Reduction of smoke formation from and flammability of thermoplastic polymers by metal oxides

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(Received 17 May 1983)

The properties of various metal oxides have recently been investigated in terms of flame retardance and smoke suppression. None of the metal oxides is an effective flame retardant on its own, but their use in conjunction with halogen compounds often results in systems which are effective as flame retardants, typically antimony(III) oxide, anhydrous aluminium(III) oxide and hydrous tin(IV) oxide phases. The two latter systems show joint flame-retardant and smoke-suppressant effectiveness. Most of the metal oxides examined have some effectiveness as smoke suppressants and, in this connection, magnesium(II) oxide hydrate and silicon(IV) oxide are outstanding, while useful influences can be obtained from anhydrous magnesium(II) oxide, molybdenum(VI) oxide and titanium(IV) oxide. A large proportion of the flame-retardant effectiveness is often derived from the volatilization of a halogenated species or of a metal halide. Some condensed-phase action is always essential at the corret temperature, as shown by the fact that synergism exists between halogen compounds and metal oxides which are catalytic but do not form volatile halides, such as iron(III) oxide, while antagonism is found with some metal oxides with easily volatile halides, such as zinc(II) oxide.

Keywords Smoke suppressants; flame retardants; metal oxides; flammability; organic polymers; metal oxide-halogen systems

INTRODUCTION

The inhibition of polymer combustion involves substrates which are to be employed either under conditions where they may be exposed to local high temperatures or in applications where their breakdown may produce undesirable hazards. The conferment of flame retardance is the process by which polymers are either protected from undergoing a rather more complete destruction of the material than simple loss of mechanical properties or forced to change the course of this decomposition so as to form products that are less hazardous.

The production of smoke from a burning system involves loss of visibility in the surrounding area and is usually accompanied by the formation of lachrymatory and other toxic products. Most fire victims are, in fact, overcome by the effects of smoke rather than by those of heat. Reduction of the smoke-forming tendency of a polymeric system will thus increase the safety limit by allowing the fire victims additional time to escape.

In practice the technology of flame retardance usually involves either the use of additives or the replacement of monomers by less flammable analogues[1-3]. These compounds do not, very often, confine their action to one of the separate stages involved in polymer combustion. Many, if not most, flame retardants may function simultaneously by several different mechanisms, often depending on the nature of the organic polymer.

The use of metal oxides as flame retardants had already been suggested by Sir William Perkin at the turn of the century[4-7]. It was not, however, until World War II, that antimony trioxide began to be used, and it was soon shown that Sb_2O_3 is generally ineffective in the absence of

halogens[8-10]. It is the apparent synergism between antimony and halogens which has been the cause of the wide use of antimony as a flame retardant[11-13]. The mechanism of action of antimony–halogen systems has been the subject of much research and is the butt of deep controversies. The greatest amount of work has initially been devoted to the identification of the active species and to the determination of the phase in which the flame-retardant action takes place. Lately, the halogen-to-metal ratio has also received significant attention[14].

Aluminium oxide trihydrate is the flame retardant most abundantly used for plastics during the last few years (representing almost 44% of the total in the United States in 1978)[15]. This implies a phenomenal rise since hydrated alumina was introduced only around the mid-1960s as a flame retardant for unsaturated polyester resins, on account of its low cost[16]. Another early source of interest was its effect as a smoke suppressant[17]. Its use in conjunction with halogen compounds, however, is relatively novel[18,19].

Although hydrous tin(IV) oxide was the first metal oxide used as a flame retardant[5,7], its effectiveness has only recently been reinvestigated[20]. Other metal oxides which have been investigated include molybdenum(III) oxide, magnesium(II) oxide, silicon(IV) oxide[21-23], iron(III) oxide and titanium(IV) oxide. None of these metal oxides is a very efficient flame retardant at low loadings in the absence of halogen compounds.

The present paper thus starts with a brief description of the mechanism of action of halogen compounds on their own and subsequently presents some recent findings related to the use of metal oxides as flame retardants

and/or smoke suppressants, principally in the presence of halogens.

EXPERIMENTAL

For those experiments carried out at the City University, the samples were prepared by milling and pressing[18], the flammability of polymer–additive systems was measured by the limiting oxygen index (LOI) method and smoke production was measured by means of a dynamic photometric method, as described previously[20,21]. Simultaneous thermal analyses were carried out on a Mettler Thermoanalyser II thermobalance[24].

RESULTS AND DISCUSSION

Mechanism of action of halogen compounds on their own

The fact that chlorine exerts some kind of flame-retardant action can be deduced from the relatively low flammability of polymers containing this halogen chemically bound in their structure. The chemical nature of the environment surrounding the bonded chlorine is very important as is apparent from plots of limiting oxygen indices (LOI) of chlorinated polyethylenes and polypropylenes against the chlorine content[2]. When the chlorine atom is attached to a tertiary carbon atom, as in polypropylene, a large flame-retardant effect is found at very low levels of chlorine[25]. When the chlorine is attached to secondary carbon atoms, the flame-retardant effect is much smaller and there is also a clear change of slope, so that at low loadings the chlorine is much less effective than at high loadings. The change in slope occurs at a chlorine level that would roughly correspond to a structure such as C_4H_7Cl. These studies, and others showing the LOI and LNOI (limiting nitrous oxide index) curves to be parallel suggest predominantly condensed-phase action[26].

It has traditionally been assumed that chlorinated additive flame retardants act by virtue of their ease of elimination of hydrogen chloride. Thermogravimetric studies of the decomposition of liquid and solid chlorinated alkanes frequently used as flame retardants have shown that hydrogen chloride is in fact evolved, at least in the absence of polymer[27,28]. This suggests that HCl is effective only in the later stages as a gas-phase flame inhibitor. Thus the flame chain carriers would react with HCl and transform reactive radicals into relatively unreactive ones such as chlorine atoms.

It can thus be concluded that, although there may be some gas-phase action for chlorine compounds, it is relatively inefficient and the bulk of the flame-retardant effect takes place in the condensed phase[2].

The most widely accepted mechanism for the action of bromine-containing compounds as flame retardants involves the release of volatile species, mainly hydrogen bromide, into the gas phase, where they then inhibit the flame reactions[29]. Hydrogen bromide is produced by the thermal decomposition of many organic bromine compounds; it then interacts with the highly reactive free radicals which are the chain carriers responsible for the propagation of combustion, forming bromine atoms[30,31] which are relatively unreactive but can still eventually abstract hydrogen from the polymeric fuel or its combustible decomposition products to regenerate hydrogen bromide.

This series of reactions reduces the concentration of the oxidizing hydroxyl radicals and inhibits the normal flame reactions, as well as the subsequent oxidation of CO to CO_2.

An alternative, purely physical theory[32,33], suggests that all four halogens have a relative effectiveness which is in direct proportion to their atomic weights,

$$I:Br:Cl:F :: 6.7:4.2:1.9:1.0$$

This theory assumes that the principal role of the halogens is to increase the total mass of material that must be introduced into the gas phase per unit time, without at the same time producing an increase in the heat flux back from the flame to the polymeric fuel.

It can be concluded that, although there may be some effect on the condensed-phase decomposition of the polymer, bromine probably acts mainly by a free-radical mechanism in the gas phase.

Metal oxides on their own

Table 1 shows that, while none of the metal oxides discussed here are efficient, on their own, in reducing the flammability of the polymeric substrate, several of them have significant effects on smoke production. Thus, for example, antimony oxide may increase the smoke-forming tendency of the polymer with which it is associated, as is the case, for example, with a thermosetting chlorinated polyester resin[34] and with HDPE, or it may decrease smoke production, as with ABS or polystyrene. Hydrated compounds are normally effective smoke suppressants on account of the production of water in the vapour phase, although the injection of water as such into the oxidant gases does not reduce smoke formation[35]. This work shows that, in fact, there is, in many cases, little difference between the hydrated and anhydrous forms of the oxide, at least on their own. Moreover, most of the oxides studied show some effectiveness in decreasing the amount of smoke generated from the polymer, the most effective additives being silica (pyrogenic) and hydrated magnesium oxide. Another oxide which can be an effective smoke suppressant is nickel(II) oxide[36,37]. A recent comprehensive study has also shown that many oxides are useful smoke suppressants for poly(vinyl chloride)[38].

Antimony oxide

There must be some gas-phase contribution to the flame-retardant action of the antimony–halogen system. This is shown by the non-parallel behaviour of the LOI and LNOI curves[26] and further evidence for a gas-phase mechanism is provided by the fact that at least 50% of the antimony is volatilized from polymers also including halogens[39], while 95% of the antimony remains in the solid residue when halogen-free polymers are burnt[26].

Thermogravimetric analysis of the polymer–additive system shows, however, that the stage of polymer decomposition in which the substrate gives off most of the volatile products is the one most affected by the antimony[27,28]. This is clear evidence for condensed-phase action, which probably occurs before the gas-phase reactions.

The optimum ratio for the Cl–Sb or the Br–Sb systems has until very recently been assumed to be 3:1. This does not, however, necessarily imply that volatile trihalide is

Table 1 Flame retardance and smoke suppression* by metal oxides

System	Loading (phr) 0 LOI	D_s	10 LOI	D_s	20 LOI	D_s	30 LOI	D_s	40 LOI	D_s
Sb_2O_3/ABS	18.6	732	18.9	711	19.6	607	20.5	542	20.8	499
Sb_2O_3/HDPE	18.5	71	18.5	86	19.4	112	20.3	117	20.7	161
Sb_2O_3/PS[a]	18.4	530			19.8	435				
Al_2O_3/ABS	18.6	732	19.1	629	19.2	504	19.3	381	19.5	293
Al_2O_3/HDPE	18.5		18.5		18.6		18.6		18.7	
AlOOH/ABS	18.6	732	18.9	585	19.0	456	19.2	307	19.6	181
AlOOH/HDPE	18.5		18.6		18.7		18.8		18.8	
$Al_2O_3.3H_2O$/ABS	18.6	732	18.8	547	18.9	398	19.0	263	19.8	150
$Al_2O_3.3H_2O$/HDPE	18.5		18.6		18.8		19.0		19.2	
SnO_2/ABS	18.0	732	18.2	311	18.3	285	18.4	213	18.6	161
$SnO_2.xH_2O$/ABS	18.0	732	18.7	304	18.9	271	19.2	234	19.4	206
SiO_2/PS[b]	18.4	983	18.5	910[c]	18.6	480[d]	18.6	330[e]	19.2	330[f]
MoO_3/PP	17.4	42	17.5	41	17.7	38	17.9	36	18.1	34
MoO_3/PS	15.8	2556	18.6	1804	18.9	1668	19.0	1451	19.2	1346
$Mg(OH)_2$/ABS	18.0	732	18.4	726	18.8	450	19.2	322	19.7	107
$Mg(OH)_2$/PP	17.4	42	17.5	28	17.6	18	17.7	17	17.7	16
$Mg(OH)_2$/PS	15.8	2556	17.2	375	18.5	346	18.6	263	18.7	149
MgO/PS	15.8	2556	17.8	730	18.4	500	18.9	306	19.9	293
Fe_2O_3/PP	17.4	42	18.3	57	18.3	87	18.3	79	18.3	75
Fe_2O_3/PS	15.8	2556	17.5	2373	17.6	2193	18.3	1634	19.5	1019
TiO_2/PP	17.4	42	17.4	45	17.8	48	18.3	40	18.9	37
TiO_2/PS	15.8	2556	17.7	2294	18.9	2223	19.2	2103	19.7	1988

[a] Berk smoke chamber
[b] Berk smoke chamber; Silica: Aerosil 200
[c] 1 phr
[d] 3 phr
[e] 5 phr
[f] 10 phr
* LOI = limiting oxygen index; D_s = maximum smoke density

the active intermediate. The initial assumption made was that antimony oxyhalide was the species responsible for the flame-retardant action[9,13,40]. Studies of the thermal decomposition of antimony oxychloride do in fact show that this compound decomposes, yielding, in three endothermic steps, gaseous antimony trichloride and a solid residue of Sb_2O_3. Thermogravimetric studies led to the conclusion that SbOCl is formed *in situ* and then produces $SbCl_3$, which is the actual flame retardant[40]. Antimony trichloride is unfortunately too unstable to be incorporated into a polymer and cannot thus be used in this form as a flame retardant. This means, of course, that the theory cannot be tested directly. However, mass spectrometric studies of the flames above polymers containing antimony and chlorine have indicated that there is no $SbCl_3$ in the flame zone, although solid antimony monoxide (SbO) and even metallic antimony (Sb) can be detected[41]. A sequence of reactions has therefore been suggested where the active species proposed are solid antimony monoxide and gaseous hydrogen chloride, the inhibitory action being at least partly heterogeneous. Thermal analysis of systems containing simply antimony oxide and a chlorinated additive show that there is extensive volatilization of the antimony, and that it is virtually complete only at a Cl/Sb ratio significantly above stoichiometric[42].

In conclusion, it now seems probable that some reaction takes place in the condensed phase to produce the antimony trihalide, possibly via the intermediate formation of a Lewis acid. Once antimony halide is formed, it volatilizes and breaks down rapidly in the hot pre-flame zone to produce SbO and hydrogen halide,

which are the active species reaching the flame zone. It is probably the existence of the additional heterogeneous scavenging action of SbO, reminiscent of the effect of lead oxide formed from lead alkyls added to motor gasolines, that is the key factor allowing the drastic reduction in the proportion of halogen required to render a polymer flame-retardant.

It is also of interest, in this connection, to identify the optimum atomic ratio of halogen to antimony for flame retardance. A study of polyester laminates showed that the extinction time passed through a minimum at a value that could be 3 (that is, stoichiometry), but other interpretations of those results are also possible[43]. The main objection to such studies is that the concentrations of all three components are not varied simultaneously and that a preferred result is sought and frequently found. A comprehensive analysis with full variation of the concentrations of all components, by LOI, of the HDPE–Sb_2O_3–chlorinated wax and of the ABS–Sb_2O_3–decabromobiphenyl systems showed that the optimum ratio is ~7 for polyethylene and ~9 for ABS[14]. Furthermore it is clear from *Figure 1* that different, incorrect, ratios would be found if these were only partially (e.g. linearly) varied.

Partial replacement of antimony oxide by other metal oxides can be very effective, as in the case of ferric oxide, or antagonistic, as in the case of zinc oxide[44]. This is very interesting because zinc halides are even more volatile than antimony halides and ferric halides are involatile. This shows that the action in the gas phase is not pronounced enough to explain the mechanism of antimony–halogen flame retardance[42,45]. Zinc halide
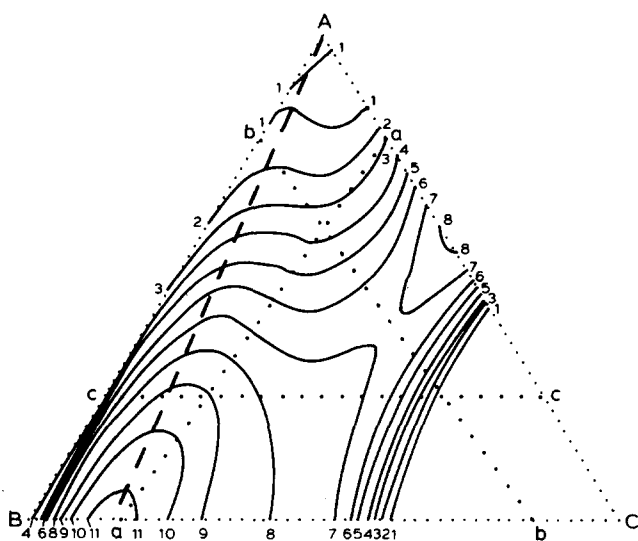
Figure 1 Flammability of the system containing ABS, decabromobiphenyl (DBB) and antimony(III) oxide: A, (1.0, 0.0, 0.0); B, (0.6, 0.4, 0.0); C, (0.6, 0.0, 0.4). *LOI* values: curve 1, 19.5; 2, 21.5; 3, 23.5; 4, 25.5; 5, 27.5; 6, 29.5; 7, 31.5; 8, 33.5; 9, 35.5; 10, 37.5; 11, 39.5. The broken line represents the optimum atomic Br/Sb ratio for flame retardance; the dotted line aa represents the addition of DBB to a mixture of ABS and 10 phr of Sb_2O_3; the dotted line bb represents the addition of Sb_2O_3 to a mixture of ABS and 10 phr of DBB; the dotted line cc represents the addition of mixtures of DBB and Sb_2O_3 at a fixed total loading of 30 wt%

volatilizes too early to be effective, while ferric oxide catalyses the volatilization of antimony halide at just the right stage in the process[42].

Aluminium oxide

Aluminium oxide trihydrate has a greater effect on kinetic smoke parameters than on the maximum smoke density for SBR rubber[2,46], suggesting a chemical effect of the additive in the condensed phase. This was confirmed by studies of alumina and halogen compounds[18,19].

Thermogravimetric studies of mixtures of anhydrous alumina with chlorinated wax showed no volatilization of aluminium chloride. This only served to confirm that alumina is unlikely to act in the gas phase. Perhaps more important is the fact that little apparent effect is found on the thermal decomposition pattern of the chlorowax. Samples of ABS containing decabromobiphenyl and of high-density polyethylene (HDPE) containing chlorinated wax, in both cases in conjunction with either anhydrous alumina, alumina monohydrate or alumina trihydrate, were heated in the source of a mass spectrometer and the volatile products were analysed. In no case were Al–Cl or Al–Br species found, which is a further confirmation that the alumina acts primarily in the condensed phase.

The limiting oxygen indices of ABS treated with decabromobiphenyl (DBB) and with each of the aluminium oxides show very definite signs of synergism[18]. The LOI of the polymer containing the mixture is compared with the LOI which would correspond to an additive effect of the flame retardants (LOI_{add}):

$$LOI_{add} = LOI_{Br} + LOI_{Al} - LOI_P$$

where LOI_{Br} is the LOI value of the polymer containing bromine, LOI_{Al} is that of the polymer containing Al_2O_3 or

$Al_2O_3 \cdot 3H_2O$ and LOI_P is that of the untreated polymer. It can be seen from such a figure that, particularly with ABS, a very pronounced synergism occurs between the halogen compound and anhydrous alumina. This is slightly less marked with the trihydrate, where the effect occurs principally at high loadings of Br (Br:Al > 3:1), and is much less noticeable with the monohydrate.

A comprehensive analysis by means of a triangular diagram shows that the optimum atomic ratio Br/Al is very different for all three grades of alumina and is lowest for the anhydrous compound[19], at ~1.5. This system produces very high LOI values, that is to say very low flammability, similar to the values found for antimony oxide. The other two hydrates are much less effective and there is little difference in effectiveness between them although the optimum ratios increase with increasing water content. The anhydrous oxide is also a very effective smoke suppressant since there is an area in the middle of the triangular diagram where the amount of smoke produced is not greater than that found from ABS itself and where there is an LOI value of almost 30 (*Figure 2*).

Even though alumina seems to have a chemical mechanism of action, its efficiency in the absence of bromine is relatively low so that fairly high concentrations must normally be used as compared with those of other flame retardants. This limits its use to polymers where considerable proportions of other material can be incorporated without causing an unacceptable alteration in the physical or mechanical properties. Its abrasiveness may also be a disadvantage during the processing of the polymer.

Finally, aluminium oxides have also been found to be possible partial replacements for antimony oxide in the system Sb_2O_3–Br–ABS[44]. At equal loadings the cost is significantly reduced and the LOI is, under certain conditions, even slightly improved. The monohydrate appears to be the most effective of the three oxides.

Tin oxide

Hydrous tin(IV) oxide phases are quite effective, in the presence of halogen compounds, both as flame retardants and as smoke suppressants for thermoplastic polymers[20,47,48]. They have also been shown to be promising smoke suppressants for glass-reinforced polyesters[49].

Because tin(IV) oxide hydrate is not a 'hydrated' oxide but a 'hydrous' oxide, it can contain variable amounts of water associated with the metal oxide, both chemically and physically adsorbed. The water thus present is, generally speaking, helpful in attaining a higher degree of flame-retardant and smoke-suppressant effectiveness, as is the case for many metal oxides. However, when a compound was prepared that contained more water than the commercial metastannic acid, it was found to be less effective than the commercial samples[20]. This was found to be due to the fact that most of the additional water was physically adsorbed on it and was thus lost endothermically at low temperatures, at least partly during processing, producing cratering of the polymeric samples. Comprehensive studies by triangular diagrams have shown that the optimum atomic ratio of halogen to tin is ~9 and that, similarly to the case of aluminium oxide, there is a rather wide zone in the centre of the triangle where good flame retardance is obtained with smoke production which is no higher than that of the base
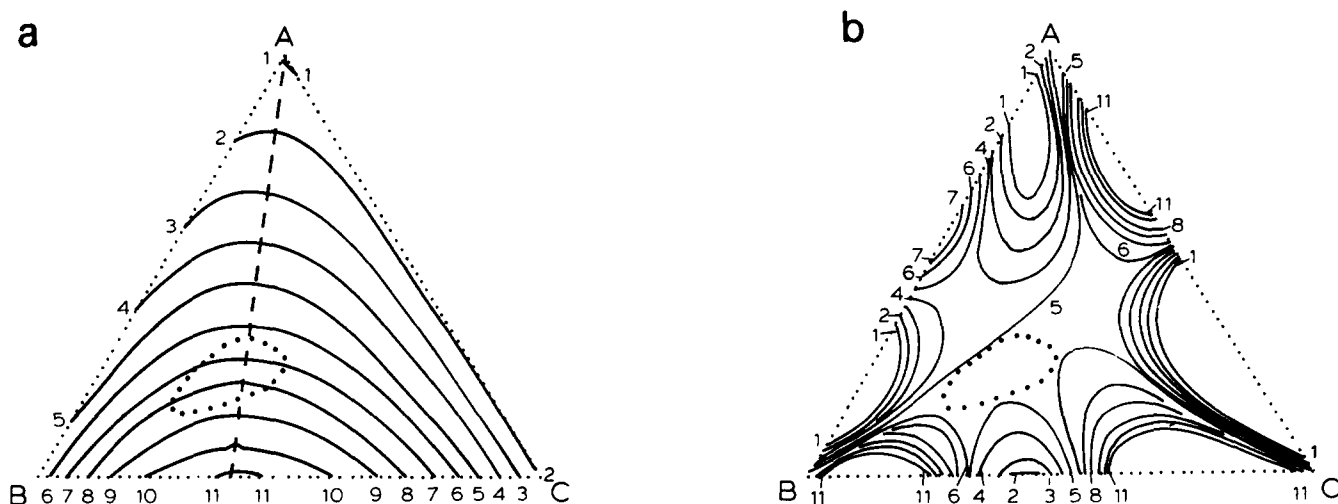
Figure 2 Flammability and maximum smoke density of the system containing ABS, DBB and anhydrous alumina: A, (1.0, 0.0, 0.0); B, (0.6, 0.4, 0.0); C, (0.6, 0.0, 0.4). (a) *LOI* values: curve 1, 1.85; 2, 20.4; 3, 22.2; 4, 24.1; 5, 26.0; 6, 27.9; 7, 29.7; 8, 31.6; 9, 33.5; 10, 35.3; 11, 37.2. (b) D_s values: curve 1, 218; 2, 343; 3, 469; 4, 594; 5, 719; 6, 845; 7, 970; 8, 1095; 9, 1221; 10, 1345; 11, 1471. The broken line represents the optimum Br/Al atomic ratio for flame retardance; the dotted line surrounds the area of good flame retardance and smoke suppression

polymer itself. The action takes place in both the condensed and vapour phases, as witnessed for example by the fact that maximum volatilization of tin(IV) halide occurs at the stoichiometric ratio[42], while the optimum ratio for flame retardance is much higher[20].

Not surprisingly on account of the very different mechanisms of flame retardance involved and the loss of catalytic effect, hydrous tin(IV) oxide is not an efficient partial replacement for antimony(III) oxide as a flame retardant[42].

Silica

Pyrogenic silica is probably the most efficient smoke suppressant yet found for polystyrene[21-23]. Its action takes place mainly by the production of a skin, consisting of a crosslinked polymer structure with silica particles embedded in it and preventing the escape of the volatile decomposition products of the polymer which would otherwise lead to smoke formation[23]. There is virtually no effect of silica as a flame retardant, beyond the action of any filler; there is also no synergistic interaction between silica and halogen compounds as flame retardants. Thermomechanical measurements have shown that this rigid skin, found at the surface of the polystyrene substrate, is formed in a way that depends on a parameter, the adsorption capacity, A_c, defined as:

$$A_c = \frac{W_s}{W_{P_0}} \times a_s$$

where W_s and W_{P_0} are the initial weights of silica and polymer respectively and a_s the specific surface area of the silica. This parameter governs relationships with a wide variety of other properties, among them char formation, smoke formation per unit mass burnt, rate of burning and skin parameters.

In conclusion, the skin formed by the interaction of silica and polystyrene was shown to be related to the formation of hydroperoxide groups along the polymer

chain which then react with silanol groups to produce the crosslinked polymeric skin.

Molybdenum oxide

Molybdenum compounds, such as molybdenum(VI) oxide or ammonium molybdate, are said to exhibit flame-retardant synergism with halogens, as well as being very effective smoke suppressants[34,50]. In the case of MoO_3, the metal has been found virtually quantitatively in the char, rather than in the gas phase[51]. The effect of molybdenum oxide on the combustion and pyrolysis of PVC is particularly interesting. This compound lowers the temperature for the start of the dehydrochlorination of PVC by an ionic mechanism[52]. After dehydrochlorination, the additive acts as a Lewis acid to promote the isomerization of the *cis* double bonds (formed from isotactic PVC) to *trans* double bonds[53-55]. In this way, the formation of aromatic products, which occurs by an intramolecular mechanism[56], is inhibited. No flammable volatile products are thus formed if the heat supplied to the polymer is small, so that the molybdenum compound acts as a flame retardant. This effect does not occur, however, at the higher temperatures involved in real fires, because other volatile flammable products, mainly aliphatic straight-chain hydrocarbons, are then formed; the action of the molybdenum is then reduced to that of a smoke suppressant. Molybdenum compounds are useful as partial replacements for antimony oxide in the presence of bromine[44,57]. Over 90% of the molybdenum added to PVC is recovered from the char remaining after the polymer has burnt[34]. These findings suggest that the flame-retardant action takes place in the condensed phase but that there is some additional gas-phase effect of ammonia, particularly in nitrous oxide atmospheres. This is, of course, consistent with the other, earlier, results presented for PVC.

In the case of thermoplastics other than PVC, molybdenum oxide has also been found to be of little use as a flame retardant, but quite effective as a smoke
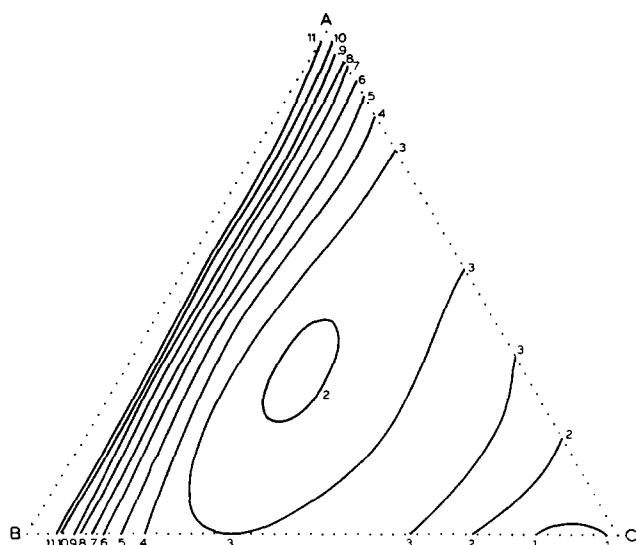
Figure 3 Maximum smoke density of the system containing polystyrene, decabromobiphenyl oxide (DBBO) and magnesium hydroxide: A, (1.0, 0.0, 0.0); B, (0.714, 0.286, 0.000); C, (0.714, 0.286, 0.000). D_s values: curve 1, 117; 2, 256; 3, 395; 4, 534; 5, 672; 6, 811; 7, 950; 8, 1089; 9, 1227; 10, 1366; 11, 1505

suppressant, in the presence of halogenated additives which simultaneously decrease flammability and increase the smoke-forming tendency[58].

Magnesium oxide

Magnesium hydroxide undergoes dehydration in the vicinity of 630–680K, and can be used as a smoke suppressant for polystyrene[58,59], polyester coatings[59] and elastomers[60], including SBR[61]. In many of these cases it has been found to be more effective than other more traditional smoke suppressants, such as trihydrate alumina. *Figures 3* and *4* show how the maximum smoke density from polystyrene is reduced by over 90% by systems containing magnesium hydroxide and deca-bromobiphenyl oxide and by over 70% in systems containing magnesium oxide and the brominated compound. It is very symptomatic that the effect of the anhydrous oxide is not very different from that of the hydrated compound, suggesting that the action is unlikely to be strongly associated with the elimination of water. There is obviously a certain degree of synergism between the halogen compound and the metal oxide because the minimum smoke density is not found at the vertex corresponding to the pure metal compound.

The flame retardant activity of magnesium oxide and of magnesium hydroxide is of little consequence, even in the presence of the halogen compounds.

Ferric oxide, titanium dioxide and zinc oxide

These oxides are of very limited effectiveness as flame retardants[58], but titanium dioxide can, in the presence of decabromobiphenyl oxide, although not in its absence, reduce by over 90% the maximum smoke density derived from polystyrene (*Figure 5*). It is of considerable interest, although the reasons for this finding are not clear, that a compound that induces excess smoke production, like the bromine compound, can interact synergistically with a metal oxide with very little smoke suppressant activity on its own, to produce a very effective smoke-suppressant system. Iron(III) oxide is of rather limited smoke-suppressant activity[58] but it can be used as a very efficient partial

substitute for antimony oxide as a flame retardant[44]. It is very interesting to compare it, in this respect, with zinc oxide. Zinc oxide, in the presence of halogenated compounds, volatilizes very efficiently as the zinc halide[28,42] but is antagonistic, in its flame-retardant action, to antimony oxide as a partial replacement[42,44,45]. It has been used as a smoke suppressant for PVC, albeit not a very efficient one[59]. Ferric oxide is a catalytic oxide[28] and, although it does not volatilize at all as a halide[28,42], it is a synergistic partial replacement for antimony oxide as a flame retardant and could be used as a weak smoke suppressant. This is probably all related to the fact that the weight loss in the full system (polymer, metal oxide, halogen) occurs continuously over a wide temperature range for ferrix oxide while it occurs at very low temperatures for zinc oxide and subsequently leaves a
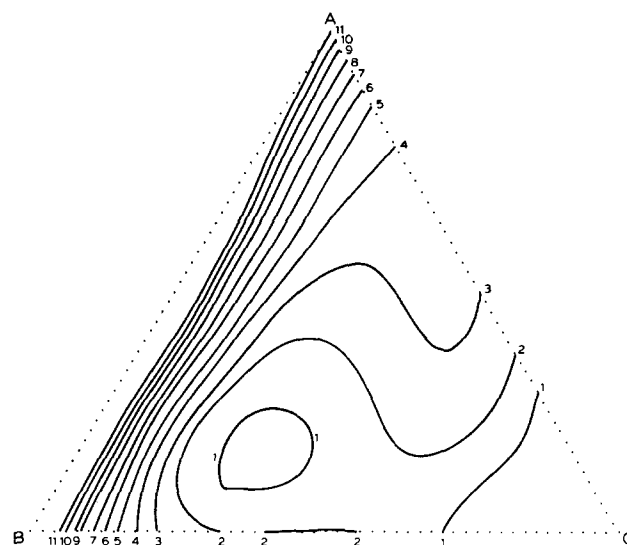

Figure 4 Maximum smoke density of the system containing polystyrene, DBBO and magnesium oxide: A, (1.0, 0.0, 0.0); B, (0.714, 0.286, 0.000); C, (0.714, 0.000, 0.286). D_s values: curve 1, 375; 2, 488; 3, 601; 4, 714; 5, 827; 6, 940; 7, 1053; 8, 1166; 9, 1279; 10, 1392; 11, 1505
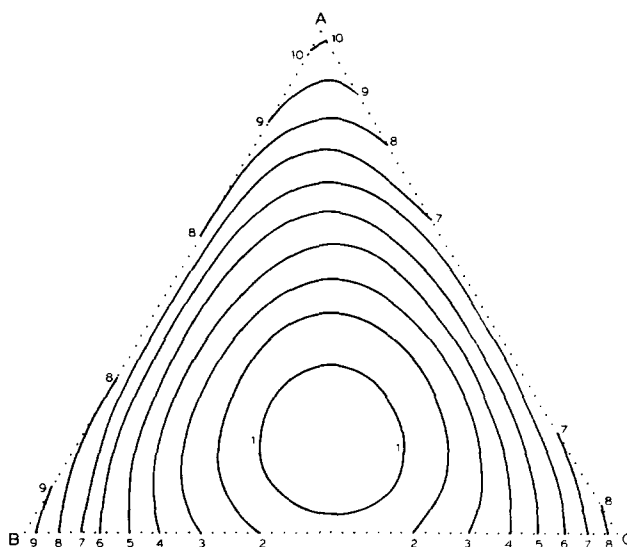

Figure 5 Maximum smoke density of the system containing polystyrene, DBBO and titanium dioxide: A, (1.0, 0.0, 0.0); B, (0.714, 0.286, 0.000); C, (0.714, 0.000, 0.286). D_s values: curve 1, 190; 2, 426; 3, 663; 4, 900; 5, 1136; 6, 1373; 7, 1609; 8, 1846; 9, 2083; 10, 2319

'gap' with no thermal activity at the temperature of the critical reactions[42].

CONCLUSIONS

No metal oxide is an effective flame retardant on its own, but many of them are of considerable interest as smoke suppressants. The use of metal oxides in conjunction with halogen compounds often results in systems which are effective both as flame retardants and as smoke suppressants. A large proportion of the effectiveness is often derived from the volatilization of a halogenated species or of a metal halide. Some condensed-phase action, at the right temperature, is always essential, however, as witnessed by the fact that synergism exists between halogen compounds and metal oxides which do not form volatile metal halides, while antagonism is found with some metal oxides with easily volatile halides.

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