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# THE EFFECT OF RED PHOSPHORUS ON THE FLAMMABILITY AND SMOKE-PRODUCING TENDENCY OF POLY(VINYL CHLORIDE) AND POLYSTYRENE

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**Abstract**—Studies have been made of the ways in which red phosphorus, both on its own and in conjunction with a bromine and a nitrogen compound, affects the combustion behaviour of two thermoplastic polymers. With plasticised poly(vinyl chloride) (PVC), red phosphorus by itself considerably increases both flammability and smoke formation; but in the additional presence of bromine and nitrogen, reasonably good flame retardance can be obtained with smoke levels not much higher than those from the base polymer. Thermal analysis of PVC–phosphorus mixtures shows that oxidation of the phosphorus is largely inhibited until all the chlorine has been lost. Microanalysis indicates that the major part of the phosphorus remains initially in the solid residue. Red phosphorus by itself has some flame-retardant action on polystyrene (PS) but greatly enhances smoke formation. Even with a bromine and a nitrogen compound present, it is difficult to obtain satisfactory flame retardance without an unacceptable increase in smoke levels. Thermoanalytical studies show that phosphorus incorporated into PS is readily oxidised; and microanalytical measurements indicate that the greater part of the phosphorus is volatilised. Thus, with PVC, where phosphorus acts principally in the condensed phase, the formation of reactive phosphoric and phosphonic acids is apparently inhibited; whereas with PS, the reduced species which cause flame quenching are largely converted to inactive phosphorus oxides.

## INTRODUCTION

Several types of phosphorus compound are effective in reducing the flammability of organic polymers, and both additive and reactive phosphorus-based flame retardants are commercially available. Additive compounds, such as phosphate esters, are the more widely used, especially for cellulosics, certain other oxygen-containing polymers and halogenated polymers such as poly(vinyl chloride); the commonest reactive flame retardants are the phosphorus-containing polyols which are incorporated into polyurethane foams.

The species directly responsible for inhibiting the combustion of organic polymers are not usually the flame retardants themselves but are formed from them as a result of various thermal or thermo-oxidative reactions. With cellulosics and other oxygen-containing polymers, phosphorus oxyacids, formed from the initial flame retardant, generally alter the mechanism of decomposition in the condensed phase, encouraging the formation of carbonaceous chars rather than volatile flammable compounds by causing catalytic dehydration, phosphorylation, cross-linking and finally skeletal rearrangement of the polymer [1]. With hydrocarbon-based thermoplastic polymers, phosphorus-containing flame retardants tend to act in the gas phase, possibly as a result of the formation of simple phosphorus species, such as $P^{\cdot}$, $P_2$ and $PO^{\cdot}$, which catalyse the recombination of the radicals responsible for flame propagation [2]:

$$^{\cdot}OH + P^{\cdot} \rightarrow PO^{\cdot} + H^{\cdot} \quad (1)$$

$$H^{\cdot} + PO^{\cdot} + M \rightarrow HPO + M \quad (2)$$

$$^{\cdot}OH + HPO \rightarrow H_2O + PO^{\cdot}. \quad (3)$$

Many of the common phosphorus-based flame retardants contain only a small proportion of phosphorus together with relatively large amounts of carbon, hydrogen and oxygen. Elemental phosphorus is thus clearly the form which is, in principle, capable of producing the highest possible yields of the reactive phosphorus species responsible for flame retardance. Red phosphorus was first employed to decrease the flammability of polyurethanes [3] and quite detailed mechanistic studies have lately been made of its action with other nitrogen-containing polymers, such as ABS terpolymer [4]. This same form of phosphorus has also been shown to exhibit useful flame-retardant properties when incorporated into oxygenated polymers [5–8]. With polyolefins, rather large concentrations of the element are required for good flame retardance, but the use of very high loadings of organic phosphorus compounds can sometimes be avoided if red phosphorus is employed instead [9]. However, for red phosphorus to be an effective flame retardant for a given polymer, it clearly must be converted, at the correct stage of the burning process, to species which will inhibit the combustion of the polymer in question.

The present paper describes studies of the effects of red phosphorus, both on its own and in conjunction with a bromine-containing and a nitrogen-containing additive (shown to enhance its flame-retardant action in other systems [4]), on the combustion of two common thermoplastics viz. poly(vinyl chloride) and polystyrene. Explanations are advanced to show why this form of elemental phosphorus is not in general a good flame retardant for either of these polymers.

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## EXPERIMENTAL

### *Materials*

*Polymers.* Poly(vinyl chloride) (PVC, Corvic), in powdered form, was kindly donated by Imperial Chemical Industries Ltd and polystyrene (PS, Carinex), in pelleted form, was generously provided by Shell U.K. Ltd.

*Additives.* Red phosphorus containing 98.6% P and a small concentration of di-2-ethylhexylphthalate (Exolit 405) was kindly donated by Hoechst U.K. Ltd; decabromobiphenyl (DBB, Adine 102) was generously supplied by Produits Chimiques Ugine Kuhlmann; melamine (MEL) was kindly provided by Imperial Chemical Industries Ltd and di-2-ethylhexylphthalate (DOP) was a BDH product.

*Procedures.* Plasticised PVC was prepared containing 40 phr of DOP. The techniques used for milling and pressing the polymer samples have already been described [10, 11]. With PVC-additive mixtures, the temperatures of the front and back rollers of the mill were set at 378 and 373 K respectively and with PS-additive mixtures the corresponding temperatures were 443 and 438 K. The resulting homogeneous crepes were pressed for 5 min at $5 \times 10^3$ kPa and 433 K (PVC) or 443 K (PS). Measurements of flammability involved determination of the limiting oxygen index (LOI) using Stanton–Redcroft equipment; maximum smoke density ($D_s$) was calculated from measurements of light obscuration in a Michigan-type dynamic chamber, details of which have already been given [11]. Thermal analyses were performed on a Mettler Thermoanalyser II thermobalance [12]; the conditions used were: sample size, *ca* 10 mg; air flow rate, 60 $cm^3$ $min^{-1}$; heating rate, 5 deg $min^{-1}$. Standard microanalytical techniques were used to determine the elemental composition of polymer-additive samples before and after various stages of heat treatment.

## RESULTS AND DISCUSSION

### *Poly(vinyl chloride)*

Red phosphorus on its own increased the flammability of PVC, the LOI of a sample containing 30% P being more than 3 units less than that of the polymer on its own; in addition, it caused marked enhancement of smoke formation (Table 1). Studies were therefore made of the effects, on the flammability and smoke-forming tendency of plasticised PVC, of phosphorus in conjunction with DBB and MEL at a total additive loading of 30 wt% and some results are shown in Table 1.

In general the LOI increased with increasing Br:P ratio, and melamine, while having little effect on flammability, tended to decrease the very large amounts of smoke liberated in the presence of phosphorus or bromine to the levels characteristic of the combustion of PVC on its own.

In view of the generally unfavourable effects of red phosphorus, studies were also made of the combustion behaviour of PVC containing mixtures of DBB + MEL only, with total additive loadings ranging from 0 to 30 wt%. The representative results in Table 2 show that, although the flammability is not quite so effectively reduced by DBB + MEL as by the best P + DBB + MEL mixtures (Table 1), a useful degree of flame retardance can nevertheless be obtained in the absence of phosphorus and that under appropriate conditions smoke formation can also be significantly decreased.

The results for both the ternary and the binary additive systems are also shown in the form of triangular diagrams. Their construction involves the fitting of the LOI and $D_s$ values determined for the system concerned by a polynomial function of the composition coordinates. Coefficients are calculated by a least-squares regression analysis procedure; polynomials of orders 1–4 are then tested and the quality of the fit is assessed as described elsewhere [13]. Figures 1 and 2 show triangular diagrams for the flammability of, and smoke production from, the ternary and binary additive systems respectively. It can be seen that both a significant degree of flame retardance (LOI, 33–34) and smoke formation no higher than that from the polymer alone can be obtained by the use of ternary mixtures containing relatively large proportions of DBB and MEL and smaller quantities of red phosphorus (Fig. 1). However, binary mixtures of DBB + MEL give results which are almost as satisfactory from the flammability point of view and considerably more so as regards smoke formation (Fig. 2).

Table 1. The effect of mixtures of P + DBB + MEL on the combustion of plasticised poly(vinyl chloride) at a total additive loading of 30%

| % P | % DBB | % MEL | LOI | $D_s$ |
|---|---|---|---|---|
| 30.0 | — | — | 21.8 | 3126 |
| 24.0 | 2.4 | 3.6 | 24.9 | 2295 |
| 21.0 | — | 9.0 | 26.0 | 1277 |
| 19.2 | 4.8 | 6.0 | 26.0 | 1085 |
| 15.0 | 10.0 | 5.0 | 28.1 | 1235 |
| 15.0 | 5.0 | 10.0 | 27.8 | 1050 |
| 12.6 | 14.4 | 3.0 | 29.0 | 1157 |
| 10.0 | 10.0 | 10.0 | 29.7 | 799 |
| 10.0 | 6.0 | 14.0 | 29.3 | 646 |
| 9.6 | 18.6 | 1.8 | 31.4 | 1157 |
| 8.0 | 2.0 | 20.0 | 29.8 | 646 |
| 6.0 | 6.0 | 18.0 | 31.0 | 708 |
| 5.0 | 20.0 | 5.0 | 31.5 | 1345 |
| 4.0 | 20.0 | 6.0 | 32.4 | 1157 |
| 3.0 | 23.4 | 3.6 | 33.0 | 1085 |
| 2.5 | 20.0 | 7.5 | 33.5 | 1052 |
| 2.4 | 25.8 | 1.8 | 33.9 | 1176 |

Plasticised PVC: LOI, 25.2; $D_s$, 569.

It is possible to obtain information regarding the fate of additives when they are heated both in the absence and presence of a polymer from thermoanalytical [14] and microanalytical [15] measurements. Table 3 shows some thermoanalytical data for the main weight loss and weight gain stages during the heating of PVC, red phosphorus and some PVC–additive mixtures. At first sight, one of the most striking features is the fact that the relatively large weight gain found for phosphorus on its own (undoubtedly attributable to its oxidation to phosphorus oxides) is almost completely absent in all systems also containing PVC. The first (and main) weight loss stage for this polymer corresponds principally to the

Table 2. The effect of mixtures of DBB + MEL on the combustion of plasticised poly(vinyl chloride) at various total additive loadings

| % PVC | % DBB | % MEL | LOI | $D_s$ |
|---|---|---|---|---|
| 100.0 | — | — | 25.2 | 569 |
| 94.0 | 3.0 | 3.0 | 25.8 | 551 |
| 88.0 | 9.0 | 3.0 | 26.9 | 959 |
| 88.0 | 3.0 | 9.0 | 25.9 | 218 |
| 82.0 | 12.0 | 6.0 | 28.0 | 551 |
| 82.0 | 6.0 | 12.0 | 27.5 | 451 |
| 76.0 | 6.0 | 18.0 | 28.3 | 404 |
| 76.0 | 15.0 | 9.0 | 29.2 | 404 |
| 73.0 | 24.0 | 3.0 | 31.2 | 626 |
| 73.0 | 3.0 | 24.0 | 28.1 | 230 |
| 70.0 | 25.5 | 4.5 | 31.9 | 499 |
| 70.0 | 15.0 | 15.0 | 30.8 | 390 |

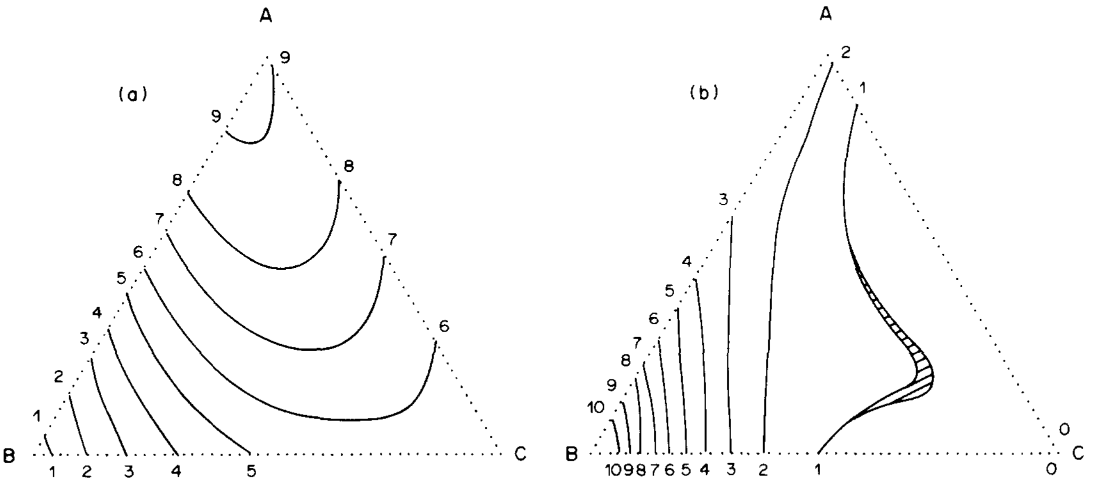

Fig. 1. Flammability and maximum smoke density of systems containing PVC, P, DBB and MEL. Vertices: (A) PVC 70%, DBB 30%; (B) PVC 70%, P 30%; (C) PVC 70%, MEL 30%. (a) LOI: 1, 23.0; 2, 24.3; 3, 25.5; 4, 26.7; 5, 27.9; 6, 29.1; 7, 30.3; 8, 31.5; 9, 32.7. (b) $D_S$: 0, 390; 1, 664; 2, 937; 3, 1211; 4, 1484; 5, 1758; 6, 2032; 7, 2305; 8, 2579; 9, 2852; 10, 3126.

loss of chlorine as hydrogen chloride; this accounts for about 60 wt% of the polymer itself (excluding the plasticiser) [16, 17]. It is during the second weight loss stage, with a maximum rate at *ca* 700 K, that most of the carbon scission and subsequent ring closure takes place to yield aromatic compounds and smoke [17]. Thus, when red phosphorus is also present, any weight gain will coincide with, and indeed tend to be masked by, the smoke-producing stage. Nevertheless it seems reasonable to assume that the negligibly small weight gains observed in all systems where phosphorus is incorporated into PVC (Table 3) indicate that oxidation of the phosphorus is largely inhibited in the presence of the polymer, perhaps by the hydrogen chloride released.

Thus, in PVC there is clearly, in the initial stages, little formation of phosphorus oxides or oxyacids, which are the species probably responsible for conferring some degree of flame retardance on plasticised PVC [18].

Microanalysis of a PVC + 30% P mixture heated in air (Table 4) shows that scarcely any phosphorus is volatilised until virtually all the chlorine has been lost from the polymer. Indeed only *ca* 10 wt% of the phosphorus is volatilised before the weight gain stage, while over 60 wt% of the original phosphorus is still present at the end of this stage. The overall gain in weight is small (Table 3), presumably because oxygen absorption is constantly competing with volatilisation. However, it is clear from the weight of the final solid residue that at least some more phosphorus is lost at higher temperatures (Table 3). Furthermore all samples containing phosphorus exhibit a highly exothermic weight loss stage at the same temperature

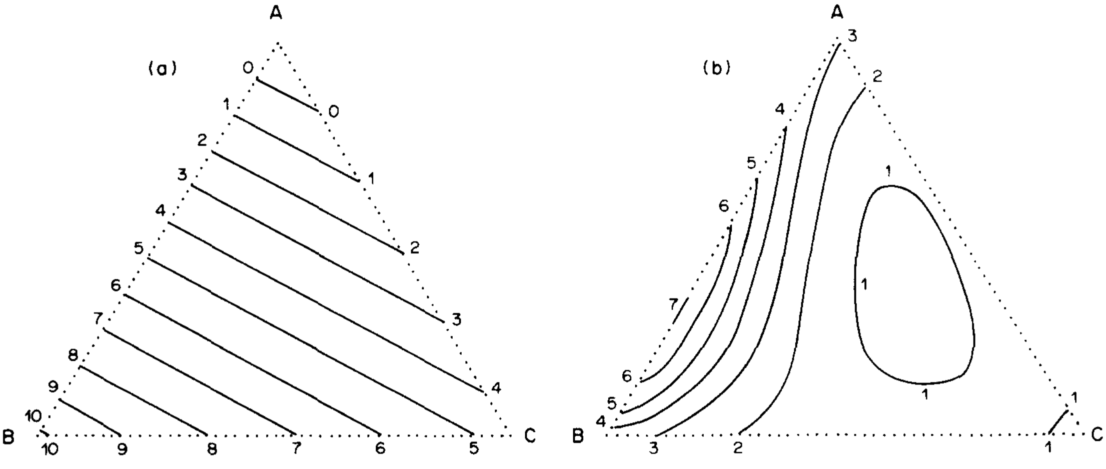

Fig. 2. Flammability and maximum smoke density of systems containing PVC, DBB and MEL. Vertices: (A) PVC 100%; (B) PVC 70%, DBB 30%; (C) PVC 70%, MEL 30%. (a) LOI: 0, 25.2; 1, 25.9; 2, 26.6; 3, 27.3; 4, 28.1; 5, 28.8; 6, 29.5; 7, 30.2; 8, 30.9; 9, 31.6; 10, 32.3. (b) $D_S$: 1, 346; 2, 474; 3, 602; 4, 730; 5, 858; 6, 987; 7, 1115.

Table 3. Simultaneous thermal analyses of poly(vinyl chloride), red phosphorus and PVC-additive mixtures

| PVC(%) | 100.0 | — | 70.0 | 70.0 | 70.0 | 70.0 | 70.0 |
|---|---|---|---|---|---|---|---|
| P(%) | — | 100.0 | 30.0 | — | — | 15.0 | 15.0 |
| DBB(%) | — | — | — | 30.0 | — | 15.0 | — |
| MEL(%) | — | — | — | — | 30.0 | — | 15.0 |
| *First wt loss* | | | | | | | |
| Wt(%) | 66.4 | — | 49.5 | 48.8 | 49.0 | 50.0 | 47.8 |
| *T* range(K) | 421–624 | — | 431–614 | 443–607 | 446–689 | 426–633 | 406–614 |
| $T_{MR}$(K) | 537 | — | 556 | 554 | 525 | 554 | 520 |
| *Second wt loss* | | | | | | | |
| Wt(%) | 10.1 | — | — | 19.5 | 15.4 | 9.2 | 5.7 |
| *T* range(K) | 624–752 | — | — | 607–736 | 689–780 | 633–730 | 614–714 |
| $T_{MR}$(K) | 712 | — | — | 633 | 734 | 666 | 641 |
| *First wt gain* | | | | | | | |
| Wt(%) | — | 30.7 | 0.9 | — | — | — | — |
| *T* range(K) | — | 451–695 | 614–705 | — | — | — | — |
| *Third wt loss* | | | | | | | |
| Wt(%) | 22.8 | 69.3 | 5.3 | 24.4 | 27.7 | 1.2 | 2.6 |
| *T* range(K) | 752–871 | 695–699 | 705–708 | 736–828 | 780–875 | 730–740 | 714–716 |
| $T_{MR}$(K) | 813 | 695 | 705 | 804 | 865 | 732 | 714 |
| DTA(μV) | 20 | 299 | 125 | — | 48 | 202 | 184 |
| *Second wt gain* | | | | | | | |
| Wt(%) | — | — | 1.6 | — | — | — | 0.4 |
| *T* range(K) | — | — | 708–718 | — | — | — | 716–720 |
| $T_{MR}$(K) | — | — | 710 | — | — | — | 720 |
| *Fourth wt loss* | | | | | | | |
| Wt(%) | — | 36.3 | 42.1 | — | — | 13.2 | 18.2 |
| *T* range(K) | — | 699–859 | 718–1037 | — | — | 740–816 | 720–800 |
| $T_{MR}$(K) | — | 776 | 786 | — | — | 780 | 770 |
| *Fifth wt loss* | | | | | | | |
| Wt(%) | — | — | — | — | — | 18.5 | 20.3 |
| *T* range(K) | — | — | — | — | — | 816–1024 | 800–993 |
| $T_{MR}$(K) | — | — | — | — | — | 865 | 846 |
| TL(%) | 99.3 | 74.9 | 94.4 | 92.7 | 92.1 | 92.1 | 94.2 |
| $T_{1\%}$(K) | 458 | — | 460 | 484 | 481 | 460 | 446 |

$T_{MR}$ = temperature of maximum rate of weight change. DTA = differential thermal analysis. TL = total weight loss. $T_{1\%}$ = temperature of 1% weight loss.

Table 4. Microanalysis of polymer–red phosphorus mixtures before and after being heated in air

| | C | | H | | Cl | | O | | P | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | wt % | mg | wt % | mg | wt % | mg | wt % | mg | wt % | mg |
| *70% PVC + 30% P* | | | | | | | | | | |
| Initially | 34.3 | 3.43 | 4.2 | 0.42 | 28.4 | 2.84 | 3.1 | 0.31 | 30.0 | 3.00 |
| Before wt gain | 33.5 | 1.67 | 2.8 | 0.14 | 0.6 | 0.03 | 9.9 | 0.49 | 52.6 | 2.63 |
| After wt gain | 20.9 | 1.07 | 2.7 | 0.14 | 0.4 | 0.02 | 40.0 | 2.05 | 36.1 | 1.85 |
| *70% PS + 30% P* | | | | | | | | | | |
| Initially | 64.6 | 6.46 | 5.4 | 0.54 | — | — | — | — | 30.0 | 3.00 |
| Before wt gain | 49.8 | 2.49 | 3.6 | 0.18 | — | — | 7.6 | 0.38 | 39.0 | 1.95 |
| After wt gain | 20.9 | 1.21 | 4.9 | 0.28 | — | — | 54.1 | 3.14 | 20.1 | 1.17 |

10 mg of each mixture heated at 5 deg min$^{-1}$ in air (flow rate, 60 cm$^3$ min$^{-1}$).

as red phosphorus itself. Whatever flame-retardant action is exerted by the phosphorus clearly takes place in the condensed phase.

### *Polystyrene*

Red phosphorus on its own causes a modest decrease in the flammability of PS but greatly enhances smoke formation from this polymer (Table 5). Better flame retardance can be obtained by the use of combinations of phosphorus and DBB and the highest LOI values are achieved with mixtures containing a high Br:P ratio (Table 5). Although there are no very well-defined trends, melamine generally decreases smoke formation. Nevertheless, in virtually all the ternary additive systems, the smoke levels are higher than those encountered with PS on its own (Table 5). Results obtained with mixtures of P + MEL (Table 6) show that it is not possible to raise the LOI significantly without markedly increasing the amounts of smoke generated. Binary mixtures of DBB + MEL cause smaller increases in smoke formation but do not decrease the flammability so effectively (Table 7).

When triangular diagrams are constructed for the ternary additive system (Fig. 3), it can be seen that the flammability is lowest along the P–DBB axis, although there is another region of high LOI along the P–MEL axis (Fig. 3a). The lowest values of LOI are obtained in the region where the melamine level

Table 5. The effect of mixtures of P + DBB + MEL on the combustion of polystyrene at a total additive loading of 30%

| % P | % DBB | % MEL | LOI | $D_s$ |
|---|---|---|---|---|
| 30.0 | — | — | 21.8 | 1804 |
| 24.0 | 2.4 | 3.6 | 23.1 | 1589 |
| 19.2 | 4.8 | 6.0 | 23.9 | 1235 |
| 15.0 | 10.0 | 5.0 | 24.9 | 1369 |
| 15.0 | 5.0 | 10.0 | 23.9 | 1157 |
| 10.0 | 10.0 | 10.0 | 24.6 | 1528 |
| 10.0 | 6.0 | 14.0 | 24.5 | 1369 |
| 7.8 | 14.4 | 7.8 | 24.2 | 824 |
| 4.5 | 23.7 | 1.8 | 25.2 | 959 |
| 3.8 | 25.0 | 1.2 | 25.8 | 730 |

Polystyrene: LOI, 17.5; $D_s$, 646.

Table 6. The effect of mixtures of P + MEL on the combustion of polystyrene at various total additive loadings

| % PS | % P | % MEL | LOI | $D_s$ |
|---|---|---|---|---|
| 100.0 | — | — | 17.5 | 646 |
| 94.0 | 3.0 | 3.0 | 20.1 | 551 |
| 89.5 | 5.1 | 5.4 | 20.6 | 435 |
| 85.0 | 4.5 | 10.5 | 21.4 | 427 |
| 82.0 | 9.0 | 9.0 | 23.3 | 1195 |
| 82.0 | 3.0 | 15.0 | 21.5 | 280 |
| 77.5 | 19.5 | 3.0 | 23.4 | 2097 |
| 77.5 | 3.0 | 19.5 | 23.0 | 1235 |
| 76.0 | 15.0 | 9.0 | 24.8 | 1256 |
| 73.0 | 18.0 | 9.0 | 24.5 | 1528 |
| 73.0 | 3.0 | 24.0 | 23.4 | 902 |
| 70.0 | 15.0 | 15.0 | 24.1 | 1891 |
| 70.0 | 6.6 | 23.4 | 24.4 | 1120 |

Table 7. The effect of mixtures of DBB + MEL on the combustion of polystyrene at various total additive loadings

| % PS | % DBB | % MEL | LOI | $D_s$ |
|---|---|---|---|---|
| 100.0 | — | — | 17.5 | 646 |
| 94.0 | 3.0 | 3.0 | 19.5 | 588 |
| 88.0 | 9.0 | 3.0 | 21.2 | 534 |
| 82.0 | 12.0 | 6.0 | 22.3 | 875 |
| 76.0 | 15.0 | 9.0 | 21.1 | 959 |
| 76.0 | 6.0 | 18.0 | 20.5 | 776 |
| 73.0 | 24.0 | 3.0 | 23.3 | 1235 |
| 73.0 | 3.0 | 24.0 | 20.5 | 708 |
| 70.0 | 15.0 | 15.0 | 22.7 | 849 |
| 70.0 | 9.0 | 21.0 | 21.4 | 626 |
| 70.0 | 3.6 | 26.4 | 20.7 | 404 |

is high (Fig. 3a). However the smoke density along the P–DBB axis is quite low compared with that along the P–MEL axis (Fig. 3b). Thus the best combination of low flammability and low smoke formation appears to be achieved when the levels of DBB are high compared with those of P and MEL. In systems containing only P + MEL (Fig. 4), the highest LOI values are obtained when approximately equal amounts of the two additives are incorporated (Fig. 4a). However, in this region the amounts of

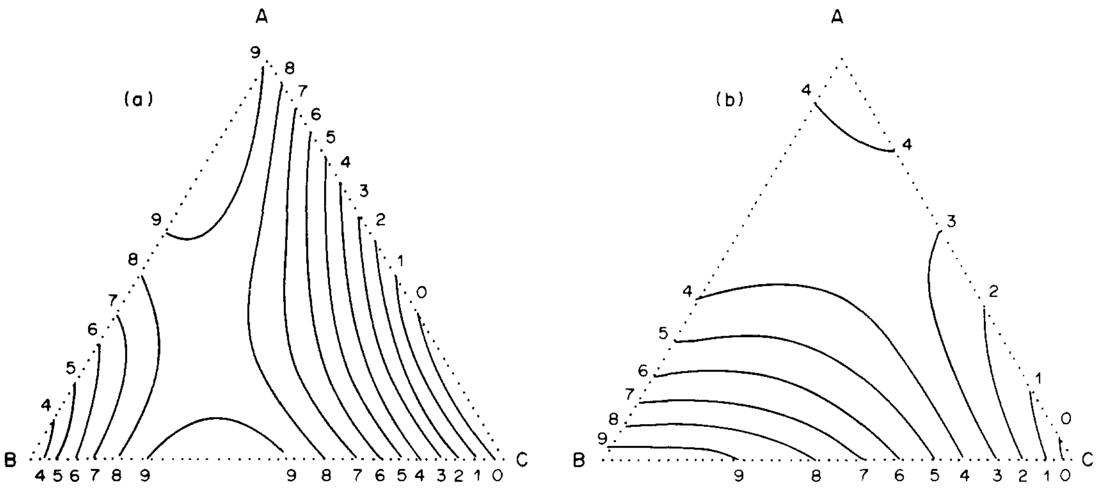

Fig. 3. Flammability and maximum smoke density of systems containing PS, P, DBB and MEL. Vertices: (A) PS 70%, DBB 30%; (B) PS 70%, P 30%; (C) PS 70%, MEL 30%. LOI: 0, 20.1; 1, 20.7; 2, 21.4; 3, 22.0; 4, 22.6; 5, 23.2; 6, 23.9; 7, 24.5; 8, 25.1; 9, 25.8. (b) $D_s$: 0, 319; 1, 476; 2, 633; 3, 791; 4, 948; 5, 1105; 6, 1262; 7, 1419; 8, 1577; 9, 1734.

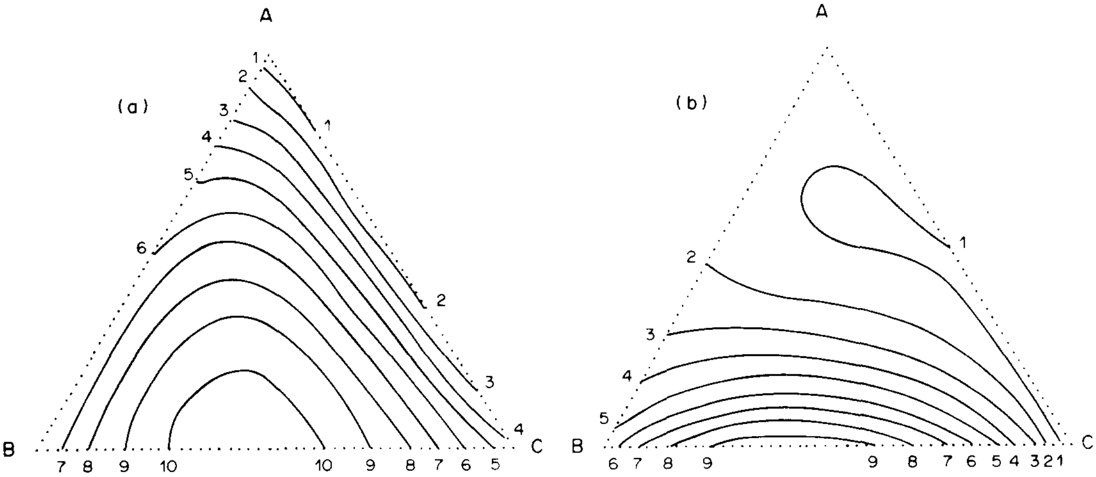

Fig. 4. Flammability and maximum smoke density of systems containing PS, P and MEL. Vertices: (A) PS 100%; (B) PS 70%, P 30%; (C) PS 70%, MEL 30%. (a) LOI: 1, 18.2; 2, 19.0; 3, 19.7; 4, 20.4; 5, 21.1; 6, 21.9; 7, 22.6; 8, 23.3; 9, 24.1; 10, 24.8. (b) $D_s$: 1, 462; 2, 643; 3, 825; 4, 1007; 5, 1188; 6, 1370; 7, 1552; 8, 1734; 9, 1915.

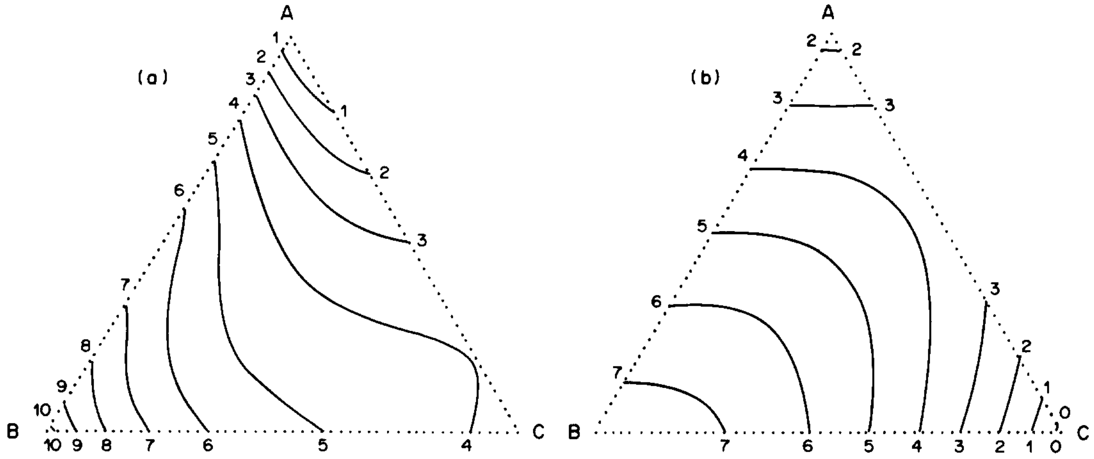

Fig. 5. Flammability and maximum smoke density of systems containing PS, DBB and MEL. Vertices: (A) PS 100%; (B) PS 70%, DBB 30%; (C) PS 70%, MEL 30%. (a) LOI: 1, 18.3; 2, 19.1; 3, 19.9; 4, 20.7; 5, 21.5; 6, 22.4; 7, 23.2; 8, 24.0; 9, 24.8; 10, 25.6. (b) $D_s$: 0, 319; 1, 419; 2, 520; 3, 620; 4, 720; 5, 820; 6, 921; 7, 1021.

smoke generated are also large (Fig. 4b). In the binary DBB + MEL system (Fig. 5), both LOI and $D_s$ increase with increasing levels of DBB. The optimum combination of low flammability and low smoke formation appears to be obtained with fairly high levels of DBB and relatively low levels of MEL.

Thermoanalytical experiments show that, in contrast to the behaviour found with PVC, there is extensive oxidation of red phosphorus when it is incorporated into PS (Table 8). The complete oxidation of elemental phosphorus to phosphorus pentoxide would involve a gain of about 130% of the weight of phosphorus initially present, although phosphorus vapour may, in practice, be oxidised only to PO [19]. Since $P_2O_5$ would volatilise significantly at the temperatures concerned, it is difficult to estimate from the observed weight gain of *ca* 30% for pure phosphorus (Table 3) the extent of oxidation to phosphorus oxides. However one very significant finding is that the extent of oxidation of red phosphorus in the form of a 70% PS + 30% P mixture (Table 8) is roughly the same as when phosphorus is oxidised on its own (Table 3). The occurrence of extensive oxidation of red phosphorus to readily volatile higher oxides is also consistent with the results of microanalysis of a PS + 30% P mixture (Table 4). This shows that by far the greater part of the phosphorus is lost by the end of the weight gain stage with 35% having been volatilised in the highly exothermic first weight loss stage. However the large amount of solid residue left in this case and the fact that the following weight loss is almost thermoneutral suggest that very little phosphorus is lost beyond this stage.

All the available evidence suggests that, with hydrocarbon-based thermoplastics, phosphorus compounds inhibit combustion mainly as a result of the intervention of species such as $P^{\cdot}$, $P_2$ and $PO^{\cdot}$ in the flame reactions [16, 20, 21]. If red phosphorus is extensively oxidised directly to $P_2O_3$ or $P_2O_5$, reactions (1)–(3) are unlikely to occur to a significant extent. This would explain why red phosphorus is unable to inhibit effectively the combustion of PS.

## CONCLUSIONS

Red phosphorus is not a good flame retardant for either PVC or PS, either on its own or when used in combination with an organic bromine and an

Table 8. Simultaneous thermal analyses of polystyrene and PS-additive mixtures

| | | | | | | |
|---|---|---|---|---|---|---|
| PS(%) | 100.0 | 70.0 | 70.0 | 70.0 | 70.0 | 70.0 |
| P(%) | — | 30.0 | — | — | 15.0 | 15.0 |
| DBB(%) | — | — | 30.0 | — | 15.0 | — |
| MEL(%) | — | — | — | 30.0 | — | 15.0 |
| *First wt loss* | | | | | | |
| Wt(%) | 93.1 | 50.9 | 90.7 | 86.1 | 71.7 | 74.4 |
| $T$ range(K) | 439–703 | 447–687 | 445–677 | 455–679 | 460–677 | 406–691 |
| $T_{MR}$(K) | 665 | 685 | 648 | 656 | 662 | *ca* 700 |
| DTA($\mu$V) | 32 | 221 | 10 | 14 | 31 | 27 |
| *Wt gain* | | | | | | |
| Wt(%) | — | 8.0 | — | — | 9.8 | 11.0 |
| $T$ range(K) | — | 687–710 | — | — | 677–756 | 691–756 |
| $T_{MR}$(K) | — | 687 | — | — | 679 | 740 |
| *Second wt loss* | | | | | | |
| Wt(%) | 4.7 | 46.3 | 6.0 | 7.2 | 30.6 | 30.3 |
| $T$ range(K) | 703–985 | 710–1000 | 677–844 | 679–892 | 756–993 | 756–971 |
| $T_{MR}$(K) | 780 | 795 | 790 | 792 | 812 | 804 |
| TL(%) | 97.8 | 89.2 | 96.7 | 93.3 | 92.5 | 93.7 |
| $T_{1\%}$(K) | 507 | 534 | 516 | 507 | 525 | 484 |

$T_{MR}$ = temperature of maximum rate of weight change. DTA = differential thermal analysis. TL = total weight loss. $T_{1\%}$ = temperature of 1% weight loss.

organic nitrogen compound. When red phosphorus is incorporated into PVC, it is apparently unable to undergo, at the right temperature, oxidation to the higher phosphorus oxides and oxyacids, which are the species likely to be involved in the condensed-phase reactions responsible for the inhibition of the combustion of this polymer. With PS, where phosphorus compounds probably act in the gas phase as a result of species such as $P^{\cdot}$, $P_2$ and $PO^{\cdot}$ interfering with the flame reactions, red phosphorus is rapidly converted to higher oxides which do not interact with the reactive free radicals responsible for flame propagation.

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## REFERENCES

1. E. D. Weil, *Flame Retardancy of Polymeric Materials* (Edited by W. C. Kuryla and A. J. Papa), Vol. 3, p. 185. Dekker, New York (1975).
2. J. W. Hastie, *J. Res. natn. Bur. Stand.* **77A,** 733 (1973).
3. H. Piechota, *J. cell. Plast.* **1,** 186 (1965).
4. J. R. A. Broadbent and M. M. Hirschler, *Eur. Polym. J.* **20,** 1087 (1984).
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. Ballistreri, S. Foti, G. Montaudo, E. Scamporrino, A. Arnesano and S. Calgari, *Makromolek. Chem.* **182,** 1301 (1981).
8. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporrino, D. Vitalini and S. Calgari, *J. Polym. Sci., Polym. Chem.* **21,** 679 (1983).
9. E. N. Peters, *J. appl. Polym. Sci.* **24,** 1457 (1979).
10. F. K. Antia, C. F. Cullis and M. M. Hirschler, *Eur. Polym. J.* **17,** 451 (1981).
11. J. D. Donaldson, J. Donbavand and M. M. Hirschler, *Eur. Polym. J.* **19,** 33 (1983).
12. M. M. Hirschler, *Eur. Polym. J.* **18,** 463 (1982).
13. F. K. Antia, P. J. Baldry and M. M. Hirschler, *Eur. Polym. J.* **18,** 167 (1982).
14. C. F. Cullis and M. M. Hirschler, *Polymer* **24,** 834 (1983).
15. M. M. Hirschler and O. Tsika, *Eur. Polym. J.* **19,** 375 (1983).
16. C. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers.* Oxford University Press, Oxford (1981).
17. M. M. Hirschler, *Eur. Polym. J.* **22,** 153 (1986).
18. M. M. O'Mara, W. Ward, D. P. Knechtges and R. J. Meyer, *Flame Retardancy of Polymeric Materials* (Edited by W. C. Kuryla and A. J. Papa), Vol. 1, p. 195. Marcel Dekker, New York (1973).
19. L. B. Soroka, *Dokl. Akad. Nauk SSSR* **236,** 1162 (1977).
20. A. W. Benbow and C. F. Cullis, *Proceedings of the Combustion Institute European Symposium* (Univ. Sheffield, Sept. 1973) p. 183. Academic Press, New York (1973).
21. M. M. Hirschler, *Developments in Polymer Stabilisation* (Edited by G. Scott), Vol. 5, p. 107. Applied Science, London (1982).