Intumescent Fire-retardant Systems

G. Camino, L. Costa & G. Martinasso
Istituto di Chimica Macromolecolare dell’Università,
V.G. Bidone, 36–10125 Torino, Italy
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ABSTRACT

The use as fire retardants of intumescent systems which on heating give a swollen char is reviewed. Early developments in intumescent organic coatings are described, which provided fundamental knowledge on the chemical composition of intumescent systems. The more recent introduction of intumescent additives into polymeric materials is discussed, with reference to specific problems derived from dilution in the polymeric matrix. The results obtained so far in studies of chemical processes which occur on heating typical intumescent systems, such as mixtures of ammonium polyphosphate with pentaerythritol, are presented.

INTRODUCTION

Ever-improving performance is required from fire-retardant systems for polymeric materials. Concern for the increasing fire hazard accompanying the increasing use of polymeric materials leads to ever more stringent regulations. Reduction of the ease of ignition and of the rate of flame spread were the major objectives previously pursued with fire retardants. However, this approach is rapidly evolving towards a comprehensive appraisal of the overall fire hazard, which also involves the obscuring power, toxicity and corrosiveness of smokes evolved on burning. In fact, it has been recognised that in the sequence of events which leads to lethal consequences in fire,
obscuration by smokes and their toxicity are of overwhelming importance.\textsuperscript{1–3} Moreover, corrosive products may damage equipment and structures well beyond the fire zone, with dramatic effects even in fires of relatively small size, when expensive or strategically important systems such as computing or telecommunication centres are concerned.

These considerations have recently led to the re-examination, in terms of overall fire hazard, of halogen-based systems which are among the most widely used fire retardants. Indeed, on burning, they generally evolve halogen acids and metal halides whose proven efficiency as fire retardants has to be balanced against their known potential effect in increasing the formation of obscuring, toxic and corrosive smokes. Moreover, it has recently been suggested that, on burning, some currently used brominated aromatic fire retardants, highly toxic brominated dibenzodioxines and dibenzofurans may be formed.\textsuperscript{4–8}

In the search for halogen-free fire retardants, increasing attention is being given to intumescent systems which, on heating, give a swollen multicellular char capable of protecting the underlying material from the action of the flame. Fire protection by coatings with intumescent properties has been in use since about 50 years ago, whereas incorporation of intumescent additives in polymeric materials is a relatively recent approach. On burning, these additives should develop the foamed char on the surface of the polymeric material. The suggested mechanism of fire retardance assumes that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the polymer to volatile combustible products. The flame then extinguishes because it is not adequately fed. Since intumescence should occur with limited evolution of volatile products, this condensed-phase mechanism of fire retardance should minimise the undesired secondary effects of halogen-based fire-retardant systems described above. Furthermore, the intumescent char adhering to the molten section of the burning polymer prevents it from dripping, thus eliminating a possible source of propagation of fire which is often enhanced with halogen-based additives.

\textbf{INTUMESCENT COATINGS}

Intumescent fire retardants for polymer materials have generally been developed on the basis of formulations used in coatings, which have been reviewed by Vandersall\textsuperscript{9} and Kay \textit{et al.}\textsuperscript{10} Most of the published information on intumescent coatings is in the patent literature, whereas little is reported on the chemical–physical mechanism of intumescence. Jones \textit{et al.}\textsuperscript{11} defined as ‘carbonifics’ the compounds that in intumescent formulations act as a
source of carbon for the char and 'spumific' those which, evolving gaseous products, induce foaming. Vandersall\textsuperscript{9} classified the chemical compounds of intumescent systems into four categories:

1. Inorganic acid, either free or formed \textit{in situ} by a precursor on heating at 100–250°C.
2. Carbon-rich polyhydric compound.
3. Organic amine or amide.

Examples are shown in Table 1.

The exact function of each component of intumescent mixtures is difficult to know in the absence of detailed studies of the chemical reactions which occur in the intumescence process. Furthermore, some of the compounds listed in Table 1 bear more than one functional group and may perform more than one function, as, for example, melamine phosphate which is both an amine and a source of phosphoric acid. Current speculations indicate that the major source of char is the polyhydric compound (carbonific) which is dehydrated by the action of the acid. Volatile products evolved on heating amines/amides or halogenated compounds (e.g. halogen acid) should perform the spumific function. Also gaseous products formed in the charring step (e.g. water vapour) may contribute to blowing the char. In addition, catalysis of the charring reactions by amines/amides was suggested.

The presence of a compound in each of the above four classes does not

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
A. Inorganic acid source & B. Polyhydric compounds \\
1. Acids & Starch \\
Phosphoric & Dextrin \\
Sulphuric & Sorbitol \\
Boric & Pentaeerythritol, monomer, dimer, trimer \\
2. Ammonium salts & Phenol–formaldehyde resins \\
Phosphates, polyphosphates & Methylo1 melamine \\
Sulphates & \\
Halides & \\
3. Amine/amide phosphates & C. Amines/amides \\
Urea & Urea \\
Guanylurea & Urea–formaldehyde resins \\
Melamine & Dicyandiamide \\
Product of reaction of ammonia with \( P_2O_5 \) & Melamine \\
4. Organophosphorus compounds & Polyamides \\
Tricresyl phosphate & D. Halogenated compounds \\
Alkyl phosphates & Chlorinated paraffins \\
Haloalkyl phosphates & Tetrachlorophthalic resins \\
\hline
\end{tabular}
\caption{Examples of Components of Intumescent Coatings\textsuperscript{9}}
\end{table}
ensure, by itself, intumescent behaviour by the mixture. In fact, a series of chemical and physical processes must occur in an appropriate sequence, while the temperature of the mixture increases, to produce the intumescent phenomenon. It is evident that the carbonific compound must not decompose or volatilise before the acid is available to play its dehydrating role. Furthermore, the foaming gases must evolve as small bubbles through the charring mass to give a multicellular char on subsequent gelling and solidification. This requires appropriate matching of rate of evolution of foaming gases and of viscosity of the mass, both of which depend on the temperature. Intumescent coatings generally give foamed chars with mostly closed cells of diameter 20–50 μm and walls 6–8 μm thick. Assisted nucleation by finely divided solid inert fillers like common pigments, such as titanium dioxide and silica, may allow the control of the size of bubbles formed in the foaming step. Improvement of the mechanical and thermal resistance of the swollen char might improve its protective action. For example, it was suggested that addition of vitrifying agents such as borates or reinforcing mineral fibres may increase the resistance of the resulting intumescent char to physical impact of air currents in fires. In the presence of some pigments, such as titanium dioxide, an inorganic–organic glass char is obtained. Degradation of the organic char and vaporisation of the volatile portion of the inorganic glass at fire temperatures may not alter the physical structure of the foam, leaving a refractory foam which can withstand fire temperatures.

Although there is a vast choice of compounds from which to formulate intumescent compositions, only a few of those listed in Table 1 are used in practice and they have mostly been selected empirically. The inorganic acid, which must be high boiling and not too strongly oxidising, is very often phosphoric acid in the form of an ammonium salt, amide or amine salt, or organic ester, or amide or imide. A linear high-molecular-weight ammonium polyphosphate is most widely used:

$$\begin{array}{c}
\text{O} \\
\text{P=O} \\
\text{ONH}_\text{n}
\end{array}, \quad n = 20–3000$$

which is sparingly soluble in water as required by the weathering characteristics of coatings. Pentaerythritol and its oligomers are traditional polyhydric compounds while polyurethane pentaerythritol or suitable epoxy resins are examples of char precursors for external use. Urea, melamine, dicyandiamide and their derivatives are commonly used amines/amides. Chloroparaffins are the halogenated compounds most widely used. There is now a tendency to avoid halogenated compounds on account of
their potential negative secondary effects described above. Furthermore, their suggested contributions to intumescence, that is the blowing action of HCl eliminated on heating and the concurrent formation of char, are performed to a much larger extent by other components of the intumescent system. Finally, HCl is a known flame poison which could add a gas-phase fire-retardant action to the typical condensed-phase action of the intumescent char. However, it has recently been shown that the contribution of HCl to fire retardance by flame poisoning in polymeric materials might be negligible, depending on the chemical structure of the polymer.14–19

Formulation of intumescent coatings must comply with specific characteristics such as good weatherability, can stability, aesthetic qualities, covering ability, etc., which are difficult owing to the chemical structure and to the relatively large amounts of the intumescent mixtures which must be used for satisfactory fire retardance.9,10 In addition, organic polymers generally used as binders may interact negatively with the process of intumescence. For example, thermosetting resins seem to hinder expansion during foaming.9 On the other hand, special epoxy resins used as binders were shown to act as carbonifics,10 thus partially contributing to the build-up of the char. The major aims for the improvement of intumescent coatings are improving the weatherability by using less water-soluble intumescent components and the synthesis of single chemicals displaying intumescent behaviour.

INTUMESCENT POLYMERIC MATERIALS

The approach generally used in the preparation of intumescent polymeric materials involves blending of the polymer with an additive system which shows intumescent behaviour when heated by itself. The guidelines supplied by Vandersall9 and discussed above are generally followed to select appropriate additives. However, their use in polymers involves specific problems which are different from those encountered in the case of coatings.

1. The additive must be thermally stable at polymer processing temperature, which is often in excess of 200°C.

2. The thermal degradation process of the polymer, which gives large amounts of volatile products and possibly leaves a charred residue depending on the chemical structure of the polymer, must not adversely interfere with the intumescence process.

3. The additive must form the protective foamed char over the entire surface of the burning polymer, in spite of being diluted within the polymer itself rather than being concentrated at its surface as in the case of coatings.
4. The additive must not impair the physical and chemical properties of
the polymeric material. In particular, it should not interact adversely
with fillers or other additives such as stabilisers, which ensure
protection of the polymer during processing and outdoor exposure.

Low water solubility as well as low hygroscopicity of the additives is
required when they are added to polymers used as coatings.

Although intumescence is of general application in polymers, it is
particularly interesting in the case of polyethylene (PE), polypropylene (PP)
and polystyrene (PS), which are among the most widely used of synthetic
polymers (c. 60% of total) and are difficult to render fire retardant since, on
heating, they volatilise quantitatively to mixtures of flammable hydro-
carbons.

Fire-retarded PP was obtained by addition of typical intumescent
mixtures of dipentaerythritol with either ammonium polyphosphate or
melamine pyrophosphate which, however, was unstable at processing
temperature. A suitable intumescent additive for PP was obtained by
heating $\text{P}_2\text{O}_5$ with dipentaerythritol and melamine.$^{20-23}$ The chemical
structure of the intumescent additive was not investigated. Adverse
interactions between the fire-retardant additive and other additives in
polymeric materials is illustrated by the fact that the fire retardance rating of
this PP (30% of intumescent additive) was significantly lowered in the
presence of 1% of some pigments such as carbon black or phthalo cyanine
green. The intumescent additive was much less effective when it was added to
other polymers (e.g. PE, PS, etc.), probably because of improper matching of
the thermal behaviour of the additive with the temperature of degradation
of the polymer, which depends on its chemical structure.$^{20}$

Mixtures of ammonium polyphosphate and nitrogen-containing com-
ounds such as products of condensation of formaldehyde with substituted
ureas or products of reaction between aromatic diisocyanate and
dipentaerythritol or melamine have been used as intumescent additives for
polymeric materials, in particular polyolefins and polystyrene.$^{24-26}$

Compound I (dimelamine salt of 3,9-bis(hydroxy)-2,4,8,10-tetraoxa-3,9-
diphosphaspiro[5,5]undecane-3,9-dioxide), which contains in one molecule
the three chemical structures required for intumescence listed by
Vandersall$^9$ (phosphoric acid, dipentaerythritol and melamine), was syn-
thesised and showed intumescent behaviour.$^{27,28}$
Compound I was shown to be an efficient fire retardant for PP\textsuperscript{29} and other polyolefins.\textsuperscript{30} However, in the case of PP it was found that the efficiency of I was increased by using it in conjunction with tripentaerythritol. This indicates that in I the optimum balance between carbonific and spumific functions is not achieved. Compound I seems, in fact, to be deficient in the carbonific ingredient.\textsuperscript{27} Indeed compound II (melamine salt of bis(2,6,7-trioxa-1-phosphabicyclo[2,2,2]-octane-4-methanol) phosphate), which is richer in pentaerythritol structures than I, imparted equivalent fire retardance to PP as the mixture of I with tripentaerythritol:\textsuperscript{27}

\[
\begin{array}{c}
\text{O} \\
\text{O--O} \\
\text{O--P--O} \\
\text{O} \\
\text{NH}_3 \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{H}_2\text{N} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{H}_2\text{N} \\
\end{array}
\]

This approach, involving the synthesis of additives in which a well-defined compound has intrinsic intumescent behaviour, offers obvious advantages over the use of additives which are mixtures of several compounds, generally two or three. In this latter case the components of the additive must interact chemically to originate the intumescence phenomenon and this might occur with low efficiency since the components are diluted in the polymer matrix. However, experimental evidence grows that fire retardants must be tailored to the type of polymer as regards thermal behaviour, chemical species formed on heating, etc. Therefore, when more than one chemical structure is participating in the fire-retardant action, the optimum ratio between them must be sought by exploring, for each polymer, the complete range of compositions, since the ratio itself might depend also on the overall fire-retardant loading.\textsuperscript{31,32} Thus, in the case of intumescent systems composed of phosphoric acid, pentaerythritol and melamine, it is convenient, at least in the exploratory stage, to use a ternary mixture of additives. In Fig. 1 is shown the dependence of the oxygen index (OI) of PP, to which the ternary additive ammonium polyphosphate–pentaerythritol–melamine is added up to an overall content of 30%. The OI–composition relationship is obtained by applying a statistical computational method previously described\textsuperscript{31,32} to experimental data referring to selected compositions. In Fig. 1 only data for overall loadings of 10, 20 and 30% are illustrated. However, the method supplies data for any mixture in the compositional range examined. It can be
seen that in this case the additive composition corresponding to maximum OI does not depend on the overall loading between 20–30%, which is the range of practical interest. Since, on the basis of data reported below, it is likely that the ternary additive gives, on heating, structures of the type I or II in the PP matrix, the data of Fig. 1 can be compared with those of Halpern et al.27 These authors found that the OI of PP increases if, instead of I, in which the ratio phosphorus atoms:pentaerythritol structure molecules:melamine molecules (P:PER:M) is 1:0.5:1, compound II is used in which the ratio is 1:0.7:0.3. This is in agreement with the data in Fig. 1 since compound II is characterised by a ratio P:PER:M closer to that of maximum OI in Fig. 1 (1:0.5:0.3) than compound I. Compositions corresponding to maximum OI were found to be strongly dependent on the chemical structure of the polymer.

It has recently been pointed out that organic-based self-intumescent systems used as polymer additives are generally characterised by several disadvantages. In particular, the reactions which occur in the intumescence process are exothermic, thus limiting the thermal insulating value of the additive system. Furthermore, the char obtained often lacks structural integrity and may have low thermal resistance.33 This has led to the evaluation of low melting glasses or glass ceramics34 (melting, softening point <600°C) and of inorganic glass-forming systems33,35 as potential intumescent fire retardants and/or smoke suppressants for polymers (Table 2). A blowing agent may be added to the glass or the glass itself may decompose on heating, generating gaseous products. In addition, it was
TABLE 2
Inorganic Intumescent Glasses and Glass-forming Systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Components (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>K₂SO₄ 25</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄ 25</td>
</tr>
<tr>
<td></td>
<td>ZnSO₄ 50</td>
</tr>
<tr>
<td>Phosphate–sulphate</td>
<td>P₂O₅ 36.6</td>
</tr>
<tr>
<td></td>
<td>ZnSO₄ 19.5</td>
</tr>
<tr>
<td></td>
<td>Na₂O 18.3</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄ 9.7</td>
</tr>
<tr>
<td></td>
<td>K₂SO₄ 9.7</td>
</tr>
<tr>
<td></td>
<td>ZnO 6.2</td>
</tr>
<tr>
<td>Borate–carbonate</td>
<td>B₂O₃ 86.2</td>
</tr>
<tr>
<td></td>
<td>Li₂CO₃ 11.2</td>
</tr>
<tr>
<td></td>
<td>CaCO₃ 2.6</td>
</tr>
</tbody>
</table>

suggested that in the presence of carbon char this may be oxidised by components of the glass with formation of CO. Finally, gaseous decomposition products of the polymer may provide the foaming action.

For example, low melting sulphate glasses and glass ceramics promote intumescence and additional charring in poly(vinyl chloride) with the formation of an effective thermal barrier on exposure to flame. Ammonium pentaborate was shown to be an effective intumescent char-forming fire retardant for thermoplastic polyurethanes, in combination with conventional fire retardants. Boric acid derivatives have indeed been used as fire retardants for cellulosic materials and zinc borate is currently used in synthetic polymers. The mechanism of action of these compounds is likely to be of the char-forming intumescent type, although the occurrence of the intumescent behaviour was not generally discussed.

There is, in fact, overlap in the literature between char-forming and intumescent fire-retardant systems and ambiguity in their definition. Char-forming systems should increase the char yield of the polymer which, by itself, reduces the flammability of the polymer because it leads to a decrease of the total amount of combustible volatiles formed. For example, for halogen-free polymers, in the absence of additives, the following relationship was shown to hold between weight % of pyrolysis char at 850°C (CR) and OI:

\[ OI = 17.5 + 0.4CR \] (1)

Quantitative definition of intumescent systems is not yet available, owing
to insufficient understanding of the detailed mechanism of their fire-retardant action. The swollen multacellular structure and the overall insulating action are qualitative characteristics presently associated with intumescent chars. Since the structure of the char was often not discussed in char-forming systems,\textsuperscript{38} it is difficult to classify them among intumescent systems unless the intumescent characteristics of the char are specified.

Evidence of a contribution by the polymer to the intumescent char was given in the case of PP with added ammonium polyphosphate and either pentaerythritol\textsuperscript{39} or polyurea\textsuperscript{40} or polyurethane.\textsuperscript{41} It was also suggested that volatile degradation products of PP might perform a blowing action.\textsuperscript{40,41}

One of the major problems of intumescent fire-retardant additives developed so far is that they have to be used at relatively high loading (20–30\%) with adverse implications in terms of costs, processability, properties of the polymeric material, etc. The ideal target, which is the development of highly efficient systems capable of involving the polymer in the charring and blowing process, requires a detailed knowledge of the chemical and physical processes through which intumescence occurs.

### CHEMICAL REACTIONS IN INTUMESCENT SYSTEMS

Charring which occurs on heating most traditional intumescent systems is due to interaction between an inorganic acid and a polyhydric compound.\textsuperscript{9} Cellulose is the polyhydric compound whose charring process by reaction with inorganic acids has been most studied, since cellulose is the most abundant natural organic material and therefore a major source of fuel in fires. These studies, which have been reviewed,\textsuperscript{38,42–44} have supplied mechanisms for the dehydrating action of inorganic acids leading to the char which might be assumed to occur also with other polyhydric compounds of similar structure. Extension of these mechanisms to pentaerythritols (monomer, dimer, etc.), which are the polyhydric compounds often used in polymeric materials, is not possible owing to structural differences between them and cellulose.

Vandersall\textsuperscript{9} reported that, on progressive heating, dipentaerythritol–ammonium polyphosphate mixtures soften and melt at 215°C, remaining clear up to 238°C when evolution of gases begins. The mass then darkens, undergoing gelation at 360°C. The following sequence was suggested:

1. Decomposition of the phosphate at 215°C.
2. Esterification of the alcoholic groups shortly thereafter, with evolution of water.
3. Solidification of a foamed carbon–phosphorus char at c. 360°C.
A maximum carbon content in the char at 500°C was observed with an initial molar ratio $\text{CH}_2\text{OH}:\text{P} = 6:1$.

A detailed study of reactions which occur on heating mixtures of ammonium polyphosphate (APP) and pentaerythritol (PER) was carried out by measuring weight loss, rates of evolution of water and ammonia, and using $^{31}$P-NMR characterisation of products of reaction.\textsuperscript{45–48} On progressive heating, reactions between APP and PER occur in several steps. The first step, studied at 210°C, leads to disruption of the polyphosphate chain while phosphoric ester bonds, $\equiv\text{P}($O$\text{CH}_2\text{)}\equiv$, are formed. The process begins with alcoholysis of APP by PER (or phosphorylation of PER by APP) without elimination of gaseous products:

\[ \begin{align*} 
\text{ONH}_4\text{ONH}_4\text{ONH}_4\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{ONH}_4\text{ONH}_4\text{ONH}_4\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{ONH}_4\text{ONH}_4\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \end{align*} \] \hspace{1cm} (2)

Cyclic phosphate ester structures are then formed with elimination of ammonia and water, e.g.

\[ \begin{align*} 
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \end{align*} \] \hspace{1cm} (3)

Repetition of reactions (2) and (3) leads to pentaerythritol diphosphate structures which are identified in the product of reaction:

\[ \begin{align*} 
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \\
\text{HO--CH}_2\text{CH}_2--\text{OH} & \rightarrow \text{HO--CH}_2\text{CH}_2--\text{OH} \end{align*} \] \hspace{1cm} (4)
The final structure of the product of reaction depends on the original PER/APP ratio. Up to a molar ratio $-\text{CH}_2\text{OH}/P (R)=2$ bicyclic structures (4) bridged by $P-O-P$ groups are stoichiometrically possible. However, simultaneous formation of pentaerythritol tri- or tetraphosphate cannot be ruled out. At $R > 2$ other structures could be formed, such as (5) or (6):

The triesterified phosphate groups were not detected by solution $^{31}P$-NMR, but it is known that they hydrolyse at a higher rate than mono- and diphosphate esters.\textsuperscript{49}

PER-richer mixtures evolve water in excess of that corresponding to complete esterification of alcoholic groups. It is therefore likely that intermolecular dehydration of PER also takes place with formation of ether bonds, since APP was shown to induce dehydration of $1-4$ butanediol to tetrahydrofuran:\textsuperscript{50}

These results show that the first step of the reaction between APP and PER leads to a product characterised by pentaerythritol phosphate and possibly ether structures which, on further heating, display the intumescent behaviour. Chemical reactions which occur in the intumescent process have been studied using a well-defined pentaerythritol diphosphate (the acid corresponding to the melamine salt I), which is a model compound with structures identified in the first step of the reaction between APP and PER:
The main features of the thermal behaviour of III are summarised in Fig. 2 and Table 3. Compound III degrades with evolution of high yields of gaseous products in steps 1 to 3 and 5, whereas in step 4 high-boiling \( \text{P}_2\text{O}_5 \) is mostly formed. Swelling of the mass, as measured by a previously described technique,\(^5\) begins at about 300°C. It is at a maximum at 325°C (charring steps 1 and 2) and tends to disappear at higher temperatures when extensive volatilisation of the sample takes place.

These data show that foaming takes place in a relatively narrow range of temperature by the effect of a limited fraction of the overall volatile products of degradation of III. Agreement is found between the thermal behaviour of III and that of APP-PER mixtures above the range of temperature corresponding to formation of phosphate esters in the mixtures (\( > 250^\circ\text{C} \)).\(^4\)

**TABLE 3**

Degradation Steps of III Heated at 10°C/min under Nitrogen, 60 ml/min

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature range (°C)</th>
<th>( T_m ) (°C)</th>
<th>Weight loss (%)</th>
<th>Main volatile products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Partial</td>
<td>Cumulative</td>
</tr>
<tr>
<td>1</td>
<td>280–320</td>
<td>310</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>320–350</td>
<td>330</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>350–500</td>
<td>425</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>500–700</td>
<td>550–600</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>( &gt; 750 )</td>
<td>875</td>
<td>( &gt; 14 )</td>
<td>( &gt; 84 )</td>
</tr>
</tbody>
</table>
It is likely that any blowing agent to be used in combination with III or APP–PER mixtures would supply gaseous products in the range of temperature in which swelling of the phosphate ester structure occurs (300–350°C). Urea, which is a common blowing agent for intumescent coatings, would be unsuitable for such systems since it eliminates volatile products on heating, mostly in the range 150–300°C. In fact it was found that urea tends to depress rather than increase intumescence and fire retardance of APP–PER mixtures added to PP. On the other hand, melamine volatilises in the range 270–400°C, which overlaps that of swelling in Fig. 2. Assuming that melamine does not significantly modify the thermal behaviour of III, this might be one of the reasons for the effectiveness of compound II.

As far as interactions which occur on heating between the intumescent additive and the polymer are concerned, it was shown that dilution of APP–PER mixtures in PP does not apparently modify the steps of ester formation and of swollen char production from the additive ($T < 400°C$). Partial charring of PP seems to take place in the presence of the additive which, however, does not modify the composition of the hydrocarbon mixture evolved by degrading PP.

In this respect reactive species, either original or formed on heating the additive and the polymer, have to be taken into account. For example, APP, which is most often used as the acid source in intumescent systems, eliminated ammonia on heating, forming polyphosphoric acid (PPA), a well-known highly reactive condensing agent or acid catalyst for organic reactions. Data are reported in the literature on the effect of in-situ generated PPA on the degradation or combustion behaviour of polymers. The degradation of acid-sensitive polymers such as polyesters, polyurethanes, etc., is generally modified in the presence of APP with increase of char yield. PPA is less effective in modifying the degradation of hydrocarbon polymers with a possible slight reduction in the rate of volatilisation. Significant promotion of charring of polystyrene in the presence of ammonium phosphate is reported, however. Detailed mechanistic studies of the reactions induced by PPA in these systems have not been reported. It was suggested that a film of PPA could cover the degrading material and might physically trap volatile products, thus favouring their further degradation to char. A similar mechanism might explain the slightly reduced rate of volatilisation of PP in the presence of APP and acid catalysed isomerisation of oligomers evolved by PS degrading in mixtures with APP.

Reactive species may also be formed by reaction of APP or PPA with coadditives in intumescent systems. For example, with intumescent additives for PP, APP–polyureas or APP–polyurethanes, a high yield of
oligomers with amine reactive end-groups is formed on heating. It was speculated that these end-groups, probably phosphates, might induce charring by reaction with olefinic double bonds of degrading PP molecules.\textsuperscript{40,41}

**CONCLUSIONS**

It is shown that intumescent behaviour can be imparted to polymers by means of suitable halogen-free additives. Fire-retardant polymeric materials characterised by reduced overall fire hazard in terms of amount, obscuring power and toxicity of smokes evolved on burning can indeed be prepared.\textsuperscript{71–73} The effectiveness of such additives is, however, still inadequate to allow their general use. This is a consequence of the current poor understanding of the mechanism of intumescence. Only a detailed mechanistic knowledge of chemical and physical processes which occur in intumescent polymeric materials may lead to the development of highly efficient intumescent systems.

Future mechanistic work should be mainly directed to the understanding of the chemistry of charring processes, to the correlation between gas evolution and swelling of the charring mass, and to the characterisation of the char in terms of chemical structure and physical properties. Furthermore, the precise mechanism of fire retardance of the intumescent systems should be defined. In fact, mechanisms involving, in general, the physical insulating action of the char are presently stated without sufficient experimental support. In this connection mechanistic studies on intumescence should also be related to models developed for heat and mass transfer in intumescent systems.\textsuperscript{12,74}

**REFERENCES**

Intumescent fire-retardant systems

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