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Mechanisms and modes of action in flame retardancy of polymers

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2.1   Introduction

Some basic mechanisms of flame retardancy were recognised as early as 1947 when several primary principles were put forward.[1] These included the effect of the additive on the mode of the thermal degradation of the polymer in order to produce fuel-poor pyrolytic paths, external flame retardant coatings to exclude oxygen from the surface of the polymer, internal barrier formation to prevent evolution of combustible gases, inert gas evolution to dilute fuel formed in pyrolysis and dissipation of heat away from the flame front. Discovery of the flame-inhibiting effect of volatile halogen derivatives subsequently led to the postulation of the radical trap-gas-phase mechanism.[2] The gas-phase and the condensed-phase proposals have long been generally considered as the primary, though not the only, effective mechanism of flame retardancy. This situation is now being modified as new mechanisms of new flame-retarding systems, especially those based on physical principles, evolve and as new insights into the performance of flame retardants is being gained. In many cases several mechanistic principles operate simultaneously and consequently it is difficult to identify one dominant mechanism. In such cases *modes of action* of particular flame-retarding formulation may be defined and described.

This paper attempts to review some of the principles, mechanisms and modes of action which prevail at present in the field of flame retardancy of polymers.

2.2   General considerations

Pyrolysis and combustion of polymers occur in several stages. The polymeric substrate heated by an external heat source is pyrolysed with the generation of combustible fuel. Usually, only a part of this fuel is fully combusted in the flame by combining with the stoichiometric amount of atmospheric oxygen. The other part remains and can be combusted by

drastic means, e.g. in the presence of a catalyst and by an excess of oxygen. A part of the released heat is fed back to the substrate and causes its continued pyrolysis, perpetuating the combustion cycle. Another part is lost to the environment. The energy needed to heat the polymer to the pyrolysis temperature and to decompose and gasify or volatilise the combustibles and the amount and character of the gaseous products determines the flammability of the substrate. A flame retardant acting via a condensed-phase chemical mechanism alters the pyrolytic path of the substrate and reduces substantially the amount of gaseous combustibles, usually by favouring the formation of carbonaceous char and water.[3] In this case the heat released in the combustion decreases with an increase in the amount of the flame-retarding agent.

In the gas-phase mechanism the amount of combustible matter remains constant but the heat released in the combustion usually decreases with an increase in the amount of the flame-retarding agent. The amount of heat returned to the polymer surface is therefore also diminished and the pyrolysis is retarded or halted as the temperature of the surface decreases. The flame-retarding moiety has to be volatile and reach the flame in the gaseous form. Alternatively it has to decompose and furnish the active fraction of its molecule to the gaseous phase. The char remaining in the substrate will contain less of the active agent. The pyrolysis of the polymer should, in the limiting case, proceed as if there would have been no flame-retarding agent incorporated in it. In addition presence of the gas-phase active agent should not influence the composition of the volatiles reaching the flame.[3]

2.3   Gas-phase mechanisms

The gas-phase activity of the active flame retardant consists in its interference in the combustion train of the polymer. Polymers, like other fuels, produce upon pyrolysis species capable of reaction with atmospheric oxygen and produce the H_2–O_2 scheme which propagates the fuel combustion by the branching reaction:[4]

$$H^{\bullet} + O_2 = OH^{\bullet} + O^{\bullet} \qquad\qquad [2.1]$$

$$O^{\bullet} + H_2 = OH^{\bullet} + H^{\bullet} \qquad\qquad [2.2]$$

The main exothermic reaction which provides most of the energy maintaining the flame, is:

$$OH^{\bullet} + CO = CO_2 + H^{\bullet} \qquad\qquad [2.3]$$

To slow down or stop the combustion, it is imperative to hinder the chain-branching reactions [2.1] and [2.2]. The inhibiting effects of halogen derivatives, usually chlorine and bromine, is considered to operate via the

gas-phase mechanism. This effect in the first instance occurs either by releasing a halogen atom, if the flame-retardant molecule does not contain hydrogen, or by releasing a hydrogen halide:

$$MX = M^{\bullet} + X^{\bullet} \qquad\qquad [2.4]$$

$$MX = HX + M^{\bullet} \qquad\qquad [2.5]$$

where $M^{\bullet}$ is the residue of the flame-retardant molecule. The halogen atom reacts with the fuel, producing hydrogen halide:

$$RH + X^{\bullet} = HX + R^{\bullet} \qquad\qquad [2.6]$$

The hydrogen halide is believed to be the actual flame inhibitor by affecting the chain branching:

$$H^{\bullet} + HX = H_2 + X^{\bullet} \qquad\qquad [2.7]$$

$$OH^{\bullet} + HX = H_2O + X^{\bullet} \qquad\qquad [2.8]$$

Reaction [2.7] was found to be about twice as fast as [2.8] and the high value of the ratio H_2/OH in the flame front indicates that [2.7] is the main inhibiting reaction.[5] It is believed that the competition between reactions [2.7] and [2.1] determines the inhibiting effect. Reaction [2.1] produces two free radicals for each H atom consumed, whereas reaction [2.7] produces one halogen radical which recombines to become the relatively stable halogen molecule.

2.3.1 Comparing flame-retardant activity of halogen derivatives

Equation [2.7] represents an equilibrium with a forward reaction and a reverse reaction. The equilibrium constants of equation [2.7] for HBr and HCl are:[6]

$$K_{HCl} = 0.583 \exp(1097/RT); \quad K_{HBr} = 0.374 \exp(16760/RT)$$

The equilibrium constants decrease strongly with increase in temperature, which explains the decreasing effectivity of halogen derivatives in large hot fires.[6] Petrella[5] calculated that in the temperature range 500–1500 K the forward reaction predominates and K_{HBr} is much higher than K_{HCl}. Both are highly effective at the ignition temperature range of polymers. The flame-retardant effectivity of the halogens was stated to be directly proportional to their atomic weights, i.e. $F:Cl:Br:I = 1.0:1.9:4.2:6.7$.[7] On a volumetric basis 13% of bromine was found to be as effective as 22% of chlorine when comparing the tetrahalophthalic anhydrides as flame retardants for poly-

esters.[8,9] A similar effect was found for PP, PS and PAN[3] and when comparing NH_4Cl to NH_4Br in cellulose.[9]

The activity of the halogens is also strongly affected by the strength of the respective carbon-halogen bonds. The low bond strength of I–C and consequently the low stability of the iodine compounds virtually exclude their use. The high stability of the fluorine derivatives and the high reactivity of the fluorine atoms in reactions [2.7] and [2.8] will prevent the radical quenching processes in the flame. The lower bond strength and stability of the aliphatic compounds, their greater ease of dissociation as well as the lower temperature and earlier formation of the HBr molecules are responsible for their higher effectivity as compared to the aromatic halogen compounds. The higher stability of the latter along with their higher volatility allow these compounds to evaporate before they can decompose and furnish the halogen to the flame.

2.3.2 Physical modes of action of halogenated flame retardants

The radical trap activity is not the only activity of the halogenated flame retardants. The physical factors such as the density and mass of the halogen and its heat capacity, have a profound influence on the flame-retarding activity of the agent. In addition, its dilution of the flame which thus decreases the mass concentration of combustible gases present are effective. Larsen[7,199,200] demonstrated the important role of the heat capacity of the flame retardant. In flame retardant polymer systems the halogens appear to work by reducing the heat evolved in the combustion of the gases given off by the decomposing polymer (low or zero fuel value plus action as a heat sink) such that to sustain burning the mass rate of gasification must be increased by the application of an increased external heat flux.[10] Other authors[11] showed by thermochemical computation that most of the action of a wide variety of halocarbon flame inhibitors could be correlated to a combination of heat capacity and endothermic bond dissociation.

A physical effect, often mentioned but rarely demonstrated or evaluated, is the 'blanketing' effect of excluding oxygen from the surface of the pyrolysing polymer. Ignition generally takes place in the vapour phase adjacent to the condensed phase, when an ignitable fuel–air mixture is reached. There is, however, evidence that the rate of pyrolysis may be affected by the oxygen getting to or into the condensed phase, and that in polyolefins surface oxidation may provide energy for pyrolysis.[12] The rate of isothermal pyrolysis of cellulose was found to be higher in the presence of air as compared to vacuum pyrolysis by an order of magnitude.[13,14] The rate of pyrolysis in the presence of air was also found to decrease lin-

earily with increase in orientation of rayon fibres. Increase in chain orientation brings about a decrease in distance between chains and their more compact packing with consequent decreased penetrability and rate of diffusion of oxygen into the polymer resulting in a decreased rate of pyrolysis.[13,14] Although some doubt has been cast on the significance of the blanketing effect,[15] it is self-evident that an outgoing stream of bulky halogen and other non-fuel molecules emitted from the pyrolysing polymer could retard the penetration of the oxygen into the polymer and slow down the pyrolysis.

The proponents of the *physical theory* of the flame-retardant activity of halogenated additives compare the halogen activity to that of inert gases, CO_2 and water.[7] The physical theory takes into consideration the basic parameters of the flame as well as the processes occurring in the solid phase leading to the production of the combustibles, and enables in certain cases an estimate to be made of the amount of flame-retardant agent needed to inhibit a flame. There appears to be no contradiction between the radical trap theory and the physical theory with regard to halogens. Both approaches complement each other. It is difficult to determine in a general way the relative contribution of each of the two modes of activity. This will usually depend on the structure and properties of the polymer and of the flame retardant as well as on the conditions and parameters of the flame and on the size of samples used.
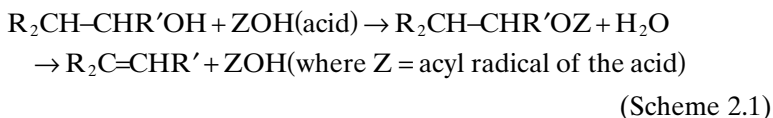
2.4   The condensed-phase mechanism

The condensed-phase mechanism postulates a chemical interaction between the flame-retardant agent, which is usually added in substantial amounts, and the polymer. This interaction occurs at temperatures lower than those of the pyrolytic decomposition. Two principal modes of this interaction were suggested: dehydration and cross-linking. They have been established for a number of polymers including cellulosics and synthetics.[16,17,202]

2.4.1 Principal modes of the condensed phase mechanism: dehydration and char formation

The varying effectivity of phosphorus compounds in different polymers has been related to the polymers susceptibility to dehydration and char formation: this explains the decreasing activity with decreasing oxygen content of the polymer. Whereas cellulosics are adequately flame retarded with around 2% of phosphorus, 5–15% of it is needed for polyolefins.[18] The interaction of phosphorus derivatives with the polymers not containing hydrox-

yls is slow and has to be preceded by an oxidation. It has been suggested that 50–99% of the phosphorus derivatives may be lost by evaporation, possibly of P_2O_5 or other oxides formed in the pyrolysis of the phosphorus derivatives.[19]

Two alternative mechanisms have been proposed for the condensed phase in cellulose: dehydration of cellulosics with acids and acid-forming agents of phosphorus and sulphur derivatives. Both mechanisms lead to char formation.[20] (a) esterification and subsequent pyrolytic ester decomposition (see Scheme 2.1) and (b) carbonium ion catalysis (Scheme 2.2):

$$R_2CH–CHR'OH + ZOH(acid) \rightarrow R_2CH–CHR'OZ + H_2O$$
$$\rightarrow R_2C{=}CHR' + ZOH (where\ Z = acyl\ radical\ of\ the\ acid)$$

(Scheme 2.1)

$$R_2CH–CHR'OH \rightarrow R_2CH–CHR'OH_2^+ \rightarrow H_2O$$
$$+ R_2CH–C^+HR'$$

(Scheme 2.2)

Differential thermal analysis (DTA) and oxygen index (OI) data indicated that phosphorus compounds reduce the flammability of cellulosics primarily by the Scheme 2.1 mechanism, which, being relatively slow, is affected by the fine structure of the polymer. Less-ordered regions (LOR) pyrolyse at a lower temperature than the crystalline regions and decompose before all of the phosphate ester can decompose, which decreases the flame-retarding effectivity and necessitates a higher amount of phosphorus. Sulphated celluloses, obtained by sulphation with ammonium sulphamate, are dehydrated by carbonium ion disproportionment (Scheme 2.2) and show a strong acid activity which rapidly decrystallises and hydrolyses the crystalline regions. The fire-retardant activity was accordingly found not to be greatly influenced by the fine structural parameters, and the same amount of sulphur was needed to flame-retard celluloses of different crystallinities.[20]

2.4.2   Cross-linking and char formation

It was early recognised that cross-linking promotes char formation in pyrolysis of celluloses.[21] Cross-linking has been assumed to be operative in P–N synergism.[22] Cross-linking reduces in many cases, albeit not always, the flammability of polymers. Although it increases the OI of phenolics, it does not markedly alter the flammability of epoxides.[23] A drastic increase in char formation is observed when comparing cross-linked polystyrene (PS), obtained by copolymerising it with vinylbenzyl chloride, to uncross-linked PS. PS pyrolyses predominantly to monomer and dimer units almost without char. Cross-linked PS yielded 47% of char.[24] Cross-linking and

char formation were recently obtained by an oxidative addition of organometallics to polyester.[25]

Cross-linking promotes the stabilisation of the structure of cellulose by providing additional covalent bonds between the chains, which are stronger than the hydrogen bonds, and which have to be broken before the stepwise degradation of the chain occurs on pyrolysis. However, low degrees of cross-linking can decrease the thermal stability by increasing the distance between the individual chains and consequently weakening and breaking the hydrogen bonds. Thus, although the OI of cotton increases marginally with increasing formaldehyde cross-linking, that of rayon markedly decreases.[26]

The formation of char in celluloses is initiated by rapid *auto-crosslinking* due to the formation of ether oxygen bridges formed from hydroxyl groups on adjacent chains. The auto-crosslinking is evidenced by a rapid initial weight loss, due to evolution of water, in the first stage of pyrolysis at 251 °C, and is linearly related to the amount of char. Formaldehyde cross-linking of rayon interferes with the auto-crosslinking reaction, decreases the initial weight loss and reduces char formation.[26]

It was suggested that cross-linking may increase the viscosity of the molten polymer in the combustion zone, thereby lowering the rate of transport of the combustible pyrolysis products to the flame.[27]

2.4.3   Structural parameters

In addition to bond strength and intermolecular forces, there are several other parameters, such as chain rigidity, resonance stability, aromaticity, crystallinity and orientation, that have a pronounced influence on pyrolysis and combustion. The linear correlations of van Krevelen between OI and char and between the char-forming tendency (CFT) and char residue (CR), are well known.[3] The CFT (equation 2.9) is defined as the amount of residue at 850 °C per structural unit, divided by 12, i.e. the amount of C equivalents per structural unit, where each group has its own CFT. These equations hold only for untreated polymers and for polymers containing condensed-phase flame retardants. They do not hold if halogen is present.[3]

$$\text{CR} = 1200 \left\{ \sum_i (\text{CFT})_i \right\} \Big/ \text{M} \qquad [2.9]$$

where M is the molecular weight per structural unit

Recent work on the relationship between chemical structures and pyrolysis and on the effects of introducing substituent functionalities into aromatic and heterocyclic structures on the modes of pyrolysis has been reviewed by Pearce.[28,29]

An interesting attempt to develop a generalised kinetic model of polymer pyrolysis was recently made by Lyon.[30] The model is based on some of the mechanisms important in the burning process, i.e. generation of combustible gases and char formation, but can be solved for the overall mass loss history of the specimen; for verification, special thermogravimetric techniques can be used.

2.4.4   Fine structural parameters and pyrolysis of polymer blends

In addition to orientation, crystallinity and degree of polymerization (DP) also have a strong influence on the energy required to melt and degrade polymers, on the rates of vacuum and air pyrolysis and on char formation and yield. That the DP has an effect on the degradation temperature of various polymers is known. Vacuum pyrolysates of purified celluloses were found to increase with increasing orientation and less-ordered regions (LOR) and to be inversely proportional to the square root of the DP.[13,14] The decrease in thermal stability with increasing orientation was ascribed to the straining of the hydrogen bonds. The extent of the auto-crosslinking reaction, discussed earlier, was found to be directly proportional to the percentage of char. The char increases with the increase in LOR of the polymer.

The energy of activation of pyrolysis of cellulose was found to increase strongly with the increase in crystallinity, indicating different mechanisms operating for the crystalline and less-ordered regions.[14]

Little is known of the effect of the fine structural parameters on the pyrolytic behaviour of polymers other than cellulose. The inclusion of these parameters in mechanistic models might prove to be of considerable interest. One such area might be the pyrolysis and flame retardancy of blends, as evidenced in the case of cotton-wool blends.[31] The DSC endotherm of cotton at 350°C, which is due to the decomposition of the levoglucosan monomer formed on pyrolysis, disappears with the addition of relatively small amounts of wool. Since levoglucosan is formed from the crystalline regions of the cellulose, its disappearance was attributed to the swelling decrystallization of the amino derivatives formed in the pyrolysis of the wool, which occurred at 225°C, i.e. lower than the 300°C at which the cotton pyrolysis begins. This is also manifested by a 'synergism' in char production. There is a strong increase in char in these blends, beyond the char amounts predicted by the composition of the blend. This rise stems from the increase in the LOR due to the swelling. Consistent with the above is also the decrease in activation energy of the pyrolysis from 220.1 for cotton to 103.4 kJ mol^{-1} for the blend with 18% of wool. It is

important to note that the above interaction between the ingredients of the blend is physicochemical in nature and depends on temperature. Pyrolysis-gas chromatography of a series of wool–cotton blends at 1000 °C for 30s yielded all the peaks in the relative area ratios as expected from a simple additive calculation in the absence of any interaction. The degree of interaction of components in a blend is therefore to be considered as a kinetic process governed by temperature and time.[31] The increase in char does not result in improved flammability. Actually more additive is needed for the blend than for the individual components.[31] A similar situation exists in the case of cotton–polyester blends. In this case more flammable gases, such as ethylene, are evolved from the blend than from the individual components.[9,16]

2.5   Modes of action of halogen-based flame retardants: synergistic systems

Halogen derivatives are used as a rule together with co-additives enhancing their flame inhibiting activity. These co-additives are usually termed *synergists*. There is a considerable number of such co-additives, the most prominent one being antimony trioxide. Their effects are based on widely differing modes of action, embracing both the radical trap and physical effects mechanisms as well as principles of the condensed-phase mechanism and intumescence. The differences between the various co-additive-synergistic systems are not only in the modes of action but also in the extent of the synergistic effect.

The term *synergism*, as currently used in the FR-terminology is poorly defined. Strictly speaking, it refers to the combined effect of two or more additives, which is greater than that predicted on the basis of the additivity of the effect of the components. In order to characterise and compare synergistic systems we introduced the term *synergistic effectivity* (SE), used in this and previous publications of this laboratory.[31–34,201] It is defined as the ratio of the FR-effectivity (EFF) of the flame-retardant additive plus the synergist to the EFF of the additive without synergist, compared at the same additive level. EFF is defined as the increment in OI for 1% of the flame-retardant element, at a given level of the flame-retardant element. The values of EFF and SE cited in this paper were computed from results of work in this laboratory as well as from data published in the literature, and were tabulated and published in previous publications.[35] The SE values are based in most cases on results obtained for additive/synergist ratios yielding the highest effect. More general mathematical definitions of synergism have been proposed.[53]

2.5.1 Halogen–antimony synergism

Formulations based on the halogen–antimony synergism are being widely used and have been described for a variety of polymers: cellulosics,[1] polyesters, polyamides, polyolefins, polyurethanes, polyacrylonitrile and polystyrene.[24]

The mode of action responsible for this synergism appears to depend both on condensed-phase as well as vapour-phase activities.[36,37] It is believed that during the pyrolysis, first, some hydrogen halide is released in the self-decomposition of the halogenated compound or by interaction with antimony trioxide and/or with the polymer. The HX reacts with the Sb_2O_3 producing either SbX_3 or SbOX.[36,37] Although some SbX_3 is found in the first stage of the pyrolysis, the weight loss pattern found in one study implied the formation of less volatile Sb-containing moieties, obtained by progressive halogenation of Sb_2O_3.[38] During the transformations gaseous SbX_3 is evolved and released to the gas phase, whereas SbOX, which is a strong Lewis acid, may operate in the condensed phase, facilitating the dissociation of the C-X bonds.[39]

Several cases of condensed-phase activity of Sb_2O_3 are known. Lowering the charring temperature by adding Sb_2O_3 to cellulosic fabrics treated with chlorine compounds has been observed.[16] Adding Sb_2O_3 to polyolefins treated with Dechlorane Plus was found to increase the char yield substantially.[3]

The main effect of Sb_2O_3 is, however, in the gas phase. The antimony halides, after reaching the gas phase, react with atomic hydrogen producing HX, SbX, SbX_2, and Sb. Antimony reacts with atomic oxygen, water and hydroxyl radicals, producing SbOH and SbO, which in turn scavenge H atoms. SbX_3 reacts with water, producing SbOH and HX. A fine dispersion of solid SbO and Sb are also produced in the flame and catalyse the recombination of H$^\bullet$. In addition, it is believed that the antimony halides delay the escape of halogen from the flame, and thus increase its concentration, and at the same time also dilute the flame. The antimony halides may also exert a 'blanketing' effect by hindering the penetration of oxygen into the pyrolysing polymer.[13,14]

Values of EFF and SE of aromatic and aliphatic bromine derivatives with antimony trioxide, computed from data of van Krevelen,[3] show SE of 2.2 and 4.3, respectively. Similarly, for aliphatic chlorine derivatives with antimony trioxide an SE value of 2.2 is computed for polystyrene.

2.5.2 Mode of action of ammonium bromide

Ammonium bromide was recently found to have a high FR-effectivity of bromine, i.e. 1.24 for NH_4Br encapsulated in PP as compared to 0.6 for

aliphatic bromine compounds. It has been explained by the low dissociation energy of NH_4Br to HBr and NH_3 which is much lower than the dissociation energy of the C–Br bond. The degree of dissociation is 38.7% at 320 °C, so that sizable amounts of HBr are readily available when PP begins to decompose. The radical trap activity of the HBr as well as the physical effects exerted by the HBr and the ammonia clearly operate here simultaneously. The possibility of synergism between the HBr and NH_3 in the gaseous phase should, however, not be discarded, as both compounds reach the flame at about the same time. Little is known about the behaviour of ammonia in the flame, particularly in the presence of H$^•$, Br$^•$, OH$^•$, and O$^•$ radicals.

2.5.3 The mode of action of mixtures of bromine-based and chlorine-based additives

Attention has recently been drawn to the enhancement in the flame retardancy when mixtures of brominated and chlorinated flame retardants are applied to ABS, HIPS and PP and a synergistic interaction was postulated and discussed in several papers.[40-44] In most cases the maximum effect is found with a Br:Cl ratio of 1:1 and with 10–12% of the sum of chlorine and bromine. When using Dechlorane Plus and brominated epoxy resin (51% Br) with ABS in the presence of 5% Sb_2O_3, the FR-EFF was calculated as 0.80. The SE obtained was 1.67. This synergism is *in addition* to the Hal–Sb synergism and is known until now to be effective only in the presence of antimony trioxide. The synergistic effect increases with the amount of antimony and reaches a maximum at 6% level.

Some light was thrown on the Br–Cl synergism in pyrolysis experiments, carried out in the ion source cell of a mass spectrometer with mixtures of polyvinyl bromide (PVB) and polyvinyl chloride (PVC) or polyvinylidene chloride (PVDC).[45] Whereas relatively high concentrations of both HCl and HBr were found, the amounts of $SbCl_3$ were very low compared to those of $SbBr_3$, which points to a much slower interaction of HCl with the oxide than that of HBr, which is not surprising, considering the higher stability and lower reactivity of HCl. This indicates that the Br–Cl synergism operates via the bromine–antimony route,[45] and is supported by the fact that no information is available on the FR-behaviour of Br–Cl systems without antimony. Additionally, it is also conceivable that the radicals Br$^•$ and Cl$^•$ might recombine not only to Br_2 and Cl_2 but also to BrCl, which is polar and more reactive and will react with the H$^•$ radicals to produce HBr and another Cl$^•$ radical, thus increasing the effectivity. This may explain the higher effectivity of the formulations containing Br- and Cl-based additives as compared to formulations in which *only* Br-based additives are applied.

The extent of the contribution of this essentially radical trap effect to the overall synergism of the bromine–chlorine system cannot be estimated at present. Experiments on identical formulations with and without antimony trioxide could elucidate the matter.

The Br–Cl synergism has been investigated up to now for a small number of polymers and little systematic work reported on it. The chemical structure and stability of the brominated and chlorinated additives and their concentrations and ratios in the formulations, with different amounts of antimony trioxide or other synergists, may have a profound effect on the synergistic activity in various polymers and provide a new picture of this phenomenon.

2.5.4   Modes of action – synergism of mixtures of bromine- and phosphorus-based additives

Synergistic interactions between bromine- and phosphorus-based derivatives are described in several publications.[46,47] Of particular interest is the case of polyacrylonitrile (PAN) treated with varying ratios of ammonium polyphosphate (APP) and hexabromocyclododecane (HBCD).[46] An SE value of 1.55 was calculated in this case. It was demonstrated in the study that the system acts via an intumescent mechanism. The bromine compound was proven by OI and nitrous oxide index (NOI) tests not to operate in the gas phase in the flame in the radical trap mode, but rather as a *blowing agent* to foam the char. This appears to be the first reported case in which a condensed-phase activity is shown for a bromine-based additive. This finding opens the way for reconsidering the mechanism of operation of bromine compounds as flame retardants in other polymers and systems. A similar phenomenon is observed in flexible polyurethane made from polyols containing bromine and phosphorus; the bromine was found to enhance the formation of a more copious foamed char.[47]

Similar SE values are computed from data given by Roderig et al[26] for a polycarbonate–polyethylene terephthalate (PC–PET) blend treated with varying ratios of triphenyl phosphate (TPP) and brominated PC. An SE value of 1.38 is found. It was suggested that when the bromine and the phosphorus atoms are included in the same additive molecule the synergism is more pronounced.[48,49] This is indeed the case when a brominated phosphate, with the ratio of bromine to phosphorus of 7:3, is added to the same blend; the SE value is 1.58.[48] These SE values are similar to those of the PAN /APP/HBCD system discussed above. There are some indications from the foamed bulky appearance of the char, that in these cases bromine may also serve, at least partly, as a blowing agent in an intumescent process, operative in these Br–P formulations, instead of or together with the radical

trapping activity in the gas phase. The Br–P SE values are considerably lower than the bromine–antimony values, i.e. 2.2–4.3, as well as the PP/pentaerythritol/APP intumescent values, i.e. 5.5–11.3,[31–35] pointing to the possibility of a different complex mechanism.

It has recently been suggested that phosphorus compounds may replace antimony as a halogen synergist.[28, 49] In the case of oxygen-containing polymers, such as nylon 6 and PET a strong synergism was demonstrated. For PET the total amount of additives (Br-based plus P-based) decreased by over 90% compared to the regular Br-based and Sb additive. A similar synergistic activity of bromine and phosphorus was obtained for PBT, PP, PS, HIPS and ABS. A decrease in the amount of total additive of 40% was obtained for PE.[49] The P–Br synergism was also demonted in a case when both atoms are part of the same molecule of dialkyl 4-hydroxy-3,5-dibromobenzyl phosphonates, developed as a flame retardant for ABS.[50] The results were based on comparative experiments with related compounds having only the bromine related structures or only phosphorus related structures. A similar synergism was also lately obtained for UV-curable urethane acrylate to which variable amounts of tribromophenyl acrylate and triphenyl phosphate were added. A Br:P ratio of 2:1 was found to yield the maximum synergism.[51] This suggests a stoichiometric interaction, but is not consistent with the occasionally postulated formation of $POBr_3$. This requires a Br:P molar ratio of 3:1 which was actually the case in a red phosphorus-decabromodiphenyl system.[52] The mode of action of these synergistic formulations has not yet been elucidated and needs further research. It has been pointed out that synergism of halogens and phosphorus is not a general phenomenon: additivity is often observed.[53]

2.6   Modes of action of phosphorus-based flame retardants

2.6.1   General comments

Several reviews of phosphorus flame retardants, or of flame retardants more broadly, contain discussions of mode of action of phosphorus compounds.[54–61] A review by Granzow in 1978[62] is still highly useful and contains results not readily found elsewhere. Overviews have been published by Brauman in 1977[63] and by Weil in 1992–4.[55,64,65] More recent results have further emphasised the multiple modes of action of phosphorus.

Various phosphorus-based flame retardants have been shown to exert action in both the condensed phase and in the flame. Physical and chemical actions have been implicated in both phases. Flame inhibition, heat loss due to melt flow, surface obstruction by phosphorus-containing acids, acid-

catalysed char accumulation, char enhancement and protection of char from oxidation have all been noted in particular polymer systems containing phosphorus-based flame retardants,[63] although the relative contribution of each mode of action depends on the polymer system and the fire exposure conditions. It is quite likely that in many cases, more than one mode of action is involved.

2.6.2   Condensed-phase modes of action

2.6.2.1   Charring modes of action

There is very convincing evidence, especially in oxygen-containing polymers such as cellulose and rigid polyurethane foam, that phosphorus compounds can increase the char yield. Formation of char means that less material is actually burned. Secondly, char formation is often accompanied by water release, which dilutes the combustible vapours. Moreover, the char can often protect the underlying polymer and the char-forming reactions are sometimes endothermic.

The pyrolysis behaviour of cellulose (cotton, paper, wood) has been discussed in sections 2.4.2–2.4.4, and a great deal of work has been published on the flame-retardant action of phosphorus in cellulose; several detailed reviews are available.[66–68,203] When cellulose is heated to its pyrolysis temperature, it normally depolymerises to a tarry carbohydrate product (mainly levoglucosan) which further breaks down to smaller combustible organic fragments. However, when a phosphorus-containing flame retardant is present in the cellulose, the retardant breaks down to phosphorus acids or anhydrides upon fire exposure. These reactive phosphorus species then phosphorylate the cellulose, generally with release of water (see Scheme 2,1). Phosphorylated cellulose then breaks down and forms char. A flame-retardant effect results from the formation of a non-combustible outward-flowing vapour (water), the reduction in fuel, and in some cases the protective effect of the char. A greater degree of flame retardancy seems likely if the char resists oxidation, although even a transitory char may have some inhibitory effect. Even if the char does undergo oxidation (usually by smouldering), the presence of a phosphorus compound tends to inhibit complete oxidation of the carbon to carbon dioxide, and thus the heat evolution is lessened. Besides its effect in enhancing the amount of char, the phosphorus flame retardant may coat the char and thus help prevent burning and smouldering by obstruction of the surface.

Another mode of action in which phosphorus is important as a char former is in intumescent fire-retardant paints and mastics. These typically have a phosphorus compound such as ammonium polyphosphate and a char-forming polyol such as pentaerythritol, along with a blowing agent

such as melamine, and, of course, a binder.[69] Briefly stated, the phosphorus compound provides a phosphorylating agent which reacts with the pentaerythritol to form polyol phosphates which then break down to char through a series of elimination steps.[70–78] In some such formulations, melamine is combined with the phosphorus acid as melamine phosphate or melamine pyrophosphate,[79–80] and the released melamine and/or its breakdown products provide an endothermic action and a blowing action.

It has been known for a long time that certain nitrogen compounds such as melamine, ureas or dicyandiamide will enhance (perhaps synergise) the action of phosphorus in cellulose. This is not a general phenomenon, and it depends on the nitrogen compound[81] and the polymer system. The effect has been attributed to the formation of P–N bonded intermediates which are better phosphorylating agents than are the related phosphorus compounds without the nitrogen.[82] Another theory is that the nitrogen compounds retard the volatility loss of phosphorus from the condensed phase[83] while another study with urea-formaldehyde–diammonium phosphate on polyester–cotton blend fabric suggests just the opposite[84] and proposes that the nitrogen resin somehow enhances the vapour-phase action of the phosphorus. A further study of red phosphorus with melamine and various other nitrogen compounds in several thermoplastics also suggested that the nitrogen compounds enhanced the oxidation of phosphorus and gave off inert gases including ammonia. The only nitrogen compound which did not enhance retardancy was benzotriazole which did not give off ammonia.[85] We could find no study on effects of ammonia, hydrogen cyanide or cyanamide on flames from the burning of other fuels. Even considered as a source of 'inert gas,' ammonia can make a significant physical impact on the fuel value of the evolved fuel gases, and thus enhance flame retardancy, aside from chemical effects.[86] Physical effects are rarely assessed in studies of flame retardancy. A related effect of the nitrogen compounds, noted in a study referenced above,[85] was the reduction of the average rate of production of volatiles (presuming limiting fuel to the flame). This may also be partly a physical effect, shared with endothermic additives.

The topic of phosphorus–nitrogen synergism has been further studied at Polytechnic University.[87,88] As previously believed, it was confirmed not to be general; for example, phospham in nylon-4,6 was no more active than its elemental phosphorus equivalent.[89] In the case of a synergistic mixture of melamine phosphate and a cyclic phosphonate in EVA, enhanced rate of char formation at the optimum ratio was noted and the char was found by X-ray photon spectroscopy (XPS) to contain phosphorus acids with P–NH bonds, which may have contributed to faster charring and/or to better retention of phosphorus.[90]

Besides that quantity of char and its rate of formation, the char quality as a mass-transfer and heat-transfer barrier is also important. If the char is

porous, a prevalence of closed cells over open cells is best and freedom from cracks and channels is also important. However, the amount of char rather than its volume seems to be dominant, at least in one Russian study.[91]

Another case where char enhancement by phosphorus is important is in rigid polyurethane foams.[92–95] The analytical evidence shows that phosphorus appears to be largely retained in the char[96–97] which is usually noted to be more coherent and thus better as a protective barrier.[94,95] However, there is also evidence that, besides char formation, part of the mode of action of phosphorus additives in rigid polyurethanes involves vapour-phase action in the flame zone.[98]

In contrast to the situation in rigid foams, char formation is probably not the basis of the action of phosphorus retardants in flexible polyurethane foam, and the formation of a small amount of char, insufficient to protect, can even reduce the flame retardancy of the flexible foam if the char acts as a wick.

In poly(ethylene terephthalate)[99–101] and poly(methyl methacrylate),[102–105] various phosphorus flame retardants cause an increase in the amount of residue and a retardation of the release of volatile fuel. This is probably the result of acid-catalysed cross-linking, perhaps by way of anhydride linkages.

Based on a study in nylon-6,[106] red phosphorus flame retardants may work by a condensed-phase mode of action if the classical interpretation is given to the very similar curves of OI and nitrous oxide index vs concentration: this evidence points away from flame chemistry. The red phosphorus becomes oxidised to phosphoric acids and some of the nylon structure becomes attached to the phosphoric acid in the form of alkyl ester structures suggested by the infrared spectrum.

It appears that phosphorus flame retardants may not produce enough char in nylons to be entirely effective in a non-dripping mode of extinguishment. Recently, studies at Du Pont have shown that melamine pyrophosphate can be further activated by a latent strong heteropoly acid such as phosphotungstic or silicotungstic acid to make sufficiently enhanced char, thus achieving UL 94 V-0 ratings.[107] Levchik et al[108] showed that at sufficient concentration of ammonium polyphosphate in nylon-6, a flame retardant intumescent char could be produced; a 5-aminopentyl polyphosphate was identified as an intermediate. Besides the protective action of the char, a protective P–N-containing cross-linked ultraphosphate coating was postulated on the basis of infrared evidence.

In oxygen-free hydrocarbon polymers such as polyolefins and styrenics, which generally do not char very easily, phosphorus flame retardants are usually not very effective unless they are supplemented by other char-forming additives. In the absence of such a char-forming additive, the flame-retardant action which the phosphorus compound still does exert seems to involve some combination of vapour-phase activity, protective acid coating

and melt-drip enhancement. In polymers that do not contain reactive functional groups, the phosphorus flame retardant may react with oxygen groups or double bonds produced in the surface as the polymer burns.[109–113] Some evidence was also adduced by XPS spectroscopy that the ammonia of ammonium polyphosphate may also interact with oxygen groups eventually to form nitrogen heterocycles comprising part of the intumescent char.[114]

An important approach to effective use of the charring mode of action of phosphorus in those polymers such as polyolefins and styrenics, which are poor char formers, is to introduce a char-forming additive. Some of these char-forming additives are the same ones which were earlier found effective as 'carbonifics' (char formers) in intumescent paints and mastics.[69] Others are good char-forming smaller molecular weight additives such as tris(hydroxyethyl)isocyanurate[115] or polymers deliberately synthesised mainly as char-formers such as a polyester made from tris(hydroxyethyl) isocyanurate[116] or a triazine-piperazine-morpholine condensation polymer.[117] Char-forming polymers having, *per se*, useful thermomechanical properties such as poly(2,6-dimethylphenylene oxide) can be used in main ingredients where they contribute to a useful plastic blend as in GE's NORYL, a PPO-HIPS blend flame retarded by aryl phosphates[118] or as minor ingredients where they help the flame retardancy but not the mechanical properties.[119]

In some instances, the phosphorus flame-retardant moiety is built chemically into a char-forming structure. No generic advantage has been found to this approach, but it has been the subject of a great deal of industrial research. One example which reached the market place with limited success is the bis(melaminium) salt of pentaerythritol spirodiphosphate (Great Lakes' CHARGUARD 329).[120] A more recent combination of the catalytic char-forming action of phosphorus with the char-forming pentaerythritol structure is the bicyclic monophosphate of pentaerythritol (Great Lakes' NH-1197).[121]

Cyclic phosphorus ester structures such as neopentylene phosphonates are reasonably good char formers. Monsanto's XPM-1000 is a tris-neopentylene ester of nitrilotrimethylphosphonic acid, and is a fairly good char former, for example in a flame-retardant ethylene-vinyl acetate formulation enhanced by the additional char-forming catalytic action and blowing action of a melamine phosphate, giving the effect of a synergistic combination.[90]

An interesting recent development of a self-intumescing phosphorus–nitrogen compound is Albright & Wilson's ethylenediamine salt of phosphoric acid (Amgard NK, now Antiblaze NK).[122,123] When heated, it gives off a gas (probably water) and forms an expandable mass. Being stable to only about 200 °C, this salt is limited in its use to polymers processed at lower temperatures; it has been, for example, successful in caulks.

Studies have been made of both the physical and the chemical properties of the intumescent shield formed on a combustible polymer by the interaction of a char-forming additive and a phosphorus compound acting as charring catalyst. Useful overviews have been published by researchers at Lille[124] and Turin.[70–78] Evidence from a study of six commercial intumescent systems in polypropylene indicated that the yield of 'residue after transition,' which is seen as a plateau (or the last plateau) after the main weight loss in a TGA curve under air, correlated well (r = 0.99) with the oxygen index.[125]

From a mode of action standpoint, there is support by XPS and elemental analysis for the postulated formation of a protective 'phosphocarbonaceous' structure through phosphorylation of oxygenated functional groups on the 'carboniferous additive' (typically a pentaerythritol) and on the nascent char.[124,126]

2.6.2.2   Coating modes of action

Some researchers have emphasised the surface chemistry of charring in systems containing a charrable polymer such as PPO; endothermic rearrangement of the polyether to a methylene-linked polyphenol followed by a phosphate-accelerated dehydrative and endothermic dehydrogenative charring is indicated by analysis of surface material.[127] Phosphorylation of the phenolic rearrangement product is likely to be an early step in the chemistry of the char formation.

Phosphorus can also inhibit smouldering, also known as glowing combustion of the char;[128–130] the mode of action has long been postulated to involve some sort of polyphosphoric acid coating which is possibly a physical barrier action; besides this a deactivation of oxidation-active centres on the carbon can be demonstrated.[130–132]

It has been shown that incorporation of phosphorus even in amounts as small as 0.1% can inhibit oxidation of graphitic carbon by free oxygen. Hydrophilic phosphorus acid groups and other P=O structures can bond to oxidation-prone sites (the 'armchair' sites) on the surface.

Research at Alma-Ata recently showed that a phosphorus flame retardant can reduce the permeability of char, improving its barrier action.[133] Whether this is due to a coating or to a structural change in the char is not clear.

Brauman postulated that a phosphorus acid acts as a physical barrier to the vaporisation of fuel from a hydrocarbon polymer flame-retarded by ammonium polyphosphate or triphenyl phosphate[134,135] and infrared bands ascribed to the polyphosphoric acid coating were observed.

2.6.2.3   Effects on melt viscosity

In some cases, phosphorus compounds can act under fire-exposure conditions by generating acids which catalyse thermal breakdown of the polymer melt,[136] reducing melt viscosity and encouraging the flow or drip of the molten polymer from the fire zone. In poly(ethylene terephthalate) fabric, as little as 0.15% phosphorus permits the fabric to pass a vertical flame test, presumably by dripping or melting away from the flame.[137]

The melt viscosity depressing effect can be enhanced in thermoplastics prone to free-radical degradation by peroxide 'synergists'; thus, foamed polystyrene flame retarded with the now-obsolete tris(2,3-dibromopropyl) phosphate could be made more easily to pass a test allowing drip extinguishment by including dicumyl peroxide.[138] The effect of peroxides was shown to be, at least in large part, a melt degradation and flow enhancement effect by Gouinlock et al.[139] Small amounts of sulphur in styrenic polymers flame-retarded with phosphates can also produce this effect, as shown in an Albemarle patent.[140]

A melt-flow, melt-viscosity-depressant mode of action can be defeated by the presence of any non-melting solid which can retard the melt flow or which can act like a candle wick: cotton threads in a flame-retardant PET fabric can have such an effect. A particularly impressive example is the antagonistic effect of traces of silicone oil on flame-retarded polyester fabric; the fabric is rendered flammable probably because the silica formed on pyrolysis of the silicone reduces melt flow.[141] It has been shown that pigment-printing with an infusible pigment can spoil the flame retardancy of a phosphorus-containing flame-retarded polyester such as flame-retardant TREVIRA,[142] and this may be a melt flow retarding effect. Materials such as mineral or cellulosic powders or fibres, even if merely present on the surface, can defeat the action of various flame retardants in flexible urethane foams.[143]

2.6.2.4   Condensed-phase free-radical inhibition modes of action

This idea has been proposed by Russian and Czech researchers, who offer some evidence in support of free-radical inhibition, or at least of an antioxidant effect, by non-volatile phosphorus flame retardants.[144–146] Electron spin resonance data indicate that aryl phosphate flame retardants may scavenge alkylperoxy radicals in the polymer surface.[145] The contribution of this action to flame retardancy is not clear.

2.6.2.5   Condensed-phase modes of action based on surface effects on fillers

This relatively unexplored area has two principal aspects. Firstly, phosphorus compounds having characteristics of surfactants, such as alkyl acid

phosphates, can aid the dispersion of solid flame retardants such as alumina trihydrate (ATH).[147] Improved dispersion usually results in improved flame-retardant efficiency. Secondly, some char enhancement may be possible as the result of improved binding or possibly from the catalytic action of a surface active agent. Thus, certain alkoxytitanates and alkoxyzirconate coupling agents having alkyl acid pyrophosphate anions seem to enhance the UL 94 flammability ratings of polypropylene with various mineral fillers.[148] Interestingly, on one filler, barium sulphate, the effect of the titanate seemed to reach a maximum at 1% concentration, and the effect was lower at lower and higher concentrations. This needs re-examination and further study.

2.6.3   Vapour-phase modes of action

2.6.3.1   Chemical modes of action

It has been shown that volatile phosphorus compounds are efficient flame inhibitors.[149,150] Mass spectroscopy studies by Hastie at the National Bureau of Standards[151–153] showed that triphenyl phosphate and triphenylphosphine oxide break down in the flame to small molecular species such as P_2, PO, PO_2 and HPO_2. These species cause the hydrogen atom concentration in the flame to be reduced, thus quenching the flame. The step in the flame chemistry which is inhibited is the rate-controlling branching step (equation 2.1) involving the reaction of a hydrogen atom with an oxygen molecule to give a hydroxyl radical and an oxygen atom. This is the same step which is believed to be inhibited by the hydrogen atom scavenging effect of halogens (discussed earlier).

Further studies of volatile phosphorus flame retardants such as trialkyl phosphates and trialkylphosphine oxides show evidence of flame-zone mode of action.[62,154] Phosphine oxides in particular seem most apt to show vapour-phase action; they are quite unreactive in most plausible condensed-phase chemistry. Some empirical evidence has been adduced for vapour-phase flame-retardant action of phosphine oxide: for instance, trime-thylphosphine oxide in rigid polyurethane foam showed very different oxygen index- vs nitrous oxide index-concentration curves.[154] Even with the phosphine oxide structure reacted into the polymer, as in a series of modified nylons made at VPI and tested at NIST,[155] it appears that the greater part of the flame-retardant action was vapour-phase, although there was also a small char yield increase. In a similar manner, having the triphenylphosphine oxide structure reacted in or as an additive gave no significant difference in fire performance. In this rigid polyurethane foam system, the condensed-phase active additive was more efficient on a phosphorus basis than the vapour-phase active additive.

The contrary was found in studies of flame-retardant finishes on wool and wool-polyester blends. The results showed that a demonstrably more volatile phosphonium structure gave better flame-retardant results than a less volatile polymer-bonded phosphine oxide structure; in this instance, vapour phase action seems more efficacious.[156,157] Not surprisingly, the relative efficacy of condensed-phase and vapour-phase action of phosphorus is substrate-dependent, probably dependent on the relative propensity to release volatile fuel and to form char.

Vapour-phase flame-retardant activity appears to be a substantial part of the mode of action of triaryl phosphates in the commercial blends of polyphenylene oxide with high-impact polystyrene; the polyphenylene oxide gives a protective char while the triaryl phosphate provides the flame inhibition needed to suppress the combustion of the polystyrene thermal breakdown products in the vapour phase.[118]

Recent developments in regard to new and superior aryl phosphate additives have emphasised higher molecular weight diphosphates and oligomers. Examples are tetraphenyl resorcinol diphosphate and tetraphenyl bisphenol-A diphosphate, which in the commercial form also contain smaller amounts of mono- and oligo- meric phosphates. Even with these materials, in PC/ABS and in HIPS, the flammability data suggest a correlation between UL rating and volatility; the more volatile phosphates gave the higher ratings.[158] This fact implies that the action of the flame retardant in the vapour phase is an important contributor to the overall action.

Even with the more volatile triphenyl phosphate however, the vapour-phase action seems not to represent the entire mode of action. In poly(2,6-dimethylphenylene oxide) (PPO) with HIPS blends, part of the triphenyl phosphate is retained and promotes the rearrangement of PPO to a benzylic hydroxyphenylene polymer which gives an enhanced char yield.[159] Hydrogen bonding seems to delay the triphenyl phosphate volatilisation.

2.6.3.2   Physical modes of action

Vapour-phase action does not have to involve flame chemistry. A physical mode of flame inhibition, based on heat capacity and heat of vaporisation, and, possibly, endothermic dissociation in the vapour phase, may be important. This physical aspect of vapour-phase flame retardancy has been discussed in connection with halogen systems by Larsen,[7,10,160,161] and, in the same way, phosphorus compounds may contribute at least part of their flame-retardant effect by virtue of their heat of vaporisation and their heat capacity.

Weil attempted to assess the relative contribution of vapour-phase and condensed-phase modes of action with a variety of phosphorus additives in

poly(methyl methacrylate) (PMMA).[64] All the additives were compared at equivalent phosphorus loadings by OI measurement. The smallest elevation of OI was found with trimethylphosphine oxide, a stable volatile compound, and the largest elevation of OI was found with phosphoric acid or alkyl acid phosphates which are non-volatile. These results suggest that the condensed-phase mode of action is a more efficient one than the vapour-phase mode of action with PMMA, even though PMMA is a polymer which depolymerises thermally to volatile monomer.

In the study by Ravey et al,[143,162] it was found that about 80% of the tris(dichloroisopropyl) phosphate (TDCPP) vaporises from a flexible urethane foam before most of the foam decomposes. But injection of large amounts of TDCPP into the flame of a burning non-flame-retardant foam produced no flame extinguishment. In the bottom-up mode of burning the TDCPP-retarded foam, as in the usual CAL 117 test, there was neither char formation nor acid coating produced on the surface. Likewise, in a miniaturised version of the bottom-ignition CAL 117 test, it was possible to see a self-extinguishing effect from merely having the usual self-extinguishing amount of flame retardant placed only on the surface or even on just the corners of a small bar of foam. Thus a *physical* vapour-phase action is indicated which may be produced by a combination of endothermicity, fuel dilution, and the Damkoehler number effect of the outward flow of a non-combustible vapour. However, with the same foams containing TDCPP, top-down burning showed the slow accumulation of a phosphorus-containing carbonaceous barrier layer. Thus, the predominant mode of action was seen to shift depending on the geometry of burning.

2.6.4   Some comments on interaction of phosphorus retardants with other flame retardants

2.6.4.1   Further aspects of the mode of action of halogen–phosphorus combinations

Synergism has been discussed earlier in this chapter. Some problems of defining synergism, with particular attention to the question of halogen–phosphorus synergism, were critically reviewed with reference to real and dubious examples in flame retardancy.[163] Phosphorus–halogen synergism, unlike antimony–halogen synergism, does not appear to be general. Formation of phosphorus oxyhalides, while possible, lacks any direct experimental support but might be inferred from a few instances where the optimum Br:P ratio is about 3:1, such as in a red phosphorus–decabromobiphenyl system.[164] Other than a few instances of synergism,

good additive results are often obtained with combinations of halogen- and phosphorus based flame retardants. One study with tris(dichloroisopropyl) phosphate in epoxy resin showed evidence of vapour-phase action (deduced from volatility), condensed-phase (acceleration of resin degradation with char enhancement) and even some suggestion of a contribution by physical barrier action.[165] However, there are some cases where phosphorus-halogen synergism seems to have been demonstrated. These were discussed earlier in the halogen section.[48,51,59]

2.6.4.2   Interaction of phosphorus with antimony

There are quite a few published formulations showing the attempted use of antimony oxide in combination with phosphorus and halogen. Results sometimes seem to be favourable, but a number of quantitative studies show convincing evidence of an antagonism between antimony and phosphorus.[55,61] In the most pronounced cases, one element cancels out the flame-retardant effect of the other, and in less drastic cases, the flame-retardant effects of the combination are lower than might be expected from adding the effects of the two separate compounds. Detailed studies of triaryl phosphate and antimony oxide in PVC showed that this antagonism only occurred in a part of the composition range.[166,167] This antagonistic effect probably is the result of the formation of antimony phosphate which is very stable and practically inert as a flame retardant.

2.6.4.3   Interactions with mineral fillers

Good E-84 tunnel results are obtained with polyester resins containing alumina trihydrate (ATH) in combination with dimethyl methylphosphonate or triethyl phosphate.[168] By some interpretations of the data, the combination might be said to be synergistic.

A careful study by Scharf compares the effect of TiO_2 and SnO_2 on the flame-retardant char-forming effect of ammonium polyphosphate in polypropylene, together with an intumescent nitrogenous resin.[169] TiO_2 increased flame retardancy by giving a stronger and more continuous char in higher yield; SnO_2, on the other hand, was antagonistic and made the char flakier and more porous, and did not enhance the char yield. The beneficial action of TiO_2 was considered to be a physical 'bridging' effect; the deleterious action of SnO_2 was attributed to an unfavourable chemical interaction with the phosphorus compound.

Recent studies in Lille[170] have shown remarkable synergism of the ammonium polyphosphate-pentaerthritol intumescent flame-retardant system in an ethylene–butylacrylate–maleic anhydride terpolymer based formulation by low levels of an acid zeolite. The presence of the

zeolite appears to enhance the quality of the protective char by decreasing the size of the amorphous domains and preventing the formation of crack-susceptible large domains in the carbon. The formation of aluminophosphates, retention of volatile cracking products, and increased radical concentration in the char are also implicated in the protective mode of action. The relative contribution of these various effects remains to be apportioned.

2.6.4.4   Interactions between different phosphorus flame retardants

What we might call 'phosphorus–phosphorus synergism' has been reported in a few cases where two different phosphorus compounds were used together as flame retardants. Some examples are combinations of a phosphonium bromide or phosphine oxide with ammonium polyphosphate in polypropylene or polystyrene.[171,172] The use of regression analysis provides statistical evidence for, and some measure of, this interaction effect.[119] The reported cases may be instances of a vapour-phase-active phosphorus flame retardant combined with a condensed-phase-active flame retardant, but this is only a hypothesis.

2.6.5   Built-in vs additive phosphorus flame retardants

No general answer can be given as to whether there is any advantage to building a phosphorus flame retardant into a polymer rather than adding it. A review of phosphorus-containing polymers leads to the conclusion that despite the large amount of work done on the synthesis of phosphorus-containing polymers,[173,174] the number of such polymers which are commercial is much smaller than the number of successful phosphorus-containing additives. The same conclusion would certainly be arrived at on the basis of total tonnage. This may be largely because it is more difficult and costly to make a useful phosphorus-containing polymer than to make an additive. However, one study comparing a built-in phosphine oxide structure with an additive phosphine oxide in a polyester showed no advantage for the built-in phosphorus.[175] A study by Stackman[176–178] who compared additive vs co-reacted phosphonate structures in polyesters showed that at a low percentage of phosphorus, the additive was slightly better while at a higher percentage of phosphorus, the co-reactant was slightly better. Flame-retarding polyester fabric by use of built-in phosphorus structures is successful, as is flame-retarding by phosphorus additives; in both cases, less than 1% phosphorus levels are all that are needed to obtain the melt-flow type of extinguishment permitted by tests such as NFPA 701.

2.6.6 Some guidelines from consideration of phosphorus modes of action

To make use of two main categories of phosphorus modes of action, the plastics compounder may find it useful to try to combine a vapour-phase-active (i.e. relatively volatile) phosphorus flame retardant with a condensed-phase-active (i.e. relatively less volatile) phosphorus flame retardant.

To enhance further the condensed-phase mode of action, it may be found helpful to formulate with additional char-forming additives, at least in those cases where the polymer itself does not char very well. Blending good char-forming polymers into poor char-forming polymers along with phosphorus flame retardants may prove helpful. The models for success are PPO-HIPS and PC-ABS blends.

2.7   Modes of action of borates

The use of borax (sodium borate) to flame-retard cellulosics goes back over two centuries.[179] Water-soluble sodium borates as well as borate–boric acid combinations continue to be used in cellulosics and other hydroxyl-containing polymers. The mode of action appears to be a combination of the effect of the formation of a conspicuous glassy inorganic layer, which is often intumescent, and an increase in char formation perhaps through the formation of borate esters as well as through the blocking off of volatile fuel release. Borates and boric acid can also give off water, which provides a heat sink, a fuel diluent, a propellant for the fuel out of the flame zone, and a blowing agent for the glassy intumescent coating.[180]

Zinc borates have become major flame and smoke retardants. Here, a multi-modal action can also be demonstrated. Most of the zinc borates in commercial use are hydrates, with sharply defined endothermic water release temperatures.[181] The use of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, US Borax's FIRE-BRAKE ZB, provides release of 13.5% water at 290–450 °C, which is a good match to the decomposition temperature of PVC and many other common polymers. The water released from FIREBRAKE ZB absorbs $503 \, J \, g^{-1}$ of heat, serves to blow char to a foam, and dilutes the fuel. A more thermally stable hydrate, FIREBRAKE 415, loses water at 415 °C so it is a good match for the decomposition temperature of high-temperature engineering ther-moplastics. Hydrated barium borate is of value as a flame retardant with low water solubility. Hydrated calcium borate has been proposed as a flame retardant.[182] Both these borates share at least the endothermic water-release mode of action with the hydrated zinc borates.

The largest use of FIREBRAKE ZB is in PVC where it can replace part of the usual antimony oxide synergist with good or even superior flame

retardancy, greatly reduced smoke, and lower heat and carbon monoxide release. Part of the smoke-reducing action is due to promotion of char, which represents carbon that did not get into the vapour phase. Most of the boron remains in the char, as does the zinc.

The zinc chloride formed in the condensed phase can catalyse dehydrochlorination and cross-linking. The minor part of the zinc chloride which volatilizes may have flame-inhibiting action. The boric oxide released from zinc borate by the action of acid is a glassy melt which can stabilize the char and inhibit afterglow.[183]

In halogen-free systems, FIREBRAKE ZB still can work by the water-release mechanisms. The flame-retardant action of anhydrous zinc borate in non-halogen systems may be due to an improved char (barrier) layer. Moreover, in the presence of alumina trihydrate, zinc borates can form a porous and ceramic-like sintered layer at temperatures above about 550 °C. This layer can act as a barrier for heat and mass transfer.[184,185]

Detailed studies have been done on the way in which boron compounds inhibit the oxidation of the graphitic structures which are present in char along with amorphous carbon.[186] The boron appears to poison specific oxidation-prone sites on the graphite crystal surface whereas phosphorus poisons a different set of sites.[131]

The question arises whether boron chlorides or boron bromides play a role in the action of zinc borate in halogenated polymers. It has been shown that boron halides are flame inhibitors with about the same order of magnitude of radical-scavenging efficacy as hydrogen halides.[187] However, in a recent Chinese study using zinc borate in PVC, it was found that only a small amount of the boron is lost, presumably as volatile boron halides. In fact this small boron halide release action was suggested to be deleterious – it was not enough to contribute much inhibition but enough to break up the integrity of the barrier layer formed.[188]

2.8   Modes of action of metal hydroxides and other hydrated inorganic additives

Alumina trihydrate (aluminium trihydroxide) and magnesium hydroxide actually do not have water of hydration in their structure as such. The hydroxyl groups bonded to the metal have to undergo endothermic decomposition to produce free water, and this starts at about 220 °C and 330 °C for ATH and magnesium hydroxide respectively. The enthalpy of water release is $1.17\,kJ\,g^{-1}$ for ATH and $1.356\,kJ\,g^{-1}$ for magnesium hydroxide.[189] This endothermicity is certainly part of the mode of action of ATH and magnesium hydroxide.[190]

It has been suggested that this endothermic fuel-diluting water release is not the total explanation for the action of ATH or magnesium hydroxide.

In fact, it has been shown that at low levels, anhydrous alumina can be a more potent flame retardant than hydrated aluminium; this was the case in an epoxy resin, for instance.[191] Anhydrous alumina is an acid catalyst and may be expected to aid charring of polymers prone to acid-catalysed dehydration. Moreover, a layer of refractory mineral can act as a heat barrier. In a case where catalysis can scarcely be invoked, a layer of silica was shown to have a profound depressing effect on heat release, perhaps as a heat-transmission barrier by poor conduction and by reflection of radiant heat.[192,193,194] Magnesia (MgO) is a good thermal insulator, often used as such, and it may be playing this role in magnesium hydroxide-retarded plastics after the water-release mode of action has been exhausted.

Further enhancement of magnesium hydroxide by certain additives may be due to development of the barrier action; novolac synergists which increase the action of magnesium hydroxide in polypropylene visibly retard melt flow at fire-exposure temperatures.[195] Certain acrylonitrile copolymer fibres (which presumably have charring capabilities) enhance the efficiency of magnesium hydroxide in rubber and probably act as physical reinforcement of the barrier.[196] Polycarboxylic resins, perhaps aided by polysiloxanes, enhance the action of alumina trihydrate or magnesium hydroxide by forming barriers during fire exposure.[197]

In a few cases, simple hydrates can be used as flame retardants probably operating mainly by the heat sink/fuel dilution effect. Gypsum, calcium sulphate dihydrate, is a good example; because of its very low cost it has been used as part of the flame retardant system in carpet backing and in polyester resin.[198] Gypsum begins to lose its two moles of water at about $120\,°C$ (too low for use in most thermoplastics). Various clays have flame-retardant action by endothermic water loss; indeed, this mode of flame retardancy was known and used in ancient times.

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