Kirk-Othmer Encyclopedia of Chemical Technology.

FLAME RETARDANTS, ANTIMONY AND OTHER INORGANIC AGENTS

Flame retardancy can be imparted to plastics by incorporating elements such as bromine, chlorine, antimony, tin, molybdenum, phosphorus, aluminum, and magnesium, either during the manufacture or when the plastics are compounded into some useful product. Phosphorus, bromine, and chlorine are usually incorporated as some organic compound. The other inorganic flame retardants are discussed herein.

Addition of approximately 40% of the halogen flame retardants are needed to obtain a reasonable degree of flame retardancy. This usually adversely affects the properties of the plastic. The efficiency of the halogens is enhanced by the addition of inorganic flame retardants, resulting in the overall reduction of flame-retardant additive package and minimizing the adverse effects of the retardants.

Hydrated metal oxides such as alumina hydrate are usually used alone because these are not synergistic with the halogens. They are useful in applications in which the halogens are excluded or low processing temperatures are used.

1. Antimony Compounds

1.1. Antimony Trioxide

Approximately 20,000 metric tons of antimony trioxide [1309-64-4] (commonly referred to as antimony oxide), Sb_2O_3, was used in the United States in 1990 to impart flame retardancy to plastics (see Antimony compounds). Although antimony trioxide is found in nature, it is too impure to be used. Flame-retardant grades of antimony oxides are manufactured from either antimony metal or the sulfide ore by oxidation in air at 600–800°C (1). The particle size and chemical reactivity is determined by the processing conditions, enabling the production of several different grades. The physical properties of various grades are listed in Table 1. Antimony trioxide is from 99.0–99.9 wt % Sb_2O_3. The remainder consists of 0.4–0.01 wt % arsenic; 0.4–0.01, lead; 0.1–0.0001, iron; 0.005–0.0001, nickel; and 0.01–0.0001, sulfates. It is insoluble in water and the loss on drying at 110°C is 0.1 wt % max.

Antimony trioxide has been used as a white pigment since ancient times. The pigmentation from antimony oxide in plastics can be controlled and adjusted by the judicious selection of a Sb_2O_3 grade having a specific particle size. The product with the smallest particle size and the narrowest particle-size range imparts the whitest color and highest opacity. Translucent plastics can be made by using low tint grades with relatively large particles.

Particle size during manufacture is controlled by adjusting the temperature and rate at which the antimony vapors are precipitated as these vapors exit the furnace. The lower the temperature and the slower the precipitation rate, the larger the particles. Figure 1 shows the particle size distribution of the various commercially available grades of antimony trioxides. Although particle size affects pigmentation, it does not appear to affect flame retardancy efficiency. The cost of antimony trioxide varies from $2.20–3.30/kg, depending on the grade and volume purchased. Suppliers and the grades offered are

Company	Trade name
Amspec	Antimony Oxide KR
	Antimony Oxide KRL
	Twinkling Star
Anzon	Timinox High Tint
	Timinox Low Tint
	Timinox Tru Tint
	Microfine AO3
Asarco	Antimony Oxide High Tint
	Antimony Oxide Low Tint
Elf Atochem NA	Thermoguard UF
	Thermoguard S
	Thermoguard L
	Thermoguard HPM
Laurel Industries	Fireshield H
	Fireshield L
	Ultrafine II
U.S. Antimony Co.	Montana Brand

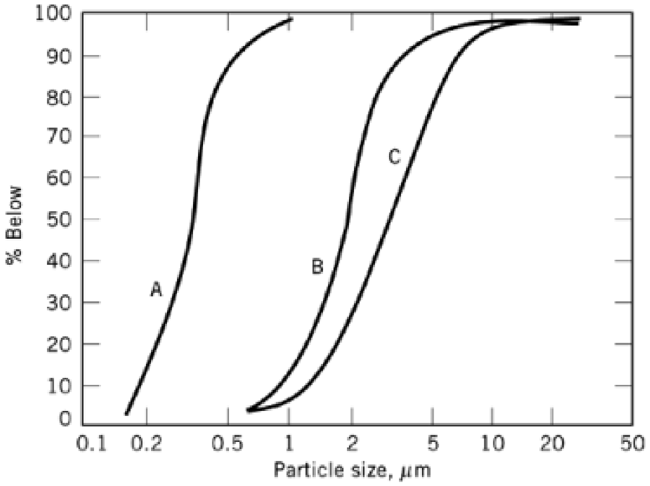

Fig. 1. Particle size distribution of the antimony oxides: A, Thermoguard UF; B, Thermoguard S; C, Thermoguard L.

1.1.1. Antimony Oxide as a Primary Flame Retardant

Antimony oxide behaves as a condensed-phase flame retardant in cellulosic materials (2). It can be applied by impregnating a fabric with a soluble antimony salt followed by a second treatment that precipitates antimony oxide in the fibers. When the treated fabric is exposed to a flame, the oxide reacts with the hydroxyl groups of the cellulose (qv) causing them to decompose endothermically. The decomposition products, water and char, cool the flame reactions while slowing the production and volatilization of flammable decomposition products (see Flame retardants for textiles).

1.2. Antimony Pentoxide

The second most widely used antimony synergist is antimony pentoxide [1313-60-9], Sb_2O_5, produced by the oxidation of the trioxide using either a peroxide or nitric acid (3–8). Antimony pentoxide is available as a

Table 1. Physical Properties of Antimony Trioxide

	Grade[a]		
Property	Ultra fine	High tint	Low tint
specific gravity	5.3–5.5	5.3–5.8	5.3–5.8
particle size, μm	0.25–0.45	0.8–1.8	1.9–3.2

[a] All grades are white powders.

nonpigmenting colloidal suspension in either water or organic media or as an agglomerated powder. It is insoluble in water, but soluble in hot concentrated acids. Properties of this unique flame retardant synergist are listed in Table 2.

Table 2. Properties of Antimony Pentoxide and Sodium Antimonate

Property	Sb_2O_5	Na_3SbO_4
particle size, μm	0.03	1–2
surface area, m^2/gm	50	
specific gravity	4.0	4.8
surface activity	weakly acidic	basic
refractive index, $n^{20}{}_D$	1.7	1.75

Table 3. Manufacturers and Trade Names of Boron Flame Retardants

Manufacturer	Trade name	Composition	CAS Registry Number
Climax Performance Materials	ZB 467	$4\ ZnO{\cdot}6\ B_2O_3{\cdot}7\ H_2O$	[12513-27-8]
	ZB 223	$2\ ZnO{\cdot}2\ B_2O_3{\cdot}3\ H_2O$	
	ZB 113	$ZnO{\cdot}B_2O_3{\cdot}3\ H_2O$	
	ZB 237	$2\ ZnO{\cdot}3\ B_2O_3{\cdot}7\ H_2O$	
	ZB 325	$3\ ZnO{\cdot}2\ B_2O_3{\cdot}5\ H_2O$	
U.S. Borax	Firebrake ZB	$2\ ZnO{\cdot}3\ B_2O_3{\cdot}5\ H_2O$	
		$Zn(BO_2)_2$	[13701-59-2]
Buckman Laboratories	Brusan M-11	$Ba(BO_2)_2$	[27043-84-1]

Submicrometer antimony pentoxide is primarily used to impart flame retardancy to fibers and fabrics. It can be added to the molten or dissolved polymer prior to forming the fiber. The antimony in this form can easily pass through the spinnerets without clogging the openings, whereas standard grades of antimony trioxide would rapidly clog the openings and necessitate frequent shutdowns for cleaning. The submicrometer antimony pentoxide is also more evenly dispersed in the fiber, resulting in better physical properties.

Powdered antimony pentoxide is used primarily in plastics. Stabilizers used to prevent the particles from growing are caustic, and can react with the halogen in the formulation. This can result in color formation and a lower flame-retarding efficiency of the system.

Antimony pentoxide is priced about two to three times higher than the trioxide. However, because it is more efficient than the trioxide, the pentoxide is at least cost-equivalent. Antimony pentoxide is manufactured by both Philadelphia Quartz and Laurel Industries under the Nyacol and Fireshield trade names.

Table 4. Physical Properties of Alumina Trihydrate

Property	Value
density, g/mL	2.42
refractive index, $n^{20}{}_{D}$	1.579
average particle size, μm	1–100
Mohs' hardness	2.5–3.5
color	white
water solubility	insoluble

Table 5. Properties of Molybdenum Flame Retarders

Property	Molybdic oxide[a]	Ammonium octamolybdate[b]	Zinc molybdate
CAS Registry Number	[1313-27-5]		[13767-32-3]
particle size, μm	25	2	1.88
bulk density, kg/m^3	38	480	
H_2O solubility, g/mL	0.68	4	0.04
specific gravity	4.67	3.18	3.0
oil adsorption per 100 g oil, g	35	20	
loss on ignition, wt %	<0.1	8.29	

[a] The refractive index of MoO_3 is >2.1.
[b] The decomposition temperature is 250°C.

1.3. Sodium Antimonate

Sodium antimonate [15593-75-6], Na_3SbO_4, another antimony synergist of commercial importance, has an antimony content of 61–63 wt % and a bulk density of 39.4–46.4 kg/m^3. Properties are given in Table 2. It is made by oxidizing antimony trioxide using sodium nitrate and caustic. It is a white powder and has a pH of around 9–11 when dissolved in water.

Table 6. Properties of Tin Flame Retarders[a]

Parameter	Zinc hydroxy stannate	Zinc stannate	Stannic oxide
molecular formula	$ZnSn(OH)_6$	$ZnSnO_3$	$SnO_2 \cdot xH_2O$
CAS Registry Number	[12027-96-2]	[12036-37-2]	
tin, wt %	47	51	67
zinc, wt %	21	28	
specific gravity	3.4	4.25	
decomposition temperature, °C	180	>570	180

[a] All materials are white powders. Particle sizes range from 1–10 μm.

Sodium antimonate contains less antimony than either antimony trioxide or pentoxide and is thus less effective. However, its unique pH and low refractive index makes the antimonate the most desirable synergist for polymers that hydrolyze when processed with acidic additives or in polymers for which deep color tones are specified. Sodium antimonate costs approximately $3.30–4.40/kg and can be obtained from either Elf Atochem NA under the Thermoguard name or from Anzon Inc. as a Timinox product.

Table 7. Effect of Plasticizer[a] on the Oxygen Index of PVC

Plasticizer, wt %	Cl, wt %	Oxygen index (OI)
0	57.0	41–49
16.6	48.5	36.4
28.5	41.0	31.5
37.5	36.4	22.2
44.4	32.0	21.2
47.5	30.0	19.2

[a] Dioctyl phthalate.

1.4. Toxicity

Antimony has been found not to be a carcinogen or to present any undue risk to the environment (9). However, because antimony compounds also contain minor amounts of arsenic which is a poison and a carcinogen, warning labels are placed on all packages of antimony trioxide.

1.5. Mixed Metal Antimony Synergists

Worldwide scarcities of antimony have prompted manufacturers to develop synergists that contain less antimony. Other metals have been found to work in concert with antimony to form a synergist that is as effective as antimony alone. Thermoguard CPA from Elf Atochem NA, which contains zinc in addition to antimony, can be used instead of antimony oxide in flexible poly(vinyl chloride) (PVC) as well as some polyolefin applications. The Oncor and AZ products which contain silicon, zinc, and phosphorus from Anzon Inc. can be used in a similar manner. The mixed metal synergists are 10 to 20% less expensive than antimony trioxide.

Table 8. Effect of Flame Retardancy of Molybdenum Oxide and Antimony Oxide[a]

Additive, parts by weight			
Sb_2O_3	MbO_3	Oxygen index	Smoke[b]
		24.5	10.7
2.0		27.5	9.2
3.0		28.3	10.9
5.0		29.0	9.4
	2.0	26.0	6.8
	3.0	27.0	4.4
	5.0	27.5	4.1
2.0	1.0	28.0	7.6
1.5	1.5	27.5	5.0
1.0	2.0	27.0	7.0
2.0	2.0	29.5	6.0

[a] Flexible PVC containing 50 phr dioctyl phthalate.
[b] Results from Araphoe Smoke Test.

1.6. Antimony–Halogen Synergism

Antimony synergists are used almost exclusively with either brominated or chlorinated organic flame retardants. These work in concert with one another and provide a highly effective flame-retardant system. Antimony and the halogens react at flame temperatures to form the corresponding trihalide or oxyhalide. The product

Table 9. Effect of Chlorine and Antimony Oxide on the Oxygen Index of Unsaturated Polyesters

Chlorine, wt %	Antimony oxide, wt %	Oxygen index
0	0	18.2
12.5	2.5	30.0
20.0	1.0	30.2
25.0	3.0	38.7
25.0	1.0	33.4
25.0	0	30.2

Table 10. Oxygen Index of Unsaturated Polyesters Containing Bromine

	Bromine, wt %				
Additive	0	5	10.0	20.0	28.0
no additive	19.1	23.1	26.7	37.2	41.2
$ZnSnO_3$					
1 wt %	19.6	24.1	28.0	42.1	52.2
2 wt %	19.6	25.3	32.7	42.4	54.2
$ZnSn(OH)_6$, 2 wt %	19.3	23.6	28.9	40.9	53.4
Sb_2O_3, 2 wt %	19.1	23.7	29.2	40.8	51.2

formed depends on the mole ratios of the reactants and the structure of the organic halogen compound. The active flame-retarding species, ie, the tribromide and the trichloride (10, 11), are formed directly when the mole ratio of halogen to antimony is at least 3-to-1 and the halogen compound is capable of dehydrohalogenating.

$$Sb_2O_3 + 6\ HCl \longrightarrow 2\ SbCl_3 + 3\ H_2O \qquad (1)$$

If there are less than three moles of halogen for each mole of antimony present or if the halogen compound cannot dehydrohalogenate, then the oxyhalide forms.

$$Sb_2O_3 + 2\ HCl \longrightarrow 2\ SbOCl + H_2O \qquad (2)$$

The formation of antimony trichloride from antimony oxychloride has been described by two different mechanisms. One asserts that formation is via a thermal disproportionation as described in equations 3–6 (12).

$$5\ SbOCl\ (s) \longrightarrow Sb_4O_5Cl_2 + SbCl_3 \qquad (3)$$

$$4\ Sb_4O_5Cl_2 \longrightarrow 5\ Sb_3O_4Cl + SbCl_3 \qquad (4)$$

$$3\ Sb_3O_4Cl \longrightarrow 4\ Sb_2O_3 + SbCl_3 \qquad (5)$$

$$Sb_2O_3\ (s) \longrightarrow Sb_2O_3\ (g) \qquad (6)$$

The other mechanism proposes that the trichloride is formed by the further chlorination of the oxyhalide as illustrated in equations 7–10 (13).

$$4\ Sb_2O_3 + 2\ HCl \longrightarrow Sb_8O_{11}Cl_2 + H_2O \qquad (7)$$

$$Sb_8O_{11}Cl_2 + 2\ HCl \longrightarrow 2\ Sb_4O_5Cl_2 + H_2O \qquad (8)$$

$$Sb_4O_5Cl_2 + 2\ HCl \longrightarrow 4\ SbOCl + H_2O \qquad (9)$$

$$SbOCl + 2\ HCl \longrightarrow SbCl_3 + H_2O \qquad (10)$$

The organohalogen compound used in the formulation also influences the formation of the trihalide. If the halogen compound can dehydrohalogenate easily, as for example do hexabromocyclododecane [25637-99-4] and poly(vinyl chloride), then the halogen decomposition products react with the antimony directly (14, 15). However if the organohalogen does not form the acid halide easily, as for example decabromobiphenyl oxide, then a third component capable of reacting with the antimony and halogen is needed. This can be the polymer itself. If a third component is not present, such as in the pyrolysis of an antimony–halogen mixture, then the decomposition products of only the halogen and antimony are recovered and no trihalide forms. Two mechanisms have been proposed (16) for this type of reaction. Both require the participation of the polymer in the reaction.

Table 11. Flammability of Flame-Retardant-Treated Flexible PVC[a]

	Flame retardant	
Parameter	Thermoguard CPA	Sb_2O_3
UL classification	V-0	V-0
flame-out time,[b] s	2.3	2.4
oxygen index	28.9	28.6

[a] Formulation is 100.0 parts by wt PVC; 54.0, plasticizer; 7.0, stabilizer; 10.0, filler; 0.5, lubricant; and 3.0, flame retardant.
[b] UL 94 Test.

One mechanism has the polymer degrading before the halogen compound does to generate a free radical which replaces the halogen of the flame retardant. The bromine radical can then react with the labile hydrogen of the polymer, forming hydrogen bromide and a new polymeric radical. The hydrogen bromide can react further with antimony oxide and generate antimony tribromide:

$$RHC{-\!\!-}CHR \longrightarrow 2\ RCH^{\cdot} \qquad (11)$$

Table 12. Oxygen Index of Flexible PVC Containing Antimony and Boron

Formulation, phr		
Zinc borate	Antimony oxide	Oxygen index
0	3	28.7
0	1.5	27.5
0.5	2.5	28.6
1.0	2.0	28.4
1.5	1.5	28.2
3.0	0	24.1
1.5	0	22.7
0	0	19.8

$$RCH^{\cdot} + Br_5O{-}O{-}OBr_5 \longrightarrow Br^{\cdot} + Br_4O{-}O{-}OBr_5 + RCH \qquad (12)$$

According to the second mechanism the polymer and antimony trioxide form a catalytic complex. The halogen flame retardant then reacts with the complex and expels antimony tribromide.

$$Sb_2O_3 + \text{polymer} \longrightarrow [Sb_2O_3{-}\text{polymer}] \qquad (13)$$

$$[Sb_2O_3{-}\text{polymer}] + RBr \longrightarrow [SbBr_3{-}\text{polymer}] + R^{\cdot} \qquad (14)$$

$$[SbBr_3{-}\text{polymer}] \longrightarrow SbBr_3 + R \qquad (15)$$

Either mechanism can be used to describe how antimony–halogen systems operate in both the condensed and vapor phases. In the condensed phase a char that is formed during the reaction of the polymer, antimony trioxide, and the halogen reduces the rate of decomposition of the polymer; therefore, less fuel is available for the flame (16).

In the vapor phase antimony trihalides inhibit the radical flame reactions. The inhibition reactions of antimony trichloride have been studied by mass spectrophotometry (17). In a flame antimony trichloride was found to decompose in a stepwise manner, enabling the chlorine to remain in the flame zone longer than it would have if it were generated directly from the organic halogen compound. Therefore the halogen becomes more effective. According to this study, chlorine deactivates the very energetic hydrogen, oxygen, and hydroxyl radicals.

$$SbCl_3 \longrightarrow SbCl_2^{\cdot} + Cl^{\cdot} \qquad (16)$$

$$SbCl_3 + H^{\cdot} \longrightarrow SbCl_2^{\cdot} + HCl \qquad (17)$$

$$SbCl_3 + CH_3^{\cdot} \longrightarrow SbCl_2^{\cdot} + CH_3Cl \qquad (18)$$

$$SbCl_2 + H^{\cdot} \longrightarrow SbCl^{\cdot} + HCl \qquad (19)$$

$$SbCl_2 + CH_3^{\cdot} \longrightarrow SbCl^{\cdot} + CH_3Cl \qquad (20)$$

$$SbCl^{\cdot} + H^{\cdot} \longrightarrow Sb + HCl \qquad (21)$$

$$SbCl^{\cdot} + CH_3^{\cdot} \longrightarrow Sb + CH_3Cl \qquad (22)$$

The chlorine radicals and hydrogen chloride inhibit the reaction in the following manner.

$$Cl^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3Cl \qquad (23)$$

$$Cl^{\cdot} + H^{\cdot} \longrightarrow HCl \qquad (24)$$

$$Cl^{\cdot} + HO_2^{\cdot} \longrightarrow HCl + O_2 \qquad (25)$$

$$HCl + H^{\cdot} \longrightarrow H_2 + Cl^{\cdot} \qquad (26)$$

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2 \qquad (27)$$

$$Cl_2 + CH_3^{\cdot} \longrightarrow CH_3Cl + Cl^{\cdot} \qquad (28)$$

The fine antimony mist formed from the decomposition of the trichloride also participates in the flame-inhibiting process, deactivating oxygen, hydrogen, and hydroxyl radicals.

$$Sb + O^{\cdot} \longrightarrow SbO^{\cdot} \qquad (29)$$

$$\mathrm{SbO^{\cdot} + 2\,H^{\cdot} \longrightarrow SbO^{\cdot} + H_2} \qquad (30)$$

$$\mathrm{SbO^{\cdot} + H^{\cdot} \longrightarrow SbOH} \qquad (31)$$

$$\mathrm{SbOH + OH^{\cdot} \longrightarrow SbO^{\cdot} + H_2O} \qquad (32)$$

2. Boron Compounds

In 1990 approximately 4500 metric tons of boron flame retardants were used in the United States to impart flame retardancy to plastics (see Boron compounds). The most widely used is zinc borate [1332-07-6], prepared as an insoluble double salt from water-soluble zinc and boron compounds. Compounds having varying amounts of zinc, boron, and water of hydration are available. The ratio of these components affects the temperature at which the flame-inhibiting powers are activated, as well as the temperature at which they can be processed (18). Zinc borates can either be used alone or in combination with other halogen synergists, such as antimony oxide. In some instances zinc borate is also used with alumina trihydrate to form a glass-like substance that inhibits polymer degradation. Manufacturers of boron flame retardants are listed in Table 3. The cost of the borates varied from $2.00–2.50/kg in the early 1990s.

2.1. Barium Metaborate

Barium metaborate is used both as a flame retarder and as an antifungicide for many flexible poly(vinyl chloride) applications (19).

2.2. Boric Acid and Sodium Borate

Boric acid [10043-35-3] and sodium borate [1303-96-4], also known as borax, have been used as flame retardants for cellulose since the 1800s (2). They are quick-fix, nondurable flame retardants. Each is applied by passing the fabric through a solution of the flame retardant. For batts, eg, cotton, a spray applicator is used. Excess solution is removed by passing the fabric through squeeze rollers. Usually an “add-on” of 20% is needed to obtain flame retardancy. However, because the flame retardants are water-soluble, they are removed after several washings or when used in high humidity atmospheres. Boric acid and borax are available from Ashland Chemical, U.S. Borax, and J.H. Henry Chemical Co.

2.3. Ammonium Fluoroborate

Ammonium fluoroborate [13826-83-0], NH_4BF_4, is unique in that when it is exposed to a flame, it generates both a halogen and a boron flame retardant (20). Antimony oxide is usually recommended as a co-synergist.

$$\mathrm{6\,NH_4BF_4 + Sb_3O_3 \longrightarrow 6\,NH_3 + 6\,BF_3 + 2\,SbF_3 + 3\,H_2O} \qquad (33)$$

Ammonium fluoroborate is both a condensed and vapor-phase flame retardant. It is available from M & T Harshaw, General Chemical Corp., and Spectrum Chemical Corp.

2.4. Boron Mechanism

Boron functions as a flame retardant in both the condensed and vapor phases. Under flaming conditions boron and halogens form the corresponding trihalide. Because boron trihalides are effective Lewis acids, they promote cross-linking, minimizing decomposition of the polymer into volatile flammable gases. These trihalides are also volatile; thus they vaporize into the flame and release halogen which then functions as a flame inhibitor (21–24).

Table 13. Fire Test Results of Laminates Containing Zinc Borate and Antimony Oxide[a]

Additive, phr			
Sb_2O_3	Zinc borate	Flame spread[b]	Oxygen index
0	0	15.0	26.0
2	0	9.1	37.3
2	6	3.7	40.2
1	6	12.5	36.8
0.5	6.5	15.4	34.1

[a] 26% fiber glass; contains 28% chlorine.
[b] Ref. 25.

Table 14. Oxygen Index and Smoke Reduction of Unsaturated Polyester Containing Molybdenum Oxide and Antimony Oxide

Additive, wt %			
Sb_2O_3	MoO_3	Oxygen index	Smoke reduction
0	0	33.0	
1		34.5	+67
3		42.0	+96
5		43.0	−26
	5	36.0	−36
	7	39.0	−49
1	1	39.5	−54
2	1	41.0	−20
1	2	40.0	−15

Boron also reacts with hydroxyl-containing polymers such as cellulose. When exposed to a flame the boron and hydroxyl groups form a glassy ester that coats the substrate and reduces polymer degradation. A similar type of action has been observed in the boron–alumina trihydrate system.

3. Alumina Trihydrate

In 1990, approximately 66,000 metric tons of alumina trihydrate [12252-70-9], $Al_2O_3 \cdot 3H_2O$, the most widely used flame retardant, was used to inhibit the flammability of plastics processed at low temperatures. Alumina trihydrate is manufactured from either bauxite ore or recovered aluminum by either the Bayer or sinter processes (25). In the Bayer process, the bauxite ore is digested in a caustic solution, then filtered to remove silicate, titanate, and iron impurities. The alumina trihydrate is recovered from the filtered solution by precipitation.

In the sinter process the aluminum is leached from the ore using a solution of soda and lime from which pure alumina trihydrate is recovered (see Aluminum compounds).

Alumina trihydrate is available in a variety of particle size distributions, ranging from less than one up to 100 micrometers. It has a low hiding power and pigmentation because of the large particles and low refractive index. Therefore formulations containing as much as 50% alumina trihydrate are translucent. Physical properties are given in Table 4. Alumina trihydrate is composed of 64.9 wt % Al_2O_3, 0.005 wt % SiO_2, 0.007 wt % Fe_2O_3, and 0.3 wt % Na_2O, of which 0.04 wt % is soluble. Water loss on ignition is 34.6 wt %.

Manufacturers of alumina trihydrate include Solem Industries, Aluchem, Alcoa, Custom Grinding Sales, R. J. Marshall, Georgia Marble, and Hitax. In 1992 the price of alumina trihydrate varied from $0.25–1.35/kg. Alumina trihydrate is the least expensive and least effective of the flame retarders. It is only about one-fourth to one-half as effective as the halogens. Usually about 50–60% of alumina trihydrate is needed to obtain some acceptable degree of flame retardancy. It is also limited to plastics that are not processed higher than 220°C.

Alumina trihydrate is also used as a secondary flame retardant and smoke suppressant for flexible poly(vinyl chloride) and polyolefin formulations in which antimony and a halogen are used. The addition of minor amounts of either zinc borate or phosphorus results in the formation of glasses which insulate the unburned polymer from the flame (21).

3.1. Mechanism

Alumina trihydrate functions as a flame retardant in both the condensed and vapor phases (26). When activated, it decomposes endothermically, eliminating water.

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O \qquad (34)$$

In the flame phase the water vapor forms an envelope around the flame, which tends to exclude air and dilute the flammable gases. The water vapor reacts endothermically with the flame radicals. The alumina residue becomes a conduit through which heat is conveyed away from the flame area, slowing down polymer decomposition.

4. Other Inorganic Materials

4.1. Magnesium Hydroxide

Magnesium hydroxide [1309-42-8] is another metal hydrate that decomposes endothermically, accompanied by the formation of water. It decomposes at 330°C, which is 100°C higher than alumina trihydrate, and can therefore be used in polymers that are processed at higher temperatures.

$$Mg(OH)_2 \longrightarrow MgO + H_2O \qquad (35)$$

Magnesium hydroxide is white, has an average particle size of 1–10 μm, density of 2.36 g/mL, refractive index of 1.58, and Mohs' hardness of 2.00. Water loss on ignition is 31.8 wt %. Magnesium hydroxide contains 1.0 wt % $Ca(OH)_2$ and is made by Solem Industries and Morton Thiokol (25).

4.2. Molybdenum Oxides

Molybdenum was one of the first elements used to retard the flames of cellulosics (2). More recently it has been used to impart flame resistance and smoke suppression to plastics (26). Molybdic oxide, ammonium octamolybdate, and zinc molybdate are the most widely used molybdenum flame retardants. Properties are

Table 15. Inorganic Synergist–Halogen Formulations

Parameter	Polyethylene				Polypropylene			
	Formulation							
polymer, wt %	82	82	60	60	56	94	60	54
antimony oxide, wt %	6	6	13	13	6	2	10	12
decabromobiphenyl oxide, wt %	12				22			
bis(tetrabromophthalimide) ethane, wt %		12						
Dechlorane Plus			27				30	
ethylene bis(dibromonorborane) dicarbanimide						4		
70% chlorinated paraffin				27				24
talc					14			10
	Flame test results							
UL 94 Class[a]	V-0	V-0	V-1	V-0	V-0	V-2	V-1	V-0
oxygen index					25.0		27.0	26.0

[a] 3.175 mm.

Table 16. Hydrated Filler Systems for Polyethylene and Polypropylene[a]

Parameter	Polyethylene		Polypropylene	
polymer, wt %	35	45	35	36
alumina trihydrate, wt %	65		65	
magnesium hydroxide, wt %		55		64

[a] Flame test results for all formulations is V-0 using the UL 94 Class (1/8 in. = 3.175 mm) designations.

given in Table 5. These materials are recommended almost exclusively for poly(vinyl chloride), its alloys, and unsaturated polyesters (qv).

Molybdenum trioxide is a condensed-phase flame retardant (26). Its decomposition products are nonvolatile and tend to increase char yields. Two parts of molybdic oxide added to flexible poly(vinyl chloride) that contains 30 parts of plasticizer have been shown to increase the char yield from 9.9 to 23.5%. Ninety percent of the molybdenum was recovered from the char after the sample was burned. A reaction between the flame retardant and the chlorine to form $MoO_2 \cdot Cl_2 \cdot H_2O$, a nonvolatile compound, was assumed. This compound was assumed to promote char formation (26, 27).

Molybdenum is also a smoke suppressant for poly(vinyl chloride). It promotes the formation of cis- rather than the trans-polymeric decomposition products which are the precursors for smoke. The sources for molybdates are Climax Performance Material Corp. and Sherwin Williams.

4.3. Tin

Tin has been used as a flame retardant for cellulose since the latter 1800s (2). Only since the 1970s has it been used as a synergist for halogen flame retarders in the same manner as antimony oxide (28, 29). Anhydrous and hydrated zinc stannate and stannic oxide are the three most important tin flame retardants. Properties are given in Table 6.

The mechanism by which tin flame retardants function has not been well defined, but evidence indicates tin functions in both the condensed and vapor phases. In formulations in which there is at least a 4-to-1 mole ratio of halogen to tin, reactions similar to those of antimony and halogen are assumed to occur. Volatile stannic tetrahalide may form and enter the flame to function much in the same manner as does antimony trihalide.

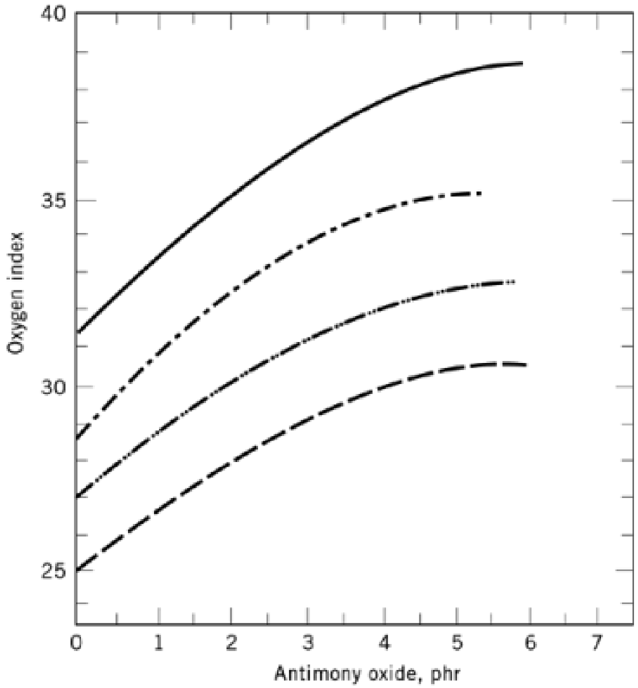

Fig. 2. The effect of antimony oxide on the oxygen index of poly(vinyl chloride) plasticized with dioctyl phthalate (DOP), (___), 20 phr, (_ _ _), 30 phr; (_.._), 40 phr; (_ _ _), 50 phr, where phr=parts per hundred resin.

If the tin source is anhydrous, very little volatile tin tetrahalide is formed. If the mole ratio of halogen to tin is less than 4-to-1 or if there is no halogen present, yet flame retardancy is observed, condensed-phase activity is assumed. The only supplier of tin flame retardants is Alcan Inc. The price in 1992 was $7.70/kg.

5. Applications

5.1. Poly(vinyl chloride)

PVC is a hard, brittle polymer that is self-extinguishing. In order to make PVC useful and more pliable, plasticizers (qv) are added. More often than not the plasticizers are flammable and make the formulation less flame resistant. Flammability increases as the plasticizer is increased and the relative amount of chlorine decreased, as shown in Table 7. The flame resistance of the poly(vinyl chloride) can be increased by the addition of an inorganic flame-retardant synergist.

5.1.1. Antimony Oxide

The effect of antimony trioxide on the oxygen index of flexible poly(vinyl chloride) containing from 20 to 50 parts of plasticizer is shown in Figure 2. The flame resistance as measured by the oxygen index increases with the addition of antimony oxide until the oxygen index appears to reach a maximum at about 8 parts of Sb_2O_3. Further addition of antimony oxide does not have any increased beneficial effect.

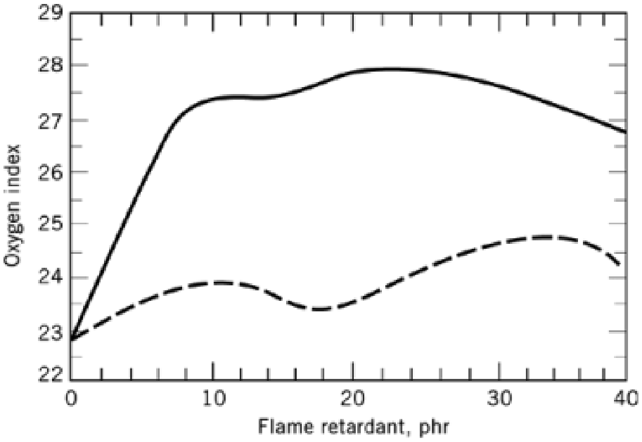

Fig. 3. A comparison of the effect of antimony oxide (___) and Firebrake ZB (_ _ _) on the oxygen index of PVC containing 50 phr DOP.

5.1.2. Mixed Metal Antimony Synergists

A similar increase in the oxygen index can be achieved using the mixed metal synergist Thermoguard CPA as illustrated in Table 11.

5.1.3. Zinc Borate

Zinc borate is also effective in enhancing the flame-inhibiting powers of chlorine. Although zinc borate increases flame resistance, it is not as effective as antimony oxide, as is illustrated in Figure 3. However, zinc borate can be used in combination with antimony oxide to obtain equivalent and in some instances enhanced effects over what can be obtained using either of the two synergists alone (Table 12).

5.1.4. Molybdenum Oxide

Molybdenum compounds incorporated into flexible PVC not only increase flame resistance, but also decrease smoke evolution. In Table 8 the effect of molybdenum oxide on the oxygen index of a flexible PVC containing 50 parts of a plasticizer is compared with antimony oxide. Antimony oxide is the superior synergist for flame retardancy but has little or no effect on smoke evolution. However, combinations of molybdenum oxide and antimony oxide may be used to reduce the total inorganic flame-retardant additive package, and obtain improved flame resistance and reduced smoke.

5.1.5. Zinc Stannates

The zinc stannates are also effective synergists for flexible PVC; however, as shown in Figure 4**a,** antimony oxide is more effective. If more chlorine such as in a chlorinated paraffin such as Cereclor is added, then the stannates become more effective and eventually outperform antimony oxide (Fig. 4**b**).

5.1.6. Alumina Trihydrate

Alumina trihydrate is usually used as a secondary flame retardant in flexible PVC because of the high concentration needed to be effective. As a general rule the oxygen index of flexible poly(vinyl chloride) increases 1% for every 10% of alumina trihydrate added. The effect of alumina trihydrate on a flexible poly(vinyl chloride) formulation containing antimony oxide is shown in Figure 5.

Table 17. Inorganic Synergists–Halogen System for Polystyrene and ABS

Parameter	High impact polystyrene		ABS	
	Formulation			
polymer, wt %	84	84	78.2	79.0
antimony oxide, wt %	4	4	3.1	5.0
brominated biphenyl oxide, wt %	12[a]	0	18.8[b]	0
brominated polystyrene, wt %	0	12	0	16.0
	Flame test results			
UL 94 Class[c]	V-0	V-0	V-0	V-0
oxygen index	26.0	24.5	32.0	

[a] Decabromobiphenyl oxide.
[b] Octabromobiphenyl oxide.
[c] 3.175 mm = 1/8 in.

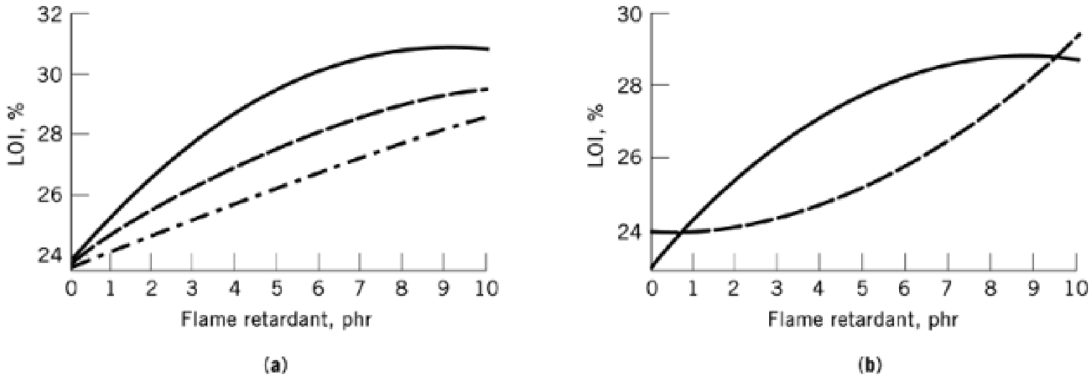

Fig. 4. Effect on limiting oxygen index (LOI) of (__) antimony trioxide (___) Flamtard S, and (___) Flamtard H added to (**a**) the basic unfilled PVC formulation, and (**b**) PVC containing Cereclor and 100-phr chalk (29).

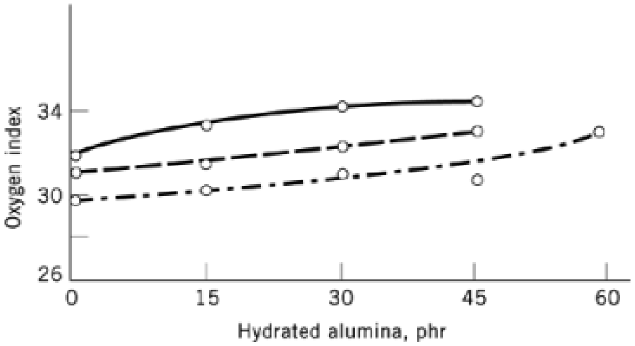

Fig. 5. Effect of alumina trihydrate on the oxygen index of flexible PVC (30) having 5 phr Tribase XL, 3 phr Sb_2O_3, 0.05 phr petroleum wax, and (__) 35, (___) 40, and (___) 45 phr 711 phthalate.

5.2. Unsaturated Polyesters

There are two approaches used to provide flame retardancy to unsaturated polyesters. These materials can be made flame resistant by incorporating halogen when made, or by adding some organic halogen compound when cured. In either case a synergist is needed. The second approach involves the addition of a hydrated filler. At least an equal amount of filler is used.

5.2.1. Synergists

The effect of antimony oxide on the flammability of unsaturated polyesters that contain chlorine is shown in Table 9. A similar effect on the flammability of unsaturated polyester containing zinc stannates and bromine instead of chlorine is given in Table 10.

Antimony oxide and zinc borate are also used as synergists for unsaturated polyesters. Their combined effect on the flame spread index (25) is shown in Table 13. The combination of molybdenum oxide and antimony oxide is used to reduce both flammability and smoke evolution as illustrated in Table 14.

5.2.2. Alumina Trihydrate

Alumina trihydrate must be used at high concentrations in order for it to be effective. The flammability and smoke of a general-purpose polyester (75 wt %) containing 20 wt % glass mat gave values of 780 and 1000 on flame spread and smoke in ASTM E84 testing. The same polyester (40 wt %) containing 40 wt % alumina trihydrate and 20 wt % glass mat gave values of 70 and 300 for the flame spread and smoke tests (18).

5.3. Olefin Polymers

The flame resistance of polyethylene can be increased by the addition of either a halogen synergist system or hydrated fillers. Similar flame-retarder packages are used for polypropylene (see Olefin polymers). Typical formulations of the halogen synergist type are shown in Table 15; the filler-type formulations are in Table 16.

Table 18. Flame–Retarded Nylon-6,6

Parameter	Value			
	Formulation			
nylon-6,6, wt %	48.0	48.0	50.0	55.0
glass fibers, wt %	30.0	30.0	30.0	30.0
antimony oxide, wt %	6.0	4.4		
ferric oxide, wt %			3.0	
zinc oxide, wt %				4.0
brominated polystyrene, wt %	18.0			
Dechlorane Plus, wt %		17.0	16.0	12.0
	Flame test results			
UL 94 Class[a]	V-0	V-0	V-0	V-0
oxygen index	34.8	31.2	36.0	34.2

[a] 3.175 mm = 1/8 in.

Halogen and inorganic synergists are used to impart flame retardancy to polystyrene rather than fillers. ABS is slightly more difficult to flame retard and requires higher concentrations of the inorganic synergist–halogen system. Fillers are rarely if ever used. Table 17 contains typical formulations.

Nylons, because of the high processing temperatures needed, are generally flame retarded using an inorganic halogen system (Table 18). Linear polyesters are susceptible to acid hydrolysis during processing. Thus sodium antimonate, the synergist having a basic pH, is favored as indicated in Table 19.

Table 19. Flame-Retarded Linear Polyesters

Parameter	Value		
Formulation			
polybutylene terephthalate, wt %	57.7	57.7	55.0
glass fibers, wt %	25.0	25.0	25.0
sodium antimonate, wt %	3.4	3.4	3.4
brominated polystyrene, wt %	14.0		
bis(tetrabromophthalimide) ethane, wt %		14.0	
tetrabromobisphenol A carbonate, wt %			18.0
Flame test results			
UL 94 Class[a]	V-0	V-0	V-0
oxygen index	32.7	37.1	35.8

[a] 3.175 mm = 3/4 in.

BIBLIOGRAPHY

"Antimony and Other Inorganic Compounds" under "Flame Retardants" in *ECT* 3rd ed., Vol. 10, pp. 355–372, by J. M. Avento and I. Touval, M & T Chemicals, Inc.

Cited Publications

1. I. Touval and H. H. Waddell, *Handbook of Fillers and Reinforcements for Plastics,* Van Nostrand Reinhold, Co., Inc., New York 1978, p. 219.
2. J. E. Ramsbottom, *Fire Proofing of Fabrics,* His Majesty's Stationary Office, London, 1947.
3. U.S. Pat. 3,873,451 (Mar. 25, 1975), C. C. Combo and Y. C. Yates (to E. I. du Pont de Nemours & Co., Inc.).
4. U.S. Pat. 3,994,825 (Nov. 30, 1976), C. E. Crompton (to Chemetron Chemical Corp.).
5. D. K. Kintz in *2nd International Conference on Flame Retardants 85,* BPF, Luton, Ltd., London, 1985, p. 9/1.
6. U.S. Pat. 4,017,418 (Apr. 12, 1977), C. E. Crompton and A. M. Z. Kazi (to Chemetron Chemical Corp.).
7. U.S. Pat. 4,022,710 (May 10, 1977), T. Kopbashi and H. Shiota (to Japan Exlan Corp.).
8. E. A. Myszak, Jr., *Use of Submicron Inorganic Flame Retardants in Polymeric Systems,* PQ Corp., Valley Forge, Pa., 1991, p. 19,482.
9. A Sheldon, *FRCA Flammability Conference,* Ponte Vedra Beach, Fla., Oct. 21, 1990, p. 1.
10. R. W. Little, *Flame Proofing Textile Fibers,* American Chemical Society Monograph Series 40, American Chemical Society, Reinhold, N.Y., 1947.
11. J. A. Rhys, *Chem. Ind. London,* 187 (1969).
12. J. J. Pitts, P. H. Scott, and J. Powell, *Cell. Plast.,* 635 (1970).
13. L. Costa, G. Paganetto, G. Bertelli, and G. Camino, *J. Therm. Anal.,* 36 (1990).
14. P. J. Gale, *Int. J. Mass Spectrom. Ion Phys.* **100,** 313–322 (1990).
15. E. R. Wagner and B. I. Joensten, *J. Appl. Polym. Sci.* **20,** 2143 (1976).
16. M. J. Drew, C. W. Jarves, and G. C. Lickfield in G. L. Nelson, ed., *Fire and Polymers,* ACS Symposium Series 425, American Chemical Society, Washington, D.C.
17. J. W. Hastie, *High Temperature Vapors,* Academic Press, Inc., New York, 1975, p. 353.
18. R. W. Sprague, *Systematic Study of Firebrake ZB as a Flame Retarder for PVC, Parts III, IV, and V,* U. S. Borax.
19. Technical data sheet, Buckman Labs. Inc., 1992.
20. J. A. Finn, in *6th International Symposium on Flammability and Flame Retardants,* Nashville, Tenn., 1979.
21. K. K. Shen and T. S. Griffen in G. L. Nelson, ed., *Fire and Polymers,* ACS Symposium Series 245, American Chemical Society, Washington, D.C., 1990, p. 157.
22. C. J. Hilado, *Flammability Handbook for Plastics,* 2nd ed., Technomic Publications, Lancaster, Pa., 1974.
23. G. A. Byrne, D. Gardiner, and F. H. Holmes, *J. Appl. Chem.* **16,** 81 (1966).
24. P. H. Kemp, *Chemistry of Borates, Part 1,* Borax Consolated, Ltd., London, 1956.

25. F. Molesky in *Recent Advances in Flame Retardancy of Polymeric Materials,* Stamford, Conn., 1990; F. Molesky, “The Use of Magnesium Hydroxide for Flame Retarded Low Smoke Polypropylene,” *Polyolefins IV International Conference,* Feb. 24, 1991, Houston, Tex.
26. F. W. Moor, *Molybdenum Compounds as Smoke Suppressants for Polyvinyl Chloride,* Society of Plastics Engineers (SPE ANTEC), Montreal, Canada, 1977.
27. *Smoke Suppression of Rigid Vinyl Using Molybdenum Compounds,* Technical Bulletin No. 2 Climax Performance Materials Corp.
28. I. Touval, *J. Fire Flam.* **3,** 130 (1972).
29. P. A. Cusack and J. Killmeyer, in Ref. 21, p. 189.
30. S. Kaufman and C. A. Landrith, *Development of Improved Flame Resistant Interior Wiring Cables,* 24th ICCS, Nov. 18, 1975.

IRVING TOUVAL
Touval Associates

Related Articles

Flame retardants, overview; Flame retardants, halogenated flame retardants; Olefin polymers