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Oxygenated Hydrocarbon Compounds as Flame Retardants for Polyester Fabric

by

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Synopsis

Synthetic polymers tend to be more flammable than conventional materials such as wood. To reduce the hazards of fire, flame retardants may be added. Typical systems are based on compounds based on halogens (Cl, Br), transition metals (Zn, Sb) or phosphorous and boron. Modifications involving both the physical and the chemical characteristics of char in intumescent flame retardants, might be related to chemical reactions between fillers and phosphorous compounds of the flame retardant. Fillers that modify the structure of the char tend to decrease the efficiency of the flame retardant system. It is shown that a recently developed non-halogen flame retardant system can provide flame retardancy to polyolefins at surprisingly low levels. The purpose of flame retardant treatments is to reduce the rates of burning and flame spread. With flame retarded fabrics it is usually required that they must pass some type of standard vertical flame test (e.g. UL 94V, NFPA 701, BS5867, DIN 4102, X65020-1991, etc.). Recently it was discovered that unsized polyester fabric can be flame retarded with certain organic compounds that are based on carbon, hydrogen and oxygen only. These flame retardants operate by altering characteristics such as the polymer melt viscosity and the melt surface tension.

Keywords

Flame retardants, phosphorous, halogen, inorganic, hydrocarbon, intumescent.

Sinopsis

Sintetiese polimere is meer geneig om te brand as konvensionele materiale soos byvoorbeeld hout. Om vuurbestandheid te verbeter kan vlamvertragers bygevoeg word. Hierdie vlamvertragers is gebaseer is op halogene (Cl, Br), transisiemetale (Zn, Sb) of fosfor en boor verbindings. Veranderinge in beide die chemiese en fisiese karakteristieke van die beskermingslaag by opskuimingsvlamvertragers kan die gevolg wees van chemiese reaksies tussen die vuller en die fosfor verbindings van die vlamvertrager sisteem. Vullers wat die struktuur van die beskermingslaag verander, is geneig om die effektiwiteit van die vlamvertrager sisteem te benadeel. Dit word aangetoon dat 'n onlangs ontdekte nie-halogeen vlamvertrager sisteem 'n poli-olefien kan vlamvertraag deur baie klein hoeveelhede by te voeg. Die doel van flamvertraging is om die tempo van brand en vlamverspreiding te velaag. Dit word gewoonlik van vlamvertraagde materiale verlang om aan 'n sekere vertikale brandtoets te voldoen (b.v. UL 94V, NFPA 701, BS5867, DIN 4102, X65020-1991, ens.). Daar is egter onlangs uitgevind dat ongestyfde polyester materiaal vlamvertraag kan word met sekere organiese koolwaterstowwe wat slegs suurstof, waterstof en koolstof bevat. Hierdie vlamvertragers verander die eienskappe van die materiaal soos byvoorbeeld die gesmelte polimeer viskositeit en die oppervlakspanning van die gesmelte materiaal,

Sleutelwoorde

Vlamvertragers, fosfor, halogeen, anorganies, koolwaterstof, opskuiming.

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1. Introduction

Back in the nineteenth century the need for flame retarded plastics became important owing to the commercialisation of the highly flammable cellulose nitrate plastics (Green, 1997). The traditional volume plastics such as phenolics, melamine resins and rigid PVC possess adequate intrinsic fire resistance. The more recent volume polymers, e.g. the polyolefins, styrenics and polyesters, are significantly more flammable than wood. This also led to the development of new flame retardants for these products.

Flame retardants generally function by interfering with the polymer thermal decomposition pathways. Their use is therefore very specific to the particular substrate for which they are designed. For example, phosphates are only used in PVC, polyurethanes (PUR) and unsaturated polyesters (UPE). Flame retardant efficiency also relies on synergy between formulation components. Its favourable interaction with halogens has made antimony one of the most popular and frequently used compounds over the years (Gann, 1993).

1.1 Historical review

Each year 29 000 injuries and 4500 deaths are caused by fires in the United States alone, and the annual cost to the global society has been estimated at over $100 billion (Gann, 1993). Something has to be done to reduce the loss of life and damage caused by fire.

By 1970, the major groups of flame retarded polymers used were the unsaturated polyesters, PVC and cellulose films for the photographic industry. By the early 1970's, the consumption of flame retardant chemicals already approached 30 kT per year and was still growing fast (Green, 1997). The main flame retardant used at that time was alumina trihydrate (ATH) with unsaturated polyesters consuming the largest quantity (Green, 1997). Other early flame retardants were mainly based on halogen and antimony compounds (Green, 1997; Gann, 1993).

1.2 Halogenated flame retardants

In 1972, the consumption of halogen based flame retarding compounds was much less than other compounds. The next five years saw the development of a number of new chlorinated and brominated flame retardant compounds. Table 1 shows the consumption of flame retardants in the United States for the plastics industry in 1972 (Green, 1997).

Table 1: Consumption of flame retardants for plastics in 1972 for the United States (Green, 1997).

Additive type	**Quantity (kT/y)**
ATH	17.7
Antimony	6.35
Halogen	2.7

The aromatic bromine additives used at that time were hexa-, octa- and decabromodiphenyl compounds. However, the chlorinated polyphenyls and brominated biphenyls were quickly withdrawn after Monsanto discovered that they could induce cancer. While brominated diphenyl compounds have a low acute toxicity, they are fat-soluble and therefore tend to accumulate in fatty tissue and the liver (Green, 1997).

In the early 1990's the trend in flame retardant usage suggested that the market was moving away from halogenated compounds (Green, 1997). There are only a few companies that produce halogenated flame retardants. Three companies (Dead Sea Bromine, Albemarle and Great Lakes Chemical Company) produce more than 80% of the total world consumption. Table 2 shows the usage of halogenated flame retardants in the world.

Table 2: Total world comsumption of halogen flame retardants (Pettigrew, 1993).

Flame Retardant	**Quantity (1989) (kT)**	**Quantity (1994) (kT)**
Brominated	106.7	236
Chlorinated	40.5	90

1.3 Inorganic flame retardants

Other flame retardant compounds used during the 70's included antimony oxide and zinc borate. When antimony oxide became scarcer and more expensive, zinc borate was used as a partial substitute (Green, 1997).

The next decade ('80s) was marked by a significant increase in flame retardant development; especially bromine containing compounds. They found application in PVC and polyethylene wire insulation, epoxy based printed circuit boards, poly(ethylene terephthalate) (PET) fabrics and acrylonitrile butadiene styrene (ABS). Table 3 shows that flame retardant usage moved away from the chlorinated substances towards the brominated substances. The use of the non-halogen additive ATH increased dramatically compared to halogenated flame retardant consumption (Green, 1997). The '80s also saw the introduction of new phosphorous flame retardants.

Table 3: Flame retardant consumption in the United States (kT/y) (Green, 1997).

Compound	1972	1977	1984
Organohalogens	2.72	12.24	31.29
Chlorophosphates	4.53	14.51	9.07
ATH	17.69	31.75	81.64

1.4 Phosphorous flame retardants

Phosphorous compounds that form phosphorous oxides upon decomposition were proposed as a partial or complete substitute for bromine compounds in PET. The resultant non-halogenated flame retardant showed excellent promise, but the price was too high to attract the cost sensitive flame retardant market (Green, 1997).

1.5 New trends in flame retardant systems

Smoke is the major killer in the case of fire, because it causes asphyxia or oxygen deprivation in victims (Green, 1997). It also obscures visibility making it difficult for victims to find escape routes. Smoke is an unavoidable consequence of the thermal decomposition process in organic materials. Polymers that unzip to monomer units when heated, e.g. polyacrylates and polyacetals burn cleanly and give very little smoke. Aromatic polymers such as styrenics; or polymers that decompose and rearrange to aromatic products such as PVC give very dense smokes.

Smoke suppressants can be added to the flame retardant formulation, but they are effective in PVC only, and to a lesser extent in unsaturated polyesters. The only real way to combat smoke is to prevent the start of fire in the first place (Green, 1997).

Table 4 shows recent data on the consumption of flame retardants. These include brominated and chlorinated compounds, antimony oxide and ATH. All show a steady increase in tonnage. However the growth rate of for ATH is higher than the others revealing the new market preference for non-halogenated products (Green, 1997).

Table 4: Consumption of flame retardants in the United States (kT/y) (Green, 1997).

Compound	**1983**	**1988**	**1991**	**1996**
Brominated	18.59	23.58	24.94	28.12
Chlorinated	12.70	15.42	13.60	14.51
Antimony oxide	13.15	20.41	20.41	22.68
ATH	81.64	106.59	113.40	131.54

1.5.1 Intumescent flame retardants

A new trend in flame retardancy of plastics is the use of intumescent flame retardants. Under fire conditions they form a sponge like insulating layer on top of the burning polymer substrate and prevent heat and mass transfer to and from the polymer (Camino, Costa & Martinasso, 1989; Gilman & Kashiwagi, 1997). The first systems used, during the early 1980's, were mixtures of ammonium polyphosphate, dipentaerythritol and melamine (Green, 1997). A problem encountered with these formulations was their water solubility.

1.6 Problem Statement

There is widespread public concern about the use of halogen containing compounds. This can be attributed to the perceived high level of toxicity and environmental unfriendliness of such chemicals. Some tend to accumulated in natural water sources, are not easily biodegradable and form highly reactive halogen radicals that may cause ozone depletion. Current efforts therefore focus on the replacement halogen flame retardants with more environmentally friendly systems. The purpose of this study was to evaluate non-halogenated compounds as flame retardants for polyester fabric.

2. Fundamentals of flammability.

Fire is the oxidative destruction of a combustible material. This process is accompanied by the release of heat and light energy. There are certain mechanisms of combustion as well as fundamental terms and definitions that must be clearly understood. Some of the relevant terms and definitions are clarified below.

2.1 Terms and Definitions.

Inert gas dilution involves the use of additives to produce large quantities of non-combustible gas when the polymer decomposes thermally. This gas dilutes the oxygen concentration in the air. Insufficient oxygen is then present for complete combustion and the fire extinguishes (Pettigrew, 1993).

Thermal quenching refers to the method by which the polymer surface temperature is kept low due to some endothermic degradation reaction, e.g. dehydration of ATH. This reaction acts as a heat sink, causing insufficient energy to be available for the production of flammable decomposition products (Pettigrew, 1993).

Protective coatings. Some flame retardants function by producing a protective char or liquid barrier. These minimise the flux or diffusion of the volatile decomposition products from the substrate to the flame front and act as an insulating layer to reduce heat transfer (Pettigrew, 1993).

Physical dilution. Inert fillers such as glass fibres and some minerals such as talc act according to this mechanism when added in large quantities. This reduces the amount of flammable polymer available, i.e. the effective heat of combustion of the substrate. Fillers may also increase the heat capacity of the polymer, creating a thermal heat sink (Pettigrew, 1993).

Chemical interaction. Halogens and phosphorous flame retardants act by chemical interaction. The flame retardant dissociates into radical species that interfere with the gas-phase combustion process (Pettigrew, 1993).

Terms that are applicable to intumescent flame retardants include (Pettigrew, 1993):

The *carbonific* (e.g. dipentaerythritol) provides the carbon source that produces the char layer.

The (latent acid) *catalyst* (e.g. ammoniumpolyphosphate) makes the intumescent reaction kinetically feasible; so that the carbonisation reaction takes place fast enough.

The *blowing agent* produces a gas, e.g. ammonia that inflates the char layer by a foaming process.

Polymer flammability can be expressed in terms of a *Limiting Oxygen Index* (LOI). The LOI refers to the minimum amount of oxygen that must be present to just sustain combustion in a vertical burn test. It involves a polymer strip lit from above with the gas streaming upwards. A higher LOI implies that a higher oxygen concentration in the gas stream is required to sustain the combustion of the strip.

2.2 Mechanism of combustion and flame retardancy.

In order for a solid polymer to burn it must be volatile, or produce volatile products, because combustion usually occurs in the gas phase. An exception is glowing combustion, a type of flameless combustion usually accompanying intumescent flame retardant systems. In the case of polymers, the solid substrate has a high molecular mass, i.e. consists of long chain molecules. Heat causes decomposition (e.g. depolymerisation) and volatilisation of the polymer. Decomposition begins in the solid phase and continues in the melt and gas phases. It produces decomposition products of low molecular mass. These volatile decomposition products enter the gas phase where they burn to produce more heat, driving further polymer decomposition. This provides the feed-back loop that sustains the combustion process. For a compound to function as a flame retardant it must interrupt the burning cycle in some way (Pettigrew, 1993).

The above process can be visualised in terms of the so-called fire triangle shown in Figure 1 (Gilman & Kashiwagi, 1997). It shows the interaction between the three elements essential for a fire:

- Heat generated by the flames.
- Fuel from the thermal decomposition of the polymer.
- Oxygen from the air.

The fire generates heat, part of which is absorbed by the substrate via radiation. The polymer substrate thermally decomposes into combustible gas fractions. These mix with the oxygen in the air to form a combustible mixture that fuels the fire. Once started, this process can sustain itself via the feed-back loop.

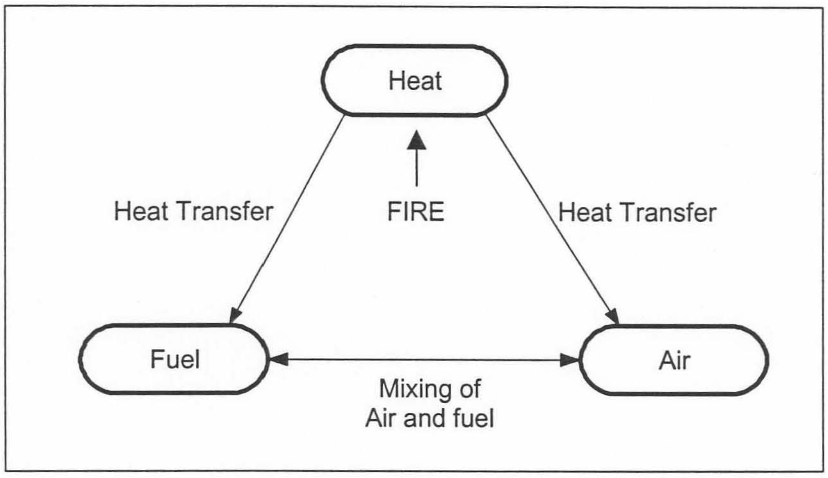


Figure 1: The Fire Triangle (Gilman & Kashiwagi, 1997).

In order to stop the fire, it is necessary to interrupt one or more of the pathways between the three major elements. This can be done in several ways, for example, by preventing the mixing of the polymer decomposition gas with the air. Alternatively, one could prevent the transfer of heat to the polymer substrate. The latter is a more sensible strategy and is easier to achieve (Srinivasan, Gupta & Horsey, 1998).

Flame retardants can modify flammability by several mechanisms. Usually a combination of several separate mechanisms is operative. Endothermic flame retardants such as metal hydroxides absorb heat during decomposition, causing thermal quenching. They also cause inert gas dilution by releasing water in the form of steam. Furthermore, so much of the flame retardant is added that it also causes a physical dilution effect (Srinivasan, *et al.*, 1998). Intumescent and halogenated flame retardants operate according to different mechanisms that are discussed in more detail in later chapters.

2.3 Flammability testing.

One of the problems related to the fire resistance of polymers is the fact that there is no clear, uniform definition of flammability. The American Society for Testing and Materials (ASTM) lists over one hundred methods for the assessment of material flammability (Pettigrew, 1993).

Table 5 shows some of the flammability tests applied to flame retardant polymers to determine their performance and characteristics. As can be seen these tests are primarily from the American Society for Testing and Materials and the vertical burning test is from Underwriters Laboratory (UL) (Pettigrew, 1993).

Table 5: Flammability tests for polymers (Pettigrew, 1993).

Designation	**Description**	**Characteristic measured**
ASTM E162-87	Radiant panel	Flame spread
ASTM D2863-87	Limiting oxygen index	Ease of ignition
UL 94	Vertical burn	Ignition resistance
ASTM E1354-90	Cone calorimeter	Heat release and smoke

The most common flame test for flame retarded polymers is the UL 94 vertical burn test. This test uses a vertical burn method to determine the ignitability towards a small flame. Test specimens are mounted vertically and ignited with a Bunsen flame at a 30° angle. A layer of cotton is placed under the sample to test for flaming drips. The flame is applied for 10 seconds and then removed, and a further 10 seconds if the first application has self-extinguished. The flammability classifications include:

- **V-0** if no sample burns for longer than 10 seconds. The sum of the after-flame times, for five samples (i.e. 10 ignitions) must not be greater than 50 seconds, and the cotton must not ignite.
- **V-1** if no sample burns longer than 30 seconds. The sum of the after-flame times, for five samples (i.e. 10 ignitions if necessary) must not exceed 250 seconds, and the cotton must not ignite.
- **V-2** is the same as V-1 but the cotton can be ignited.

Cone calorimeters measure the rate of heat release during the burning of a sample. The specimens are exposed to a radiation flux of up to 100 kW/m^2. Some of the measured parameters include the heat released, percentage mass loss, ignition time, heat flux and smoke production. The advantage of cone calorimeter testing is that the sample can be subjected to heat fluxes similar to those encountered in real fires (Pettigrew, 1993).

During this literature survey, a modified version of the Underwriters Laboratory vertical burn test (UL94) was used. A vertically mounted unsized polyester fabric sample was ignited twice with a spirit burner flame using an exposure time of 10 seconds. This test is referred to as British Standard 5438 (BS 5438) in accordance with BS 5867 Part 2 (CSIR, 1999).

3. Halogenated Flame Retardants

A significant application area of halogenated flame retardants is flame retarded plastic used in consumer electronics. The environmental issues concerning brominated flame retardants clouds their future. Consequently, the manufacturers of computers and business machines are re-evaluating the use of halogenated flame retardants.

This is particularly true for the European market place where eco-friendly labels are becoming a major factor in marketing computers and other electronic equipment. To qualify for the label such as the White Swan of Sweden the product must comply with certain environmental ground rules. This includes not using any halogenated flame retardants. Computer manufactures are therefore considering switching from halogenated flame retardant system, to a PC/ABS (polycarbonate/acrylonitrile butadiene styrene) polymers flame retarded with a phosphorous compound (Miller, 1996).

3.1 Mechanism of halogen flame retardants

It is generally accepted that the combustion of gaseous fuel proceeds via a free radical mechanism. A number of propagating and chain branching mechanisms are illustrated below. These are necessary to maintain the combustion process. Methane is used in the example as the fuel or the decomposition gas coming from the polymer (Green, 1986):

$$CH_4 + O_2 \rightarrow {}^{\bullet}CH_3 + H^{\bullet} + O_2$$

$$H^{\bullet} + O_2 \leftrightarrow HO^{\bullet} + O^{\bullet}$$

$$CH_4 + HO^{\bullet} \rightarrow {}^{\bullet}CH_3 + H_2O$$

$${}^{\bullet}CH_3 + O^{\bullet} \rightarrow H_2CO + H^{\bullet}$$

$$H_2CO + HO^{\bullet} \rightarrow CHO^{\bullet} + H_2O$$

$$CHO^{\bullet} + O_2 \rightarrow H^{\bullet} + CO + O_2$$

$$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet}$$

Here $H^{\bullet}$, $HO^{\bullet}$ and $O^{\bullet}$ are radicals and chain carriers. The reaction of the $H^{\bullet}$ radical and the O_2 molecule is an example of chain branching in which the number of carriers is increased. The reaction of the CO molecule with the $HO^{\bullet}$ radical, converting CO to CO_2, is a particularly exothermic reaction (Green, 1986).

3.2 Brominated Flame Retardants

The performance of halogens as flame retardants is rated as follows (Green, 1986):

$$I > Br > Cl > F$$

Iodine compounds, apparently the most effective, are not used in polymers because they do not have adequate thermal stability. Iodine flame retardants decompose thermally at a low temperature and cause brown stains in the polymer. Fluorocarbons are inherently non-burning, but they generally do not impart flame retardancy to other plastics because either the C-F bond is too thermally stable or the highly reactive hydrogen fluoride or fluoride radicals that may form react rapidly in the condensed phase. An exception is that small amounts of Teflon will significantly increase the oxygen index of polycarbonate resins, due to the increase in viscosity that inhibits dripping.

Commercial organohalogen flame retardants include aliphatic, alicyclic and aromatic chlorine and bromine compounds. Aliphatic compounds are the most effective and the aromatic compounds are the least effective with the alicyclic compounds in between (Pettigrew, 1993).

$$\text{aliphatic} > \text{alicyclic} > \text{aromatic}$$

The above is true for e.g. polypropylene, but for polyethylene the opposite is observed. This is in the same direction as the thermal stability indicating that the more easily available the halogen the more effective. The actual type of compound used in an application will depend on the processing temperature of the plastic. Bromine compounds are about two thirds more effective than chlorine compounds. The expected relative effectiveness is indicated in Table 6.

Table 6: General effectiveness of halogen compounds for flame retardancy (Pettigrew, 1993).

Element	Effectiveness
Fluorine	1.0
Chlorine	1.9
Bromine	4.2
Iodine	6.7

It takes about 3% bromine of an aliphatic brominated flame retardant plus 1.5% antimony oxide to obtain a polypropylene composition to a UL94 V-2 rating. When burning, profuse dripping is observed. The flaming polymer droplets remove heat from the flame zone. Addition of inert filler to inhibit dripping leads to a burning product. This demonstrates the utility of dripping as a method for passing a small-scale laboratory test. Dripping also allows heat to be removed from the flame zone in large-scale tests, significantly reducing the total heat release. The flame dripping polymer will self-extinguish and the actual amount of polymer burned could be significantly less (Pettigrew, 1993).

3.2.1 Mechanism of Brominated flame retardants

In the radical trap theory of flame inhibition, it is believed that HBr competes for the radical species $HO^{\bullet}$ and $H^{\bullet}$ that are critical for flame propagation (Green, 1986):

$$H^{\bullet} + HBr \rightarrow H_2 + Br^{\bullet}$$

$$^{\bullet}OH + HBr \rightarrow H_2O + Br^{\bullet}$$

The active chain carriers are replaced with the much less active $Br^\bullet$ radical. This slows the rate of energy production resulting in flame extinguishing.

It also has been suggested that halogens simply alter the density and mass heat capacity of the gaseous fuel-oxidant mixture so that flame propagation is effectively prevented. This physical theory is equivalent to the way inert gases such as carbon dioxide and nitrogen may influence combustion (Larsen, 1973).

Suggestions have been made that the flame retardant mechanism of some bromine compounds acts mainly in the condensed phase and also depends on the type of polymer being treated. Reaction of the flame retardant or its decomposition products with the polymer can inhibit the decomposition of the polymer, thereby influencing the flame retardancy (Green, 1986).

3.3 Halogen Synergism

Antimony oxide itself usually renders no flame inhibition properties to polymers, but it is known as a synergist for halogen compounds. Antimony oxide is not volatile but antimony oxyhalide ($SbOX$) and antimony trihalide (SbX_3) formed in the condensed phase, by reaction with the halogenated flame retardant, are volatile. They facilitate the transfer of halogen and antimony into the gas phase where they function. Antimony oxide flame retardants are therefore usually used indirectly in the form of antimony trichloride ($SbCl_3$) or antimony tribromide ($SbBr_3$). These forms are very effective retardants at typical flame temperatures.

Laboratory flammability tests indicate that the optimum halogen / antimony atom ratio in many polymers is about 2:1 to 3:1. It has been suggested that antimony halides are also highly active radical traps. Although the antimony halides appear to act exclusively in the vapour phase, some effect in the condensed phase can not be ruled out (Pettigrew, 1993).

Historically, impurities such as iron and aluminium, which came from catalyst residues, limited the use of the flame retardants, much like the fouling of a catalyst. The residues tend to bind with the flame retardant, making it less volatile and more prone to condense or precipitate on the surface. The levels of these impurities have since been reduced. Some aromatic bromine compounds, e.g. decabromo diphenyloxide, are thermally stable up to very high temperatures (Pettigrew, 1993).

Interference with the antimony-halogen reaction will affect the flame retardancy of the polymer. For example, metal cations from colour pigments and inert fillers such as calcium carbonate may lead to the formation of stable metal halides. These metal halides can render the halogen unavailable for reaction with the antimony. The result is that neither the halogen nor the antimony is transported into the vapour phase, where they provide flame retardancy. Silicones have also been shown to interfere with the flame retardant mechanism. Consequently, the total plastic composition must be considered in developing a new flame retardant product.

Other members of Group V of the periodic table, such as arsenic and bismuth also function as synergists for halogens. Little work has been done with these compounds for toxicity reasons. The Diels-Alder adduct of hexachlorocyclopentadiene with 1,5-cyclooctadiene (Dechlorane Plus™)

can be used to flame retard nylons, epoxies and polybutylene terephthalate using synergists other than antimony oxide. These compounds include zinc compounds such as the borate, oxide and phosphate as well as iron oxides such as Fe_2O_3 and Fe_3O_4. The use of mixed synergists is also reported to lower the level of the total flame retardant required (Green, 1986).

4. Inorganic Flame Retardants.

Plastics can be given flame retardant characteristics by introducing elements of organic, inorganic and halogen origin. Such elements include magnesium, aluminium, phosphorous, molybdenum, antimony, tin, chlorine and bromine. Flame retardants are added in either the manufacturing step of the polymer or the compounding step of the polymeric article. Phosphorous bromine and chlorine are usually included as some organic compound. Inorganic flame retardants are usually added together with other flame retardants to provide a more efficient flame retardant action through synergism.

Halogen flame retardants usually need an addition of about 40% in order to be effective, and this affects the properties of the polymer quite negatively. Structural integrity of the polymer article is often very important, and a drastic decrease in strength and other mechanical properties is simply not acceptable. The efficiency of halogen flame retardants is often enhanced by the addition of inorganic flame retardants. A smaller mass percentage halogen flame retardant is now needed, so the adverse effect on the polymer properties is also reduced (Touval, 1993).

4.1 Antimony Compounds

The antimony compounds used for flame retardancy include antimony trioxide, antimony pentoxide and antimony-metal compounds. In 1990 in the United States alone, the use of antimony trioxide amounted to 20 000 metric tons just for the flame retardancy of plastics. Antimony oxide is readily found in nature but in very impure form. This is not suitable for direct use as flame retardant, so antimony oxide is often rather produced from antimony metal. There are therefore many different grades of antimony oxide that can be used for flame retardants. Some of the physical properties of antimony trioxide are listed in Table 7.

Table 7: Physical properties of commercial antimony trioxide (Touval, 1993).

Property	**Grade**		
	Ultra fine	High tint	Low tint
Specific gravity	5.3-5.5	5.3-5.8	5.3-5.8
Particle size (μm)	0.25-0.45	0.8-1.8	1.9-3.2

Antimony oxide with a small particle size will for example give a polymer with a high opacity and white colour whereas the larger particle sizes produce translucent polymers. Although particle size affects pigmentation, it does not appear to affect the flame retardant efficiency. The price for antimony oxide is quite high, depending on the purity (Touval, 1993).

With cotton textiles, antimony oxide is usually applied by impregnating the fabric with a water soluble antimony solution, followed by secondary treatment (such as evaporation) that deposits the oxide on the fibres. When the treated sample is exposed to a flame, the fibres decompose endothermically. The decomposition products, apart from the volatile components, are water and char, and this reduces the combustion temperature of the flame (Touval, 1993).

The second most widely used antimony compound for flame retardancy is antimony pentoxide (See Table 8). Unlike the trioxide, the pentoxide does not cause a pigmenting effect on the treated polymer. Furthermore, the average particle size for a typical commercial pentoxide is 0.03 μm, which causes a more even distribution throughout the polymer. This implies a less drastic change in the polymer properties, and overall better flame retardancy. Antimony pentoxide is however priced two to three times higher than the trioxide.

Table 8: Typical properties of commercial grades of antimony pentoxide and sodium antimonate (Touval, 1993).

Property	**Sb_2O_5**	**Na_2SbO_4**
Particle size (μm)	0.03	2
Surface area (m^2/g)	50	Not available
Specific gravity	4.0	4.8
Surface activity	Weak acid	Base
Refractive index $n^{20}{}_D$	1.7	1.75

Another antimony synergist of commercial importance is sodium antimonate (Refer to Table 8). As it only contains 60 percent antimony on a mass basis, it is less effective. than either the trioxide or pentoxide. Sodium antimonate has an average pH of 9-11 when dissolved in water. The bacisity of this antimony form makes it ideal for a polymers that are easily hydrolysible (Touval, 1993). For example, it is used instead of antimony trioxide in PET applications. The sodium antimonate price is in the range of $3.30 to $4.40 per kilogram.

It has to be mentioned that antimony compounds are not currently used on their own as flame retardant. Antimony in combination with elements such as chlorine and bromine shows remarkable flame retardant synergism.

Due to the world-wide scarcity of antimony, new products containing antimony-metal synergists have been found. Some of these contain zinc, silicone or phosphorous and were found to be as effective as antimony alone. These antinomy compounds are also typically 10 to 20 percent less expensive than antimony trioxide.

4.1.1 Mechanism of Antimony compounds

The antimony flame retardants follow the mechanism of the formation of antimony chloride with an oxychloride as a highly reactive intermediate. The antimony oxide reacts with the halogen containing compound forming highly volatile antimony oxychloride (Touval, 1993).

$$Sb_2O_3 + 2\ HCl \rightarrow 2\ SbOCl + H_2O$$

The antimony oxychloride is a very reactive intermediate that forms antimony trichloride through several reactions (Touval, 1993).

$$5\ SbOCl\ (s) \rightarrow Sb_4O_5Cl_2 + SbCl_3$$

$$4\ Sb_4O_5Cl_2 \rightarrow 5\ Sb_3O_4Cl + SbCl_3$$

$$3\ Sb_3O_4Cl \rightarrow 4\ Sb_2O_3 + SbCl_3$$

$$Sb_2O_3\ (s) \rightarrow Sb_2O_3\ (g)$$

By means of the above reactions, antimony helps to quickly move the halogen into the gas phase, where it acts as an effective flame retardant.

Antimony oxide was found not to be a carcinogenic nor to pose a risk to the environment. Some antimony products do however contain trace amounts of arsenic, so caution should nevertheless be taken during handling (Touval, 1993).

4.2 Boron Compounds

In the United States the consumption of boron flame retardants for plastics amounts to approximately 4500 metric tons per annum. The most widely used is zinc borate, prepared from water-soluble zinc and boron compounds. Zinc borate can be used on its own or in combination with other flame retardants such as antimony oxide, to form a glass-like substance that prevents further polymer decomposition. Borates, like all other flame retardants, vary in grade and effectiveness, depending on the composition, varying from $2ZnO{\bullet}3B_2O_3{\bullet}5H_2O$ to $4ZnO{\bullet}6B_2O_3{\bullet}7H_2O$ (Green, 1997).

The ratio of zinc, boron and water in the borate flame retardants determines the performance properties of the compound such as the temperature at which the flame-inhibiting powers are activated. Some of the other boron flame retardants used are barium metaborate ($Ba(BO_2)_2$), boric acid, sodium borate and ammonium fluoroborate (NH_4BF_4) (Touval, 1993).

4.2.1 Mechanism of Boron compounds

Boron functions as a flame retardant in both the condensed and the vapour phases, forming the corresponding trihalide as shown in the reaction below. The boron trihalides are volatile and vaporise to produce halogens in the gas phase, which act as a flame inhibitor. Boron trihalides are Lewis acids so they promote cross-linking of the polymer, producing a minimum of polymer vapour during decomposition (Touval, 1993). Borates are also known to be after-glow inhibitors (Green, 1997).

$$6\ NH_4BF_4 + Sb_2O_3 \rightarrow 6\ NH_3 + 6\ BF_3 + 2\ SbF_3 + 3\ H_2O$$

Zinc borate is used in polyvinyl chloride to replace, in part, antimony oxide. The hydrogen chloride generated from PVC reacts with the zinc borate (Green, 1997). The cost of borates varies from $2.00 – 2.50 per kilogram (Touval, 1993).

Mixtures of boric acid and borax are used as flame retardants for cellulose. Boric acid decomposes endothermically releasing water in two stages. The first stage is at 130-200°C to form HBO_2 and again at about 265°C. When heated the mixture dissolves in its own water of hydration, froths, and fuses to form a surface coating. Similar to the phosphoric acids resulting from phosphate esters, boric acid dehydrates oxygen-containing polymers, yielding char. The glassy coating and the char protect the substrate from oxygen and heat.

4.3 Aluminium Compounds

The most commonly used aluminium flame retardant compound is alumina trihydrate, $Al(OH)_3$. Alumina trihydrate is the most widely used flame retardant for plastics at low temperatures. In 1991, the use of alumina trihydrate was approximately 113 400 metric tons. Alumina trihydrate is available in many different particle size distributions from 1 – 100 μm. The low refractive index of the particles gives it only slight pigmentation properties, making it ideal for wide-spread polymer applications. Mixtures of up to 50% alumina trihydrate are therefore translucent. A typical commercial alumina trihydrate composition is given in Table 9.

Table 9: Typical composition of commercial alumina trihydrate (Touval, 1993).

Component	**Quantity (wt %)**
Al_2O_3	64.9
SiO_2	0.005
Fe_2O_3	0.007
Na_2O	0.3
Water solubles	0.04
Water loss on ignition	34.6

Alumina trihydrate is relatively cheap, in the order of $0.25 – $1.35 per kilogram. Unfortunately, it is the least effective of all flame retardants. It is only about one fourth to one half as effective as the halogen flame retardants. The physical properties of alumina trihydrate are shown in Table 10.

Table 10: Typical physical properties of commercial alumina trihydrate (Touval, 1993).

Property	Value
Density (g/ml)	2.42
Refractive index n^{20}_D	1.579
Average particle size μm	1-100
Colour	White
Water solubility	Insoluble

Usually about 50 – 60 % alumina trihydrate must be added to provide some acceptable level of flame retardancy, and the plastic processing temperature must usually not exceed 220 °C.

Alumina trihydrate is also used as a secondary flame retardant and smoke suppressant for flexible poly(vinyl chloride) plastics. It is also used in combination with antimony and halogen flame retardants. The addition of small amounts of zinc borate or phosphorous results in the formation of glasses and protects the polymer surface from the flame (Touval, 1993).

4.3.1 Mechanism of Aluminium compounds

Alumina trihydrate functions as a flame retardant in both the vapour and the condensed phases. When activated it decomposes thermally to alumina trioxide and water as shown by the reaction below.

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$

In the flame phase, the water vapour forms an envelope around the flame, excluding oxygen from the flame. It also decomposes endothermically; thereby lowering the effective flame temperature (Touval, 1993).

5. Phosphorous Flame Retardants

Various phosphorous based flame retardants have been shown to produce some action in the condensed phase (polymer melt) and the vapour phase (flame zone). Physical and chemical actions have been proven in both phases. Flame inhibition, heat loss due to melt flow, surface obstructions with char formation, acid-catalysed char formation, and char enhancement have all been noticed in polymer systems with phosphorous based flame retardants. It is therefore quite possible that more than one mechanism is involved in any given case (Weil, 1992).

5.1 Condensed phase mechanisms

5.1.1 Charring mechanisms

There is convincing evidence, that in oxygen-containing polymers, such as cellulose and rigid polyurethane foam, phosphorous containing flame retardants can increase the char yield. Char formation implies that less of the molten polymer substrate is converted to combustible gases, so the mass loss is reduced. Secondly, char formation is often accompanied by water release, which dilutes the combustible vapours, making the vapours less combustible. Char formation is also sometimes an endothermic process.

The pyrolysis behaviour of cellulose such as cotton paper and wool has been extensively studied. When cellulose is heated to its pyrolysis temperature it normally depolymerises to a tarry carbohydrate product which further breaks down to smaller combustible organic compounds (Weil, 1992).

Upon fire exposure, phosphorous containing flame retardants decompose to phosphorous acids or anhydrides. These active phosphorous species phosphorylate the cellulose. Phosphorylated cellulose then breaks down to form char. The presence of phosphorous also improves fire resistance by preventing further oxidation of the char by a glowing combustion (Weil, 1992).

It is also known that certain nitrogen compounds such as melamine, urea or dicyandiamide will synergise the action of phosphorous in cellulose. This is not a general phenomenon, and depends on which nitrogen compound is used with which polymer system (Weil, 1992).

Another case in which the char enhancement by phosphorous is important is in rigid polyurethane foams. The analytical evidence shows that phosphorous appears to be largely retained in the char, to make the char more coherent and provide a better protective barrier. In contrast to the situation in rigid foams, char formation is probably not the basis of the action of phosphorous retardants in flexible foams. On the other hand char formation can lessen the flame retardancy in flexible foams (Weil, 1992).

In PET (polyethylene terephthalate) and PMMA (polymethyl methacrylate), phosphorous flame retardants cause an increase in the amount of char residue, reducing the release of volatile fuel. This is probably the result of acid catalysed cross-linking of the system that increases the molecular mass and melt viscosity. In oxygen-free hydrocarbon polymers that don't char very easily, e.g. polyolefins and styrenics, phosphorous flame retardants are usually not very effective. They can be made more effective by addition of char-forming additives. In the absence of such a char-forming additive the main mechanism of flame retardancy seems to be increased dripping by reducing melt viscosity. Other mechanisms such as vapour phase reactions are not excluded (Weil, 1992).

Phosphorous can also reduce smouldering, as mentioned before. Glowing combustion of the char formed often occurs. The addition of phosphorous flame retardants can prevent this oxidative process. The mechanism is still unclear, but involves the deactivation of the active centres on the carbon atoms (Weil, 1992).

Phosphorous is also important as a char-promoting compound in intumescent flame retardants for paints and plastics.

5.1.2 Coating mechanisms

Besides its effect in enhancing the amount of char, the phosphorous flame retardant may provide a protective surface coating that inhibits further burning and smouldering. Phosphorous reduces the permeability of the char, improving its barrier properties. While this may be due to coating, a chemical connection is also possible (Weil, 1992).

Condensed phase mechanisms based on phosphorous acids coating the burning surface have often been proposed (Weil, 1992). Some researchers postulate that phosphorous acid acts as a physical barrier to prevent the vaporisation of fuel from a hydrocarbon polymer. In this case the polymer is flame retarded with ammonium polyphosphate or triphenyl phosphate.

Some infrared evidence supports the proposal regarding the polyphosphoric acid coating (Weil, 1992).

5.1.3 Melt viscosity

Phosphorous compounds can generate acids under fire conditions. In some cases, these acids catalyse the thermal degradation of the polymer melt, reducing the molecular mass and reducing the melt viscosity. This causes the melt to flow or drip away from the flame zone, reducing the material that is exposed to flame. Poly(ethylene terephthalate) provides a very impressive example. Addition of as little as 0.15% of a phosphorous flame retardant permitted a polyester fabric to pass a vertical burn test (Weil, 1992).

This mechanism of changing the melt viscosity can be defeated by adding any non-melting filler or additive that can retard the melt flow. For example, cotton threads in a flame retarded poly(ethylene terephthalate) fabric can have such an effect. A particularly illustrative example is the antagonistic effect of traces of silicone oil on flame retarded polyester fabric. The fabric is rendered flammable probably because the silica, formed during pyrolysis of the silicone oil, reduces the melt flow. Another instance where the melt flow retarding effect occurs, is when phosphorous containing flame retardant polyester (such as Trevira CS™) is pigment-printed with an infusible pigment (Weil, 1992).

5.1.4 Free radicals

This idea has been developed by Russian researchers, who offer some evidence in support of free radical inhibition, or at least of an antioxidant effect. Non-volatile phosphorous flame retardants are usually used for this purpose. By looking at electron spin resonance data, it can be seen that aryl phosphorous flame retardants may scavenge alkylperoxy radicals at the polymer surface (Weil, 1992).

5.1.5 Effects of fillers

Condensed phase mechanisms based on surface effects from fillers are still relatively unexplored. Some phosphorous compounds have characteristics of surfactants and aid the dispersion of the solid flame retardant. Improved binding by the surface-active agent improves the char cohesion. Similar effects are observed with titanate and zirconate coupling agents. They seem to enhance the UL 94 flammability rating of polymers containing various mineral fillers (Weil, 1992). Interestingly, on one filler, barium sulphate, the effect of the titanate seemed to reach maximum at 1% concentration, and the effect was lower at lower and higher concentrations (Weil, 1992).

5.2 Vapour phase mechanisms

Exactly as in the case of condensed phase mechanisms, there are a number of physical and chemical modes of action for the vapour phase. While the condensed phase reaction products cover the polymer substrate, the vapour phase reaction products may dilute the combustible polymer decomposition products (Weil, 1992).

5.2.1 Chemical methods

Volatile phosphorous compounds are also effective flame inhibitors. Mass spectroscopy showed that triphenyl phosphate breaks down in the flame to produce small species such as P_2, PO, PO_2 and HPO_2. This reduces the hydrogen atom concentration in the vapour phase, extinguishing the flame. The step in the flame chemistry which is inhibited is the rate-controlling branching step (Weil, 1992):

$$H^{\bullet} + O_2 \rightarrow HO^{\bullet} + O^{\bullet}$$

Vapour phase flame retardant activity appears to be the mechanism whereby triaryl phosphates functions. It is used in commercial blends of polyphenylene oxide with high impact polystyrene. The polyphenylene oxide gives a protective char while the triaryl phosphate provides the flame retardancy needed to suppress the combustion of polystyrene (Weil, 1992).

5.2.2 Physical methods

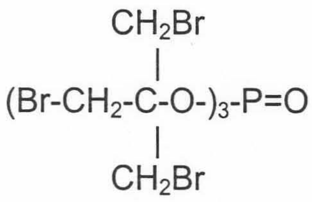
Vapour phase flame retardant action does not have to be chemical, but can be physical in nature. It can be based on heat capacities, heat of vaporisation and endothermic dissociation. Studies have shown that the condensed phase mechanisms are significantly more effective than the vapour phase mechanisms, even with polymers that depolymerise thermally to produce volatile monomers (Weil, 1992).

In flexible polyurethane foams, various chloroalkyl phosphates are effective flame retardants, however they don’t appear to increase the char formation or produce a chemical effect on the burning surface of the foam. They do appear to volatilise as the intact molecule, and cause a vapour phase retardant action. Some small degree of condensed phase action is also possible since it was shown that chloroalkyl phosphates become incorporated into the char structure (Weil, 1992).

5.3 Phosphorous flame retardant synergism

5.3.1 Halogen synergism

Halogen phosphorous synergism is often confused by analogy with the strong and well established halogen antimony synergism. Unlike antimony halogen synergism, phosphorous halogen synergism is not general. The postulated formation of phosphorous oxyhalides completely lacks experimental support. However, good additive results are often obtained with combinations of halogen- and phosphorous-based flame retardants (Weil, 1992). An instance of bromine and phosphorous synergism is found in the structure of the following brominated phosphate ester:



$$(\mathrm{Br\text{-}CH_2\text{-}}\underset{\underset{\mathrm{CH_2Br}}{|}}{\overset{\overset{\mathrm{CH_2Br}}{|}}{\mathrm{C}}}\mathrm{\text{-}O\text{-}})_3\mathrm{\text{-}P{=}O}$$

5.3.2 Antimony synergism

There are a number of published formulations showing the attempted use of antimony oxide in combination with phosphorous and halogen flame retardants. Results sometimes appear favourable, but quantitative studies show convincing evidence of an antagonism between antimony and phosphorous. In the most severe case the one element cancels out the effect from the other, and in other cases the effect is less than an additive. A detailed study of triaryl phosphate and antimony oxide in polyvinyl chloride (PVC) showed that this antagonism only occurred in a part of the composition range. The antagonistic effect probably is the result of the formation of antimony phosphates, that are very stable and practically inert fillers (Weil, 1992).

6. Intumescent Flame Retardants

Intumescence is an interesting phenomenon. The French verb *tumere* means “to swell”. The Latin equivalent *tumescere* can be translated as “to swell up”. Therefore tumid or tumescent means swollen or bulging, and the process of getting to a swollen state is intumescence. In flame retardant terms, exposure to heat initiates a series of chemical and physical processes, leading to a tumescent condition. This state is characterised by a fire-resistant insulating foam. The foam serves to isolate heat and oxygen from the fuel source, extinguishing the fire (Mount, 1992).

6.1 Condensed phase charring

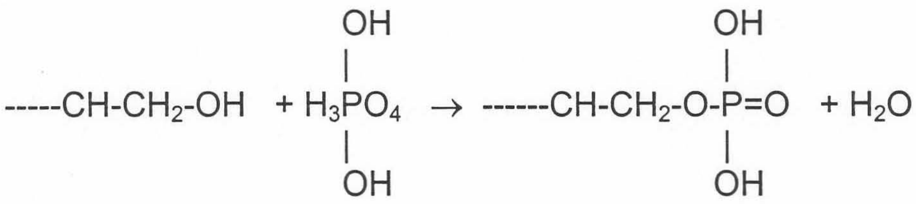
A complete description of intumescence requires analysis of both chemical and physical process.

6.1.1 Chemical mechanism of intumescence

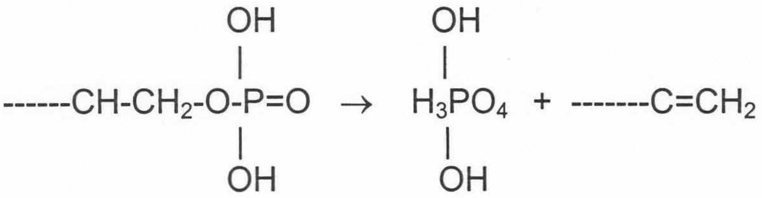
A suggested mechanism for char formation is discussed by Mount (1992). The chemistry is often written in terms of simple acid-catalysed, dehydration reactions. This is shown in the four reactions below.

$$\text{-----CH-CH}_2\text{-OH} + H^+ \rightarrow \text{-----CH-CH}_2\text{-OH}_2^+$$

$$\text{-----CH-CH}_2\text{-OH}_2^+ \rightarrow \text{-------C=CH}_2 + H_2O + H^+$$



$$\text{-----CH-CH}_2\text{-OH} \; + \underset{\substack{| \\ \text{OH}}}{\overset{\substack{\text{OH} \\ |}}{\text{H}_3\text{PO}_4}} \rightarrow \text{------CH-CH}_2\text{-O-}\underset{\substack{| \\ \text{OH}}}{\overset{\substack{\text{OH} \\ |}}{\text{P}}}\text{=O} \; + \text{H}_2\text{O}$$



$$\text{------CH-CH}_2\text{-O-}\underset{\substack{| \\ \text{OH}}}{\overset{\substack{\text{OH} \\ |}}{\text{P}}}\text{=O} \rightarrow \underset{\substack{| \\ \text{OH}}}{\overset{\substack{\text{OH} \\ |}}{\text{H}_3\text{PO}_4}} + \text{-------C=CH}_2$$

The first two reactions show the depolymerisation catalysed by an acid. The second two show the dehydration of the polymer when phosphoric acid is present. Both reactions essentially lead to the same result: producing -----C=CH$_2$ fragments at the polymer chain ends. These fragments condense to form carbon-rich char residues.

Briefly stated, the way the phosphorous compounds work is that they phosphorylate carbonifics such as pentaerythritol to make polyol phosphates. These polyol phosphates can then break down to form char (Weil, 1992).

6.1.2 Physical model of intumescence

Intumescent flame retardants were initially used, in paints and coatings. Typical formulations contained a phosphorous compound such as ammonium polyphosphate, a char forming polyol such as pentaerythritol, along with a blowing agent such as melamine. A binder is also necessary to keep the compounds in contact with each other.

With such intumescent coatings, one can visualise the burning polymer as a block consisting of several separate layers. The top char layer, is followed by the intumescent front where the foaming reactions take place. Below is an unburned polymer coating layer that still contains flame retardant. The bottom layer represents the polymer substrate that is being protected by the intumescent coating. The char-foam provides a physical barrier to heat- and mass transfer, and therefore interferes with the combustion process (Gilman & Kashiwagi, 1997).

For a mixture to be an efficient intumescent system, three ingredients are needed (Mount, 1992; Camino, *et al.*, 1989):

- An inorganic acid (dehydrating agent);
- A carbon rich polyhydric material as char former (carbonific); and
- A blowing agent – called a spumific.

The interaction of these components, to form a foamed char is illustrated in Figure 2.

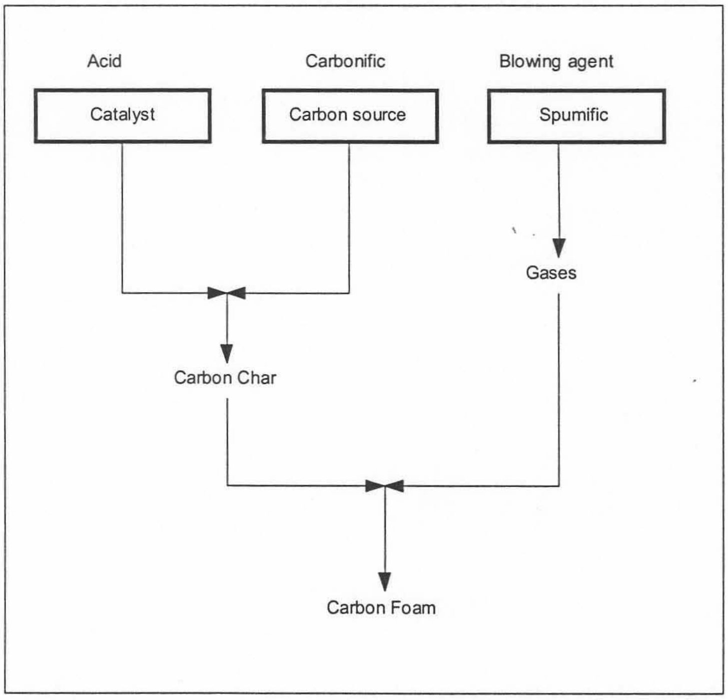


Figure 2: chematic diagram of the formation of char during intumescence (Gilman & Kashiwagi, 1997).

The ratios in which the different compounds are present are also of utmost importance. The optimum ratio must be determined experimentally. One or more of these substances could be replaced with others of the same class or group. Further studies showed that more effective intumescent systems are obtained when two or more of the elements required for intumescence are incorporated in the same molecular complex (Camino, *et al.*, 1989).

Intumescent flame retardants also work well in bulk polymers, such as polypropylene (PP) (Montaudo & Puglisi, *s.a.*).

The effectiveness of the intumescent flame retardants is due to the foamed char formed on the surface of the burning material (Camino, *et al.*, 1989). The char acts as a physical barrier against heat transfer to the surface of the combustible material. Char formation lowers the rate of temperature increase of the surface beneath the char. (See Figure 1)

The layer of char furthermore hinders the diffusion of oxygen to the site of combustion. Dripping of the molten plastic is also reduced by char formation, thereby eliminating a possible source of further flame propagation.

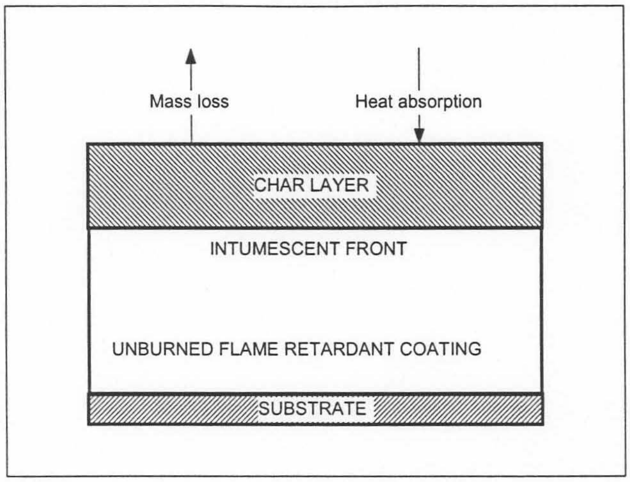


Figure 1: Schematic diagram of the different layers during the burning process (Gilman & Kashiwagi, 1997).

Halogenated compounds such as chlorinated paraffin are commonly used in intumescent coatings as carbonifics. However, they are not widely used in intumescent flame retardants for plastics. Nitrogen based compounds are widely used owing to their environmental soundness. This is true for almost all char forming flame retardant systems (Zaikov & Lomakin, 1996). Nitrogen based flame retardants have many advantages over other systems because they produce less smoke and fewer toxic gases. The smoke is also less corrosive and polymer scrap more readily disposable after use (Horacek & Grabner, 1996). The shift to such environmentally friendly flame retardants, is of high interest world wide. The market is trying to move away from halogenated flame retardants, but alternative systems are usually less effective or more expensive (Mount, 1992).

6.2 Mineral filler synergism

It was believed that the addition of inorganic fillers to the compounds used as flame retardants can improve their efficiency. This is due to the plate-like microstructure of certain fillers and the consequent stabilising effect they might have on the cell-structure of the char foam. The addition of fillers may reduce the amount of intumescent char, but should give the char a better strength and cell-structure. In the late 1980's a study on the then common and frequently used inorganic fillers proved to be a revelation. It was found that the fillers did modify the char structure but reduced the efficiency of the flame retardant system (Bertelli et al., 1989). The chars formed with the added filler were harder and more solid than those without the fillers, but were of lesser volume. The mechanism used to explain the modifications in the chemical and physical characteristics of the char was based on the possibility of the reaction between the acid phosphorus moieties and the fillers.

Recently, a careful study was made by Hoechst-Celanese comparing the effect of titanium dioxide (TiO_2) and stannous oxide (SnO_2) on the flame retardant char forming effect of ammonium polyphosphate in polypropylene. An intumescent nitrogen containing resin was also used. Titanium dioxide increased the flame retardancy by giving a stronger and more cohesive char with higher yield. Stannous oxide on the other hand was antagonistic, made the char flakier and more porous and did not enhance the char yield. Titanium dioxide probably functions by a physical bridging effect in the char, and the negative effect of the stannous oxide is probably due to some chemical interaction with the phosphorous compounds (Weil, 1992).

6.3 Other intumescent systems

Recent research showed that combinations of silica gel and pentaerythritol with potassium carbonate are effective char forming flame retardants (Gilman *et al.,* 1997; Miller, 1996). Unfortunately, these systems are water-soluble, making them unsuitable for outdoor use. It should be possible to convert these systems to intumescent ones.

Other new intumescent systems include the use of expandable graphite flakes in a special intumescent carrier resin (Miller, 1996). These flakes expand their initial thickness by up to a hundred times when exposed to heat. This material is based on natural occurring graphite and is therefore environmentally friendly. The implementation of nanocomposite clays as flame retardants in polymers is also being investigated (Gilman & Kashiwagi, 1997).

7. Experimental

7.1 Flame retardant treatment

Unsized polyester fabric (150 g/m^2) was obtained from Wesco Fabrics. The fabrics were woven from fibre produced by South African Nylon Spinners (SANS). The flame retardant treatment process occurred in three stages.

7.1.1 Pre-treatment

Strips with dimensions of 50 mm wide and 200 mm long were cut. The pre-treatment consisted of weighing the strips and then placing them in an oven for a few days. A weight measurement after drying determined the amount of water bound to the fibres.

7.1.2 Impregnation

The fabric strips were marked for identification purposes. Solutions or suspensions of the specific flame retardant candidates were prepared a variety of solvents e.g. water, ethanol, methanol, acetone and chloroform. Solvents were chosen based on the greatest solubility for the compound under consideration. The fabric strips were submerged in the solution for a few seconds. After stirring they were removed and placed in a fume cabinet with extraction fan. The samples were then left to dry for about a day.

7.1.3 Post treatment

The air-dried samples were transferred to an oven and dried at 60 °C to 80 °C for a few hours. Thereafter they were weighed again to determine the mass percentage add-on of the flame retardant.

7.2 Evaluation of fire performance

7.2.1 The bottom edge ignition test

The self-extinguishing times of the samples were tested according to the Underwriters Laboratory UL 94Vertical flame test - a common procedure specified commercially. For this test, five test specimens were evaluated and each specimen was exposed to two successive gas flame applications of 10 seconds each from the bottom edge. The chemicals used to estimate their flame retardant capabilities are listed in Table 11.

7.2.2 The Puddle flame retardancy test

Gouinlock, E.V *et al.* (1965) proposed a puddle test for evaluating the intrinsic flame resistance of dripping plastics. In this study, it comprised the placing a ca. one gram sample of the fabric on an inert surface. It was then ignited with a Bunsen burner held at a 45° angle. The flame length was ca. 25 mm flame and the ignition period 30 seconds. The burning behaviour as well as the mass loss of the sample was noted.

7.2.3 The Face ignition flame retardancy test

This test was set up as follows: A stretched fabric sample was attached to a vertical wire frame in order to keep it in place. A hole was then burned into the middle of the fabric by exposing it to a horizontal Bunsen flame. The flame was applied for ten seconds, to conform to the UL-94 flammability test. In each case the fabric was subjected to two flame applications. The fabric mass was measured before and after the flame treatments. The area of the burn-hole was also determined.

Table 11: Chemicals used to test for flame retardancy

Compound	**Other Name**
2-Furoic Acid	Furane-2-carboxylic acid
4-Hydroxybenzyl alcohol	p-Hydroxybenzyl alcohol
Benzoyl peroxide	Dibenzoyl peroxide
Diethyl phthalate	Phthalic acid diethyl ester
Fumaric acid	2-Butenedioic acid
Isophthalic acid	1,3-Benzenedicarboxylic acid
Benzyl benzoate	Benzyl benzoate
Benzoic acid	Isopropenyl benzene
Benzoin	2-Hydroxy-2-phenyl-acetophenone
Pentaerythritol	-
Phloroglucinol	1,3,5-trihydroxybenzene
Pyrogallic acid	Pyrogallol
Benzophenone	-
Benzyl phenyl ketone	2-Phenylacetophenone
Catechol	1,2-Benzenediol
Resorcinol	1,3-Benzenediol
Salicylic acid	o-Hydroxybenzoic acid
Terephthalic acid	1,4-Benzenedicarboxylic acid

7.2.4 Polymer dripping test

The experimental set-up to evaluate the flame retardancy of the treated polyester samples was relatively simple. Figure 2 shows the physical hardware involved for the sample-testing phase.

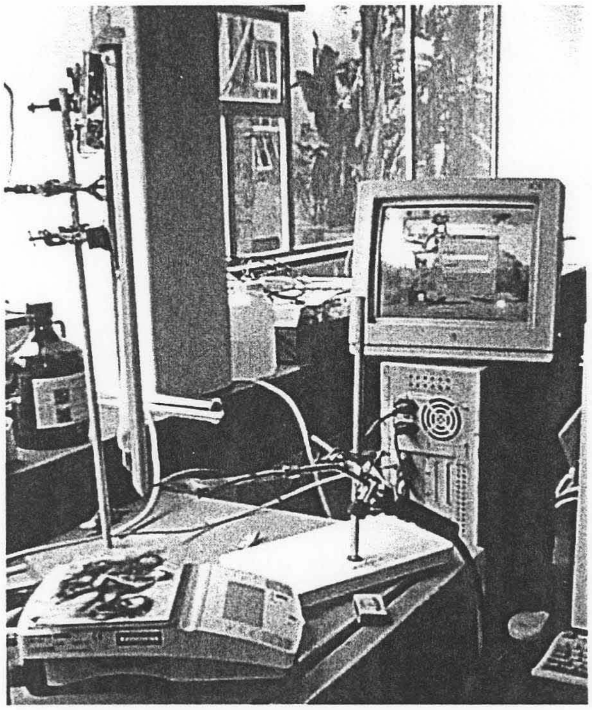


Figure 2: Experimental set-up for sample evaluation.

An OHAUS Explorer balance was used which was accurate to two decimal places and which stabilised within one second. The balance was capable of transmitting the date, time and mass to an RS232 port. It was captured on a personal computer using appropriate software.

The samples were evaluated by attaching a sample to a wire frame, which fitted into a rail to prevent the sample from rotating. The frame was attached a small 1.2V DC servomotor. A series of gears controlled the speed at which the sample was lowered into a fixed horizontal flame.

Figure 3 shows the flame and the test rig. The sample was lowered at a speed of approximately 1,8 ± 0,2 mm/s. A flat CADAC gas nozzle was used, which had almost the same width as the samples, to ensure good overall heating and melting.

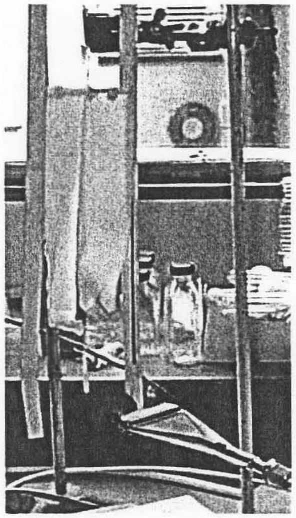


Figure 3: Sample being lowered into flame.

The molten polymer that dripped down was collected on an asbestos and stainless steel plate assembly on top of the balance load-plate. Figure 4 shows the LCD display of the balance during an actual run. The data was sampled once every second. Figure 5 shows the computer screen with the software while a sample was running.

Figure 4: Display of the balance during operation.

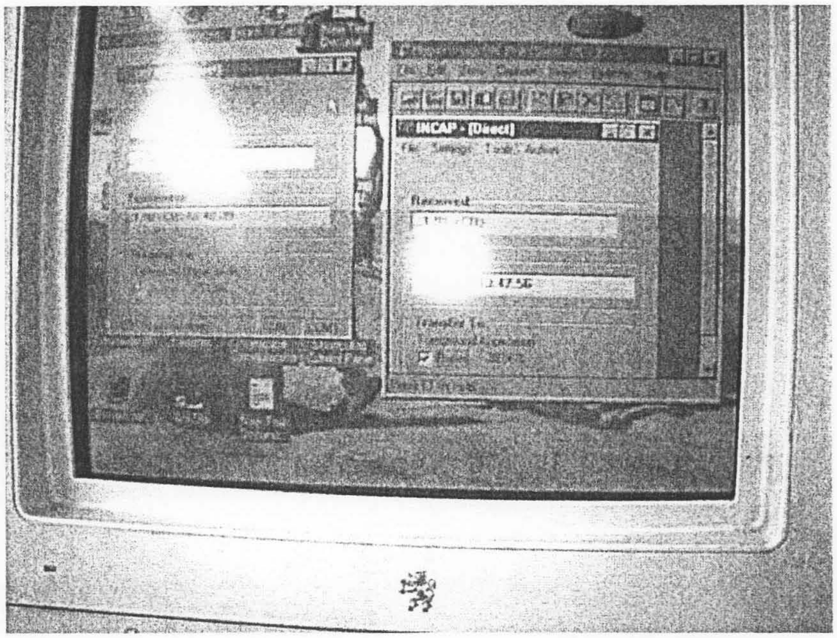


Figure 5: Computer screen showing the software in action.

Dripping was an erratic process. The rate of dripping was determined by fitting a straight line through the mass dripped versus time data. The average rate of dripping, for each treatment was obtained by averaging the data from 6 different samples.

7.3 Differential Scanning Calorimetry and Differential Thermal Analysis

When a substance undergoes a physical or chemical change, a corresponding change in enthalpy is usually observed. This forms the basis of the technique known as differential thermal analysis (DTA) in which the change is detected by measuring the enthalpy difference between the material under study and an inert reference standard. The sample is placed in a heating block and the temperature increased at a uniform rate, usually 5 to 20 °C.min^{-1}. The sample temperature is monitored by means of a thermocouple and compared with the temperature of the inert reference. An empty sample pan is usually used as reference. If the change is exothermic, the sample temperature will exceed the reference temperature, for a short period, but if the change is endothermic, the sample temperature will lag behind the reference temperature. This temperature difference are observed as peaks, e.g. for the melting endotherm associated with crystallisation. Another type of change can also be detected. Since the heat capacities of sample and reference are different, ΔT is never actually zero, and a change in heat capacity, such as that associated with glass transition, will cause a shift in the base line position. Other changes such as decomposition, crosslinking, and the existence of polymorphic forms can also be detected. DTA are usually of a qualitative nature, so the results have limited usefulness.

To overcome these drawbacks a modified method known as Differential Scanning Calorimetry (DCS) was developed. In this technique, the sample temperature is controlled, by varying the heat input, to be the same as that of the reference. The thermograms obtained look similar to those from a DTA, but actually represents the amount of energy supplied to the system. The area under the peaks is therefore proportional to the change in enthalpy that has occurred, e.g. heats of crystallisation, melting and reaction. Normally an empty sample pan is used as reference. Calibration of the instrument will allow the heat capacity of a sample to be calculated in a quantitative manner.

A Perkin-Elmer DSC9 and a Netzsch STA 409 simultaneous TG/DTA instrument were used to collect calorimetric data. Sample masses of approximately 10 to 15 mg were weighed into either aluminium or platinum pans. With the Perkin-Elmer instrument the atmosphere was oxygen supplied at a flow rate of approximately 20 ml/min. With the Netzsch instrument the atmosphere was nitrogen supplied at a flow rate of approximately 20 ml/min. In both cases the scan rate was set at 10°C per minute.

7.4 Thermogravimetric Analysis

In thermogravimetric analysis (TGA) the mass loss of a sample as a function of temperature is measured. The temperature is usually ramped at a constant scan rate. A Netzsch STA 409 simultaneous TG/DTA instrument was used to collect gravimetric data using the experimental conditions described above.

7.5 Rheometry

A Rheometric International parallel plate rheometer was used to determine melt viscosities. Sufficient fabric was placed on the hot lower plate of the instrument, and the temperature then cooled down from ca. 300°C at a rate of 10°C/min. The atmosphere used was nitrogen.

8. Results and discussion

8.1 The bottom edge ignition test

The untreated unsized polyester fabric burned out completely within 30 seconds. The vertical burn test results are presented in Appendix 12.2. The results show that excellent self-extinction times can however be achieved at relatively low add-on levels with the oxygenated hydrocarbon flame retardants. For example, dipentaerythritol requires an add-on of just above two percent to be effective as a flame retardant with a self-extinguishing time of approximately three seconds. Similar results were obtained when the fabric was treated with benzophenone and solid epoxy resin Epikote 1001 (oligomers of the diglycidyl ether of bisphenol A) from Shell Chemicals. The average self-extinguishing time for the latter was about one second, and for the former about three seconds. Interestingly, the add-on vs. self-extinction time curve for pentaerythritol starts to rise again above an add-on of about 20 percent, as shown in Figure 8.

These results imply that some of the oxygenated hydrocarbon flame retardants may be effective in an intermediate concentration range only. Such behaviour was previously also observed with hindered N-alkoxy amines (NOR-Hals) as flame retardants in polypropylene fabrics (Srinivasan *et al*, 1998).

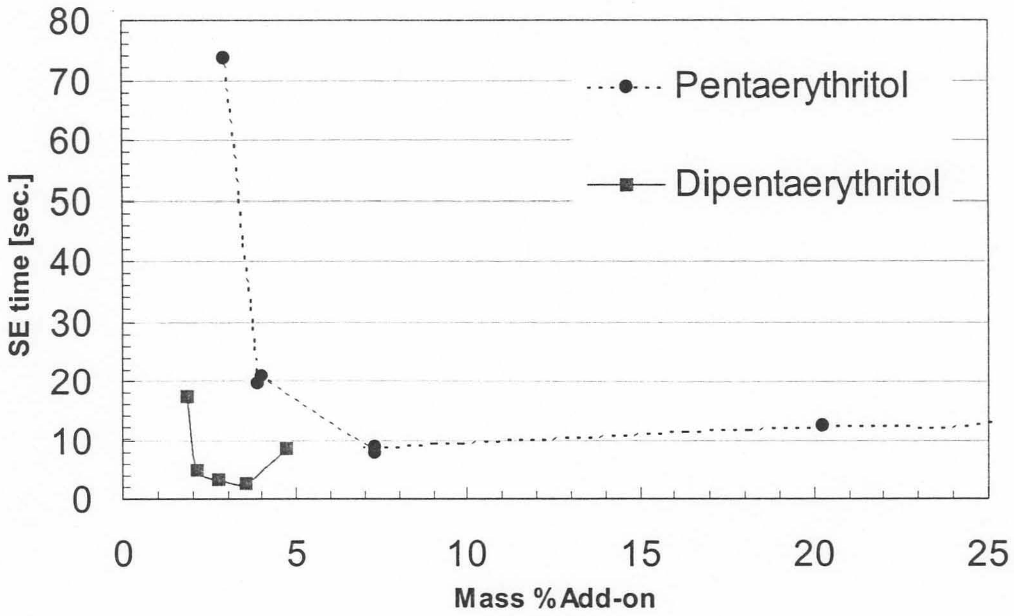


Figure 8: Self-extinguishing times versus add-on of Pentaerythritol and dipentaerythritol treated polyester fabric.

The same behaviour was also observed with phosphorous flame retardants and with phosphorous mineral filler synergism (Weil, 1992). Using vertical burn tests (NFPA 701), polypropylene fibre and films passed the test with the addition of 1% NOR-Hals, but when the concentration was raised to 10% the test was failed.

Figure 9 shows the self-extinguishing time and the mass percentage add-on for polyester fabric treated with Phloroglucinol and Inositol. The line represents the average values of the samples. The Phloroglucinol had an average self-extinguishing time of 1 second and the Inositol an average self-extinguishing time of 4 seconds.

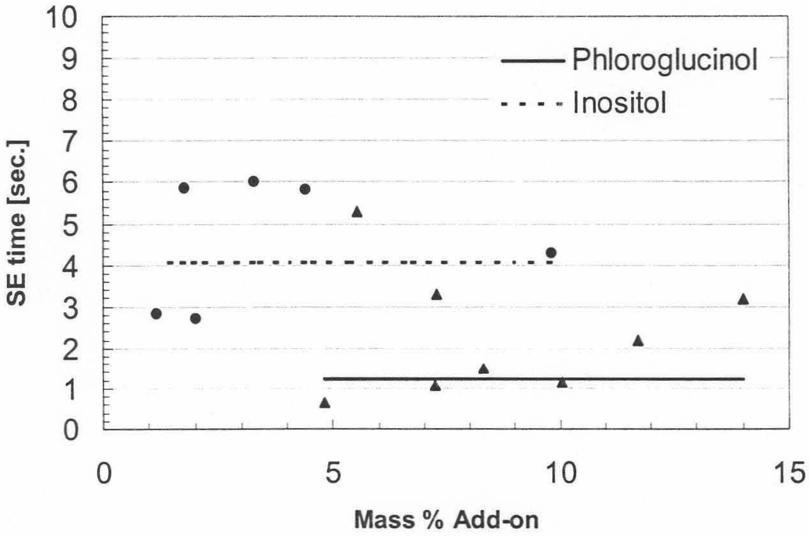


Figure 9: Self extinguishing times versus add-on of Phloroglucinol and Inositol treated polyester fabric.

Figure 10 shows the self-extinguishing time and the mass percentage add-on for polyester fabric treated with 2-Furoic acid, Epikote 1001 and Benzophenone.

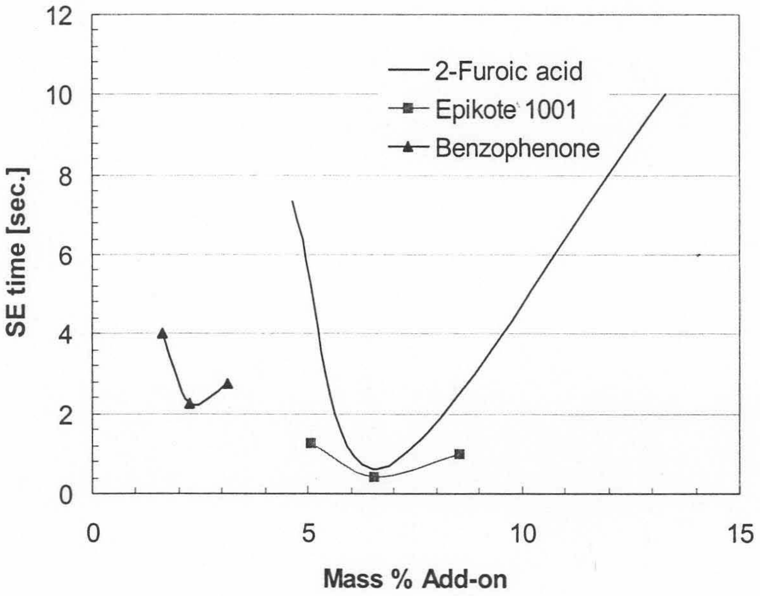


Figure 10: Self extinguishing times versus add-on of 2-Furoic acid, Epikote 1001 and Benzophenone treated polyester fabric.

From Figure 10 it is evident that some of the oxygenated hydrocarbon flame retardants exhibit the same behaviour, in that there is a parabolic relationship between the self extinguishing time and the mass percentage add-on. Benzophenone has an optimum mass percentage add-on at about 2 %, with a self-extinguishing time of 2 seconds. 2-Furoic acid and the Bisphenol A based resin Epikote 1001 both display almost the same self extinguishing time of less than one second at an mass percentage add-on level of 7.5 %. Figure 11 shows the results obtained with Benzyl phenyl ketone, Maltol and Benzoic acid. These oxygenated hydrocarbon compounds exhibit similar parabolic behaviour as Figure 12 show for Benzoyl benzoate and Diethylphthalate.

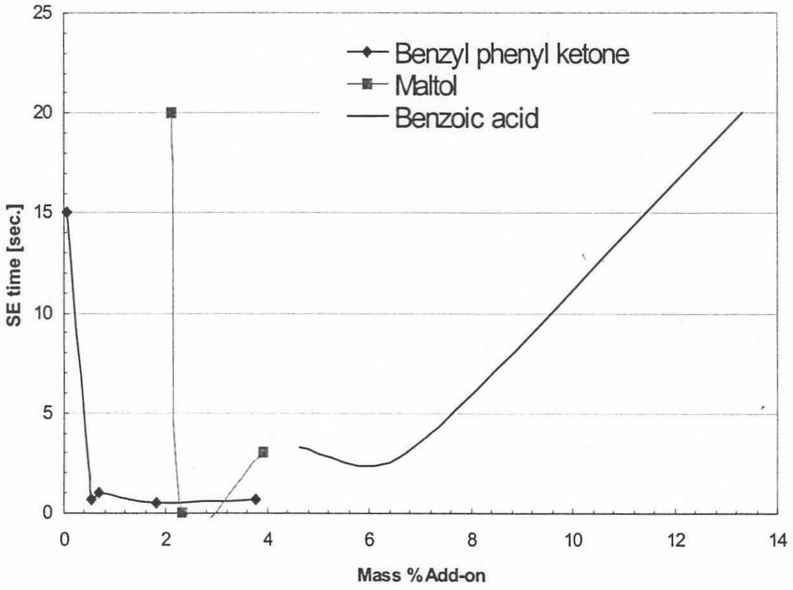


Figure 11: Self extinguishing times versus add-on of Benzyl phenyl ketone, Maltol and Benzoic acid treated polyester fabric.

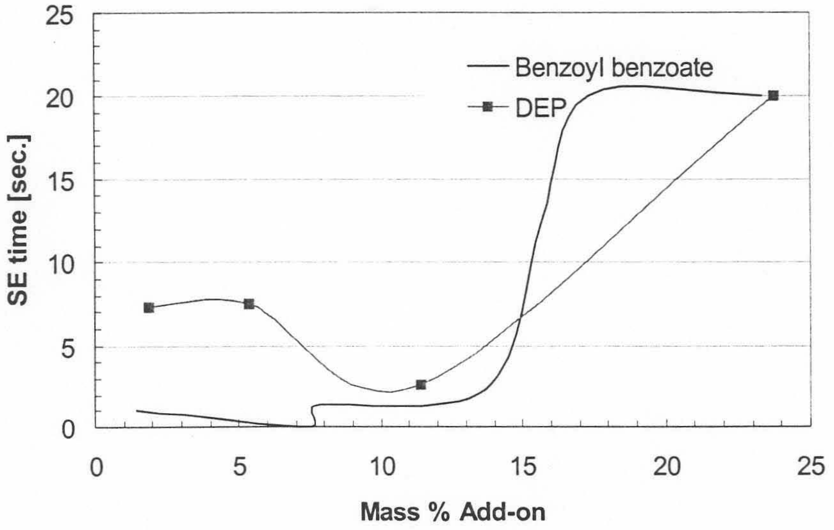


Figure 12: Self extinguishing times versus add-on of Benzoyl benzoate and Diethylphthalate treated polyester fabric.

8.2 The Puddle flame retardancy test

The purpose of this test was to determine whether the fabric ignited and burned in a situation where melt dripping was prevented Unfortunately none of the treated samples tested, ignited. However, the untreated fabric burned for approximately 3 seconds. Puddle test results are compiled in Table 12. These reported values represent average values measured for the samples tested.

Table 12 : Results obtained from the Puddle Test

Additive	**Add-on [%]**	**Percentage Mass loss**
Pure PES	-	11.5
Pentaerythritol	1.1	13.1
Dipentaerythritol	0.8	19.5
Phloroglucinol	3.2	13.7
Isophthalic acid	1.9	13.3

Surprisingly, as shown in Table 12, the pure polyester fabric showed a lower mass loss than the treated fabrics. The highest mass loss was observed with Dipentaerythritol as additive. During the vertical burn test the dipentaerythritol treated samples displayed fast melt dripping. These results suggest that the additive enhances the polymer solid to gas conversion.

8.3 The Face ignition flammability test

Table 13 shows the results obtained with the Face Ignition test on untreated fabric. The average values for the treated fabrics are shown in Table 14. Figure 13 to 17 show the fabric samples after the Face Ignition test.

Table 13 : Results of the Face Ignition Test for Pure Polyester fabric.

Sample	**Percentage mass Loss***	**Area of Hole (mm^2)**
A	1.8	8931
B	1.3	5379
C	1.4	Consumed completely
D	3.4	3183

* Corresponds to the dripped mass collected below the sample. Mass consumed by combustion was assumed negligible.

It is observed during this test that the stretched fabric first contracts at the point where the flame impinges before melting starts. Then a hole starts to form that is surrounded by a ridge of molten polymer. The hole expands owing to an apparent outward pulling force. This force might arise from build in stress caused by the oriented polymer chains in the fibres. An alternative explanation involves the surface tension forces in the molten polymer bead.

Table 14: Average results from the Face Ignition Tests.

Additive	**Percentage Mass add-on**	**Percentage mass loss**	**Hole Area [mm^2]**
Pure PES	-	2.0	>5800
Pentaerythritol	1.1	0.5	3000
Dipentaerythritol	0.8	0.6	6500
Phloroglucinol	3.2	0.4	5700
Isophthalic acid	1.9	1.5	6900

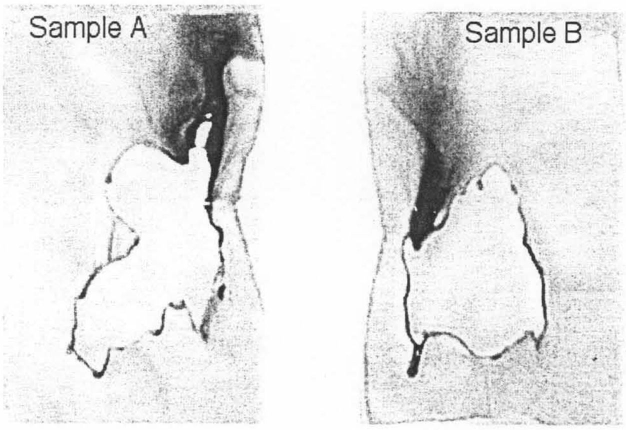


Figure 13: Untreated Polyester fabric samples after the Face Ignition test was applied.

Figure 13 shows some results after untreated samples have undergone the Face Ignition test. The black residue is char residue and/or soot from the combustion process. It deposited on the colder surfaces of the fabric during the burning process. It is evident that the shape of the burn hole is neither uniform nor symmetric in shape. The damage to the fabric is inclined towards one side of the mounted sample. Molten polymer drops can be clearly seen on the sides of the hole, as well as a downward flow of polymer melt. The area of the hole in the untreated polyester fabric is also variable ranging from the smallest to the largest of all the samples tested.

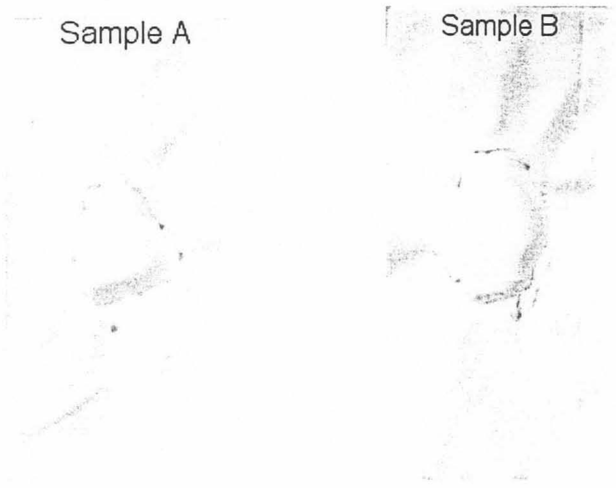


Figure 14: Polyester samples treated with Pentaerythritol.

In the case of the treated samples, there is less evidence of charring and the holes burned into the fabric have a more rounded shape. In addition, most of the samples did not ignite at all. The Pentaerythritol treated polyester samples from Figure 14 shows no black carbon residue whatsoever. Thus there was no discernable combustion of molten polymer during the test. In this case the hole in the fabric formed quickly and the molten polymer flowed away rapidly. On the fabric samples treated with Dipentaerythritol shown in Figure 15 there is almost no evidence of burning of the molten polymer melt. The Dipentaerythritol samples melted and burned slightly slower than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a fast rate.

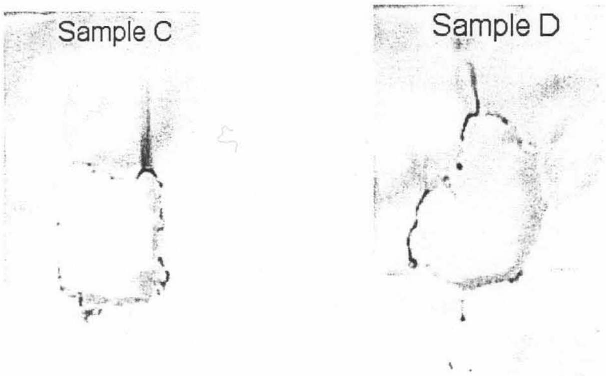


Figure 15: Polyester samples treated with Dipentaerythritol

On the fabric samples treated with Phloroglucinol shown in Figure 16 there is slight evidence of burning of the molten polymer melt. The Phloroglucinol samples melted and burned slightly faster than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a very fast rate as can be seen by the streaks of drops on the solid fabric.

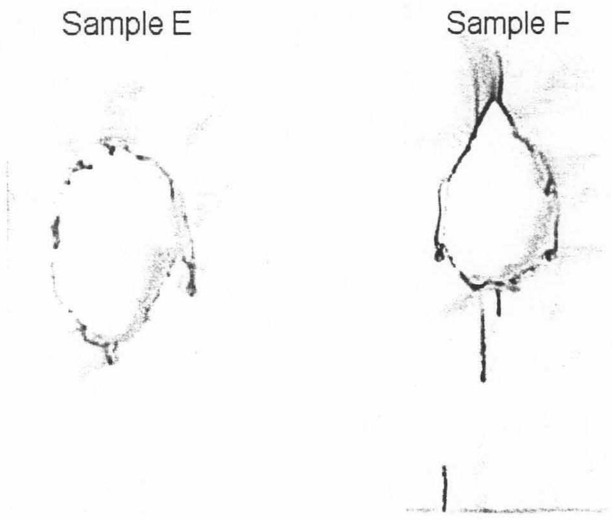

Sample E
Sample F

Figure 16: Polyester samples treated with Phloroglucinol.

On the fabric samples treated with Isophthalic acid shown in Figure 17 there is no evidence of burning of the molten polymer melt. The Isophthalic acid samples melted and burned slightly slower than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a moderately fast rate.

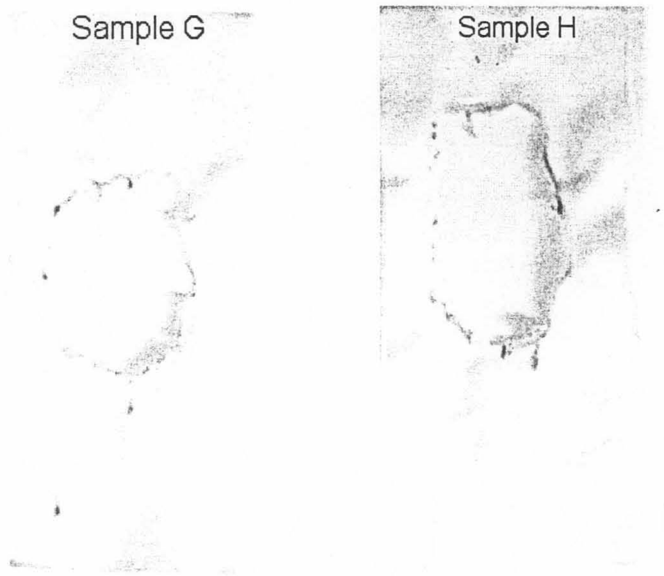

Sample G
Sample H

Figure 17: Polyester samples treated with Isophthalic acid

8.4 Polymer dripping test

Figure 18 depicts the results from a typical drip test. The average values obtained for the polymer drip test are shown in Table 15. Except for isophthalic acid, the presence of additives led to an increased tendency to drip. Pentaerythritol treated samples dripped at the fastest rate, almost 70 % faster than the observed rate for the untreated sample.

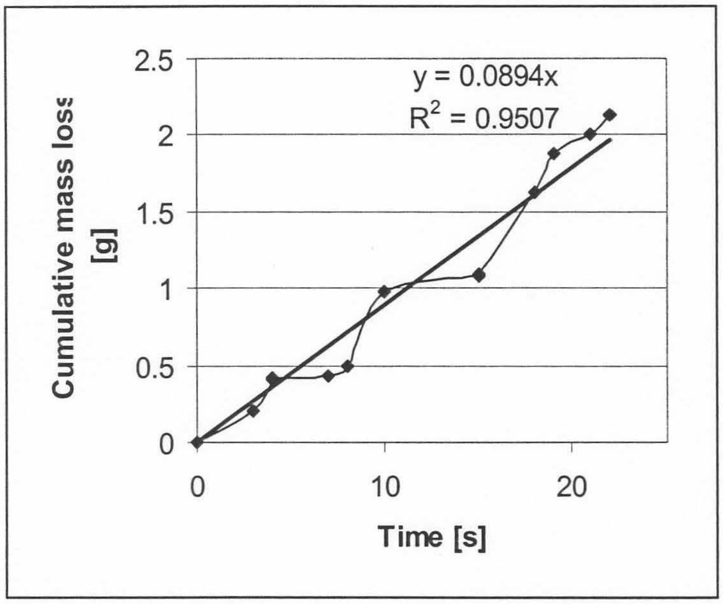


Figure 18: Typical drip test result for Pentaerythritol.

Table 15 : Results obtained from the polymer dripping tests.

Additive	Correlation coefficient, R	Rate of dripping [g/s]
Untreated	0.9289	0.077
Pentaerythritol	0.9433	0.130
Dipentaerythritol	0.9044	0.086
Phloroglucinol	0.8939	0.081
Isophthalic acid	0.8787	0.070

8.5 Differential Scanning Calorimetry and Differential Thermal Analysis

The results obtained for Differential Scanning Calorimetry are shown in Figure 19 for the untreated and the treated polyester fabrics. It is clear that the additives affect the shape and position of the melting endotherm peak for the flame retarded polymer. Interestingly, the additives shift the peak temperature to higher values. The observed heat of melting was approximately 52 kJ/g for all the samples.

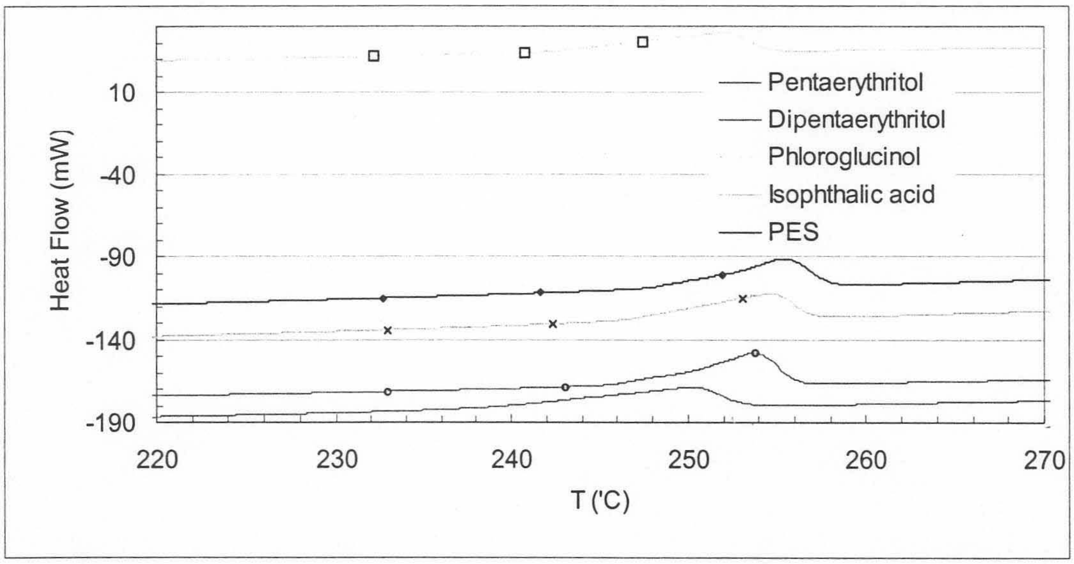


Figure 19: DSC curve of PES and treated PES samples.
Endothermic up, scan-rate of 10°C/min in oxygen atmosphere.

The results for the Differential Thermal Analysis (see Figure 20) confirm the results obtained with DSC. The melting onset-temperatures observed in the DTA were higher for treated samples than for the pure PES. The reasons for these observations are not currently understood.

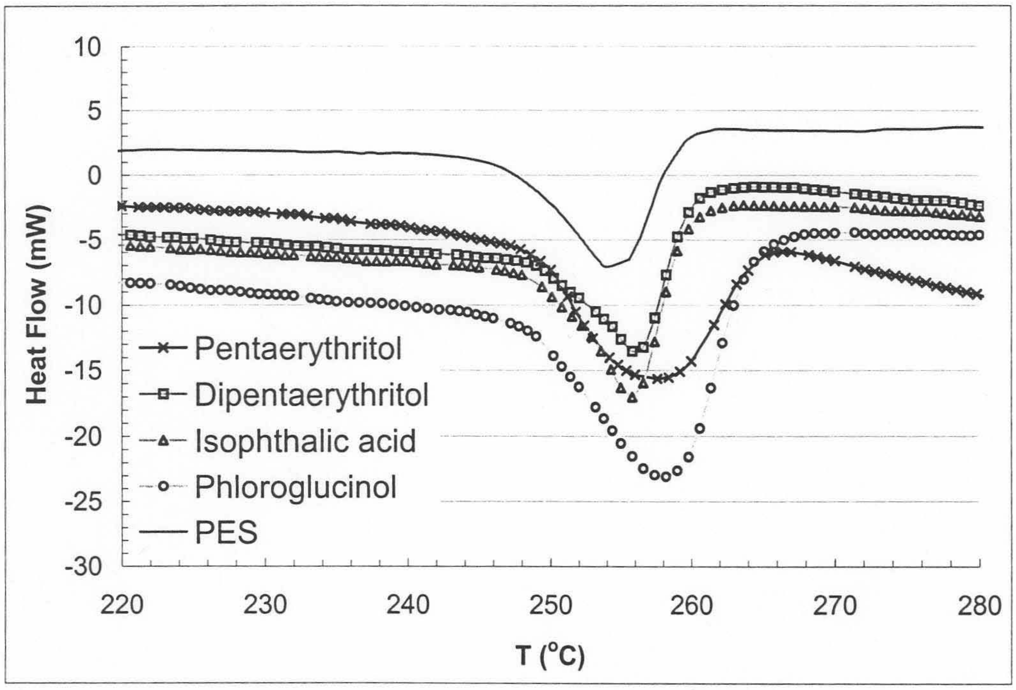


Figure 20: DTA curve of PES and treated PES samples. Endothermic down, scan-rate of 10°C/min in nitrogen atmosphere.

8.6 Thermogravimetric Analysis

The results obtained with Thermogravimetric Analysis are shown in Figure 21. All samples show similar rapid volatilisation, with a mass loss of ca. 80% between 400°C and 420°C. Further mass loss occurs at a slower rate up to about 580°C and is complete for the untreated polyester fabric. The additives appear to affect this second degradation step. The presence of the additives also appear to reduce the rate of mass loss, and also results in higher levels of char residue. For example, the Isophthalic acid treated sample provided the best performance with respect to char formation, and Phloroglucinol treated samples degraded almost completely.

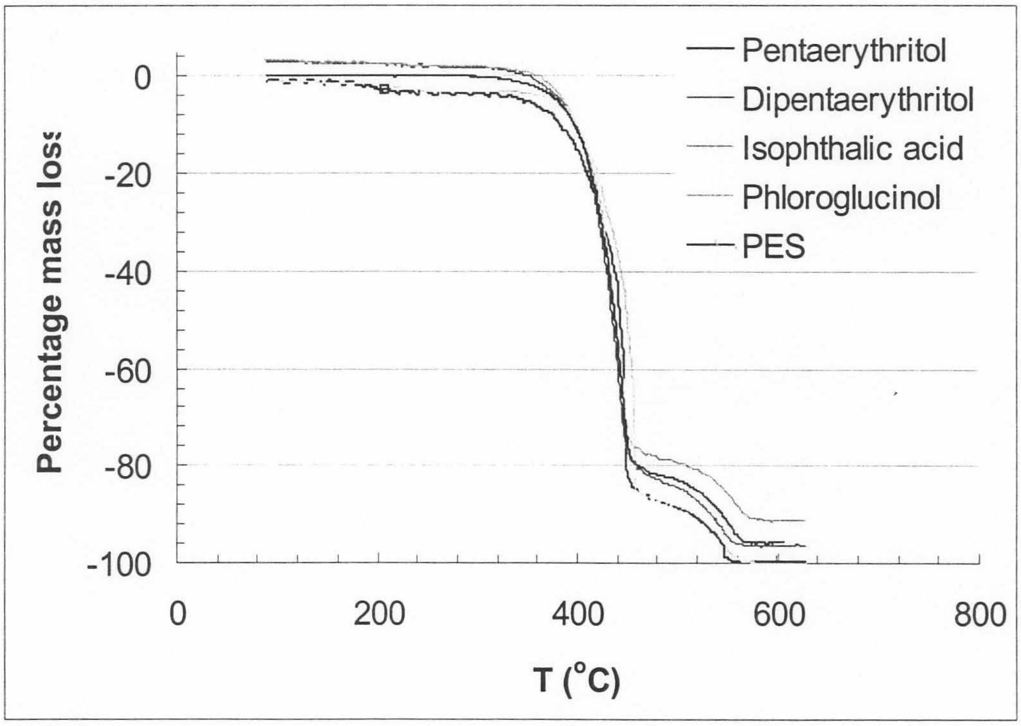


Figure 21: TGA results for PES and treated PES samples.

8.7 Rheometry

The loss modulus for the treated and untreated fabrics is shown in Figure 22.

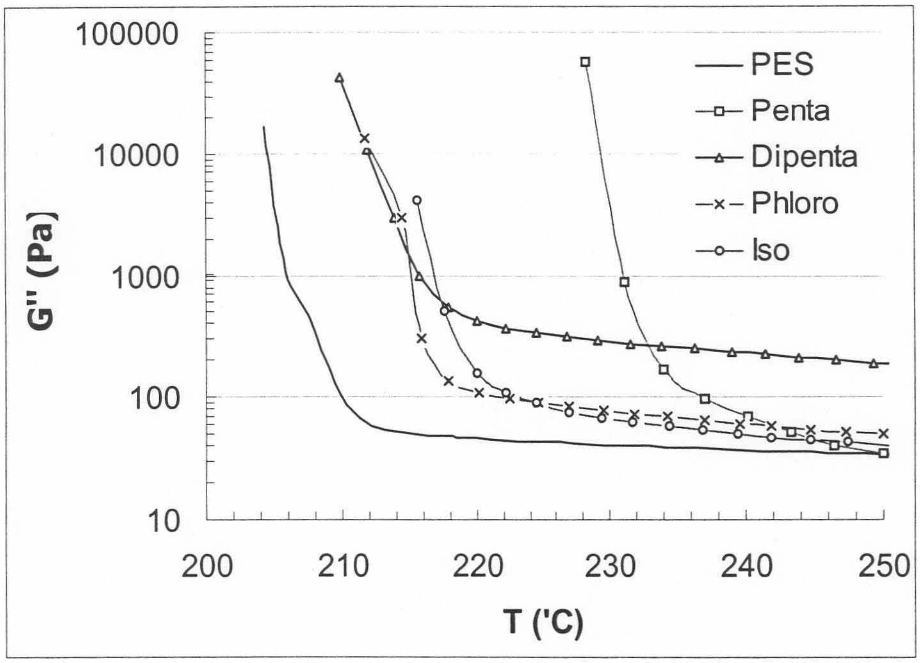


Figure 22: Loss modulus from parallel plate rheometry of PES and PES treated samples.

G*(ω) is the frequency dependant complex dynamic modulus consisting of a real and complex part. G'(ω) is the real part that is in phase with the strain and is called the storage modulus. G''(ω) is the complex part called the loss modulus, defined as the ratio of the component 90° out of phase with the stress to the stress itself.

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

G'(ω) therefore measures the amount of energy stored and G''(ω) the amount of energy dissipated by the material.

It is therefore possible to say that in Figure 22 the sample treated with Pentaerythritol, which shows the highest loss modulus, is altered in such a way that a lot of energy is dissipated and very little recovered. The untreated fabric sample exhibits the lowest loss modulus.

Figure 23 shows the storage modulus of the storage modulus of the treated and untreated fabric samples. It strengthens the results from the loss modulus, as can be expected.

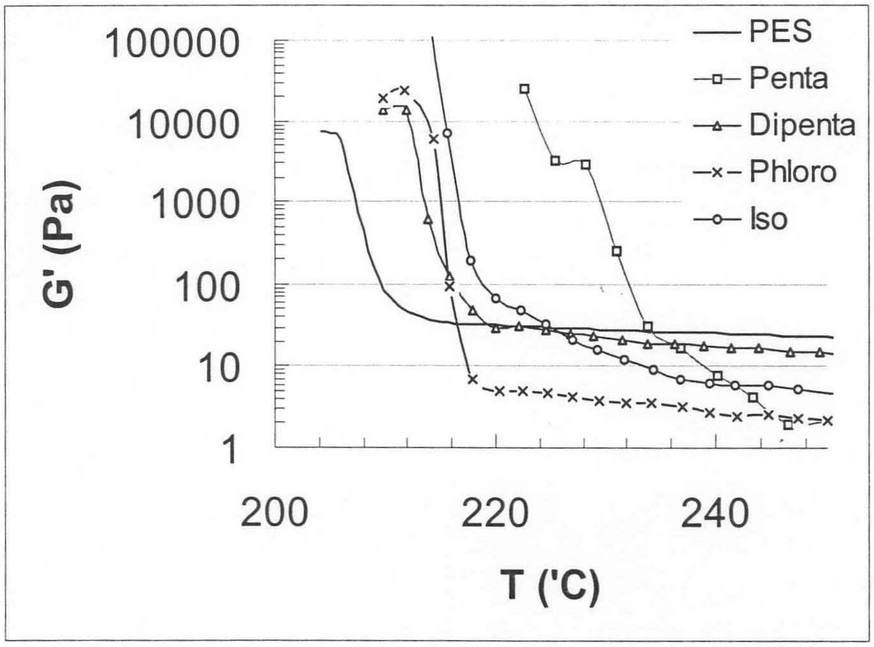


Figure 23: Storage modulus parallel plate rheometry of PES and PES treated samples.

Unfortunately, there was no clear insight into the mechanism of the oxygenated hydrocarbon flame retardants, obtained from the viscosity analysis (see Figure 24). It could however now be said that the viscosity plays not the only role in the mechanism, but is only part of a bigger picture. There was no significant increase in viscosity over the melt temperature range, so the additives did not contribute a temperature dependent viscosity alteration.

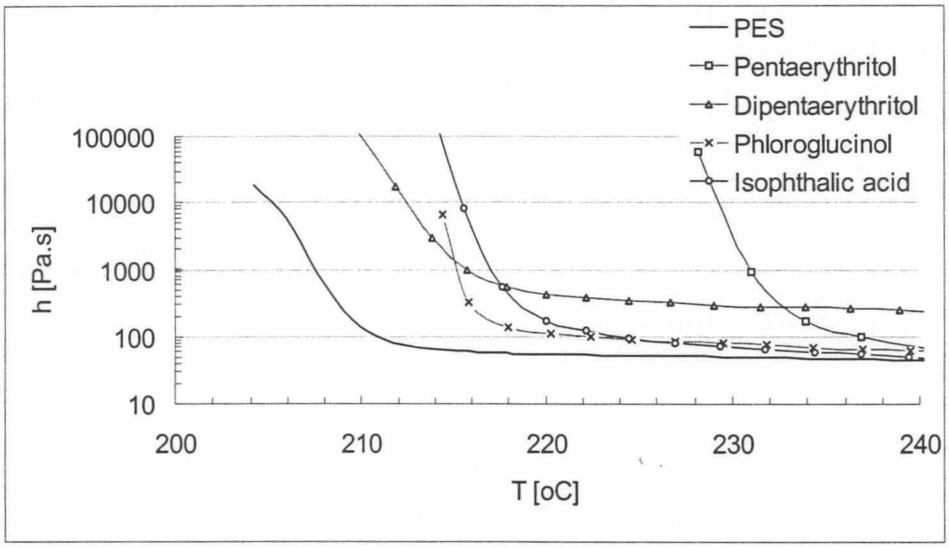


Figure 24: Viscosity response parallel plate rheometry of PES and PES treated samples.

Parallel-plate rheometry produced a surprising result. According to the data of Figure 24, the additives tend to increase melt viscosity in the temperature range of 220°C to 240°C rather than inducing the expected reduction. Unfortunately, it was not possible to measure the viscosity at higher temperatures more relevant to the flame retardancy process e.g. in the region of 400°C.

9. Proposed flame retardancy model

The results presented above show that the organic oxygen containing hydrocarbons can render the fabric flame retarded in terms of vertical flame test. Any physical model that is proposed to explain their action will require mass and energy balances that must consider the following effects:

- The effect of elongational viscosity and surface tension effects on the propensity for melt dripping; and
- The effect of the built in stresses on fibre pullback.

For the flame retardant to be effective it will have to fulfil in one or more of the following criteria:

- Providing a thermal heat sink effect to reduce the effective surface temperature of the polymer;
- Reduce the viscosity of the molten polymer in order to accelerate the drip rate M_{drip};
- Lower the surface tension in the polymer melt so as to lower the adhesion forces and accelerate drip rate;
- Decrease the rate of volatilisation of polymer degradation products;
- Change the colour of the molten polymer in order to increase the radiation heat loss; and
- Decrease the flammability of the volatile decomposition products.

As far as the elongational viscosity is concerned, Figure 25 shows a possible model that could be used.

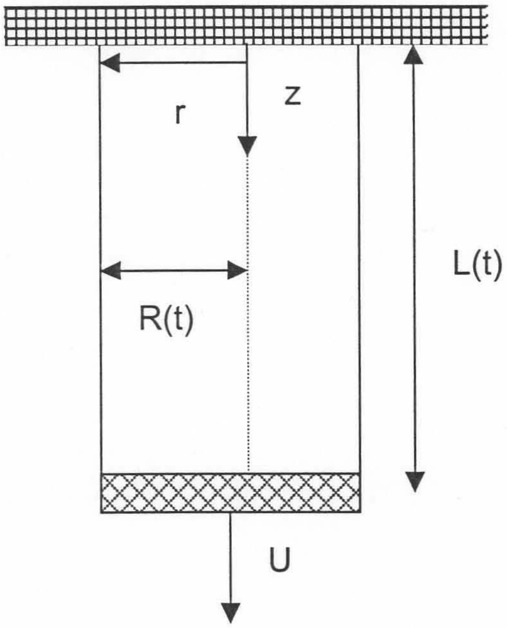


Figure 25: Schematic diagram for the model of elongational viscosity.

In this model a mass of molten polymer is drawn down by gravity forces (F=m.g) at a speed U. Therefore, the dimensions change with time, and length (L) as well as sample radius (R) has to expressed as L(t) and R(t).

Surface tension is caused by an imbalance of forces that act at the interface between the polymer melt and the air. These forces are attractive in nature and the imbalance occurs because there are only two dimensions present in any surface. The imbalance of forces tends inwards for liquids and solids, so the attractive forces in the polymer melt tend to draw the molecules on the surface to the inside of the liquid. This process causes a skin to develop that resists change, the skin being the surface tension. This is the basis for the thermodynamic principle that new surfaces will not form spontaneously, but require an input of work or a positive Gibbs Free Energy change.

Consider a bead of molten polymer at the bottom edge of a solid piece of fabric. Tate's law states that there must be a balance of forces. The force that pulls the drop downwards is the gravity force, and the upward force is the surface tension at the circumference of the drop. At the point of incipient detachment, the forces are in equilibrium. At this point the equation $mg = 2r\gamma$ holds where m is the mass of the drop in kilograms, r is the radius of the drop in meter, g is the gravitational constant in kg.m/s^2 and γ the surface tension in N/m.

The rate of dripping also depends on the surface tension of the liquid. In the case of polymer melts, there is a further complication. Polymer melts exhibit resistance to extensional flows. Enhanced polymer dripping therefore requires an effective reduction in combination of surface tension and elongational viscosity effects.

When the fibres are spun, they are stretched according to a specific draw-down ratio that can be as high as 10 to 1. This enhances the strength and crystallinity of the fibre. This stretching orients the polymer chains in the direction of the fibre axis. This unnatural conformation of the polymer chains is locked in place by subsequent recrystallisation. When the fibre melts the polymer chains become mobile and reorient themselves into random coil conformations. This process sets up a retractive force in the fibre. This retractive force of the fibre was clearly demonstrated in both the bottom edge and face ignition tests.

10. Conclusions and Recommendations

In the study of the diverse chemical and physical mechanisms which may be used to explain the burning properties of flame retarded polymer systems, molten polymer dripping and sample ignition plays an important role. Dripping is characteristic of most thermoplastic polymers. It is utilised to achieve a low level of flame retardancy in polystyrene, polypropylene and polyester. For example, in polystyrene foam aliphatic bromine compounds in combination with a free radical generating systems are extremely effective.

In most of the standard tests used to evaluate fire retardance of fabrics, it is allowed for molten polymer material to drip away from the flame zone. In the most common laboratory tests, a vertically or horizontally mounted sample is ignited with a Bunsen burner, and the self-extinguishing time or burning rate determined after removal of the flame. It may be argued that dripping molten polymer poses a hazard in the practical application of flame retardant systems. In particular this would be true if the ignited sample produces flaming drips that are capable of spreading flames beyond the initial site of ignition. However the UL 94 flammability test of the Underwriters Laboratory make provision for flaming drips for low level flame retardancy ratings. They specify that a piece of cotton placed beneath the burning sample should not ignite. In some cases, dripping may even detach the flame front from the burning specimen, mechanically extinguishing the burning sample. In any case, dripping behaviour will remove heat from the flame front both during and after ignition. This can result in inadequate ignition or in a retardation of the burning process and can ultimately cause spontaneous extinction of the flame.

Visual inspection during the flame retardancy test conducted with treated samples showed that in most cases dripping was more profuse than for the untreated samples. Yet, the melt viscosity measurements suggest that the additives actually increased the polymer melt viscosity. It is therefore speculated that reductions in surface tensions may have contributed to the increased rate of dripping. In the actual fire test, elongational viscosity is more relevant than the shear viscosity that was measured. It could be that the additives caused a reduction in the elongational viscosity, but this could not be experimentally confirmed.
The dripping rate was up to 80 % faster for the treated samples than for the untreated samples. Dripping must therefore play an important role in the self-extinguishing properties conferred by the additives studies.

Oxygenated hydrocarbon compounds have utility as flame retardants for unsized polyester fabrics. These compounds may be regular food-type additives such as Pentaerythritol, are therefore inexpensive, safe, easy to use, and apply. They render such fabrics flame retarded in terms of conventional vertical flame tests. The flame retardancy effect shows a parabolic dependence on the add-on level. This implies an optimum dosage level beyond which flammability increases again.

It is postulated that the mechanism involves a combination of enhanced melt dripping and fibre shrinkage. These effects result in efficient heat removal from the burning sample allowing it to self-extinguish. Melt viscosity measurements suggest that the increased rate of dripping can not be ascribed to a viscosity reduction alone. It is speculated that melt surface tension effects might be responsible instead.

It is recommended that a mathematical model be developed to explain the flame retardancy mechanisms described above. It is expected that such a model should proved an improved understanding on the relative importance of the different modes of action for this flame retardant system. For example, the relationship between viscosity and surface tension, and their impact on a mass and energy balance.

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12. Appendix

12.1 Chemical and Physical properties of flame retardants

12.2 Results from UL94 Vertical Burn Test

12.3 Test standard BS 5867: Part 2: 1980

12.1 Chemical and Physical properties of flame retardants

Compound	Other Name	CAS Code	Molecular formula	Molecular weight	Partition Coefficient [Log (K_{ow})]
2-Furoic Acid	Furane-2-carboxylic acid	88-14-2	$C_5H_4O_3$	112.085	0.64
4-Hydroxybenzyl alcohol	p-Hydroxybenzyl alcohol	623-05-2	$C_7H_8O_2$	124.1393	0.25
Benzoyl peroxide	Dibenzoyl peroxide	94-36-0	$C_{14}H_{10}O_4$	242.23	-
Diethyl phthalate	Phthalic acid diethyl ester	84-66-2	$C_{12}H_{14}O_4$	222.2408	2.35
Fumaric acid	2-Butenedioic acid	110-17-8	$C_4H_4O_4$	116.0734	-0.36
Isophthalic acid	1,3-Benzenedicarboxylic acid	121-91-5	$C_8H_6O_4$	166.1332	1.15
Benzyl benzoate	Benzyl benzoate	120-51-4	$C_{14}H_{12}O_2$	212.2481	3.97
Benzoic acid	Isopropenyl benzene	98-83-9	C_9H_{10}	118.1784	2.84
Benzoin	2-Hydroxy-2-phenyl-acetophenone	119-53-9	$C_{14}H_{12}O_2$	212.25	2.53
Pentaerythritol	-	115-77-5	$C_5H_{12}O_4$	136.15	-1.7
Phloroglucinol	1,3,5-trihydroxybenzene	108-73-6	$C_6H_6O_3$	126.1118	0.87

Pyrogallic acid	Pyrogallol	87-66-1	$C_6H_6O_3$	126.1118	0.87
Benzophenone	-	119-61-9	$C_{13}H_{10}O$	182.2218	3.58
Benzyl phenyl ketone	2-Phenylacetophenone	451-40-1	$C_{14}H_{12}O$	196.2487	3.19
Catechol	1,2-Benzenediol	120-80-9	$C_6H_6O_2$	110.1124	1.01
Resorcinol	1,3-Benzenediol	108-46-3	$C_6H_6O_2$	110.1124	1.26
Salicylic acid	o-Hydroxybenzoic acid	69-72-7	$C_7H_6O_3$	138.1228	1.2
Terephthalic acid	1,4-Benzenedicarboxylic acid	100-21-0	$C_8H_6O_4$	166.1332	1.15

Compound	**Molar Refractivity Refractivity [cm^3/mol]**	**Henry Constant**	**Melting point [°C]**	**NBP [K]**	**Freezing Point [K]**
2-Furoic Acid	24.61	5.354	129-130	504.82	361.96
4-Hydroxybenzyl alcohol	34.36	9.034	118-122	533.75	367.11
Benzoyl peroxide	-	3.839	104-106	619.37	384.54
Diethyl phthalate	59.37	4.792	-3	577.11	348.1
Fumaric acid	24.27	10.257	299-300	558.42	450.46
Isophthalic acid	38.90	10.049	341-343	624.54	539.56
Benzyl benzoate	62.02	3.941	18-20	591.06	342.21
Benzoic acid	40.06	0.754	-24	435.73	201.39
Benzoin	62.91	8.927	135-137	622.4	395.63
Pentaerythritol	30.72	7.777	255-259	594.02	391.31
Phloroglucinol	30.72	12.605	218-221	554.37	505.94
Pyrogallic acid	30.72	12.605	133-134	554.37	505.94
Benzophenone	56.65	4.1	48-49	572.67	338.54

Benzyl phenyl ketone	60.96	4.489	55-56.5	586.93	349.81
Catechol	28.91	8.623	104-106	502.87	394.22
Resorcinol	28.91	8.623	110-112	502.87	394.22
Salicylic acid	33.90	9.336	158-160	571.2	466.89
Terephthalic acid	38.90	10.049	> 300	624.54	539.56

Benzyl phenyl ketone	207.44	> 110	-	489	489
Catechol	117.52	137	-	343	343
Resorcinol	117.52	-	-	1465	1465
Salicylic acid	138.36	-	-	1476	1476
Terephthalic acid	159.2	-	-	1547	1547

12.2 Results from flammability tests

Functional group	Organic compound name	Carrier material	Add-on [%]	SE time* [s]
Alcohols	Pentaerythritol	Water	7	7
	Di-pentaerythritol	Water	3	3
	m-Inositol	Water	5	2
Aldehydes and ketones	Benzyl phenyl ketone	Ethanol	2	1
	Benzophenone	Acetone	2	3
Anhydrides	Phthalic anhydride	Ethanol	1	3
Carboxylic acids	2-Furoic acid	Ethanol	7	1
	Terephthalic acid	Chloroform	2	1
	Isophthalic acid	Ethanol	2	0
	Adipic acid	Ethanol	2	0
	Oxalic acid	Water	1	6
Epoxies	Epikote 1001	Acetone	5	2
	Epikote 3004	Acetone	17	1
	Epikote 3009	Acetone	16	3
Esters	Benzyl benzoate	Ethanol	2	1
	Diethyl phthalate	Ethanol	6	12
Peroxides	Benzoyl peroxide	Ethanol	1	11
Phenols	Pyrogallol	Water	3	1
	Catechol	Chloroform	≈ 1	10
	Resorcinol	Water	2	3
	Phloroglucinol	Ethanol	7	1
Combinations of functional groups	4-Hydroxybenzoic acid ethyl ester	Ethanol	15	0
	Maltol	Water	2,5	0
	Vanillin	Water	5	2
	Salicylic acid	Ethanol	10	0
	Benzoin	Ethanol	1	5
	Pyrogallic acid	Ethanol	3	0

12.3 Test standard BS 5867: Part 2: 1980

BS 5867 : Part 2 : 1980

Spec for fabrics for curtains and drapes

Part 2 : Flammability requirements

Sampling

From each batch at least every 5000m.

Test procedures

The side that has the fastest flame spread will be tested.

BS 5438 Test 3 will be used:

3 samples in the machine direction and 3 samples in the cross direction using a 10 second flame application time.

Taking the two vertical trip threads as representing one trip thread in each of at least four specimens not more than one trip thread (i.e. 300mm or either or both of the vertical trip thread) shall be severed.
In either of the 2 remaining specimens not more than 2 trip threads (i.e. 300mm and 600mm, or 300mm and either or both of the vertical trip threads) are severed on any specimen the fabric shall be deemed not to comply with the requirements for Type A of this British Standard.

No part of any hole nor any part of the lowest boundary of any flame shall reach the upper edge or either vertical edge of any specimen. If it does a further 6 specimens shall be tested and all 6 must comply.

Cleaning requirements.

All fabrics shall be tested both before and after the cleaning procedure i.e. 50 cycles of the appropriate hospital laundry procedure specified in BS 5651, except that for the hospital laundry procedure (normal) water of zero hardness shall be used and IEC test detergent type 1 but without perborate, shall be used in place of soap and sodium metasilicate.

Test 2

Template of 170mm x 220mm with four holes, one in each corner 10mm from each side. Rectangular test flame but with four pins only.

Test 3

Template of 670mm x 170 mm, two rows of five holes 10mm form each edge and spaced at 10mm, 210mm, 410mm, 610mm and 660mm from bottom edge. Rectangular test flame but fitted with two vertical rows of five pins spaced 200mm, 400mm, 600mm, 650mm above the bottom row of pins.

Combined mean afterflame and afterglow times must not exceed 2.5s

BS 5438 : 1989

Flammability of textile fabrics when subjected to a small igniting flame applied to the face or bottom edge of vertically oriented specimens.

Condition test specimens at least 24h in an atmosphere having a temperature of 20 ± 5 ° C and H = 65 ± 5 %. If testing in not carried out immediately after conditioning replace the conditioned test specimens within 2 min of removing it from either the conditioning atmosphere or the sealed container.

Testing atmosphere

T = 15 ° C - 30 ° C

H = 55 ± 20 %

Air movement less than 0.2 m/s

Apparatus

Gas burner capable of being fixed vertically, horizontally or inclined at 30 °

Tip of burner 50mm from specimen

Set burner in vertical position. Adjust flame height to 40 ± 2 mm. Return burner to horizontal position and check horizontal flame reach of 23 ± 2 mm.

Preheat the burner for 2 min. before testing.

Types of tests

Minimum ignition time: face ignition.

Specimen: 200mm x 80mm

Ignite for 1s at the bottom face of specimen.

If not ignite repeat with flame application times of 2,3,4,6,8,10,15,20s until the shortest of these times, if any, is found that causes a test specimen to ignite.

Minimum ignition time: Bottom edge ignition.

Specimen: 200mm x 80mm

Ignite for 1s at the bottom edge of specimen.

If not ignite repeat with flame application times of 2,3,4,6,8,10,15,20s until the shortest of these times, if any, is found that causes a test specimen to ignite.

Limited flame spread: Face ignition.

Specimen: 200mm x 160mm

Ignite for 10s at the bottom face of specimen.

Note the following:

a) Duration of flaming.

b) Duration of afterglow.
c) Occurrence of any flaming debris
d) Whether, for any flame, any part of its lowest boundary reaches the upper edge or one of the vertical edges of the specimen.
e) Whether a hole develops which extends to the upper edge or one of the vertical edges of the specimen
f) Whether glowing reaches the upper edge or one of the vertical edges of the specimen.
g) Maximum extent of any holes in the horizontal or vertical direction whichever is the greatest.
h) Maximum damaged length measured
i) Which face of the fabric was subjected to the flame test.

<u>Limited flame spread: Bottom edge ignition.</u>

Specimen: 200mm x 160mm

Ignite for 10s at the bottom edge of specimen.

Note the following:

a) Duration of flaming.
b) Duration of afterglow.
c) Occurrence of any flaming debris
d) Whether, for any flame, any part of its lowest boundary reaches the upper edge or one of the vertical edges of the specimen.
e) Whether a hole develops which extends to the upper edge or one of the vertical edges of the specimen
f) Whether glowing reaches the upper edge or one of the vertical edges of the specimen.
g) Maximum extent of any holes in the horizontal or vertical direction whichever is the greatest.
h) Maximum damaged length measured
i) Which face of the fabric was subjected to the flame test.

If the 10 second exposure of a specimen does not cause it to ignite the specimen is believed to be of sufficient quality to pass all the tests.