



The Applications of Flame Retardants; Types and Characteristics for Polymeric and Allied Materials

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Abstract

As a result of little or absolutely lack of control by human efforts and even professional fire quenchers over fire during fires break out at homes, offices, industries, hospitals, automobiles and consequently accounting for loss of thousands lives and millions of valuable properties almost every year across the globe informed the development and utilization of various types of flame retardants in modern foam formulations. Although, the historical development of fire retardants dates back to 450 BC when aluminum was used to reduce the flammability of wood by Egyptians. Several research methodologies have been developed to enhance the flame retardancy potentials of consumer valuable goods by providing additional protection from fires and to increase the human escape time and safety whenever fire breakout occurs. The different categories of fire retardants revealed by research includes: inorganic, organohalogen, organophosphorous and nitrogen-based compounds. Though, relevant reports unveiled plants materials to offers cheaper and easily accessible renewable natural resource for fire retardancy properties with great advantage over synthetic fossil-based chemicals which are not cost effective and equally hazardous to human life and the entire ecosystem. Nontoxic nanofiller is also gaining scientific consideration recently. Hence, the exploration and extraction of the active green plant's materials for flame retardancy properties and other uses have captured significantly scientific interest. Flame retardants are used predominantly in foam factories to reduce or delayed the combustion rate of foam materials at the time of fires outbreak thereby enhancing the escape time of human lives and also valuable properties.

Keywords: Flame Retardants, Foam Formulation, Escape Time, Combustion, Organohalogen

1. Introduction

In Nigeria and the world, there is an increasing awareness of the importance of fire-resistant-rated foams in products manufactured for industrial and other commercial finish-out and furnishing (Suhailuddin *et al.*, 2022). The polyurethanes are one of the important classes of polymeric materials which have various applications such as biomedical, construction, textile and automotive (Moon *et al.*, 2004; Rehab and Salahuddin, 2005). The properties of polyurethanes can be tailored chemically during the synthesis or physically by using certain additives (Gary, 2002). Although polyurethanes exhibit good properties for special purposes (Stefan and Veronica, 2002; Feng and Li, 2006) and their use is limited in some applications due to degradation under certain conditions, easy flammability and lack of thermal stability (Sarkar and Lopina, 2007; Melnig *et al.*, 2005; Yang *et al.*, 2001; Martin *et al.*, 2006).



In some biomedical applications and for environmentally friendly polymers, degradation is generally desired and the rate can be adjusted to meet specific needs as well (Wallstrom *et al.*, 2002; Sain *et al.*, 2004).

The widespread applications of polymeric materials require the use of conventional flame retardants based on organic, inorganic, organohalogens organophosphorous and nitrogen base compounds to satisfy fire safety regulatory standards (Aravind Dasari *et al.*, 2013). However, these compounds, particularly the halogen-based, are persistent organic pollutants of global concern and generate corrosive/toxic combustion products (Lu and Hamerton, 2002).

Safety requirements are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances, while various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment and the combined challenge thus rely in developing effective and environmentally friendly flame retardant systems for polymer materials. Although the incorporation of organic base materials and non-toxic nanofillers in polymers shows positive potential towards flame retardancy (Laoutid *et al.*, 2009). Moreover, most of the literature on these materials is qualitative, and often points to conflicting/misleading suggestions from the perspectives of short-term and long-term fire exposure tests. Hence, there is a renewed need to fundamentally understand the fire response of such materials, and complement experimental results with theoretical modelling and/or numerical simulation (Camino *et al.*, 1991).

Combining the cost effectiveness and versatility of polyurethane foam with the fire-retardant properties required by commercial construction codex makes it an innovative option product material (Yildiz *et al.*, 2009). Beds, cabinets, fixtures, furniture and various types of wall system assemblies typically used in schools, offices, hospitals and other commercial structures where fire safety is a primary concern are good examples and fire-retardant polyurethane foam may be specified for a wide range of applications where a class 1 (first class) fire rating is desired (Feske and Canaday, 2001).

Reports revealed over one million fires disasters occurs annually in Nigeria, leading to ten thousand (10,000) injuries and an estimate of one thousand five hundred (1500) deaths couple with large financial losses occurring in commercial structures such as office buildings, homes, hospitals and also transportation industries encounter fires in automobiles, aeroplanes, buses and trains (Shen *et al.*, 2022; Gann, 1993).

In view of this, there is rapid increasing utilization of flame retardants across foam formulation industries and several methodologies to enhance the flame retardance of consumer goods have been developed to provide additional protection from fires and to increase escape time when a fire break occurs. Presently, several plant materials have also been identified and reported to offer cheaper, easily accessible renewable natural resources to retard fire with great advantages over synthetic fossil-based chemicals which are more expensive and dangerous/toxic to human health and the entire ecosystem. Hence, extraction of the active substances in green plants for flame retardant properties and other uses has been considered economically viable and valuable scientifically (Nayak, *et al.*, 1997; Mohapatra, *et al.*, 1998; Bhuria, *et al.*, 1998; Purjavadi, *et al.*, 1998; Javni, *et al.*, 1999; Adamu, 1999; Ikeh, 2009; Ishidi, 2011; Obidiegwu and Ogbobe, 2011).

The two main methods to achieve flame retardancy in polymers is the additive type and the reactive type approaches. In Additive type flame retardants, which are widely in used, are generally incorporated into polymer by physical means and obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers (Lu and Hamerton, 2002). Nevertheless, challenges such as poor compatibility, leaching, and a reduction in mechanical properties tends to weaken the attraction and the application of reactive flame retardants involves either in the design of new, intrinsically flame retarding polymers or modification of existing polymers through copolymerisation with a flame retarding unit either in the chain or as a pendent group. Presently, new polymer design lacks sufficient versatility in manufacturing, processing and is uneconomical, due to the expense associated with qualifying a new material for use (Lu and Hamerton, 2002).

This makes the modification approach more advantageous, because covalently incorporating the flame-retarding unit in the polymer backbone imparts the flame retardancy permanently and the original physical and mechanical properties are maintained. The majority of the research efforts are concentrated on this approach and results show that the incorporation of even a few weight percent of the unit into the polymer chains can lead to remarkable improvements in the overall flame retardancy of the polymer (Lu and Hamerton, 2002).



Flame retardants are incorporated into foam formulations to reduce flammability of foam products especially at the times of fire accidents (Irvine *et al.*, 2000). A flame retardant may be defined as a substance other than water which when incorporated into a product raise the ignition point or reduces the flammability of fuels material or delays their combustion rate (Torioitzsch, 2003). These include chemicals used in thermoplastics, thermosets, textiles and coatings that inhibit or resist the spread of fire (Green, 1992). Flame retardants have been grouped into inorganic, organohalogens, organophosphorous and nitrogen-based compounds (Shen, 2022; Wolf and Kaul, 1992; Touval, 1993) which will be discuss in this review alongside the mechanism of action/reaction of fire on polymeric and allied materials.

2. Inorganic Compound Used for Fire Retardant.

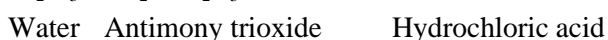
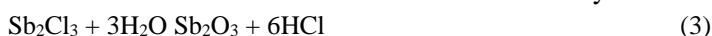
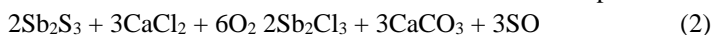
These include compounds of metallic hydroxides such as magnesium hydroxide, aluminum hydroxide; compounds of Antimony such as Antimony trioxide, Antimony pentoxide, Sodium antimonite; Boron containing compounds such as boric acid, borax, zinc borate (Shen *et al.*, 2022). This group of inorganic compound makes up about half (50 %) by volume of the total world-wide flame-retardant production and some of them are used together as synergistic flame retardant of which antimony trioxide appeared the most important (OECD, 1994).

2.1 Antimony trioxide (Sb₂O₃)

Antimony trioxide is an inorganic compound and reported to be the most important commercial compound of antimony and occurs naturally as valentinite and senarmonite. Similar to most polymeric oxides, it dissolves in aqueous solution only with hydrolysis. It is mainly produced through the smelting of stibnite ore which is oxidized to crude Sb₂O₃ using furnaces operating at approximately 850 – 1000 °C (Gann, 1993). The production of antimony trioxide is shown in equation (1.1)



AntimonyTrisulphate(stibnite) Oxygen Crude antimony trioxide Sulphur (iv) Oxide
sublimation technique is usually employed in the purification of the crude Sb₂O₃ which allows it to be separated from the more volatile arsenic trioxide. The compound can also be obtained from antimony trichloride by hydrolysis which can be lined from stibnite after fractional distillation to separate it from arsenic trichloride (Gann, 1993).



It can also be prepared by burning elemental Antimony in air



Antimony trioxide can dissolve in alkaline solution to give antimonate and in acid solution to give a range of polyantimonous acid. It can be readily oxidized to antimony pentoxide and related antimony (v) compounds but it is easily reduced to antimony, sometimes with production of stibnite (Gann, 1993).

2.2 Organic Fire Retardant

Organophosphorus compounds are among the organic fire retardants that is reported to exert the best flame retarding effects composite materials. Reports have shown that, when the mass fraction of flame retardant reached 25.0 wt%, the corresponding limiting oxygen index (LOI) becomes 30.5%. However, organic flame retardants containing multiple flame retardants can also optimize the fire retardancy properties of polymer matrix and improve the synergistic fire retardant potential between multiple elements. Consequently, increases the LOI of polymer materials to a larger extent (Tian *et al.* 2001).

2.2.1 Organohalogen Compounds Used for fire Retardant



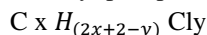
Organohalogen compounds makes up about 25 % by volume of the total production of fire retardants worldwide (OECD, 1994) and these include; organochlorines such as chlorendic acid derivatives and chlorinated paraffins, organobromines such decabromodiphenyl ether (decaBDE), decabromodiphenyl ethane (a replacement of decaBDE), polymeric brominated compounds such as brominated polystyrenes, brominated carbonate oligomers (BCOs), brominated epoxy oligomers (BEOs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and, tetrabromophthalic anhydride. Most halogenated flame retardants effects are enhanced by blending with a synergist to improve efficiency. Antimony trioxide is widely used but other forms of antimony such as the pentoxide and sodium antimonate are also in used (Di-Gani *et al*, 2010).

2.2.2 Organophosphorous Compounds Used for Fire Retardants.

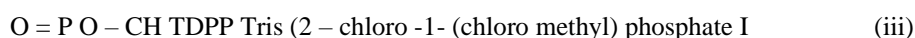
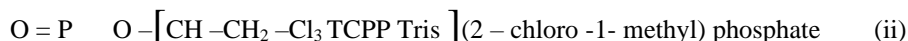
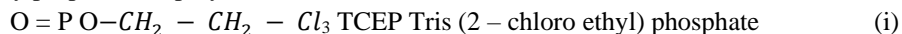
Organophosphorus products are primarily phosphate esters that makes up about 20 % by production volume worldwide and derivatives containing phosphorus, chlorine and/or bromine formed an important part of these class of organic fire retardants. These include Organophosphorus compounds such as organophosphates, tris (2,3-dibromopropyl) phosphate (TDBPP), Triphenylphosphate (TPP), Reseoucinoldiphosphete (RDP), tri-0-cresylphosphate, phosphonates such as Dimethyl-methyl-phosphinates (DMMP) and phosphinates (Gerabner, 1993). There is also an important class of flame retardants that contain both phosphorous and halogen, examples are the chlorophosphates like Tris (1,3-dichloro-2-propyll phosphate) TDCP (Gao *et al.*, 2021; Shi *et al.*, 2021; SpecialChem, 2012). The most widely used flame retardants are chlorinated paraffins, chlorinated phosphate ethers and melamine. In addition, nitrogen-based flame retardants are used for a limited number of polymers or form part of intumescent flame-retardant formulations. Polyurethane and polyamides which are Nitrogen containing products are polymers mostly incorporated with Nitrogen-based flame retardants and also utilized in PVC, polyolefins and in the formulation of 2001 intumescent paint systems (Gerabner, 1993). Inorganic flame retardants are typically applied as additive while organohalogen and organophosphorus can acts as either reactive component or additives. However, the basic action mechanisms of flame retardancy vary, which are dependent upon the specific type of flame retardant and the substrate applied. Additive and reactive flame-retardant chemicals can function in the vapour or condensed phase (barrier theory) (Ravey *et al.*, 1998).

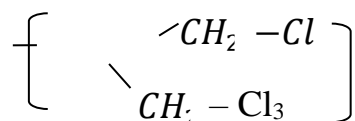
2.3 Chlorinated Flame Retardants

Compounds containing high concentration of chlorine act chemically in gas phase to delay burning rate during combustion and they are mostly used synergistically with antimony trioxide. Some of the major parameters to consider for the choice of a chlorinated compound to select are; the chlorine content, thermal stability, the volatility and physical form. The two main frequently used families of chlorinated compounds are; Chlorinated paraffins and Chlorinated alkyl phosphates. The general structure of a chlorinated resin is given as shown;



The products can variable depending on the length of the paraffinic structural chain. However, product of liquid grades are produced from short chain paraffin while solid grades constantly (70-72 %) of chlorine, are produced from higher molecular paraffin waxes. The main application of chlorinated resins is to act as plasticizer for flexible PVC in combination with Diphenyl Octyl Phthalate (DOP) as an example. This resin is known to improves flame retardant properties in applications like flooring and cables. Solid grades with high chlorine content commonly used in thermoplastics like low density polyethylene (LDPE) in Chain Transfer Index (CTI) cable jacketing in combination with antimony trioxide (Pettigrew, 1993; IPCS, 1996). The structures shown in equation i - iii below are the most common examples of chlorinated alkyl phosphate compound that are incorporated to enhance fire retardancy properties of polymeric and allied materials:





The products above are mainly applied on rigid and flexible polyurethane foam and generally introduced at concentration between 5 and 15% depending on foam density and test severity (Chen *et al.*, 2024; SpecialChem, 2012). One good example of a general purpose chlorinated phosphorous fire retardant is dodecachlorodimethanodibenzocyclo-octane (chlorinated cycloaliphatic compound) is more commercially accessible and used in numerous polymers including polyamide, and polyolefins. They can also be blend with antimony trioxide and zinc borate as synergies to enhance performance and efficiency. Some advantage of this class of fire retardants include: Good temperature resistance up to 320 °C, High resistance to UV aging, non-plasticizing product, insoluble filler and non-blooming (mould growth), Chain Transfer Index (CTI) values greater than 400 °C in FR nylon, low smoke generation, and low density and cost effective (Stapleton *et al.*, 2011; SpecialChem, 2012).

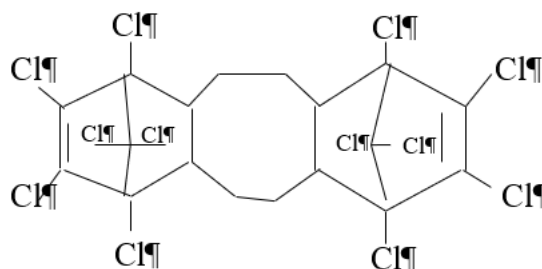


Figure. 1: Dodecachlorodimethanodibenzocyclo-octane

2.3.1 Dichloromethane (MC)

Dichloromethane or Methylene dichloride (MC) is a volatile, non-flammable, colourless liquid with a sweetish chloroform-like odour. It is slightly soluble and miscible with alcohol, ether and dimethylformamide (Pettigrew, 1993). It is an organic compound with formula CH_2Cl_2 and can be produced by treating either methyl chloride or methane with chlorine gas at temperatures between 400-500 °C which react to give series of chlorinated products as shown below;



2.4 Nano Fillers-Containing Fire-Retardant Composites

The fire retardant properties of nano-composites polymer materials obtained by formulating with nano-fillers have been reported to account for the flame-retardant mechanisms of various nano-fillers. The fire response of these materials shows that, the thermal and volatile barriers formed by the nano-clay particles is transported to the surface of the polymer, which improved the fire retardant properties of the nano-clay/polymer composites. Some fibrous nanomaterials, such as carbon nanotubes, multi-walled nanotubes and siloxanes, can greatly improve the fire retardant of the polymer composites by enhancing the formation of carbon char. Nano-clay, carbon nanotubes and siloxane show capacity to promote the fire retardancy of the polymer composites, but the effect is not evident, while nano-metal oxides and hydroxides are apparently effective (Laoutid *et al.*, 2009).

2.5 Polymer-Based Flame-Retardants in Construction and Engineering Applications

Table 1: Brief overview of the fire retardant and fire-resistant characteristics

	(FR)Fire Retardant	(FRT) Fire Resistant
WHY	To save lives	
HOW	Delaying the fire growth	Limiting the physical progression of fire from one area to another.



MEANS	Decreasing the fire kinetics	Using fire proof barriers to compartmentalize the fire areas
WHEN	At the early stage of fire delaying the flash over phenomenon	During fire from the early to the post flashover periods.
What is assessed	The reaction to fire term of contribution to fire: - nil - low - medium - high	The resistance to fire in term of maintaining certain functionalities - smoke and heat insulation - integrity - load bearing
Test scenario	To submit a sample to a heat flex To ignite the gaseous decomposition To follow the fire development Heat release	To submit the sample to an inerrancy heat flex To follow the functionality evolution during the explosive time Time failure of functionality analysis.
Key parameters	Dripping Flame spread Smoke opacity Smoke toxicity	Smoke insulation Heat insulation Integrity Load bearing

Source: SpecialChem, 2012.

3. Historical Development of Flame Retardants

Fire protection and Preventive measures including the use of fire retardants has been practiced since time memorial. Some examples of early historical developments in fire retardants are shown on Table 2

Table 2: Historical Developments Fire-Retardant

S/N	Name of Fire Retardant	Uses	Date
1.	Aluminum	To reduce the flammability of wood by the Egyptians	about 450 BC
2.	Mixture of Alum and Vinegar	To reduce flammability on wood by the Romans.	about 200 BC
3.	Mixture of clay and gypsum	To reduce flammability of theater curtains	1638
4.	Mixture of alum, ferrous sulfate and borax	Used on wood and textiles in Britain	1735
5.	Alum	Used to reduce flammability of balloons	1783
6.	Gay-lussac's mixture of $(\text{NH}_4)_3 \text{PO}_4$, NH_4Cl and Borax X	Effective on linen and hemp.	1821
7.	Perkin's mixture of sodium stannate and ammonium sulfate	Flame retardant treatment for cotton	1912

Source: Hindersinn 1990

The designed and development of synthetic polymers over a century ago was of special significance to human existence and since the water-soluble inorganic salts used earlier were of little or no utility in these largely hydrophobic materials. Hence, Modern modification concentrated on the design and development of polymer-compatible flame retardants (Ravey *et al.*, 1998). Report revealed that, at the break of Second World War (World War II), flame-proof constellate for outdoor use by the military was produced incorporated with a chlorinated paraffins and an insoluble metal oxide, mostly Antimony oxide as a glow inhibitor together with a binder resin. After the war, non-cellulosic thermoplastic polymers became more and more important as the basic fibers used for flame retardant applications. A dramatic example of the superiority of the non-cellulosic compounds is provided by the diminished use of cotton fiber in children's sleep wear since the inception of new standards (Arias, 1992).

The U. S. Patent No. 5,250,581 describes a polymer polyol formed from tribromostyrene and acrylonitrile to have improved flame resistance compared to polyurethane foams from conventional styrene-acrylonitrile-polymer polyols. However, the polymer product of this polyol contained large amount of tribromostyrene which emit toxic



fumes when burnt, coupled with its high cost, hence large quantities of tribromostyrene are highly undesirable in polyurethane foam products. More so, these foams materials already contained a second fire retardant which may contribute to fogging and difficulties in forming uniform foam matrix (Alexandre and Lopez-Cuesta, 2009).

Consequently, the used of a low molecular weight liquid fire retardant tends to volatilize with time causing the undesirable fogging of the windows in an automobile while solid fire retardants (e.g., melamine) tend to increase the viscosity of the polyol-filler dispersion which giving rise to non-uniform mixing leading to non-uniform cell opening resulting in a significant density gradient in the foam from top to bottom. The fundamental property of a material is the amount of heat it generates when burned. Wood, paper and cotton generate 14-18 KJ/Kg of heat while polyurethane and other organic materials generate 37-47 KJ/Kg of heat. A kilogram (Kg) of polyurethane gives off three times the heat of one Kg of paper or wood (Camino *et al.*, 1993).

Another property that greatly affects fire retardant performance is the burning rate which is a function of the physical state of a product which tells whether the product is expanded, as in a foam, or not. This is because, the lower the density of a product the faster it burns and hence, the low rate of burning of the chlorinated castor oil is due to its high density which depends also on its concentration as observed from the table of comparison of methylenedichloride (MC) versus chlorinated castor oil (CCO) versus Sb_2O_3 concentrations on burning rates. A product that melts generally produces a much more intense fire than one that chars. Flexible foam typically melts while rigid foam chars. The heat content and the burning rate in is a product of the heat release rate of the foam product. This property defines the challenge that the sprinkler system is going to have to control the fire, cool down the building and keep it from collapsing (Hankins, 1997).

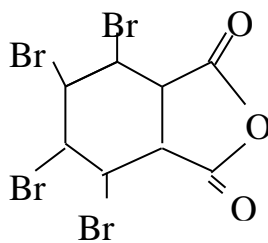
Fire retardants and flame barriers have a significant impact on the ignition characteristics of the foam and however, once the material starts burning, the fire retardants have a much more limited effect on the flame control. Fire retardants do not have any effect on the heat content of the foam which is still about 42KJ/Kg for polyurethane but the increasing use of thermoplastic and thermosets on a large scale for applications in building, transportation, electrical engineering and electronics informed the designed, formulations and development of new compatible flame-retardant systems. These fire retardants substance mainly consist of inorganic and organic compounds based on bromine, chlorine, phosphorous, nitrogen, boron, and metallic oxides, nonofillers and hydroxides. presently, these fire-retardant systems fulfill the multiple flammability requirements developed for the above-mentioned applications (Weil, 1993; Makinde, 1998).

Table 3: Some Commercial Flame Retardants

Chemical Name	Chemical Structure	CAS Registration No	Substrate Uses
Inorganic flame retardants			
Potassium fluorootitanate	K_2TiF_6	16919-27-0	Wool
Aluminum hydroxide	$Al(OH)_3$	21645-51-2	Elastomers PVC polyolefins, thermosets
Antimony trioxide	Sb_2O_3	1309-64-4	Additive type flame retardant
Zinc oxide	ZnO	1314-13-2	Additive type fire retardant synergist.
Zinc borate	$3ZnO.2B_2O_3$	1303-96-4	Synergist, polyurethane and smoke suppressant
Ammonium orthophosphate	$(NH_4)_3PO_4$	10124-31-9 32588-76-4	Cellulosic and textiles High impact polystyrene; polyethylene; polypropylene; polycinide; EPDM; rubbers; polycarbonate; ethylenecopolymers; ionomer resins; textiles M.
N,N'-Ethylene-bis (tetrabromophthalimide)Tris(2-butoxyethyl) Phosphate		78-51-3	Additive flame retardant and plasticizer in plastics and synthetic rubbers
Nitrogen-based flame retardants: Melamine			Polyurethane foams, polypropylene
Melamine phosphate			

Source: SpecialChem, 2012





3.1 Methodology for the Determination of Flame Retardancy of a Material

3.1.1. Determination of the Limiting Oxygen Index (LOI)

The LOI value which can be defined as the minimum oxygen concentration in the flowing oxygen/nitrogen mixture that can keep the flame burning for a duration of 3 min or consume or completely burnt 5 cm of a sample material. In accordance to the ISO 4589 standard, a sample of the dimension 80 mm × 10 mm × 4 mm is usually placed vertically in the center of a glass chimney, and the top of the sample is lit up with a burner. LOI testing is considered one of the most important screening and quality control methods in the development of flame-retardant polymers because of the inexpensive process and the relatively small sample size required. However, this test method is not suitable for assessing the true extent of the fire resistance of materials due to the low heat input and high simulated oxygen concentration (Wang *et al.*, 2017).

3.1.2 Flammability Determination of Plastic Materials

The UL-94 test set has been used by Underwriters Laboratories to determine the flammability of plastics used as equipment and appliance components. The UL-94 vertical test is the most common method used to determine the flammability of plastic materials and their capacity to spread flames. The control burner produces a blue flame, the height of which is 20 mm, at a power of 50 W. The distance between the top of the burner and the bottom of the sample should be kept at 10 mm and the bottom of the sample is exposed to the flame for 10 s, then removed. The time required for the flame to extinguish is denoted as residual flame time, T1. After flameout, the bottom of the sample is exposed to the flame for another 10 s. The time required for the flame to extinguish is denoted as residual flame time, T2, and the time required for the flame's glow to disappear is denoted as residual glow time, T3. According to IEC 60695-11-10, five (5) parallel samples must be tested in each run (Wang *et al.*, 2017).

3.1.3 Cone Calorimetry Measurement

This measurement is an effective small-scale test used to determine the combustion behavior of polymer materials and conform to international standards (ISO 5660). It's carried out by exposing the sample material to a conical radiant electric heater and ignited by an electric spark and then calculate the heat release rate (HRR) by measuring the gas flow rate and oxygen concentration. The peak heat release rate (PHRR) is considered one of the most important parameters when evaluating the fire resistance of materials. The total heat release (THR) value is obtained from the integral of HRR over the time curve. In addition, conical calorimetry can characterize time to ignition (TTI), flameout time (TOF), effective heat of combustion (EHC), mass loss during combustion, production of CO and CO₂, and total smoke release (TSR). There is no doubt that cone calorimetry provides more detailed fire characteristics and is a powerful tool for simulating material flammability under real-world fire conditions (Wang *et al.*, 2017).

4. Action of Flame Retardants

A flame retardant should inhibit or even suppress the combustion process, mechanism of fire retardancy depends on the nature of the fire retardant and they can act chemically or physically in the solid, liquid or gas phase. Fire retardant can be reactive additive or a combination (which provides an additive, synergistic or antagonistic effect on the polymer). They tend interfere with combustion process at a particular stage of this process, for instance, during heating, decomposition, or flame Spread and delay the overall combustion process (Baby *et al.*, 2020).



Flame-retardant systems for synthetic or organic polymers act in five basic ways or through a combination of these mechanisms: (1) Gas dilution; (2) Thermal Quenching; (3) Protective Coating; (4) Physical Dilution (5) Chemical Interaction (Pettigrew, 1993; Camino *et al.*, 2001)

1. The dilution of inert gas can be achieved by the used of additives that produce large volumes of non-combustible gases on decomposition. These gases dilute the fuel concentration below the flammability limit. Similarly, compounds such as metal hydroxides, metal salts and some nitrogen compounds can function in this manner as well.
2. Thermal quenching is the result of endothermic decomposition of the flame retardant for example metal hydroxides; metal salts and nitrogen compounds act to decrease surface temperature and the rate of burning.
3. Some flame retardants react by forming a firm protective liquid or char barrier which limits the amount of polymer material available to the flame front. It can also act as an insulating cover/layer to reduce the amount of heat transfer from the flame to the polymer surface. Phosphorous compounds and intumescent systems biased on melamine and other nitrogen compounds are examples of this category.
4. Inert fillers (glass fibers and micropores) and minerals such as (talc) act as thermal sinks to increase the heat capacity of the polymer or reduce its fuel content.
5. Active flame retardants such as halogens and some phosphorus compounds act by chemical interaction. The flame retardant dissociates into radical species that compete with chain-propagating steps in the combustion process (Gerard *et al.*, 2012)

4.1 Mechanism of Action of Flame Retardant

Fire is mainly a product of three basic ingredients; which are heat, fuel and oxygen and hence heat from the pyrolysis of polymer generates flammable gases which in adequate ratio with oxygen lead to ignition of the polymer material. The combustion leads to production of heat that is spread out (ΔH_1) and fed back (ΔH_2). Consequently, the feedback of heat pyrolyzes the polymer structure and sustain the combustion process. One or several ingredients have to be removed to reduce the formation of this combustion circle (Joseph *et al.*, 2015; Baby *et al.*, 2020). Though, several techniques are also available in order to break down this combustion circle as illustrated below;

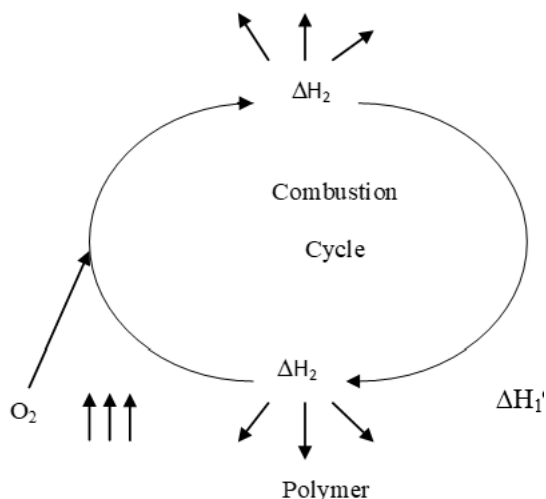


Figure 2: Combustion Cycle

Flame retardants have to inhibit or even suppress the combustion process (cycle). Flame retardants interfere greatly into one or several stages of the combustion cycle processes depending on the polymer structure and its fire safety test (heating, decomposition, ignition, flame spread, smoke process). Flame retardants can act chemically and/or physically in the condensed and/or in the gas phase. However, both of them occur during a complex process with many simultaneous reactions (Joseph *et al.*, 2015; Baby *et al.*, 2020; SpecialChem, 2012).



4.1.1 Chemical Effect of Condensed Phase

The most significant reactions interfering with the combustion process take place in the solid and gas phases

Reaction in the solid phase: The flame retardant can cause a layer of carbon on the polymer surface. This can occur for example, through the dehydrating action of the flame retardant generating double bond in the polymer. These form the carbonaceous layer by cyclizing and cross-linking.

In the condensed phase, two types of reactions can take place.

Flame retardants can accelerate the breakdown of the polymeric material and leads to pronounced flow of the polymer which decreases the impact of the flame which breaks away.

- Flame retardants can influence the formation of a carbonaceous layer (charring) on the polymer surface which occurs, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer structure. These processes form a carbonaceous layer via cyclizing and cross-linking processes cycle (Special Chem, 2012).

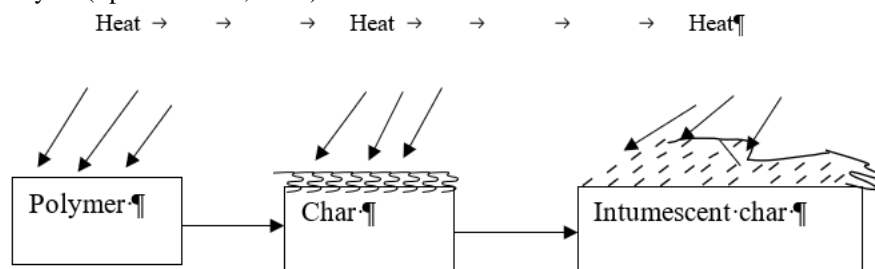


Figure 3: Char and intumescence formation

4.1.2: Intumescence Formation

The process of flame retarding polymers degradation by intumescences is essentially a special case of a condensed phase mechanism. The activity in this case occurs in the condensed phase and radical trap mechanism in the gaseous phase appears not to be involved. However, in intumescences formation, the amount of fuel produced is also greatly diminished and char rather than combustible gas is formed. The intumescent char has a special active role in the process by constituting a two-way barrier, both for the hindering the passage of the combustible gases and molten polymer to the flame as well as shielding of the polymer from the heat of the flame. In spite of the considerable number of intumescent systems developed in the last 15 years, they all seem to be based on the application of three basic ingredients; a “Catalyst” (acid source), a charring agent and a blooming agent (Spumific) (SpecialChem, 2012).

Additives combining the last three ingredients leading to the intumescent effect are commercially available. However, intumescent formulations can simply be developed and are more suitable than some commercial grades for some specific applications (Table 4).

Table 4: Summary of Used Catalyst, Charring and Blooming Agent

Catalyst Acid source	Charring agents Polyhydric Compounds	Blooming agents (Spumific compounds) Amines/amides
Ammonium salts, Phosphates, polyphosphates, Sulfates, Halides	Starch Dextrin Sorbitol pentaerythritol, monomer, trimer Phenol-formaldehyde resin Methylol melamine	Urea Urea-formaldehyde resins Dicyandiamide Melamine Polyamides
Phosphate of amine or amide Products of reaction of urea or guanidyl urea with phosphoric acids Melamine phosphate Product of reaction of ammonia with P ₂ O ₅		
Organophosphorus compounds		

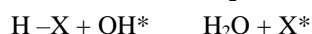
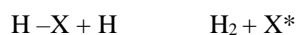


Tricresyl phosphate Akyl
phosphate Haloalkyl phosphates

Source: SpecialChem, 2012

4.1.3 Chemical Effect of Gas Phase

The flame retardant or their degradation products stop the radical mechanism of the combustion process that takes place in the gas phase. The exothermic processes, which occur in the flame, are thus stopped, the system cools down, and the supply of the flammable gases is reduced and eventually completely suppressed but high reactive radicals such as HO* and H* can react in the gas phase with other radicals, such as halogenated radicals X* resulted from flame retardant degradation and generates less reactive radicals which decrease the kinetics of the combustion Process (Fig.9) (Grover *et al.*, 2014; SpecialChem, 2012)



Flame inhibition studies have shown that the effectiveness decreases as follow:

HI > HBr > HCl > HF (SpecialChem, 2012)

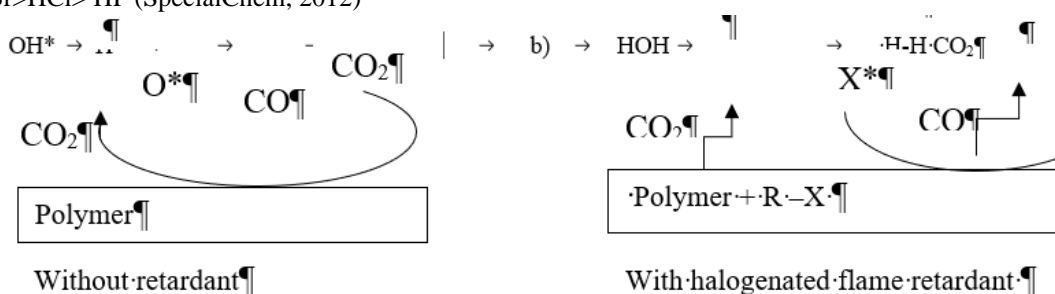


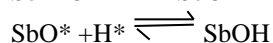
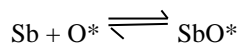
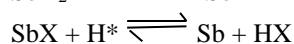
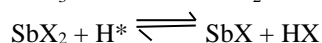
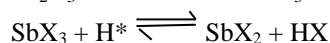
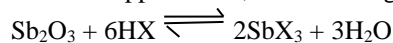
Figure 4: Mechanism of action of halogenated flame retardants

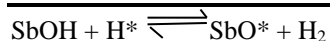
Brominated compounds and chlorinated organic compounds are generally used because iodides are thermally unstable at processing temperatures and effectiveness of fluorides in the material are among the criteria that have to be considered. More so, those additives that produce halides to the flame at the same range of temperature of polymer degradation into combustible volatile product are strongly recommended. As such fuel and inhibitor would both reach the gas phase in accordance to the principle of “right place at the right time”. The most effective fire retardant (FR) polymeric materials are halogen-based polymer (PVC, CPVC, FEP, PCDF...) and additives (CP, TBBA, DECA, BCOs...) however the improvement of fire-performance depends on the type of fire tests i.e., the application which perfectly illustrates the described chemical modes of action. Thus, some fluster of the kinetic mechanism of the combustion cycle led to incomplete combustion (SpecialChem, 2012; Di-Gani *et al.*, 2010).

4.2 Synergism with Antimony Trioxide (Sb₂O₃)

For effectiveness and efficiency, the trapping of free radicals needs to reach the flame in gas phase. Addition of antimony trioxide allows formation of volatile antimony species (antimony halides or antimonyoxyhalide) capable of interrupting the combustion process by inhibiting H* radicals via a series of reactions proposed below. These phenomenons explain the synergistic effect-between halogenated compounds and Sb₂O₃.

For most applications, these two ingredients are present in the formulations (SpecialChem, 2012)





Where X = F, Cl, Br

4.3 Physical Effect

Several ways in which the combustion process can be retarded by physical action include;

1. By cooling during which endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.
2. By formation of a protective layer (Coating): The condensed combustible layer can be shielded from gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process, is excluded and heat transfer is impeded.
3. By dilution; the incorporation of inert substances (example fillers) and additives that produce inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas is not exceeded (Bertelli, 1988).

Formation of a protective layer is achieved when the additives can form a shield with low thermal conductivity from the heat source to the material. It then reduces the degradation rate of the polymer and decreases the “flow” (pyrolysis gases from the degradation of the material) that feeds the flame however, Phosphorous additives may act in this same way too. The pyrolysis of phosphorous leads to thermally stable pyro- or polyphosphoric compounds which form a protective vitreous barrier. The same mechanism can be observed using boric based additives, zinc borates or low melting glasses (Ikeh, 2009).

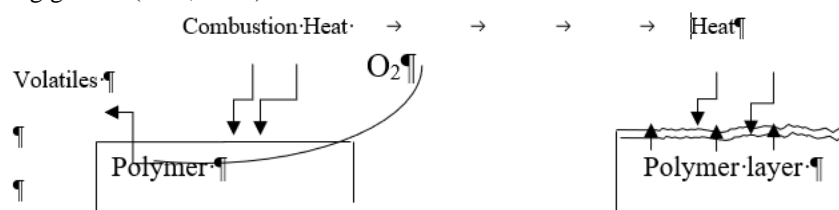


Figure. 5: formation of protective layer inhibiting, combustion and volatiles

4.3.1 The Cooling Effect of the Polymer Material

The combustion energy balance can be influenced by the degradation reactions of the additive and the additives can degrade endothermally which cools down the substrate to a temperature which is below the required for sustaining the combustion process. Metal hydroxides also exhibit this principle and its efficiency depends on the amount incorporated in the polymer material (Special chem, 2012; Grover *et al.*, 2014; Hafezeh, and Yuan, 2022).

4.3.2 Dilution

The incorporation of inert substances (e.g. fillers such as talc or chalk) and additives (which evolves inert gases on decomposition) dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not reached. In recent work, the isolating effect of a high amount of ash (resulting from certain silica-based fillers) has been shown in fire-retarded systems. Moreover, it highlights also an opposite effect as thermal degradation of the polymer in the bulk is increased by heat conductivity of the filled material (Bourbigot, and Duquesne., 2007; Specialchem, 2012).

5. Combustion of Polyurethane Foams

The mechanism of fire retardancy can be basically split into three (3) phases; initiation, propagation and after-glow. Polyurethane foam like any other material burns in a fully developed fire. The combustion of polyurethane foam is basically initiated by endothermic heating followed by the decomposition of the foam. Flammable foam mixes with atmospheric oxygen and ignites leading to the exothermic process of flame propagation and heat release. During heating and pyrolysis, endothermic processes take place for overcoming the high bond binding energies between



individual atoms. Ignition initiates the exothermic part of the process which overrides the endothermic pyrolytic reaction. Pyrolysis is reinforced by thermal feedback (heat release) which fuels the flame and increasing the level of the flame spread over the decomposed polymer surface. Diffusion flame is supported by extremely high energy H^* and OH^* radicals transfer confer a high velocity on the flame front. The schematic of the combustion process of polyurethane foam is shown in Fig.2.8 below along with combustion process for the main reaction (Grover *et al.*, 2014; Lefebvrte, *et al.*, 2004).

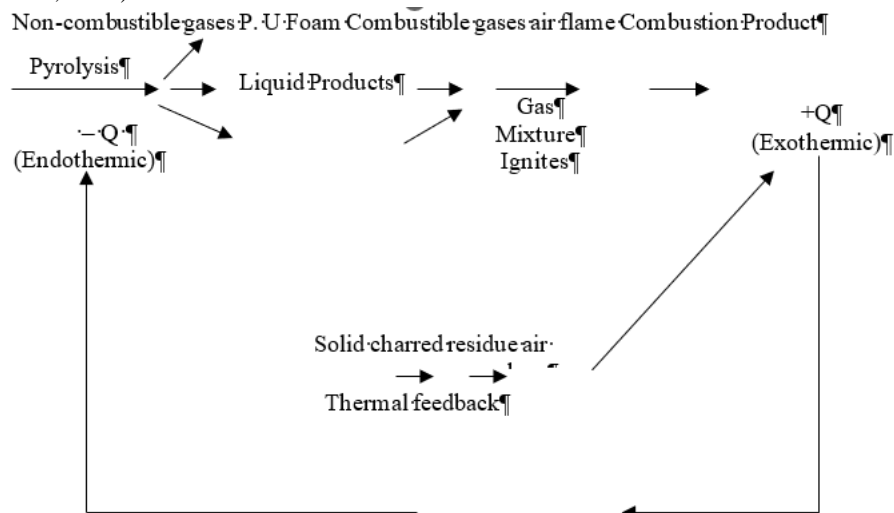


Figure 6: Combustion Process of Polyurethane (PU) Foam

Combustion process for the main reaction is given as follows:



5.1 Fire Dynamics

The goals for fire retardant are universal and can simply be stated in the following manner:

1. Prevent the fire or retard its growth and spread i.e the flash over time by controlling fire properties of combustible items, and providing for suppression of the fire

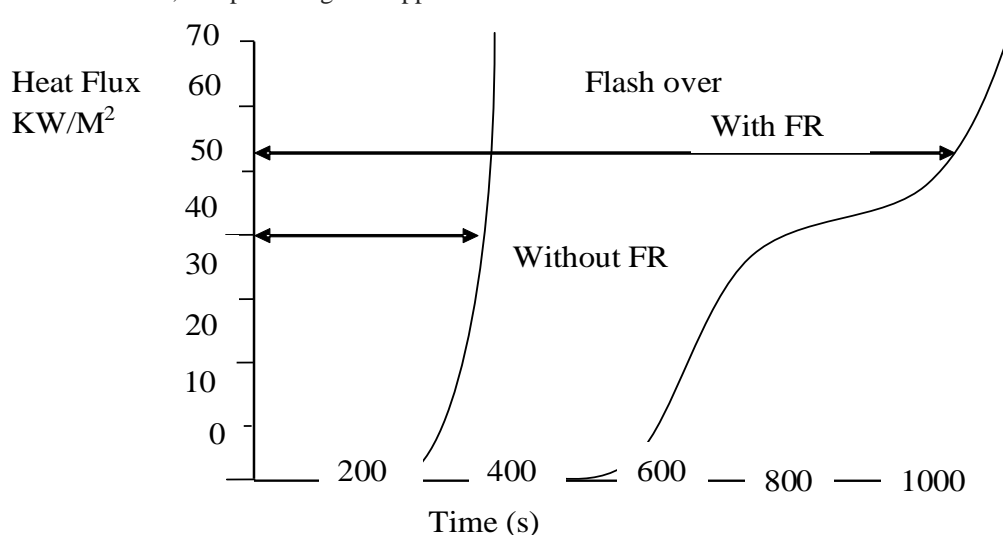


Figure 7: Flash overtime Vs Fire retardant use

Under the conditions of fire, the use of the flame retardant gives a significant increase in the escape time available.



2. Protect occupants from the fire effects by; providing timely notification of the emergency, protecting escapes routes and providing areas of refuge where necessary and possible.

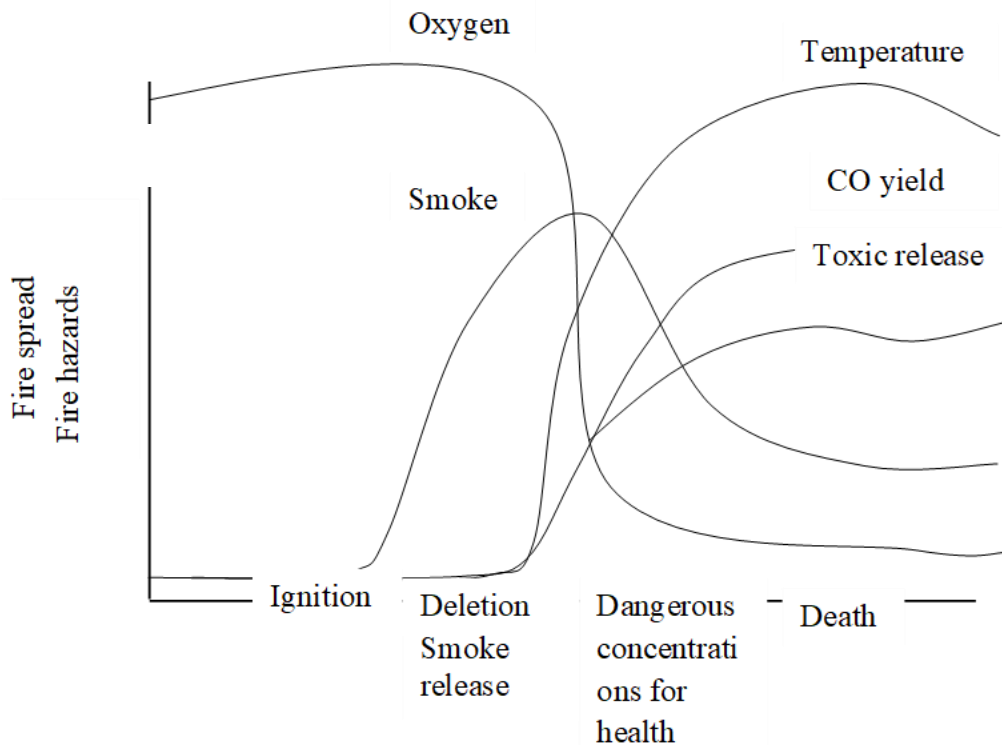


Figure 8: Smoke release Vs Fire spread

The use of fire retardant reduces the flame spread and so the rate at which the smoke develops. Less smoke production gives an increase in the escape time available.

3. Minimize the impact of fire by; providing separation by tenant, occupancy, or maximum area, maintaining the structural integrity of property, providing for continued operation of shared properties

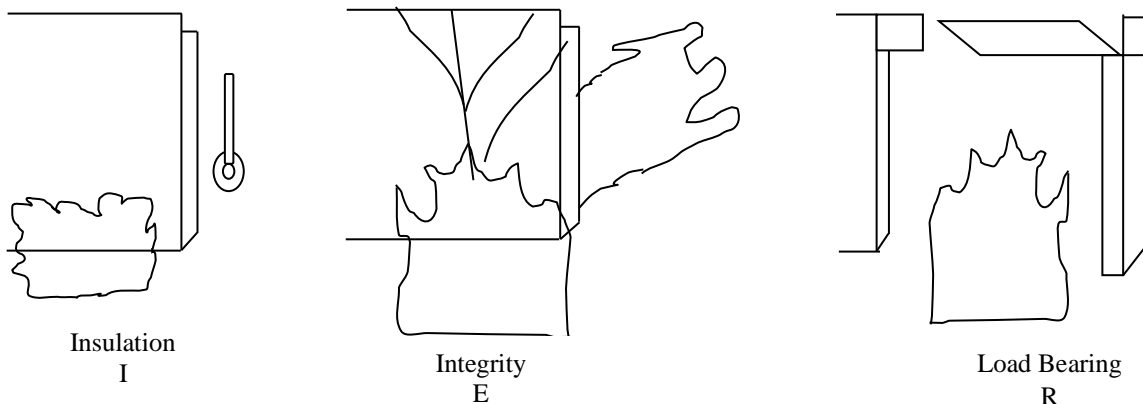


Figure 9: Example of functionalities that have to be maintained during fire spread

The use of fire retardant reduces the flame spread and so the rate at which the smoke develops. Less smoke production gives an increase in the escape time available. Support fire service operations by; providing for identification of fire location, providing reliable communication with areas of refuge, and providing for fire department access, control, communication, and selection (Tullo, 2003).

To prevent the fire or retard its growth and spread, material and product performance testing is used to set limits on the properties of items which represent the major fuels in the system. The majority of fire safety requirements

consist of material fire performance test criteria to retard its growth and spread. Based on test methods that evaluate fire properties of individual materials, the test methods are generally based on the measurement of the flame-spread speed (Special Chem, 2012; Tullo, 2003; Irvine *et al.*, 2000).

6. Conclusion

There are different classes and types of flame retardants developed to prevent or retard the growth and spread of fire during its occurrence or disastrous outbreak on valuable materials and products. The density gradient and physical state have significant effect on burning rates of materials, though the fundamental properties of material are the amount of heat generated when burnt. Wood, paper and cotton generate 14-18 KJ/Kg of heat but polyurethane foams and other organic materials generate 37-47 KJ/Kg of heat. A Kg of polyurethane, can give off three times the heat of one kg of wood or paper. Fire safety requirements consist of material fire performance test criteria to retard its growth and spread. This is basically measure of the flame spread speed. The actions of flame retardants on polymeric and allied materials have immensely improved their properties to delayed combustion and increases versatility in terms of applications.

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