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.