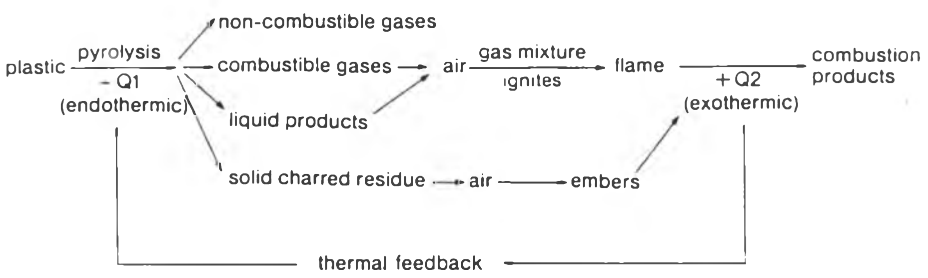
CHAPTER II

THEORY AND LITERATURE REVIEW

The Combustion Process

The combustion of plastics is a process comprising many steps, some of which are still uninvestigated. It therefore cannot be described quantitatively. A simplified schematic representation of the various phenomena which take place during the combustion of plastics is shown in Figure 2-1.

Figure 2-1 The combustion process (schematic)



Three stages are necessary to initiate the actual combustion process: heating, decomposition and ignition of the polymer.

1. Heating

The solid plastic is heated by thermal "feedback" as shown in Figure 2-1 or by an external heat source (e.g. radiation or flame). In this initial phase thermoplastics tend, on account of their linear molecular chains, to soften or melt and start to flow. Thermosetting plastics have a three-dimensional cross-linked molecular structure which prevents softening or melting. The polymers do not pass as such into the gas phase if further energy is supplied, but decompose before vaporizing.

2. Decomposition

Decomposition is an endothermic process in which sufficient energy must be provided to overcome the high binding energies of the bonds between individual atoms (between 200 and 400 kJ/mol) and to provide any necessary activation energy. As the individual plastics differ in structure, their decomposition temperatures-ranges vary within certain limits. Table 2-1 gives the range of decomposition temperatures for some plastics, and for the natural product, cellulose.

Table 2-1 Range of decomposition of some plastics (1)

Plastic	Td [°C]	Plastic/natural product	Td[°C]
Polyethylene	340-440	Polypropylene	320-400
Polypropylene	320-400	Polyacrylonitrile	250-300
Polystyrene	300-400	Polyamide 6	300-350
Polyvinyl chloride	200-300	Polyamide 66	320-400
Polytetrafluoroethylene	500-550	Cellulose	280-380

In most cases decomposition occurs via free radical chain reactions, initiated by traces of oxygen or other oxidizing impurities which are trapped in all plastics during manufacture.

This oxidative degradation of polymers usually proceeds via the formation of hydroperoxide groups whose decomposition leads to highly reactive species such as H and OH radicals and thus to chain branching. These free radicals are responsible for flame spread (see below) in the combustion process. The formation of such high energy radicals has been illustrated by the thermal oxidation of polyolefins as an example.

Start $$\text{(polyolefin) } RH \longrightarrow R^{\bullet} + H^{\bullet} \qquad (1)$$

Growth $$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \qquad (2)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \qquad (3)$$

Branching $$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (4)$$

The radical R formed in equation (1) reacts with oxygen to give ROO (2), which together with further polyolefin forms hydroperoxide(3) and decomposes to give RO and highly reactive species OH (4).

These radicals cause degradation and give rise to various decomposition products depending on the constitution of polymer:

a) Almost exclusively gaseous products are formed; e.g., the depolymerisation of polymethyl methacrylate results in the formation of over 90% monomer and the degradation of polyethylene leads to the formation of saturated and unsaturated hydrocarbons.

b) Gaseous products and carbonaceous residues are formed: for instance in the pyrolysis of polyvinyl chloride, hydrogen chloride is eliminated in the first step and the remaining polyene sequence forms aliphatics and aromatics in the second step. These escape as gaseous products or remain as solid carbonaceous residues as a result of cross-linking reactions.

c) Almost exclusively carbonaceous residues are formed ; for example in the case of polyacrylonitrile or high temperature resistant plastics such as polyimides.

3. Ignition

The flammable gases formed by pyrolysis mix with atmospheric oxygen, reach the lower ignition limit and are either ignited by an external flame or, if the temperature is sufficiently high, self ignite. The flash-ignition and self-ignition temperatures of various polymers determined to ASTM D 1929 are given in Table 2-2 together with those of cotton for comparison.

Table 2-2 Flash-ignition and self-ignition temperatures of various plastics by ASTM D 1929 (1)

Plastic/natural product	FIT* [°C]	SIT**[°C]
Polyethylene	340	350
Polypropylene	320	350
Polystyrene	350	490
Polyvinyl chloride	390	450
Polytetrafluoroethylene	560	580
ABS	390	480
Polymethyl methacrylate	300	430
Polyacrylonitrile	480	560

Plastic/natural product	FIT* [°C]	SIT**[°C]
Polyamide 6	420	450
Polyamide 66	490	530
Polyurethane (rigid foam)	310	415
Cotton	210	400

*FIT = Flash-ignition temperature

**SIT = Self-ignition temperature

These values hold only under the conditions of this Standard and should not be considered as intrinsic properties of the material. Ignition depends on numerous variables such as oxygen availability, temperature and the physical and chemical properties of the polymer. The reaction of the combustible gases with oxygen is exothermic and, if sufficient energy is available, overrides the endothermic pyrolytic reaction and initiates flame spread.

4. Flame Spread

The exothermic combustion reaction reinforces pyrolysis of the polymer by thermal feedback (see Figure 2-1) and fuels the flame at an increasing level. The hydrocarbon diffusion flame in which the following reactions take place can be taken as a simple mode:

Growth:

$$CH_4 + OH^{\bullet} \longrightarrow CH_3^{\bullet} + H_2O \quad (5)$$

$$CH_4 + H^{\bullet} \longrightarrow CH_3^{\bullet} + H_2 \quad (6)$$

$$CH_3^{\bullet} + O \longrightarrow CH_2O + H^{\bullet} \quad (7)$$

$$CH_2O + CH_3^{\bullet} \longrightarrow CHO^{\bullet} + CH_4 \qquad (8)$$

$$CH_2O + H^{\bullet} \longrightarrow CHO^{\bullet} + H_2 \qquad (9)$$

$$CH_2O + OH^{\bullet} \longrightarrow CHO^{\bullet} + H_2O \qquad (10)$$

$$CH_2O + O \longrightarrow CHO^{\bullet} + OH^{\bullet} \qquad (11)$$

$$CHO^{\bullet} \longrightarrow CO + H^{\bullet} \qquad (12)$$

$$CO + OH^{\bullet} \longrightarrow CO_2 + H^{\bullet} \qquad (13)$$

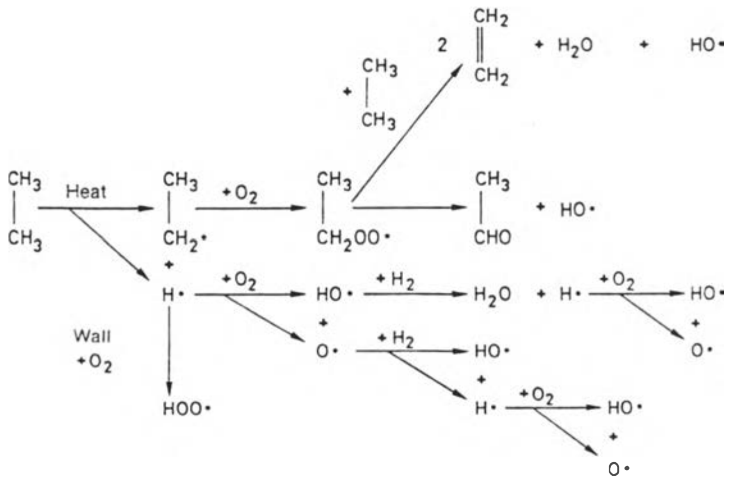
Branching:

$$H^{\bullet} + O_2 \longrightarrow OH^{\bullet} + O \qquad (14)$$

$$O + H_2 \longrightarrow OH^{\bullet} + H^{\bullet} \qquad (15)$$

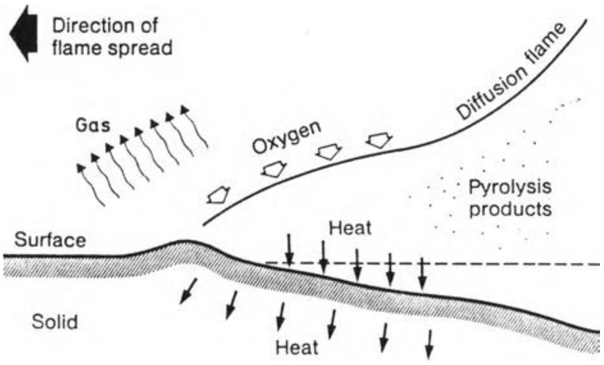
The chain branching step in which extremely high energy H and OH radicals are formed is particularly important. These radicals confer a high velocity on the flame front. Figure 2-2 illustrated the avalanche-like proliferation of these OH radicals particularly vividly.

Figure 2-2 The combustion of ethane



According to more recent investigations, however, the H radicals appear to be at least as important as the OH radicals. A phenomenological description of flame spread along a polymer surface is given in Figure 2-3. The diffusion flame advances over the decomposed polymer surface. As with the candle flame, the surface temperature of the polymer (500°C) is lower than that of the diffusion flame and of the edge of the flame, where reaction with oxygen occur (1200°C).

Figure 2-3 Flame spread (schematic) after



A further factor which determines the extent of flame spread is the heat of combustion of the polymer. The heats of combustion of various polymers are compared with those of cotton and cellulose in Table 2-3

Table 2-3 Heats of combustion of various plastics and natural products (1)

Plastic	ΔH [kJ.kg-1]	Plastic/natural product	ΔH [kJ.kg-1]
Polyethylene	46 500	Polyamide (6 or 66)	32 000
Polypropylene	46 000	Polyester resin	18 000
Polyisobutylene	47 000	Natural rubber	45 000
Polystyrene	42 000	Cotton	17 000
ABS	36 000	Cellulose	17 500
Polyvinyl chloride	20 000	Celluloid	17 500
Polymethyl methacrylate,	26 000		

One should not, however, try to relate the heat of combustion to the combustibility of individual materials, as the example of extremely flammable celluloid, with a heat of combustion of only 17,000 kJ/kg, clearly demonstrates.

Concurrent with the extremely rapid gas phase reactions controlled by diffusion flames, various slower, oxygen-dependent reactions also take place. These give rise to smoke, soot and carbon-like residues and take place partly in a condensed phase with glow or incandescence.

Retardation Approaches

Polymer combustion, a highly complex process, is believed to be composed of a vapor phase in which the reactions responsible for the formation and propagation of the flame are taking place and a condensed phase in which fuel for the gas reactions is being produced. Flame retardancy, therefore, can be improved by appropriately modifying either one or both of these phase (2).

The approaches toward reducing the flammability of polymer systems could be grouped into the following three categories:

a) Vapor phase: In the vapor-phase approach, a fire retardant or the modified polymer unit, on heat exposure, releases a chemical agent that inhibits free radical reactions involved in the flame formation and propagation. Flame retardation could be implemented by incorporating fire-retardant additives, impregnating the material with a fire-retardant substance, or using fire-retardant comonomers in the polymerization or grafting.

b) Condensed phase : In condensed-phase modification, the fire retardant alters the decomposition chemistry, which favors the transformation of the polymer to a char residue. This could be achieved by the addition of additives that catalyze char rather than flammable product formation or by designing polymer structures that favor char formation.

c) Miscellaneous: These approaches include dilution of the polymer with nonflammable material (e.g., inorganic fillers), incorporation of materials that decompose to give nonflammable gases such as CO_2, formulation of products that decompose endothermically, etc.

Mechanism of Flame Retardation

Flame retardancy is believed to be result from the presence of one or more key elements in the retardant -- such as phosphorus, nitrogen, chlorine, bromine -- or of a volatile compound (e.g., water of hydration).

Although the question of how various fire retardants work is still, in some cases, highly controversial, major advances have been made in this field during the past decade. Despite wide disagreement about how some of these substances suppress burning, the following are some of the widely accepted theories and their supporting thermoanalytical data:

1. Vapor-Phase Mechanism

The fire retardants operating by the vapor-phase mechanism are known to dissociate into species that can remove free-radical intermediates from the flame reaction or that can replace the major propagating species with those that do not propagate the flame as readily.

Halogenated fire retardants (e.g., chlorinated paraffins, chlorocycloaliphatics, and chloro- and brome-aromatic additives) have been commonly used in fire-retarding plastics. These additives are postulated to function primarily by a vapor-phase flame inhibition mechanism, which is characterized by the following criteria:

a) Fire-retardant element is lost from the substrate.

b) Flame inhibition is insensitive to substrate structure.

c) Fire retardance is sensitive to oxidant, e.g., O or N_2O.

d) Fire retardant does not change the composition or amount of volatiles.

Halogenated additives are the fire retardants known to function predominantly on the vapor phase. Since the preceding section deals with the use of thermal analysis in detecting vapor-phase activity, it may be appropriate to mention briefly how the fire retardants function in the vapor phase.

Burning of most polymers can be regarded as, a hydrogen-containing combustion system that is generally described and quantified in terms of the H_2-O_2 reaction scheme. The hydrogen-oxygen combustion scheme contains the following reactions:

$$H^{\bullet} + O_2 \longrightarrow OH^{\bullet} + O^{\bullet}$$
$$O^{\bullet} + H_2 \longrightarrow OH^{\bullet} + H^{\bullet}$$

And these dominate the combustion process because of their chain branching nature (the species like; H and H_2 originate from polymer pyrolysis). Halogenated fire retardants (MX) are postulated to function primarily by the following mechanisms, which produce HX, the actual flame-inhibiting species,

$$M\text{-}X \longrightarrow M^{\bullet} + X^{\bullet}$$
$$RH + X^{\bullet} \longrightarrow R^{\bullet} + HX$$

or

$$H_2 + X^{\cdot} \longrightarrow H^{\cdot} + HX$$

The flame-inhibiting effects of HX are manifested through reactions that inhibit the chain-branching step of the hydrogen-oxygen combustion systems, such as

$$H^{\bullet} + HX \longrightarrow H_2 + X^{\bullet}$$

and

$$OH^{\bullet} + HX \longrightarrow H_2O + X^{\bullet}$$

However, that the halogenated materials suppress the flame by a physical mechanism involving the undecomposed agents. This theory has generally not been favored.

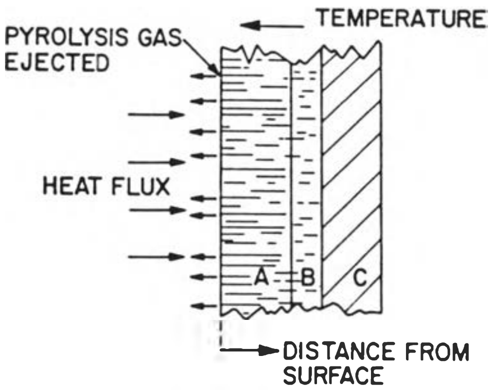
2. Condensed-Phase Mechanism

The fire retardants that function by this mechanism have the ability to increase the conversion of polymeric materials to a char residue (a carbonaceous product comprised mainly of carbon) during pyrolysis and thus decrease the formation of flammable, carbon-containing gases. The char helps to protect the substrate by interfering with the access of oxygen. Formation of char on the polymer surface can also be postulated to act as a heat shield for the base material . This is illustrated by Figure 2-4.

Phosphorus-based additives are typical examples of fire retardants that could act by a condensed-phase mechanism. The following are the indicators of a condensed-phase operation for a fire retardant:

a) Fire-retardant results in enhanced char formation.
b) Fire-retardant element is retained in the substrate.
c) Fire-retardant element is often ineffective in the vapor phase.
d) Fire retardance is sensitive to the substrate structure.
e) Fire retardance is insensitive to oxidant (e.g., N_2O or O_2)
f) Fire retardant changes the composition of volatiles.

Figure 2-4 Effect of char formation on polymer combustion



A , char layer ; B , transition zone of incomplete charring ; C , virgin polymer material .

3. Miscellaneous Mechanisms

Apart from vapor-phase and condensed-phase mechanisms described previously, fire retardants could also function in a number of other ways. The following are some other alternative model of flame inhibition:

a) Large volumes of noncombustible gases may be produced that dilute the oxygen supply to flame and / or dilute the fuel concentration needed to sustain the flame.

b) The endothermic decomposition of the fire retardant could lower the polymer surface temperature and retard pyrolysis of the polymer.

c) The fire retardant may act as a thermal sink to increase the heat capacity of the combustion system or to reduce the fuel content to a level below the lower limit of flammability.

Synergism in Flame Retardation

The effect of a mixture of two or more fire retardants may be additive, synergistic, or antagonistic. Synergism is the case in which the effect of two or more components taken together is greater than the sum of their individual effects. The concept of synergism is very important, since the development of synergistically efficient fire retardants can lead to less expensive polymer systems with reduced effects on other desirable properties. One of the classical illustrations of synergism observed in fire retardation is the addition of antimony (III and V) oxide to halogen containing polymers. Here we have described the antimony (III) - halogen synergism and the role played by thermal analysis in substantiating its mechanism.

In polymer systems containing Sb_2O_3 and halogen, it has often been suggested that fire retardance is mainly due to the gas phase flame inhibition by the volatile antimony trihalide; since maximum flame retardancy is observed when the mole ratio Sb/X is 1:3. It is believed that HC1 formed by the degradation of the chlorinated additive reacts with Sb_2O_3 to yield SbOC1 as an intermediate, and the subsequent reactions are responsible for the increased flame retardancy. The formation of an intermediate by the combination of Sb_2O_3 and a chlorine source was also confirmed by thermoanalytical data; for example, the individual TG's of Sb_2O_3 and a chlorinated paraffin showed a 0 and 67% weight loss, respectively, in the RT-375 $^{\circ}$C temperature range. Assuming that there was no interaction between the components of this system, a 34% weight loss would be expected from a 50:50 mixture. Instead, a 72% weight loss was observed in the temperature range under consideration.

In a typical substrate of R.HCl (chlorine source)+Sb_2O_3+ polymer, the formation of SbOCl has been illustrated by the following equations:

$$R\text{-}H + Cl^{\bullet} \xrightarrow{\sim 250^{\circ}C} R^{\bullet} + HCl$$

$$2HCl + Sb_2O_3 \xrightarrow{\sim 250^{\circ}C} 2SbOCl + H_2O$$

Working under the assumption that SbOCl was the primary product of the interaction between Sb_2O_3 and a chlorine source, The studied of the thermal decomposition of SbOCl by Tg and DTA proposed that the following reaction sequence in order to account for the three weight loss steps on the TG curve.

		Theoretical % wt loss	% Wt loss by TG
Step I :	$5SbPCl(s) \xrightarrow{245\text{-}280^{\circ}C} Sb_4O_5Cl_2(s) + SbCl_3(g)$	26.4	24.1
Step II :	$4Sb_4O_5Cl_2(s) \xrightarrow{410\text{-}475^{\circ}C} 5Sb_3O_4Cl(s) + SbCl_3(g)$	6.9	8.4
Step III :	$3Sb_3O_4Cl(s) \xrightarrow{475\text{-}565^{\circ}C} 4Sb_2O_3(s) + SbCl_3(g)$	10.6	9.5

A simultaneous DTA thermogram further indicated that the three weight loss steps on the TG curve were endothermic.

The endothermic release of $SbCl_3$ during the formation of flammable degradation products was considered to be responsible for the fire-retardance effect observed in flexible urethane foams containing SbOCl.

The thermal decomposition of SbOCl occurred within an appropriate temperature range that happened to match the degradation temperature range of the foam itself.

Flame Retardants for PVC

Polyvinyl chloride (PVC) resin itself inherently fire retardant. However, most organic additives incorporated to improve processing or end-use performance of PVC can act as fuels for fire propagation. To counteract this it is necessary to use other additives to regain at least a measure of the flame retardancy of the PVC resin.

Fire retardants can be classified, into two basic type: (3)

- Organics
- Inorganics

In contrast to most additives, fire retardants can appreciably impair the properties of plastics. The problem is to find a compromise between the decrease in performance of the plastic caused by the fire retardant and the desired improvement in fire safety.

An ideal fire retardant should be easy to incorporate in, and be compatible with the plastic (i.e. not bleed out), and not alter its mechanical properties. Furthermore, it should be colorless, exhibit good light stability, and be resistant to aging and hydrolysis. It should also be matched to the decomposition temperature of the polymer, i.e. its effect must begin below the decomposition temperature of the plastic and continue over the whole range of its decomposition. It must not cause corrosion, must be temperature resistant, effective in small amounts, odorless and without harmful physiological effects. It must also emit only low levels of smoke and toxic gases and finally be as cheap as possible.

To approach this unachievable range of properties, countless formulations have been developed for fire retarding each plastic for diverse applications. These are based on fire retardants to which synergists and fillers may be frequently added .

1. Inorganic Flame Retardants

Inorganic-type fire retardants can be subdivided as follow: (4)

- Antimony compounds
- Metal hydroxides, hydroxycarbonates, and carbonates
- Molybdenum, zinc, and iron compounds

Antimony Compounds are the most commonly used fire retardants for PVC. Their popularity stems from their efficiency in reducing flame spread at relatively low levels (typically up to 7 phr) without any major adverse effects on physical properties (other than the opacity introduced in most cases). Antimony compounds only work in combination with a halogen-containing compound. PVC, of course, fits this requirement. The mechanism is one of gas-phase inhibition involving the formation of antimony-halogen products. Essentially any antimony compound will provide flame retardancy; however, for the majority of applications, antimony trioxide (often called antimony oxide) is the product of choice from both cost efficiency and end-property standpoints. Some blended products containing antimony trioxide with extender synergists are also available. Because of their higher cost, other antimony compounds are only used when additional properties are required such as very low to zero tinting strength for translucent of clear applications.

Antimony Trioxide is the most commonly used antimony compound and is recommended for its cost efficiency as the primary antimony fire retardant unless special requirements preclude its use. Typical properties are shown in Table 2-4

TABLE 2-4 Typical properties of antimony trioxide (4)

Molecular weight	291.52
Melting point	1213°F (656°C)
Specific gravity at 20/20°C	5.5
Physical form	Fine white powder
Crystal type	Cubic (major)
Average particle size	1 micron
Retention on 325-mesh sieve	<0.03%
Antimony (as metal)	83.1%
Arsenic %	0.1-0.3%
Lead	0.05-0.2%
Iron	<0.002 %

In PVC applications, antimony trioxide is practically chemically inert with the exception of its flame retardancy action at elevated temperatures, Antimony trioxide is predominantly in the form of small (typically 0.1-2.0 microns) cubic crystals. Its effect on physical properties of PVC compounds, such as tensile and impact strength, is comparable to a calcium carbonate filler of similar particle size.

Antimony trioxide does have a high refractive index compared to PVC; this, combined with its fine particle size, gives it high pigmentary properties. This can be considered a benefit in white or gray applications, because it can allow the formulator to reduce or even eliminate the need for other white pigments, such as titanium dioxide. It should be noted, however, that antimony trioxide does not have the same screening action on UV light, so reduction in titanium dioxide level is not advisable for outdoor exposure where the primary purpose of the titanium dioxide is for weather protection. In some applications, particularly when bright colors are required, the high pigmentary effect of the antimony trioxide is considered an adverse effect, because it necessitates the use of higher levels of expensive pigments to achieve the desired color. For such applications, special low-tinting grades of antimony trioxide are produced. To make these products it is necessary to form the oxide under conditions which will enhance crystal growth. his imparts an extra cost, and inevitably these products carry a premium over that of regular oxide. Therefore care should be taken to establish that a true cost saving is being achieved in their use. Another point to note is that manufacturers do not all make equivalent products.

Some manufacturers provide products with a specified tinting strength range (regular oxide is used as a standard at 100%). Other just state low tint, so it is important to establish exactly what the specification is and what degree of consistency is guaranteed. Otherwise, problems of color matching may occur later.

Antimony trioxides of a finer particle size than standard are also available. These products are more pigmentary and are sometimes claimed to be more efficient and more readily dispersed, but they also carry a premium. Some acceptance of these products has been obtained in high-value added-engineering thermoplastics, although justification in most PVC applications is more difficult. Dispersion tends not to be an issue except in certain plastisol application; under very-low-shear mixing conditions it can be argued that a coarser-particle-size product may be easier to disperse because there is less surface energy to overcome to wet out the product. Flame retardancy is primarily controlled by the antimony content, and cost tends to be the driving factor in the grade selected.

Product form is becoming an increasingly important issue. The majority of antimony trioxide used is still a fine dusty powder. However, there is a growing concern and awareness of the potential hazards of all dusts, and it is certain that regulation of the handling of dusty powders will only become more stringent. For this and other reasons, several types of "low" or "nondusting" forms or packages of antimony trioxide have been made available, and it is the belief that the use of these products will be the norm in the near future.

Manufacturers of antimony trioxide in the United States and western Europe are shown in Table 2-5 .

Table 2-5 Major manufacturers of antimony trioxide (4)

			Grade[a]		
Manufacturer	Location	Trade name	High tint	Low tint	High purity
		United States			
Amspec Chemical	Gloucester City, NJ	Amstar	KR	LTS	Blue Star
Anzon Inc	Philadelphia, PA	TMS	TMS	TruTint	TMS-HP
Asarco	New York, NY		High	Low	Ultrapure
Laurel Industries	Cleveland, OH	Fire Shield	H	L	—
Elf Atochem N.A.	Philadelphia, PA	Thermoguard	S	L	—
		Western Europe			
Campine	Brussels, Belgium	Antiox	BlueStarRG	BlueStarMT	WhiteStar
Cookson Minerals Ltd	Newcastle, England	Timinox	RedStar	15S	BlueStar
La Lucette	Paris, France	Triox	WhiteStar	TL	GoldStar
Sica	Chauny, France	Naige	Super	—	Extra
Stibiox	Hungerkamp, Germany	—	MF	—	—

Metal Hydroxides, Hydroxycarbonates, and Carbonates : Alumina trihydrate and several alkaline earth metal derivatives in this category provide flame retardancy by releasing water or, in the case of carbonates CO_2 as well, to quench the flame. These product must be used at high loading (typically 20-100 phr) to provide any degree of flame retardancy. This inevitably imposes restrictions on processing and on the physical properties attainable on the finished product. In PVC applications, certain alkaline earth-based products can also affect color, causing a pink discoloration. However, these products can act as acid scavengers, reducing HCl evolution, and will lower smoke emission (covered later under smoke suppressants).

Alumina trihydrate (ATH) is generally the lowest cost of this class of this products as such has found the wide application. The main drawback of ATH is its relatively low decomposition temperature [initial water release is around $400^{\circ}F$ ($204^{\circ}C$)]. This can cause gassing problems in the processing operations involving high stock temperatures.

ATH is supplied in a range of particle sizes in ground-precipitated and fine-precipitated grades. The latter grades are more expensive but disperse more readily than do similar-particle-size ground- precipitated grades due to the tendency of the ground-precipitated types to agglomerate. Surface-modified grades are available for such applications as plastisols (low DOP absorption) and wire and cable (low electrolyte level). Specific gravity of the untreated grades is 2.42 .

Manufacturers of ATH are shown in Table 2-6 .

Table 2-6 Suppliers of alumina trihydrate (4)

Company	Location	Type[a]	Trade name/grade	Average particle size (microns)		Typical end uses[c]
				Sedigraph	Other[b]	
			North America			
Alcan Chemicals	Cleveland, OH	gmd	Baco FRF 20	13	17	FF, CF
Alcan Chemicals	Cleveland, OH	gmd	Baco FRF 80	5.5	6.5	FS
Alcan Chemicals	Cleveland,OH	gmd	Baco FRF 85	4.5	5.5	CVB
Alcan Chemicals	Cleveland, OH	—	Baco LV2	55	—	FF
Alcan Chemicals	Cleveland, OH	ppt	Baco Superfine 4[d]	1.4	—	CVB, CF, R
Alcan Chemicals	Cleveland, OH	ppt	Baco Superfine 7[d]	1.0	—	W, CF, R
Alcan Chemicals	Cleveland, OH	ppt	Baco Superfine 11[d]	0.7	—	R
Aluchem, Inc.	Reading, OH	gmd	AC-400K	7-10	—	FS
Aluchem, Inc.	Reading, OH	gmd	AC-712K	2.5	—	W, PG, R
Aluchem, Inc.	Reading, OH	gmd	AC-714K	3.0	—	FS, PG, R
Aluchem, Inc.	Reading, OH	gmd	AC-722K	4.0	—	FS, PG, R
Alcoa Industries Chemical Division	Bauxite, AR	ppt	Hydral 710	0.9	—	R
Custom Grinders Sales	Chatsworth, GA	gmd	Polyfill 402	2.7	—	CF, CVB
Custom Grinders Sales	Chatsworth, GA	gmd	Polyfill 502	1.7	—	W
Pluess-Staufer International	Stamford, CT	ppt	Martinal OL-104/C[e]	—	< 1[f]	W
Pluess-Staufer International	Stamford, CT	ppt	Martinal OL-104/LE	—	1.3-2.6	W
Pluess-Staufer International	Stamford, CT	ppt	Martinal OL-107/C[e]	—	< 1[g]	W
Pluess-Staufer International	Stamford, CT	ppt	Martinal OL-107/LE	—	0.8-1.4	W
Pluess-Staufer International	Stamford, CT	ppt	Martinal OL-111/LE	—	0.6-1.0	W
Nyco	Willsboro, NY	ppt	21 Nycoat 10734[e]	—	1	W
Solem Industries[h]	Norcross, GA	gmd	Micral 855SL	2.0	—	W, R
Solem Industries	Norcross, GA	gmd	SB-432	9.0	—	FS, PG
Solem Industries	Norcross, GA	gmd	SB-632	3.5	—	FS, PG, FF, R, W
Solem Industries	Norcross, GA	gmd	Micral 932	2.0	—	FS, PG, W
			Western Europe			
BA Chemicals, Ltd	Chalfont Park[i]	(See products listed under Alcan Chemicals)				
Martinswerke	Bergheim, Germany	(See products listed under Pluess-Staufer International)				
VAW	Bonn, Germany					

[a] ppt—precipitated; gmd—ground.

[b] Coulter counter, laser, sieve, etc.

[c] CF—coated fabrics; CVB—conveyor belts (mines); FF—foamed flooring; FS—film and sheeting; PG—plastisols, general; R—rigids; W—wire and cable.

[d] Also available in stearate-coated grades.

[e] Surface-modified.

[f] 95% less than 1 micron.

[g] 99% less than 1 micron.

[h] Division of J. M. Huber Corp.

[i] Gerrards Cross, Buckinghamshire, England.

Molybdenum, Zinc, and Iron Compound : It is well known that certain transition metal compounds can catalyze the hydrochlorination of PVC (18). It is for this reason that such materials are usually avoided in PVC compounding due to their detrimental effect on thermal stability. However, in a fire situation this property can be advantageous because it promotes char which generally improves flame retardancy and smoke suppression. Therefore, some selected transition element compounds have found application as combined fire-retardant and smoke-suppressant additives. The most common types are discussed in the following:

Zinc compounds, zinc borate is the most commonly encountered zinc compound used as combination fire retardant and smoke suppressant. In rigid PVC applications it is claimed to be useful as a total replacement for antimony trioxide, whereas in flexible PVC it is generally recommended as a partial replacement. Zinc borate does offer improvements in smoke suppression over antimony oxide alone and is cost comparative. However, it does have a notable detrimental effect on heat stability.

Other zinc compounds, including zinc oxide, will provide varying degrees of flame retardancy and in many instances reduced smoke emission. As with zinc borate, most zinc compounds have a detrimental effect on heat stability to a greater or lesser extent.

Of the zinc compounds currently available, Ongard 2 (a patented calcined blend of zinc and magnesium oxides) has only a marginal effect on heat stability while providing good fire-retardant properties (14,28). Manufacturers of molybdenum and zinc fire retardants (and smoke suppressants) are shown in Table 2-7

Table 2-7 Manufacturers of molybdenum and zinc fire retardants and smoke suppressants (4)

Manufacturer	Location	Trade name (grade)	Composition	Average particle size (microns)	Specific gravity
Alcan Chemicals	Cleveland, OH	Flamtard H	Zinc hydroxystannate	2.5[a]	3.3
Alcan Chemicals	Cleveland, OH	Flamtard S	Zinc stannate	1.7[a]	3.9
Anzon Inc.	Philadelphia, PA	Ongard 2	Mg-Zn complex	1.5	4.4
Anzon Inc.	Philadephia, PA	Smokebloc 11	Sb-Mo complex	1.9	3.9
Climax Specialty Metals	Cleveland, OH	POL-U	MoO_3	2.5[b]	4.69
Climax Specialty Metals	Cleveland, OH	AOM	$(NH_4)_4Mo_8O_{26}$	1[b]	3.18
Climax Specialty Metals	Cleveland, OH	ZB-112	$ZnO \cdot B_2O_3 \cdot 2H_2O$	6[b]	2.50
Climax Specialty Metals	Cleveland, OH	ZB-223	$2ZnO \cdot 2B_2O_3 \cdot 3H_2O$	4[b]	2.83
Climax Specialty Metals	Cleveland, OH	ZB-237	$2ZnO \cdot 3B_2O_3 \cdot 7H_2O$	2.6[b]	2.31
Climax Specialty Metals	Cleveland, OH	ZB-325	$3ZnO \cdot 2B_2O_3 \cdot 5H_2O$	2[b]	2.66
Climax Specialty Metals	Cleveland, OH	ZB-467	$4ZnO \cdot 6B_2O_3 \cdot 7H_2O$	5[b]	2.74
Sherwin Williams	Cleveland, OH	Kemgard 981	ZnO-phosphate complex	1.0[c]	4.2
Sherwin Williams	Cleveland, OH	Kemgard 425	Ca-Zn molybdate-ZnO	1.9[c]	3.0
Sherwin Williams	Cleveland, OH	Kemgard 911 A	Ca-Zn molybdate-ZnO	1.9[c]	3.0
Sherwin Williams	Cleveland, OH	Kemgard 911 B	$ZnMoO_4$-ZnO	0.7[c]	5.06
Sherwin Williams	Cleveland, OH	Kemgard 911 C	$ZnMoO_4$ on talc	10[c]	2.8
Sherwin Williams	Cleveland, OH	Kemgard 911 T	$ZnMoO_4$ on talc	10[c]	2.8
U.S. Borax	Los Angeles, CA	Firebrake ZB	$2ZnO \cdot 3B_2O_3 \cdot 5H_2O$	—	2.8
U.S. Borax	Los Angeles, CA	Firebrake ZB (fine)	$2ZnO \cdot 3B_2O_3 \cdot 5H_2O$	—	2.8

Development of Tin-based Flame Retardants

Despite the fact that tin salts have been known as fire retardants since the mid-nineteenth century, until very recently their industrial use has been limited to specialized treatments for woolen sheepskins and rugs. In view of the increasing demand for novel, non-toxic, fire-retardant additives for synthetic polymers, a program of research was initiated in the laboratories of the International Tin Research Institute during the mid-1980s, to develop tin chemicals as fire retardants and smoke suppressants for plastics, elastomers and related materials. Preliminary studies demonstrated the effectiveness of tin(IV) oxide, SnO_2, both in its anhydrous and hydrous forms, as a flame- and smoke-inhibitor for halogen-containing polymer formulations such as PVC, halogenated polyester resins and polychloprene. Subsequent work was aimed at developing tin additives with improved activity compared to tin(IV) oxide. This led to the conclusion that, of a series of metal hydroxystannates and stannates, $MSn(OH)_6$ and $MSnO_3$ respectively, the zinc compounds were clearly the most effective with regard to fire-retardant and smoke-suppressant performance.

The choice of zinc hydroxystannate (ZHS) an zinc stannate (ZS) for further study at I.T.R.I. was to prove a significant step in the quest for tin-based fire retardants for synthetic polymers. This research has reached fruition with the recent commercial introduction of fire retardants based on these compounds, and their proven range of advantages over existing products could lead to significant worldwide usage. Some important properties of these compounds are shown in Table 2-8 overleaf

Table 2-8 Properties of zinc hydroxystannate and zinc stannate (5)

	ZHS	ZS
Chemical formula	$ZnSn(OH)_6$	$ZnSnO_3$
CAS No.	12027-96-2	12036-37-2
Appearance	white powder	white powder
Analysis (approx.):Sn	41%	51%
Zn	23%	28%
Cl	<0.1%	<0.1%
free H_2O	<1%	<1%
Specific gravity	3.3	3.9
Decomposition temperature (°C)	>180	>570
Toxicity	very low*	very low*

*Acute oral toxicity, LD_{50}(rat):>5000mg/kg

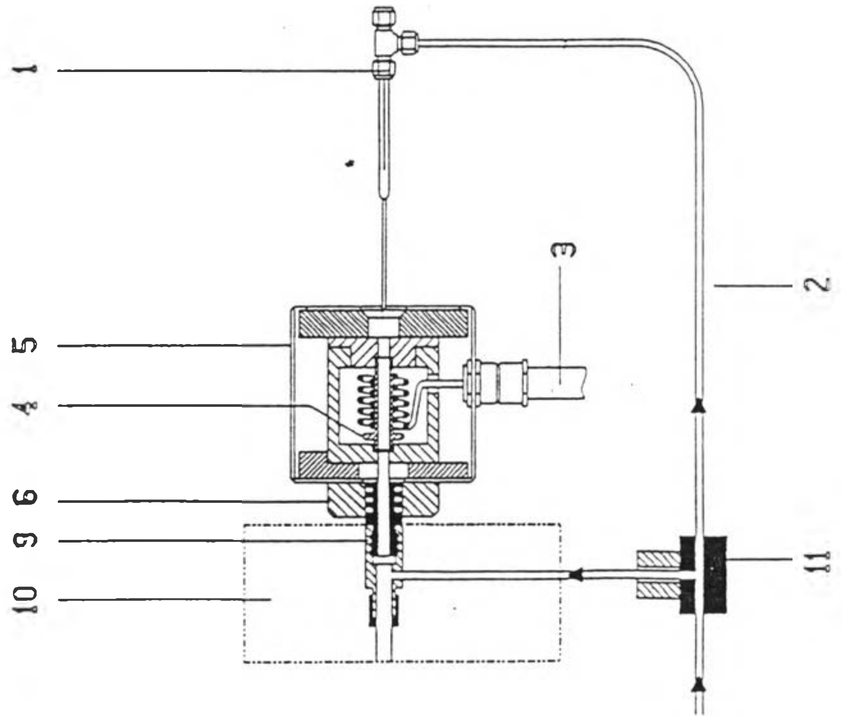
Pyrolysis Gas Chromatography

The analytical pyrolysis field has made impressive advances over the past decade with the availability of reliable instrumentation and methods. The development of analytical systems which couple pyrolysis (Py) with gas chromatography (Py-GC), gas chromatography-mass spectrometry (Py-GC/MS), or direct with mass spectrometry (Py-MS) and Fourier transform infrared (Py-FTIR or Py-GC/FTIR), has extended the applicability of pyrolysis to the analysis of nonvolatile materials such as natural and synthetic polymers, biopolymers, microorganisms, food and tabacco, forensic and art materials, and many others.(6)

The essential requirement of pyrolysis instrumentation in analytical pyrolysis is that of reproducibility. When a sample is subjected to pyrolysis, primary-bond-fission processes are initiated. These may proceed by several temperature dependent and competing reactions, which make the final product distribution highly dependent upon the pyrolysis temperature and pyrolysis time.

In the Curie-point pyrolysis (CPPY) invented by Professor W. Simon in 1965, a ferromagnetic sample support (wire, tube) is centered in a glass or quartz tube, which is connected to the inlet of a gas chromatograph, and through which the carrier gas flows. A Curie-point induction coil surrounds the tube and heats the ferromagnetic sample support until its Curie-point is reached. (See Figure 2-5)

Figure 2-5 The pyrolysis reactor and injector

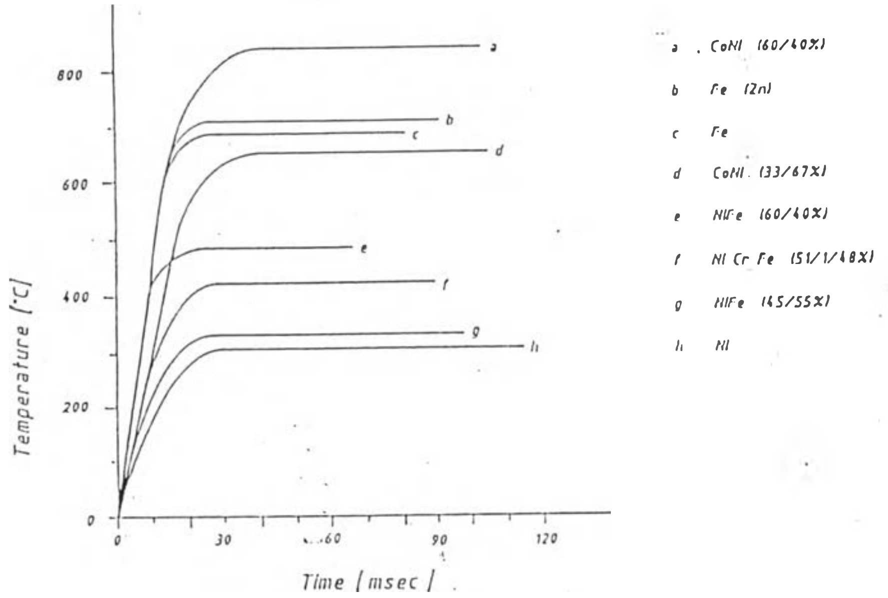


1. Pyrolysis injector, consisting of:

   Glass pyrolysis chamber with injection needle made of stainless steel, inlet made of glass quartz, axial ferromagnetic sample carrier, septum and 3-way screwing
2. Teflon carrier gas hose
3. Impulse cable for connection of pyrolysis reactor to generator
4. Induction coil
5. Aluminium housing
6. Adapter for fastening the reactor onto the GC-inlet part
7. GC-inlet
8. GC
9. Carrier gas change-over valve-3-way solenoid valve

This is the temperature at which the support becomes paramagnetic, and its energy intake drops, thus holding the temperature of the sample support at this point. Different pyrolysis temperatures are obtained by using ferromagnetic sample supports of different Curie points. A range of temperatures is obtained by using alloys containing different amounts of the common ferromagnetic metals, i.e., iron, cobalt, nickel, and chromium (see Figure 2-6)

Figure 2-6 Curie-point temperatures versus time profiles for various ferromagnetic materials and alloys



In Curie-point systems, the heating rate is dramatically affected by the position of the ferromagnetic sample support within the induction coil. Coating should therefore be as controlled as possible, so that the sample is placed in the same position each time. To achieve rapid pyrolysis, the size of the sample should be kept to a minimum (between 0.1 and 500 μg).