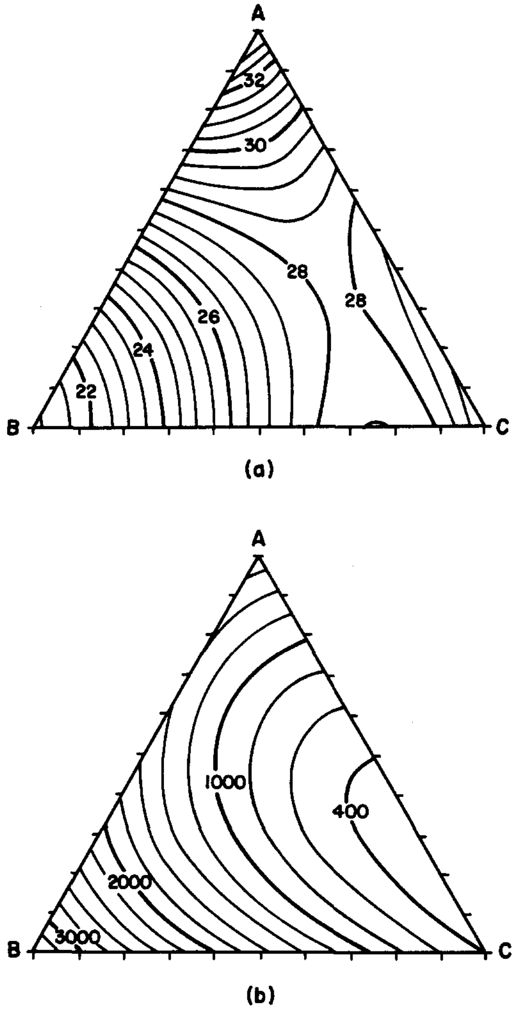


Fig. 1. The effects of P, DBB and UR on (a) the LOI and (b) D_s values for plasticized PVC. A, 70 wt% PVC + 30 wt% DBB; B, 70 wt% PVC + 30 wt% P; C, 70 wt% PVC + 30 wt% UR.

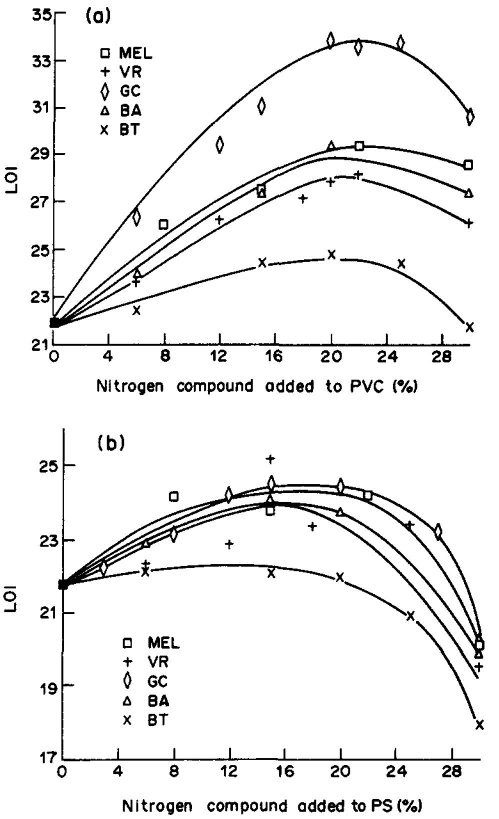


Fig. 2. The effects of 30 wt% of mixtures of P and a nitrogen compound on the LOI of (a) plasticized PVC and (b) PS.

ternary synergism. It resembles the P/DBB/UR system in Br–N antagonism but differs from it in positive P–BR synergism.

Figure 2 shows the large effect of GC, in combination with P, in decreasing the flammability of plasticized PVC. This is followed by very similar levels of effects for MEL, UR or BA, and by much smaller effects for BT. Moreover, there is clearly good flame retardant synergism for the former four materials, while the synergism is very small for BT and P.

Unlike P (in all the PVC systems studied), TEP does not increase the flammability of PVC nor does it significantly enhance smoke formation. The near linearity of the LOI (flammability) plots for ternary additive systems [Fig. 3(a)] indicates that there is no appreciable fire-retardant interaction between the various additives. If anything, the binary interactions are all antagonistic. DBB is the only individual constituent which reduces the flammability of these systems by a reasonable margin.

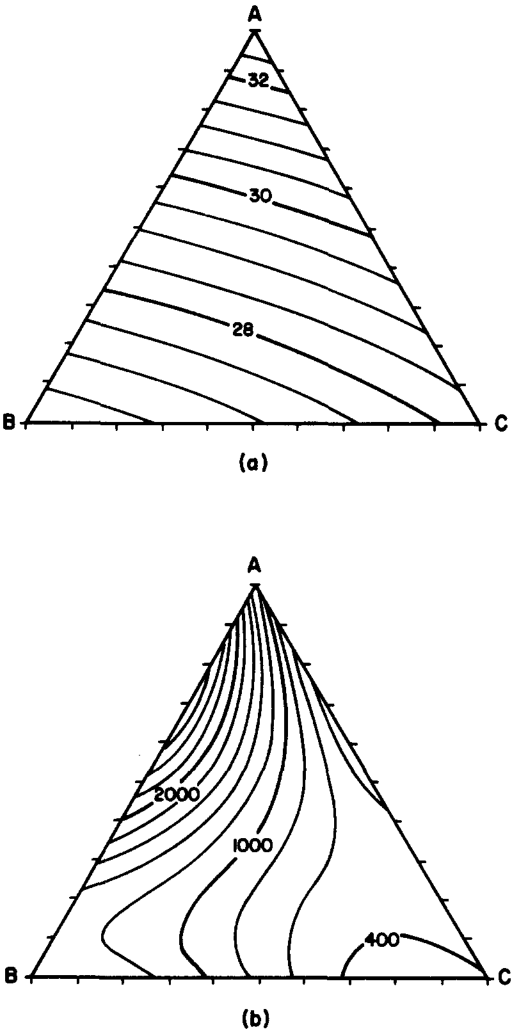
The highest smoke density in this case is found for systems along the TEP–DBB axis [Fig. 3(b)] and the interaction here is antagonistic: synergism coefficient of 44,640, corresponding to an increase in D_s of *ca* 1000 units. Although only MEL shows a mildly favourable effectiveness coefficient, most synergism coefficients are negative, indicating smoke suppression.

Polystyrene

P, on its own, slightly decreases the flammability of PS, but greatly enhances smoke formation. There is a clear flame-retardant synergism between P and all the nitrogen-containing compounds used (MEL, UR, GC, BA and BT): the P–N synergism coefficients range between 138 and 171. Again, DBB is the most effective individual FR additive. As regards smoke formation, the nitrogen compounds (MEL and UR) are effective smoke suppressants as is the P–DBB system (leading to a decrease in 610 D_s units), while P–N interaction increases smoke by *ca* 440 units.

Figure 2 shows how much less effective the P–N combined systems are in raising the LOI of PS than they are for plasticized PVC.

Overall, the effects of UR are very similar to those of MEL, on flammability and on smoke formation (Tables 1 and 2). This is also true for GC, although the results reported only address flammability (see Fig. 4 and Table 1). Both the FR effectiveness coefficient for GC and the ternary FR synergism coefficients are somewhat smaller in PS than in plasticized PVC, but the differences involved are small.



(a)

(b)

Fig. 3. The effects of TEP, DBB and MEL on the (a) LOI and (b) D_s values (b) for plasticized PVC. A, 70 wt% PVC + 30 wt% DBB; B, 70 wt% PVC + 30 wt% TEP; C, 70 wt% PVC + 30 wt% MEL.

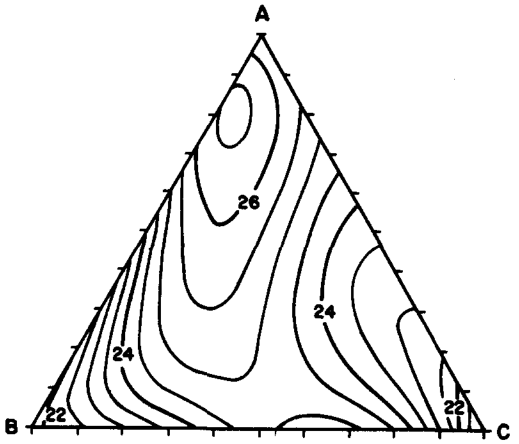
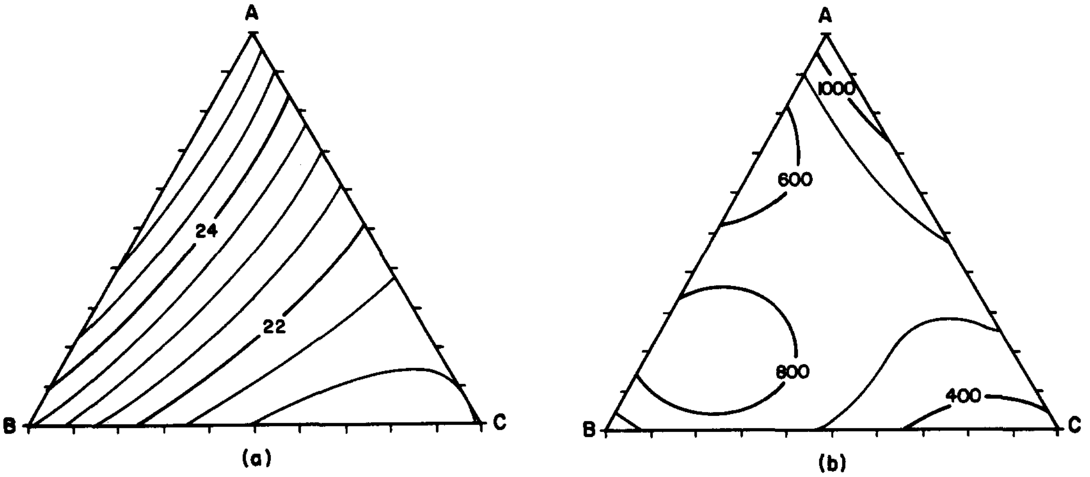


Fig. 4. The effects of P, DBB and GC on the LOI values for PS. A, 70 wt% PS + 30 wt% DBB; B, 70 wt% PS + 30 wt% P; C, 70 wt% PS + 30 wt% GC.

TTP shows some favourable individual effects as both a flame retardant and a smoke suppressant for PS. There is also some good synergism with DBB in both capacities, so that a relatively low smoke density is found on the TTP–DBB axis (Fig. 5). All other interactions are either very small or antagonistic. Comparison of results in Table 1 can be confirmed by analysis of Figs 3 and 5: they show that TTP is more effective in reducing the flammability of PS than TEP is for plasticized PVC.

Poly(methyl methacrylate)

The effectiveness of P as a flame retardant for PMMA (coefficient of 20) is slightly higher than for PS and much higher than for PVC (where it was detrimental). DBB is a less useful flame retardant for PMMA than for PVC or PS. However, in this case there is a fairly high P–Br synergism coefficient (103, equivalent to 2.3 LOI units), which is very different from the effects on the other two polymers, where synergism was either very mild or even become antagonism. The P–N interaction is also synergistic



(a) (b)

Fig. 5. The effects of TTP, DBB and MEL on the (a) LOI and (b) D_s values for PS. A, 70 wt% PS + 30 wt% DBB; B, 70 wt% PS + 30 wt% TTP; C, 70 wt% PS + 30 wt% MEL.

(coefficient of 93, corresponding to 2.1 LOI units, for MEL, and of 178 for BT, corresponding to 4 LOI units) but less so than in the case of the other polymers. The specific smoke formation tendency of PMMA (per unit mass burnt) is rather low, partially due to the oxygen in the ester group of its molecular structure. The addition of P, however, rapidly increases the smoke production tendency as the level of P increases (a coefficient of 15,250, equivalent to an increase of *ca* 4580 D_s units). The P–Br and P–N interactions, on the other hand, show synergism as smoke suppressants with coefficients of −66,430 and −55,390 (corresponding to decreases in D_s of 1500 and 2500 units respectively).

In the PMMA/P/DBB/BT system, there is good P–N flame-retardant synergism, similar to that found for P–N in the case of P.

High density polyethylene

P is not effective in reducing the flammability of HDPE and it enhances smoke formation, although perhaps not to as great an extent as with the other polymers studied. High LOI values can be obtained by using high loadings of DBB and there is evidence of good FR synergism between P and N, both for MEL and for BT (coefficients of 157 and 222 respectively). However, even the optimum combination increases the LOI by only six units and the ternary additive combination (P/DBB/MEL) is antagonistic (FR synergism coefficient of −1060).

Overall

Table 3 summarizes the flammability and smoke results by showing the individual effects of 30 wt% of each additive in changing the LOI and the maximum D_s of the various polymers. It can be seen that P decreases the flammability of all polymers except plasticized PVC but drastically enhances smoke formation in every case. DBB similarly always acts as a flame retardant (usually more effectively than P) and also increases smoke formation (but less so than P). The nitrogen compounds, other than benzotriazole, act as mild flame retardants and as reasonably efficient smoke suppressants, at least for PVC and PS. GC is a fairly efficient FR for plasticized PVC. TTP is a very efficient flame retardant for PS and has some reasonable smoke suppressant activity. On the other hand, TEP is much less efficient as a flame retardant for PVC and increases smoke formation.

Table 3 shows also that there is no simple relationship between the effects of nitrogen-containing additives on combustion behaviour and their molecular weight or their nitrogen content.

The nitrogen-containing additives also show significant interactions with the other additives in various systems. The P–N interactions, in particular, are generally synergistic as flame retardants and as smoke suppressants (except for PS on smoke, where there is antagonism).

Thermoanalytical results

Attempts were made to elucidate the mode of action of the various nitrogen compounds by studying their behaviour when they are heated both in the absence and presence of the various polymers and of P. This technique has been used effectively [15].

When PVC is heated, the first (and main) decomposition stage corresponds to dehydrochlorination. In the case of plasticized PVC, this first stage may be more complex, dehydrochlorination being accompanied by the volatilization of the plasticizer, either unchanged or decomposed [20]. The temperature range for PVC dehydrochlorination is also strongly dependent on the composition of the formulation, and principally on the level of stabilizers present.

The plasticized PVC used here, containing no stabilizers, has its main decomposition stage in the range 420 to 620 K. If MEL, UR or GC is present in the polymer, weight loss starts at temperatures 30–50 deg lower than usual and continues to considerably higher temperatures than in the absence of these compounds (Table 4). In other words, the nitrogen compounds significantly extend the temperature range over which PVC decomposition takes place.

The real thermal stability is given by the temperature at which 1% of the weight has been lost, which is, generally, higher than the minimum thermal decomposition temperature by *ca* 30 deg or more (e.g. Table 4).

P, when heated on its own, first exhibits a weight gain of *ca* 30% (due to uptake of oxygen) between 450 and 690 K, but this is followed by a very exothermic weight loss stage as the resulting phosphorus oxides volatilize. However, oxidation of P, as indicated by this initial gain in weight, seems to be largely inhibited when P is incorporated in plasticized PVC. Table 4 shows that the simultaneous presence of nitrogen compounds has little effect on the magnitude of this (small) weight gain.

In contrast, it has already been shown [15] that considerable oxidation of P takes place when it is incorporated in PS, so that the extent of weight gain

Table 3. The effects of 30 wt% of various additives on the flammability and smoke-producing tendency of some thermoplastic polymers

			Polymer							
			PVC		PS		PMMA		HDPE	
Additive	N-content (%)	Mol. wt	LOI	D_s	LOI	D_s	LOI	D_s	LOI	D_s
P	—	31	−2.7	3210	4.8	1160	6.0	4580	1.5	910
DBB	—	943	7.5	470	8.1	460	3.3	520	5.1	610
MEL	67	126	3.0	−200	2.4	−340	4.2	20	3.3	−60
UR	47	60	1.2	−190	2.1	−580	—	—	—	—
GC	47	180	6.6	—	3.0	—	—	—	—	—
BA	22	128	2.1	—	2.4	—	2.3	—	0.8	—
BT	35	119	−3.3	—	0.1	—	—	—	—	—
TEP	—	182	0.9	780	—	—	—	—	—	—
TTP	—	368	—	—	6.0	−210	—	—	—	—

Table 4. Thermal analysis of systems containing P plasticized PVC and a nitrogen compound

PVC (%)	100		70		70		70		70	70	70	70
P (%)								100	30	15	12	15
MEL (%)		100	30							15		
UR (%)				100	30						18	
GC (%)						100	30					15
Wt gain (%)								30.7	0.9	0.4	0.5	1.4
P gain (%)								30.7	3.0	2.7	4.2	9.3
1st loss (%)	66.4	94.9	49.0	59.0	28.7	56.4	13.5	69.3	49.5	47.8	15.5	6.7
T MR (K)	537	513	525	497	441	508	454	695	556	520	428	461
MR (%/min)	7.8	15.7	6.3	7.6	2.8	19.4	3.4	184	7.5	6.3	1.7	1.6
T_i (K)	421	494	416	411	369	453	406	451	431	406	375	408
$T_{1\%}$ (K)	458		481		411		430		460	446	406	445
T range (deg)	331	132	459	307	473	106	515	408	606	587	663	638
TL (%)	99.3	94.9	92.1	92.3	95.8	93.7	91.9	74.9	94.4	94.2	93.3	85.4

P gain (%), percentage of initial P that gains weight.
1st loss (%), first weight loss stage.
T MR (K), temperature at which the peak mass loss rate occurs.
MR (%/min), peak mass loss rate.
T_i (K), temperature of initial weight loss (or weight gain, for pure P).
$T_{1\%}$ (K), temperature at which 1% of weight has been lost.
T range (deg), temperature range over which weight change occurs.
TL (%), total weight loss.

of P is the same in the polymer matrix as outside it. The effect of nitrogen compounds on this weight gain is considerable: all three nitrogen compounds tested increase the extent of this oxidation [15] (Table 5).

Extensive oxidation of P also occurs when it is present in PMMA, which displays effects similar to those of PS, but only a relatively small weight gain is observed when HDPE is the supporting polymer (Table 5). In both cases, however, the co-presence of nitrogen compounds again increases the temperature range over which these polymers break down as well as enhancing the initial weight gain of P (Table 5).

When P is replaced by a phosphate ester, no weight gain stage is observed. In the presence of plasticized PVC, TEP appears to volatilize in two stages instead of one, when it is heated on its own (Table 6). Thermal analysis of PS containing 30 wt% TTP shows that most of this additive is volatilized before the polymer starts to decompose and thus has little effect on the main breakdown process (Table 6).

I.r. spectrometric analysis

I.r. analysis of the gaseous products formed when various additives and polymer-additive systems are heated shows that, in all polymer samples containing P, absorption peaks are seen in the region 930–1390 cm^{-1}. These peaks are similar to those found when P is heated in air or oxygen but are absent when P is heated in nitrogen. They are, therefore, almost certainly due to P—O and P=O stretching modes.

MEL, UR, GC and, to some extent, BA give copious amounts of ammonia, both when heated alone and when P is present. No ammonia is apparently formed from BT under similar conditions.

DISCUSSION

In general, nitrogen compounds serve as mild flame retardants but perhaps their more important effect is to decrease smoke formation from the polymers and in particular to nullify the large increase in smoke

Table 5. Thermal analysis of systems containing P, a polymer and a nitrogen compound

PS (%)	70	70	70	70				
PMMA (%)					70	70		
HDPE (%)							70	70
P (%)	30	15	15	15	30	15	30	15
MEL (%)		15				15		15
UR (%)			15					
GC (%)				15				
Wt gain (%)	8.0	11.0	6.5	8.4	9.5	6.1	0.4	14.0
P gain (%)	27	73	43	56	32	41	1.3	14
T_i (K)	687	691	669	669	669	673	766	781
$T_{1\%}$ (K)	534	484	416	460	602	510	572	510
First loss (%)	50.9	74.4	54.9	59.4	67.8	14.4	3.3	15.2
T MR (K)	685	643	653	657	671	648	673	670
MR (%/min)	17.4	4.4	6.8	6.1	9.1	9.7	14	15
T range (deg)	240	285	284	253	226	220	248	320
TL (%)	89.2	93.7	87.0	90.8	85.9	90.8	83.5	85.8

P gain (%), percentage of the initial P that gains weight.
First loss (%), first major weight loss stage.
T MR (K), temperature at which the peak mass loss rate occurs.
MR (%/min) peak mass loss rate.
T_i (K), temperature of initial weight loss (or weight gain, for pure P).
$T_{1\%}$ (K), temperature at which 1% of weight has been lost.
T range (deg), temperature range for weight loss occurring before gain.
TL (%), total weight loss.

Table 6. Thermal analysis of systems containing an organic phosphate, a polymer and MEL

PVC (%)		70	70			
PS (%)					70	70
TEP (%)	100	30	15			
TTP (%)				100	30	15
MEL (%)			15			15
T_i (K)	298	329	338	421	436	441
$T_{1\%}$ (K)		358	372		474	478
First wt loss						
Wt %	95.0	6.6	3.9	92.2	30.3	28.7
Second wt loss						
Wt %		62.2	60.3		59.4	61.0
T_i (K)		436	445		577	602
Third wt loss						
Wt %		7.6	7.3		3.0	2.9
T_i (K)		659	677		686	690
Fourth wt loss						
Wt %		15.0	19.5			
T_i (K)		759	763			
T MR (K)	396	537	531	555	669	665
Max rate (%/min)	16.2	8.9	7.6	13.1	6.0	6.8
TL (%)	95.0	91.4	91.0	92.2	92.7	92.6

T_i (K), temperature of initial weight loss for a stage or the whole.
$T_{1\%}$ (K), temperature at which 1% of weight has been lost.
First loss (%), first weight loss stage.
Second, third, fourth loss: corresponding weight loss stages.
Wt %, weight % lost in the corresponding stage.
T MR (K), temperature at which the peak mass loss rate occurs.
MR (%/min), peak mass loss rate.
TL (%), total weight loss.

levels caused by the incorporation of P. Thus, in many systems, there appears to be synergism of flame retardance, in the sense that the combination of P and the nitrogen compounds decreases flammability to an extent greater than the additive effects of the individual materials. There is also smoke-suppressant synergism, in the sense that the nitrogen compounds decrease the high additional levels of smoke per unit mass burnt attributable to the incorporation of P into the polymers.

One possible mode of action of the nitrogen compounds seems to be to extend considerably the temperature range over which the polymeric system decomposes (Table 4). This means that the average rate of production of combustible volatile products from the polymer is decreased and this would be expected to be tantamount to a reduction in flammability. However, the nitrogen compounds also appear to influence the oxidation of P, since they increase the level of weight gain, which is associated with P oxidation. The flame-retardant action of P appears to be related to this oxidation. If the oxidation of P is completely inhibited, simple species (such as P, P_2 and PO, which are believed to catalyse the recombination of free radicals responsible for flame propagation [21]) will not be formed. If, on the other hand, P is completely oxidized to P_2O_5 and other phosphorus oxides, which are inactive in interfering with combustion processes, again no flame retardant action will be exercised. Thus, the nitrogen compounds are apparently able to improve significantly the flame-retardant action of P in some of the polymeric systems studied (e.g. Figs 2–4).

Another mode of operation of nitrogen compounds is to break down to yield relatively large amounts of inert gases. These gases change the composition, and perhaps also the temperature, of the mixture of gaseous combustion products from the polymer, so that the resulting gas mixture is no longer capable of flame propagation. In this case, the flammability of the polymer and also its tendency to yield smoke on combustion will be decreased. In this context it is perhaps significant that all the nitrogen compounds used, except BT, give off quite large quantities of ammonia when they break down. Furthermore, BT is the only nitrogen compound which does not reduce flammability (Table 3). Certainly, other well-established flame retardants, such as ammonium salts and metal ammine complexes [22], owe their action, at least in part, to the fact that they release ammonia, which makes the gaseous decomposition products of the polymer less flammable as a result of dilution.

However, there appear to be no clear relationships between the effects of the various nitrogen compounds on flammability and on specific smoke production levels, which in effect differ relatively little from one another. There is no clear relationship either between the effects of nitrogen compounds and their molecular weight, N-content or other structural factors. It seems likely that several distinct modes of action are involved in the systems studied. It is also difficult to envisage chemical, or indeed other, explanations for the P–N synergistic effects observed and for their variation from one system to another.

The effects of the bromine compound used (DBB) have not been discussed at length in this paper, because they are well known and have been considered already [e.g. 2, 15]. The focus of this work was the effect of nitrogen and phosphorus compounds, and DBB was simply used as a base substrate, in combination with the polymers.

In conclusion, it must be admitted that the disadvantages of red P as a possible flame retardant additive probably outweigh its advantages and that, although nitrogen compounds are able to modify some of the worst effects of P, they are not able to do so to an extent which makes P a viable flame retardant for most polymeric systems.

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REFERENCES

1. H. Piechota. *J. cell. Plast.* **1,** 186 (1965).
2. J. R. A. Broadbent and M. M. Hirschler. *Eur. Polym. J.* **20,** 1087 (1984).
3. I. G. Williams. *IEE Conf. Publ., Dielectric Materials, Measurements and Applications*, Vol. 239, p. 205 (1984).
4. H. Staendeke. Red phosphorus—recent development for safe and efficient flame retardant applications. In *Dynamics of Current Developments in Fire Safety of Polymers, Joint SPE-FRCA Tech. Mtg*, March 20–23, 1988, Grenelefe, FL, pp. 32–46 (1988).
5. A. Granzow and J. F. Cannelongo. *J. appl. Polym. Sci.* **20,** 689 (1976).
6. A. Granzow, R. G. Ferrillo and A. Wilson. *J. appl. Polym. Sci.* **21,** 1687 (1977).
7. A. Granzow. *Acc. Chem. Res.* **11,** 177 (1978).
8. E. N. Peters. *J. appl. Polym. Sci.* **24,** 1757 (1979).
9. E. N. Peters. In *Flame Retardancy of Polymeric Materials*, Vol. 5 (edited by W. C. Kuryla and A. J. Papa), p. 113. Marcel Dekker, New York (1979).
10. A. Ballistreri, S. Foti, G. Montaudo, E. Scamporrino, A. Arnesano and S. Calgari. *Makromolek. Chem.* **182,** 1301 (1981).
11. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporrino, D. Vitalini and S. Calgari. *J. Polym. Sci., Polym. Chem.* **21,** 679 (1983).
12. F. J. Dany, J. Kandler, K. Frank and H. Weiden. *Can. Pat.* 846892 (to Knapsack A. G.) (1970).
13. F. J. Dany, K. Maier, P. Reidel and J. Wortmann. *Ger. Pat.* 2408488 (1975).
14. J. R. Bethea and C. F. Raley. *Res. Dissert.* **154,** 50 (1977).
15. C. F. Cullis, M. M. Hirschler and Q. M. Tao. *Eur. Polym. J.* **22,** 161 (1986).
16. J. D. Donaldson, J. Donbavand and M. M. Hirschler. *Eur. Polym. J.* **19,** 33 (1983).
17. M. M. Hirschler. *Eur. Polym. J.* **18,** 463 (1982).
18. F. K. Antia, P. J. Baldry and M. M. Hirschler. *Eur. Polym. J.* **18,** 167 (1982).
19. P. J. Baldry. Private communication.
20. M. M. Hirschler. *Eur. Polym. J.* **22,** 153 (1986).
21. J. W. Hastie. *J. Res. natn. Bur. Stand.* **77a,** 773 (1973).
22. J. J. Pitts. In *Flame Retardancy of Polymeric Materials*, Vol. 1 (edited by W. C. Kuryla and A. J. Papa), p. 133. Marcel Dekker, New York (1973).