

## **CHAPTER II**

### **THEORETICAL CONSIDERATION**

#### **The Burning Process [1]**

The burning process of any material, is a combination of complex physical and chemical processes, which include the transformation of initial substance into high-temperature combustion products. It is apparent that a fire proceeds in various stages, with specific physical and chemical processes occurring in each of these stages.

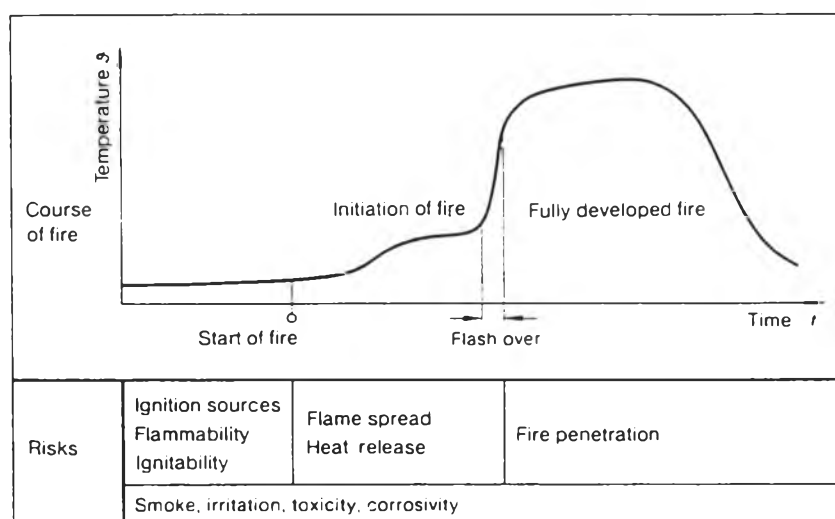
##### **1. Fire**

The course of a fire can be split into several phases as explain below ;

##### **The Initiating Fire**

An ignition source such as a cigarette ignites combustible matter (for instance, the content of a wastepaper basket). This material burns and generates heat, heating up and igniting additional combustible matter (e.g., a certain near the basket). The additional heat released and resultant rise in the temperature of the surrounding speed up the rate at which the fire develops. At

this stage radiant heat and the temperature have increased to such an extent that the fire load (i.e., all the combustible matter such as furnishings, carpets, etc.) decomposes with the evolution of a flammable gas mixture. The ignition of the gas cause an extremely high, even explosive, rate of fire spread over the entire area. This point in time is termed “flash-over” and leads to the fully developed fire which constitutes the second phase.



**Figure 2-1** Phases in the course of a fire.

### **The Fully Developed Fire**

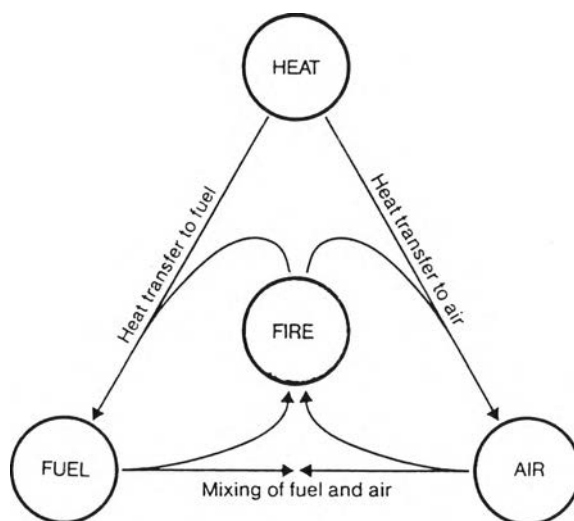
The fire penetrates doors, walls, ceilings and windows and spreads to neighboring rooms until the whole building is in flame. The room temperature exceed 1000°C and the entire fire load in the building burns. At this point the fire has reached its peak.

### **The Decreasing Fire**

Depending on the size of the fire load and the ventilation conditions, the fire passes its climax and enters the decreasing phase in which the building is more or less rapidly burnt out. These three phases and associated risks are illustrated in Figure 2-1.

## **2. Fire Determining Parameters**

In order for a fire to start, three components-fuel, oxygen and energy are necessary. The combustion process cannot take place without them. It has illustrated this clearly in a fire triangle (Figure 2-2). The extraordinary complexity of a fire springs from these three components which are themselves affected by a multitude of variables. It is therefore impossible to describe a fire quantitatively or to predict its cause exhaustively. Selected parameters which influence the above components are discussed in the following summary .



**Figure 2-2** Fire triangle

- Energy can be transferred to the fuel by radiation, sparks and flames. Of special importance for the continuation of the fire are the intensity ( distance of the energy source from combustible matter) and duration of the ignition source.

- Oxygen is necessary for the actual burning process. i.e., for chemical reaction of the fuel. It must be present in sufficient quantities (e.g., through ventilation) at the size of fire.

- The fuel itself influences the fire situation in several ways. Parameters of primary importance affecting the behavior of fuel in a fire include position in the fire room , “built-in” state, form ( shape, thickness, surface characteristic,

distribution, density, etc.) and finally physical and chemical properties ( ignition and flash points, thermal conductivity, specific heat and heat of combustion, etc.).

This variety of parameters demonstrates that the fire performance of a fuel only partially characterized by its chemical and physical properties and is therefore not an intrinsic property of the material-contrary to frequently stated opinions.

The instant at which flash-over occurs is of prime importance for the fire situation since it leads, as can be seen from Figure 2-1, to the fully developed fire. At this stage the fire situation can no longer be controlled and one must be content with preventing the fire from spreading to other parts of the building or, indeed, to other structures. Prior to flash-over, the fire can be effectively fought in the vicinity of the initiating fire and extinguished. Suitable measures at this point, such as the use of flame retardants, can effectively and permanently influence processes such as ignition, flame spread and heat release.

### 3. The Flame

In order to gain a deeper understanding of the combustion process, it is useful not only to consider its macroscopic manifestation, but also to examine the microscopic or molecular region where material properties play a determining role. While fire is the external manifestation of an uncontrolled combustion process and therefore cannot be exactly defined, the flame may be considered as the expression of controlled combustion and thus be described.

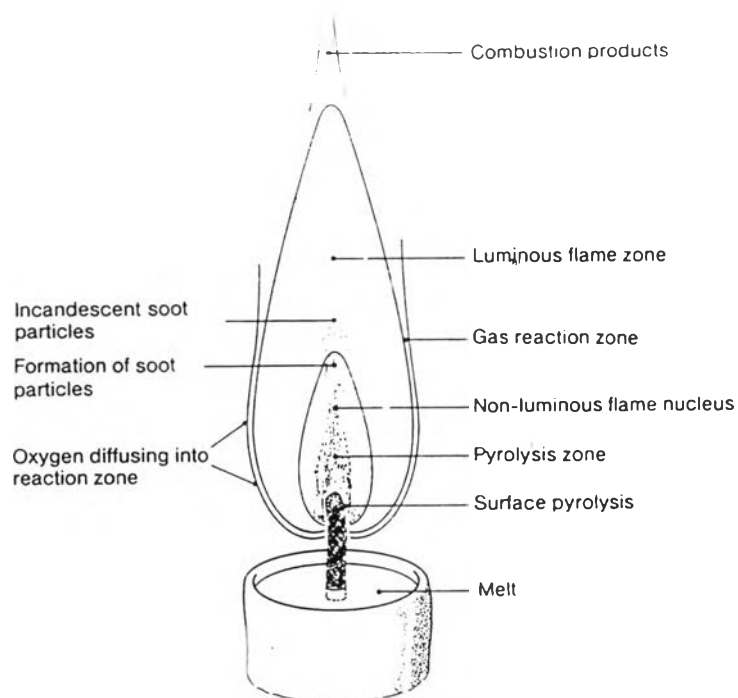
Basically, two types of flame exist: the **premixed** flame in which the gas composition is fixed prior to combustion (e.g., as in the Bunsen burner)

and the **diffusion flame**, so called because the oxygen necessary for combustion diffuses into the gas mixture from the surrounding atmosphere.

The best known example of a diffusion flame is the candle flame. An illustration detailing the individual phenomena of the combustion process in such a flame is shown in Figure 2-3 .

Wax melted by radiated heat migrates up the wick by capillary action and is pyrolysed on its surface at temperatures between 600-800°C. The pyrolysis gases migrate further and either remain in the inner part of the flame, the flame nucleus, or reach the external flame mantle.

A reducing atmosphere exists in the flame nucleus owing to the lack of oxygen. The hydrocarbon fragments from pyrolysis migrate to regions in which temperature reach 1000°C. Generation of conjugated double bonds followed by cyclisation and aromatization leads to the formation of soot particles. The latter are transported further and start to glow, causing luminescence of the flame. They are consumed in the luminescent region of the flame by reaction with water and carbon dioxide to form carbon monoxide.



**Figure 2-3** Candle flame

The pyrolysis gases are carried to the exterior and encounter oxygen diffusing inwards. In this flame mantle reaction zone, high energy, primarily oxygen-containing radicals are generated at temperatures around  $1400^{\circ}\text{C}$ . These maintain the combustion reaction. If the process is uninterrupted and an adequate supply of oxygen is maintained., the end products of combustion of the candle flame are carbon dioxide and water. The processes which take place during the combustion of plastics are, in principle, similar to those of the candle flame.

Combustion is a catalytic exothermic reaction maintained by internally generated free radicals and radiant heat. If the supply of free radicals and heat exceeds the energy required for combustion, the reaction proceeds at an increasing rate until an explosion occurs. If the energy supply is constant and equals the demand, a stationary equilibrium occurs, i.e., the rate of combustion

constant. If the available energy is less than required to maintain equilibrium, the rate of combustion decreases until extinction occurs.

The radicals, oxygen and thermal energy necessary for combustion are brought to the site of combustion by various transport mechanism :

By mass transfer:

- Flow processes such as eddy diffusivity: mass transport in turbulent flow.
- Molecular diffusion: mass transport due to concentration gradients.
- Thermal diffusion : mass transport due to temperature gradients.

By energy transfer:

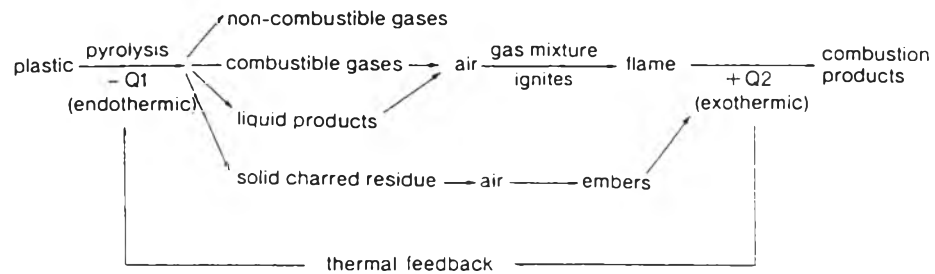
- Thermal conduction: heat transfer due to temperature gradients.
- Radiation: energy transfer due to radiation.

The flame is a combustion process which takes place exclusively in gas phase. It represents, however, only one aspect of combustion since other types exist. An example is provided by a system in which reaction components are present in gaseous and solid phases.

### **The Combustion of Plastics. [1,2]**

The combustion of plastics is a process comprising many steps , some of which are still uninvestigated. It therefore cannot be describe quantitatively, although it is possible to describe it quantitatively. A simplified schematic representation of the various phenomena which take place during the combustion of plastics is shown in figure 2-4





**Figure 2-4** The combustion process (schematic)

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

### 1. Heating

The solid plastics is heated by thermal "feedback" as shown in figure 2-4 or by an external heat source (e.g., radiation or flame). In this initial phase thermoplastic 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 prevent softening or melting. The polymer 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 temperature-range varies within certain limits. Table 2-1 gives the range of decomposition temperature for some plastics, and the nature of the product, cellulose.

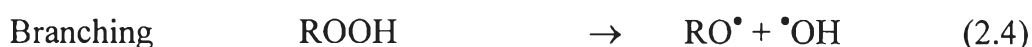
In most cases decomposition occurs via free radical chain reactions, initiated by trace of oxygen or other oxidizing impurities which are trapped in all plastic during manufacture.

**Table 2-1** Range of decomposition of some plastics.

Plastic	T <sub>d</sub> ( °C )	Plastic/natural product	T <sub>d</sub> ( °C )
Polyethylene	340-440	Polymethyl methacrylate	180-280
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

This oxidative degradation of polymers usually proceeds via the formation of hydroperoxide groups. Decomposition leads to highly reactive species such as H and OH radical and thus to chain branching. The formation of

such high energy radicals, using the thermal oxidation of polyolefins of an example.



The radical R formed in equation (2.1) reacts with oxygen to give  $\text{ROO}^\bullet$  (2.2), which together with further polyolefin forms hydroperoxide (2.3). In the branching step the hydroperoxide decompose to give  $\text{RO}^\bullet$  and the highly reactive species  $\text{}^\bullet\text{OH}$  (2.4).

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

(a) Almost exclusively gaseous products are formed ; e.g.,the depolymerization of polymethyl methacrylate results in the formation of 90% monomer and the degradation of polyethylene leads to the formation of saturated and unsaturated 2 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 a second step .

(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 by an external flame or, if the temperature 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. These values hold only under the condition of this standard and should not be considered as intrinsic properties of the material.

**Table 2-2** Flash-ignition and self-ignition temperature of various plastics by ASTM D 1929

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
Polyamide 6	420	450
Polyamide 66	490	530
Polyurethane (rigid foam)	310	415
Cotton	210	400

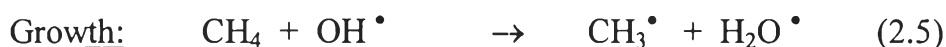
\* FIT = Flash-ignition temperature

\*\* SIT = Self-ignition temperature

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

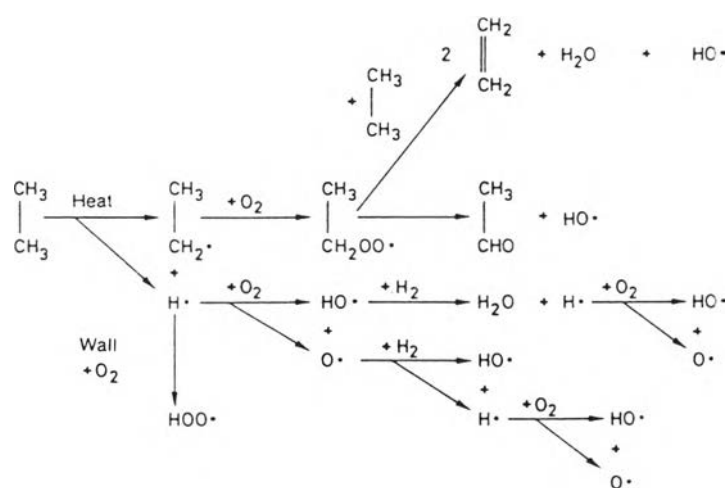
The exothermic combustion reaction reinforces pyrolysis of the polymer by thermal feedback (see Figure 2-4) and fuels the flame at an increasing level. The hydrocarbon diffusion flame in which the following reactions take place can be taken as a simple model;



Branching:

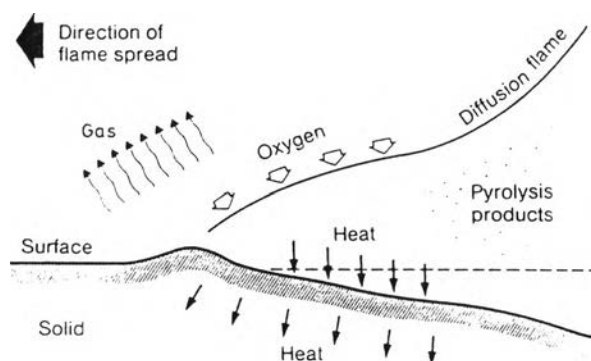


The chain branching step in which extremely high energy H and OH radicals are formed is particularly important. These radicals confer a high velocity on the flame front. Figure 2-5 illustrated the avalanche-like proliferation of these OH radicals particularly vividly.



**Figure 2-5** Combustion of ethane

According to more recent investigation, 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 2-6. The diffusion flame advances over the decomposed polymer surface. As with the candle flame, the surface temperature of the polymer ( $500^\circ\text{C}$ ) is lower than that of the diffusion flame and of the edge of the flame, where reaction with oxygen occurs ( $1200^\circ\text{C}$ ).



**Figure 2-6** Flame spread (schematic).

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

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 17,500 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.

**Table 2-3** Heats of combustion of various plastics and natural products [3].

Plastic	$\Delta H$ [kJ.kg <sup>-1</sup> ]	Plastic/natural product	$\Delta H$ [kJ.kg <sup>-1</sup> ]
Polyethylene	46500	Polyamide	32000
Polypropylene	46000	Polyester resin	18000
Polyisobutylene	47000	Natural rubber	45000
Polystyrene	42000	Cotton	17000
ABS	36000	Cellulose	17500
Polyvinyl chloride	20000	Celluloid	17500
Polymethyl methacrylate	26000		

### Flame Retardants. [4,5]

Flame retardants are chemical compounds or mixtures of chemical compounds that are added to plastics resins, compounds, alloys, and blends to reduce the combustibility (ease of ignition and rate of burning) of the finished article. They are defined as substances that, when added to another substance, material, or product, will suppress, reduce or delay the propagation of flame to the mass and/or the surface of that substance, material, or product. Flame retardant are added to plastics resins, compounds, alloys, and blends, for two purposes:



(1) To change the combustion characteristics of the plastic material so that it will be more difficult to ignite or

(2) Once ignition has occurred, to cause the fire to die out or cause the material to burn more slowly so that the flame spread, rate of heat release, or both will be substantially lowered.

It would be ideal if the addition of flame retardants to plastics would totally prevent ignition of the article, or, in the alternative, cause the fire to go out once ignition had occurred. This usually does not happen, because of the chemical and physical nature of the flame retardants.

All of the foregoing specifications are severely affected by the addition of the flame retardant chemical. To satisfy all requirements for the finish article, the processor must choose a flame retardant carefully.

Plastics compounders or engineers are therefore constantly seeking the proper loading level of the flame retardants to provide the proper balance to flame retardation and all the other properties required by the end user.

The compounder in the processing plant or the chemical engineer in the polymerization plant (the flame retardant may be added in either place) must constantly search the ideal flame retardant for the particular plastic compound and end application of the finish product.

The ideal flame retardant material will, at a minimum :

- Be efficient at a low loading level in the compound.
- Provide maximum flame retardation safety.
- Be totally compatible with the compound.
- Process easily in all processing equipment normally use for the particular thermoplastic in question.

- Operate at a temperature high enough so it will not degrade during processing but will release its flame retardant efficiency early in a fire.
- Not volatilize out of (or otherwise leave) the compound.
- Not produce hazardous by products either during processing or when functioning as a flame retardant.
- Not detract from the performance of the plastic material.
- Allow the final product to have proper surface characteristics.
- Be easily colorable to the color desired by the end user.
- Be low cost.

## **1. Types of Flame Retardants**

Flame retardant chemicals may be classified into two basic types,

- inorganic flame retardants
- organic flame retardants

### **1.1 Inorganic Flame Retardants**

Inorganic flame retardants are largely used as synergists with halogenated organics or to release water which cools a flame. Two inorganic materials, alumina trihydrate and antimony oxide, constitute over 50% of flame retardant market. High loadings of these materials are used, in part, because they act as filler in addition to their function as flame retardants.

**Alumina Trihydrate** has the highest usage of all flame retardants. This additive is used in products where demands for physical properties of the polymer and flame retardancy are not stringent. Heating of alumina trihydrate above 250°C forms water and alumina. The water approximately 34.5% by weight of additive, absorbs heat, cools the flame, and dilutes flammable gases and oxidant in the flame. Alumina trihydrate may be used as the sole flame retardant, or may be applied in combination with more efficient chemicals.

**Antimony Trioxide** is the most widely used flame retardant in commercial production of plastics. Antimony trioxide is used in conjunction with the halogen flame retardants for its synergistic effect. This chemical forms antimony trichloride and antimony oxychloride. Volatile antimony trichloride (b.p. 280 °C) participates directly in flame quenching by reaction with flame-propagating free radicals. In some polymers antimony trioxide tends to retain heat after flaming has ceased (afterglow). The heated inorganic may then serve as a source for reignition for some components.

**Boron Compounds**, led by zinc borate which does offer improvements in flame retardant over antimony trioxide alone and is cost comparative. This compound acts in both the flame and condensed phases to promote char formation, inhibit the release of combustible gas, and suppress. They generally form boron trihalides, Other boron compounds, used as flame retardants include ammonium fluoroborate, barium metaborate, boric acid, borax, ammonium pentaborate and disodium octaborate.

## 1.2 Organic Flame Retardants

For organic flame retardant, halogens are the most efficient flame retardant, because of the manner in which they interrupt the combustion process. Bromine compounds are the most common class of organic flame retardant material, followed by chlorine compounds. As a flame retardant, bromine is the more efficient of the two. Another class of organic flame retardant chemicals in large volume is the group known as esters of phosphoric acid.

**Chlorinated Flame Retardants** such as chlorinated paraffins, are usually used in combination with a synergist. These are largely straight-chain, saturated,  $C_{10}$  -  $C_{30}$  paraffins with chlorine contents from 20 to 70%. They act as secondary plasticizers, but have limited heat stability ( $<220^{\circ}\text{C}$ ).

**Brominated Flame Retardants** include the variety of aromatic and aliphatic compounds. These flame retardants have high heat stability and tend to be more effective than chlorine compounds on a weight basis such as decabromodiphenyl oxide, pentabromocyclohexane and hexabromocyclodecane.

**Phosphorus-containing Flame Retardants** are largely liquid at room temperature. they include phosphates ( $(\text{RO})_3\text{PO}$ ), phosphites ( $(\text{RO})_3\text{P}$ ), phosphine oxide ( $\text{R}_3\text{PO}$ ), and phosphine ( $\text{R}_3\text{P}$ ).

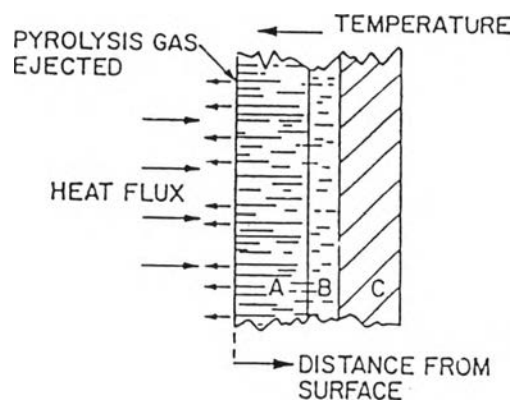
## Mechanism of Flame Retardation

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 flame 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 widely accepted theories and their supporting thermoanalytical data:

The most significant chemical reactions interfering with the combustion process take place in the condensed and vapor phases:

### 1. Condensed Phase Retardation.

The flame retardants that function by this mechanism have 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. Formulation 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 2-7.



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

**Figure 2-7** Effect of char formation on polymer combustion

These are several mechanisms by which flame retardants can operate in the condensed phase:

i) Diversion of pyrolysis towards char formation, instead of volatile, flammable compounds, result in a reduction of flammability. The formation of a thermally stable barrier during combustion at the polymer surface reduces the amount of fuel fed to the flame. However, char formation can only occur if the degradation path of the polymer involves extensive cross-linking and

consequently, polymers which were depolymerised easily do not leave carbonaceous chars.

ii) The retardation of the flow of fuel to the flame may also be accomplished by absorption of part of the heat combustion of the polymer in an endothermic reaction at the pyrolysis temperature. The most important of this process is dehydration although dehydrochlorination reaction, can also be observed in the condensed phase.

iii) Inert materials can show some effect as flame retardants when blended into the polymers. Their mode of action involves conduction of heat away from the hot region more rapidly than that in the untreated polymer. When used in higher concentrations, fillers also act as diluents of the flammable materials.

iv) Flammability may greatly be reduced by inhibition of fragmentation reactions in the condensed phase, following primary breakdown of the polymer.

In wool, certain metal complexes (e.g.,  $ZrF_4$ ,  $SnF_4$ ) are used to inhibit pyrolysis by direct complexing with the proteinaceous substrate or by yielding involatile derivatives of the low molecular weight pyrolysis products.

v) Materials that melt and flow (or drip) easily tend to burn slowly because heat is removed from the advancing flame (although ignition and burning of the drippings can increase the fire hazard). Hence, substances which accelerate physical or chemical changes that cause this flow (particularly in thermoplastic fiber), can be classified as flame retardants.

vi) The final type of solid phase retardation is the formation of a glassy, protective layer on the fiber, and is the basis of sodium tetraborate boric acid flame-retardant treatments.

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

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

## 2. Vapor Phase Retardation.

Whereas condensed-phase reactions leading to a change in primary pyrolysis patterns are mostly heterolytic (ionic) in character, vapor phase inhibition involves homolytic (free radical) processes. Halogenated flame retardant (e.g., chlorinated paraffins, chlorocycloaliphatics, chloro- and bromo-aromatic additives) have been commonly used in flame-retarding plastics. These additives are postulated to function primarily by a gas-phase flame inhibition mechanism, which is characterized by the following criteria:

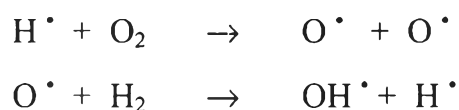
- a) Flame-retardant element is lost from the substrate.
- b) Flame inhibition is insensitive to substrate structure.
- c) Flame retardance is sensitive to oxidant, e.g.,  $O$  or  $N_2O$ .
- d) Flame retardant does not change the composition or amount of volatile.

Halogenated retardants yield HCl or HBr, which break the chain of reactions in the flame by scavenging highly active radicals .

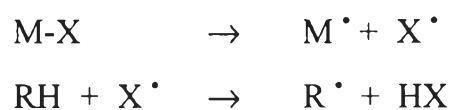


In general, brominated compounds are better than chlorinated compounds, since they breakdown more readily. The compounds used for this purpose must, however, be stable up to the pyrolysis temperature to prevent halogen loss before pyrolysis occurs. Since the preceding section deals with the use of thermal analysis in detecting gas-phase activity, it may be appropriate to mention briefly how the fire retardants function in the gas phase.

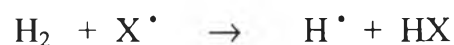
Burning of most polymers can be regarded as, a hydrogen-containing combustion system that is generally described and quantified in terms of the  $H_2$ - $O_2$  reaction scheme contains the following reactions:



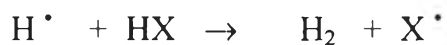
And these dominate the combustion process because of their chain branching nature (the species like;  $H$  and  $H$  originate from polymer pyrolysis). Halogenated flame retardants (MX) are postulated to function primarily by the following mechanisms, which produce HX, the actual flame-inhibiting species,



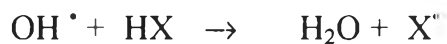
or



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



and



A second gas-phase mechanism involves the catalysis of radical recombination. The introduction of heterogeneous, finely divided metal or metal oxide particles into the flame is a very effective way of inhibiting flame reaction. The free radicals in the flame recombine on the metal oxide surface, giving up a fraction of the collision energy to this third-body intermediate. This type of mechanism is found in the antimony oxide/chlorine retardants where, through the formation of the volatile  $\text{SbCl}_3$  or  $\text{SbOCl}$ , finely divided antimony or antimony oxide is released in the flame.

### Neutron Activation Analysis (NAA)

Basic concepts of Neutron Activation Analysis (NAA) :

Activation analysis is commonly considered a method of analysis for chemical elements in trace quantities. A radioactive nuclide is formed when an element is bombarded by neutrons or charged particles such as electrons and protons etc.

A reaction used extensively in activation analysis is the  $(n,\gamma)$  reaction, which is shown as examples in the following equations:



In a nuclear reactor, stationary conditions are established when the number of neutrons released in a given volume is about equal to the number of neutrons which participate in new fission acts. Neutrons from a nuclear reactor are composed of thermal and fast neutrons. Thermal neutrons are neutrons with an energy of about 0.025 eV.

The interactions between thermal neutrons and most of the nuclides through the  $(n,\gamma)$  reaction produce radioisotopes which can be identified by their characteristic decay rates and energies of the emitted radiations. The amount of radioisotope produced can be calculated from the well-known activation equation:

$$A = A_0 e^{-\lambda t} \quad (2.16)$$

$$A_0 = A e^{\lambda t} \quad (2.17)$$

from  $\lambda = 0.693 / T_{1/2} \quad (2.18)$

$$A_0 = A e^{0.693t/T_{1/2}} \quad (2.19)$$

where:

$$\begin{aligned} A &= \text{Activity at time } = t \\ A_0 &= \text{Activity at time } t = 0 \\ \lambda &= \text{Decay constant of product nuclide} \\ t &= \text{Decay time} \\ T_{1/2} &= \text{Half-life of product nuclide} \end{aligned}$$

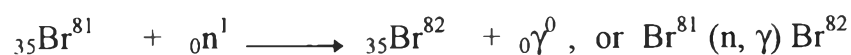
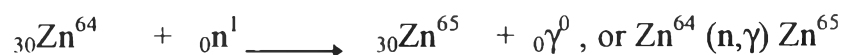
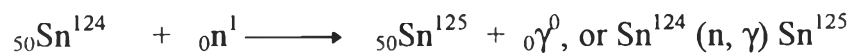
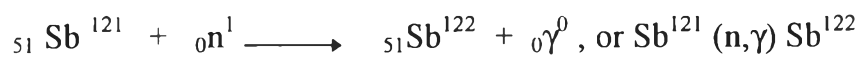
Half-life ( $T_{1/2}$ ) and decay time ( $t$ ) must be the same unit of time. If the half-life of product nuclide is long when compared to decay time the term  $e^{\lambda t}$  in equation (2.17) will approach to 1.

Theoretically it is possible to calculate the amount of element present in a sample by comparing the count rate of a standard with that of the sample, one can determine the amount of each element in the sample by the following equation:

$$\% \text{ EX} = \frac{C_{\text{EX}}}{C_{\text{STD}}} \times \frac{W_{\text{STD}}}{W_{\text{EX}}} \times \% \text{ STD} \quad (2.20)$$

where :	% EX	=	% Element in sample
	%STD	=	% Element in standard
	C <sub>EX</sub>	=	Count rate of sample
	C <sub>STD</sub>	=	Count rate of standard
	W <sub>EX</sub>	=	Weight of sample
	W <sub>STD</sub>	=	Weight of standard

Reaction of element Br, Sb, Sn, Zn when bombarded by neutrons shown in following equation :



Element Characteristic as follow:

**Table 2-4** Characteristic of elemental.

Element	Molecular weight	Half-life	Energy (Kev)
Sb <sup>122</sup>	121.75	2.7 days	564.1
Sn <sup>125</sup>	118.71	9.5 mins.	332
Zn <sup>65</sup>	65.39	243.8 days	1115.5
Br <sup>82</sup>	79.904	1.471 day	776.5

Kev = Kilo electron volt.

### Literature Review

The studies that concerned about flame retardant of polypropylene, which is considerable interested in developing novel flame retardants for this polymer are;

The experiment pertaining to flame retardancy of polypropylene with magnesium hydroxide, to study the relationships between the physical properties and the burning characteristics. It was shown that incorporation of not less than about 57% by weight of magnesium hydroxide made the composite nonflammable, but at the same time considerably reduced its impact, flexural, and tensile yield strengths. [8]

Granzow and Savides [10] investigated the effect of the phosphonium salt Cyagard RF-1 ammonium polyphosphate on the oxygen index of polypropylene and high-impact polystyrene. The oxygen index of these polymer was increased by the individual addition of the phosphonium salt Cyagard RF-1 flame retardant and ammonium polyphosphate.

In 1986, Jha, Bajaj, Misra and maurya studied the flame retardation of polypropylene : Effect of organoantimony compounds on the flammability and thermal behavior. They described that maximum limiting oxygen index of 31.5 against 18.2 for unfilled polypropylene was obtained in a sample containing 10 phr of triphenylstibinedibromide. For thermal analysis, the residue obtained in isothermal treatment at 450°C for 1/2 hour in air was analyzed for antimony and halogen which established the role of these flame retardants in vapor phase.[9]

In the research of Hornsby and Watson [11], polypropylene composition containing a suitably modified form of sea water magnesium hydroxide were shown to yield improved toughness and stiffness together with enhanced flame retardant and smoke suppression properties.

In the studies of Rigolo and Woodhams, a basic form of magnesium carbonate , magnesium carbonate hydroxide pentahydrate  $[(MgCO_3)_4.Mg(OH)_2.5H_2O]$  was evaluated as a flame retardant for polypropylene. Which this filler was most effective as a high load near 60% where it was found to impart a limiting oxygen index of 28.2 with a V-O rating. This was slightly more effective than the flammability ratings for ATH and  $Mg(OH)_2$  under the same conditions.[12]

In 1992, Schleifstein studied the based formulation of flame retardant polypropylene which contained a flame retardant amount of dacabromodiphenyl oxide and a polybrominated cycloalkane having an 8 to 12 carbon atom ring which were synergisted with antimony trioxide.[13]

Vyazovkin, Bogdanova, Klimovsova and Lesnikovich [14] studied the influence of antimony trioxide and hexabrominecyclododecane (HBCD) as fire-retardant additives on polypropylene thermolysis. The addition to polypropylene of individual HBCD and in a mixture with antimony trioxide increased the flame

retardancy and permitted the mechanism of flame retardant action proceeding in the condense phase of polypropylene.

Earlier studies have demonstrated the effectiveness of tin compounds as flame retardant and smoke suppressant additives for preparing thermoplastics and thermosettings such as;

The effect of stannic acid and antimony trioxide as flame retardant on poly(vinyl alcohol) / poly(vinyl chloride) blend, was studied using thermogravimetric and differential analysis. It was found that the O.I. value of PVA/PVC blends with flame retardants increased rapidly with increasing concentration of flame retardants. [16]

Bains, Cusack and Monk investigated the effectiveness of  $\text{ZnSn(OH)}_6$  and  $\text{Sb}_2\text{O}_3$  as flame retardants in brominated polyester resins containing inorganic fillers. The effectiveness of zinc hydroxystannate [ $\text{ZnSn(OH)}_6$ ] and zinc stannate [ $\text{ZnSnO}_3$ ] as flame retardants depended on several factors including incorporation level of the additives and fillers, and bromine content of resin. Furthermore, the  $\text{ZnSn(OH)}_6$  - $\text{Al}_2\text{O}_3$  combination inhibited the evolution of carbon monoxide from burning resins and was an excellent flame-retardant system for this type of polymer.[6]

Hornsby, Mitchell and Cusack (1991) suggested that tin(IV) oxide and zinc hydroxystannate increased flame retardancy and reduced rates of smoke evolution when used with chlorinated paraffin wax. It was apperanted that tin acted mainly in the condense phase by a char formation. However, at high Cl/Sn ratios, volatilisation of tin chloride or oxychlorides might occurred, resulting in a vapor phase flame retardation.[15]

In the studies of Hornsby and Winter indicated that the introduction of small amounts of tin(IV) oxide or zinc hydroxystannate into chlorosulphonated polyethylene results in a large improvement in oxygen index. Formulation

containing tin(IV) oxide and additional highly chlorinated compound (Dechlorane plus) increased in flammability resistance, suggested the formulation of volatile tin halides or oxyhalides, which acted in the vapor phase.[7]

Furthermore the thesis study of Siriphan [18] which investigated the effectiveness of inorganic tin compounds, zinc hydroxystannate, zinc stannate and hydroromarchite  $[\text{Sn}_2\text{O}_3(\text{OH})_2]$  as flame retardants in flexible and rigid polyurethanes found that increasing of metal stannate contents gave reduction in flammability. In addition, the LOI values of zinc hydroxystannate, zinc stannate and hydroromarchite were 23%, 20% and 20% , respectively. However, the mechanism of flame retardant of the tin compounds in polyurethane foams was not clearly understood.

In 1995, the thesis of Surasak [19], suggested that zinc hydroxystannate and zinc stannate could be used as industrial fire retardants in plasticized polyvinyl chloride and offered the advantages over antimony trioxide which they were non-toxic additives and could reduced the toxic benzene that evolved from burning of the polymer.