İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ZINC BORATE AS A FLAME RETARDANT AND SMOKE SUPPRESSANT AGENT

M.Sc. Thesis by
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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

NOVEMBER 2011

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ALEV GECİKTİRİCİ VE DUMAN AZALTICI AJAN OLARAK ÇİNKO BORAT

YÜKSEK LİSANS TEZİ

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FOREWORD

This study has been carried out in laboratory of Ahmet Akar, Faculty of Science and Letters, Istanbul Technical University.

I would like to offer the most gratitude to my advisor, Prof. Dr. Ahmet AKAR, for sharing his knowledge, experience, his precious time with me generously, for his guidance, and motivation throughout this study and over all of these for the support he gave me in many ways.

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September 2011

Berrin DEĞİRMENCİ

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ABBREVIATIONS

PU **:** Polyurethane
PVC **:** Poly vinyl chloride
TCPP **:** Tris (chloroisopropyl) phosphate)
TCP **:** Tricresyl phosphate
CaAIP **:** Calcium aluminum phosphate (CaAIP)
ZnB **:** Zinc borate
ATH **:** Aluminum trihydrate
FR **:** Flame retardant

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ZINC BORATE AS A FLAME RETARDANT AND SMOKE SUPPRESSANT AGENT

SUMMARY

In recent years, trend for fire retardancy of plastics is towards non-halogen and non-antimuan compounds due to their hazardous effect. Among all-known traditional fire retardants, the best candidate for fire retardancy is zinc borate. Though the fire retardance mechanism of zinc borate is not very well-known, the synergy of zinc borate and ATH mixture gives the best results thus it can be seen that this fire retardant will be an important player in future's flame retardants world.

In this thesis a mixture of zinc borate, and other fire retardants such as aluminium trihydrate, hidro talcide were used for fire retardant material in flexible PVC. And fire retardance effect was obtained using zinc borate at 8% and ATH 18% by weight. Similarly in rigid Polyurethane, fire retardance effect of zinc borate and modified zinc borate, in the presence of aluminium trihydrate, TCPP, synthetic borates was studied. Fire retardant effect of them could only be achieved at high percentage addition. Best result was obtained when using zinc borate 10%, ATH 40% and TCP 8%.

ALEV GECİKTİRİCİ VE DUMAN AZALTICI AJAN OLARAK ÇİNKO BORAT

ÖZET

Son yıllarda plastiklerde yanmazlık sağlayıcı maddelerdeki tercih halojensiz ve antimuansız alev geciktiricilere doğru oldu. Bütün bilinen geleneksel yanmazlık sağlayıcı maddeler içinde çinko borat en iyi aday olarak gösterilebilir. Çinko boratın alev geciktirici olarak çalışma sistemi çok iyi bilinemese de, en iyi sonuçların ATH ve çinko boratın sinerjisinden doğduğu söylenebilir. Bu da bize çinko boratın ilerleyen yıllarda yanmazlıkla ilgili konularda çok daha ön planda olacağının bir göstergesidir.

Bu çalışmada flexible PVC için yanmazlık çalışmaları çinko borat, ATH ve hidro talsit gibi madde lelerle gerçekleştirildi. Yanmazlık değerleriyle ilgili en iyi sonuçlar çinko boratın karışımda ağırlıkça %18 ve ATH'nin de ağırlıkça %18 oranında kullanılmasıyla elde edildi. Aynı şekilde rijit Poliüretanın yanmazlığı için de çinko borat, modifiye çinko borat, ATH, TCPP ve sentetik boratlar kullanıldı. Yanmazlık etkisi ancak yüksek miktarlarda alev geciktiricilerin kullanılmasıyla elde edildi. En iyi sonuç çinko boratın ağırlıkça %10, ATH'nin ağırlıkça %40 ve TKP'nin ağırlıkça %8 kullanılmasıyla sağlandı.

1. INTRODUCTION

Advances in polymer science over the past 50 years has led to the introduction of a large number of polymers with different properties and applications. As a result, polymers take in place in clothes, furniture, electronics, vehicles, computers etc. Most of these polymers are petroleum-based and hence are flammable. In order to meet fire safety regulations, flame retardants are added into combustible materials. In this thesis, two of these polymers were examined in terms of their flammability and smoke suppressant properties as well as their physical and chemical properties: PVC and Polyurethane.

Recent years, a trend has started in the world and encourage most of the company that produces PVC and polyurethane to use zinc borate and boron compounds instead of halogenated compounds and Sb_2O_3 due to the hazardous effect of them. Thus boron compounds, such as zinc borates, are today's most favourite flame retardants. where 90% amount of them are present in The United States and Turkey. Due to this important reserve of Turkey, this subject should be payed more attention in Turkey.

Borax and boric acid are well-known fire retardants in cellulosic products and coatings. However, the use of boron compounds such as zinc borate, ammonium pentaborate (APB), melamine borate, boric oxide, boron phosphate, and other metal borates in polymers has become prominent only since early 1980s.

Overall, in the U.S., the $827 -million flame- retardant industry is expected to grow at an annual rate of 3% through 2011. Rapid gains are expected for smaller volume flame retardants, such as magnesium hydroxide. Alumina trihydrate (ATH) will remain the largest-volume flame retardant through 2011, comprising 45% of demand. [1]. Nowadays, non-halogenated FRs, take place in the markets. This thesis will review zinc borate's –which is non-halogenated and toxic- chemical and physical properties and its use as a flame retardant and smoke suppressant agent in rigid polyurethane foam and flexible PVC applications.

2. THEORETICAL PART

2.1 Flame Mechanism and Combustion

Combustion is initiated by heating a plastic material to its decomposition point. The three critical sources required to sustain combustion process are ignition source, fuel and oxygen. The combustion cycle can be stopped by isolating any of the mentioned sources. Numerous combustible decomposition products like hydrocarbons, hydrogen and carbon monoxide are formed.

$RH \rightarrow R^* + H^*$ (Start)

$H^* + O_2 \rightarrow HO^* + O^*$ (Branching)

$HO^* + CO \rightarrow CO_2 + H^*$ (Propagation, highly exothermic)

The reaction of combustible gases with oxygen is an exothermic reaction, which upon exceeding the endothermic pyrolysis reaction, initiates flame propagation. A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act as physically or chemically. Flame retardants function in three ways:

a) Vapour phase reactions disrupt the free- radical oxidation process.

b) Endothermic reactions act as heat sinks which reduce temperatures

c) Char promoters act as insulators and protect underlying polymers. [2]

2.2 Physical Action

a) By cooling: The additives cool the substrate to a temperature below the combustion temperature (e.g. ATH).

b) By formation of protective layer: A solid or gaseous protective layer, which excludes the oxygen necessary for the combustion process (e.g.phosphorus compounds).

c) By dilution: The inert gases from the additive dilutes the fuel in the solid and gaseous phase (e.g. Aluminium hydroxide).

2.3 Chemical Action

Reaction in gas phase **occurs in** the radical mechanism of combustion is interrupted and exothermic reactions are stopped. System cools down (e.g. halogenated flame retardants).

Reaction in solid phase occurs by forming carbonaceous layer on the polymer surface (e.g. phosphorus compounds). [3]

2.3.1 Types of flame retardants

Flame-retardants are classified into two categories: additives (mechanically blended with polymeric substrate) and reactives (chemically bound to the polymer). Additive types are used especially for thermoplastics., while reactives are typically used for thermosets. Different classification has been made in fire retardants. Below are widely used flame retardants are described.

2.3.1.1 Halogen flame retardants

The effectiveness of halogen containing flame retardances increases in the order F<Cl<Br<I. Fluorine and iodine-based flame retardants are not used in practice because neither type interferes with the combustion process at the right point. Fluorine, due to its strong bond with carbon, and iodine is loosely attached to carbon. Bromine compounds are the most effective compound.

According to table 2.1 all type of flame retardants which are used for both applications and effectiveness can be seen.

Table 2.1 : Flame retardants used in polymers [3]

Flame retardants	Polymers	Applications and effectiveness
Aluminium tri hydroxide ATH Magnesium dihydrate MDH Boehmite ATH (aluminium oxide hydrates)	Low density polyethylene LDPE Ethyl vinylacetate Polyolefins	In fire, these mineral FRs decompose,absorbing energy, releasing water(reducing fire intensity and diluting fire gases), and causing charring(fire barrier)
Phosporus flame retardants	Used in fire resistant coatings for cables	
Silicon dioxide SiO2		
Zinc borate	Synergist with ATH	
Red phosporus	Polyolefins Other insulating resins	
Phospate esters (e.gTricresyl Phospate T.C.P)	PVC Rubber	Plasticizer properties Flame inhibition and charring fire resistance properties of phosporus
Antimony trioxide Sb_2O_3	PVC	Synergist fo fire safety with brominated or chlorinated flame retardants, or in chlorinated polymers(including PVC)
Zinc oxide(ZnO), Tin dioxide SnO_2	PVC	
Melamine cyanurate, melamine phospate,	Polyamides Polypropylene	
Chlorinated paraffins	PVC	
Tetrabhromopthalate ester	PVC Elastomer	
Ammonium polyphospate APP	Polyolefins	
Deca-BDE and decabromodiphenyl ethane	Various polymers	

Halogen/antimony synergism

Antimony trioxide shows no flame-retardant action on its own. However, it shows good synergistic effect with halogen containing compounds.

At 250 ^{0}C, $Sb_2O_3 + HBr \rightarrow 2SbOBr + H_2O$

245 to 280 ^{0}C, $5SbOBr \rightarrow Sb_4O_5Br_2 + SbBr_3$

410 to 465 ^{0}C, $4Sb_4O_5Br_2 \rightarrow 5Sb_3O_4Br + SbBr_3\uparrow$

475 to 495 ^{0}C, $3Sb_3O_4Br \rightarrow 4Sb_2O_3 + SbBr_3\uparrow$

The antimony trihalides and various antimony oxihalides act as radical interceptors like HCl or HBr.

2.3.1.2 Phosphorus-containing flame retardants

Phosporus based flame retardants can be organic, inorganic or elemental. They can be active in the vapour phaseor in the condensed phase, or sometimes in both phases. Phospine oxides and phosphate esters are thought to act in the vapour phase through the formation of PO* radicals, which terminates the highly active flame propagating radicals (OH* and H*). The condensed phase mechanism arises as a consequence of thermal generation of phosphoric acid from the flame retardant, e.g. phosphoric acid or polyphosphoric acid. These acids act as dehydrating agents, altering the thermal degradation of the polymer, and promoting the formation of char.

2.3.1.3 Aluminium hydroxide

$Al(OH)_3$ is the most widely used flame retardant. Its cost is low and it is easy to incorporate in plastics. Aluminium hydroxide starts to break down in the temperature range of 180 to 200 ^{0}C. Conversion to aluminium oxide takes place in an endothermic reaction as below:

$Al_2O_3.3H_2O \rightarrow Al_2O_3 + 3H_2O$ [4]

ATH acts as a heat sink by giving off “water of hydration” when the dehydration reaction temperature is reached. This reaction temperature needs to be above the maximum temperature seen during processing, as premature water vapor evolution can cause porosity problems. The release of water from ATH reduces the temperature of the substrate and retards the combustion reaction. [3]

2.3.1.4 Magnesium hydroxide

Magnesium hydroxide acts in a similar way as aluminium hydroxide, but magnesium hydroxide has a higher decomposition temperature of 300 ^{0}C.

Magnesim hydroxide acts as heat sink as in the case of aluminium hydroxide:

$Mg(OH)_2 + 1220 \text{ kj/kg} \rightarrow MgO + H_2O$

The mechanism of $Mg(OH)_2$

During this process, energy is detracted from the ignition source, as the decomposition is an endothermic reaction. At the same time, the released water vapour cools the surface of the polymer and particularly dilutes the concentration of burnable gases in the surrounding area. The remaining metal oxide residue has a high internal surface where sooty particles are absorbed. Additionally, the oxide residue acts as a barrier, disabling the further release of low molecular weight decomposition products as well as a heat barrier protecting the polymer against further decomposition. In figure 2.1 the flame retardancy mechanism of metal hyroxise takes place.

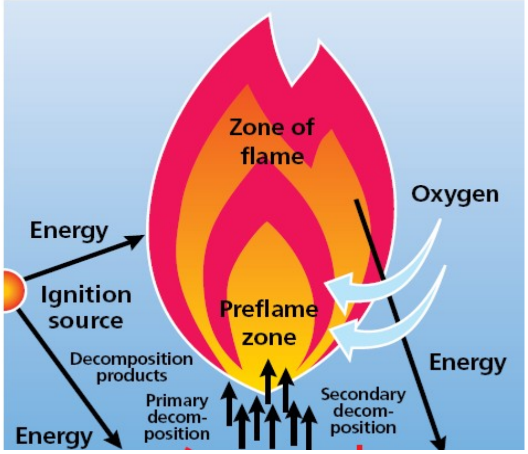


Figure 2.1 Flame retardancy mechanism of metal hydroxide [5]

2.3.1.5 Boric acid

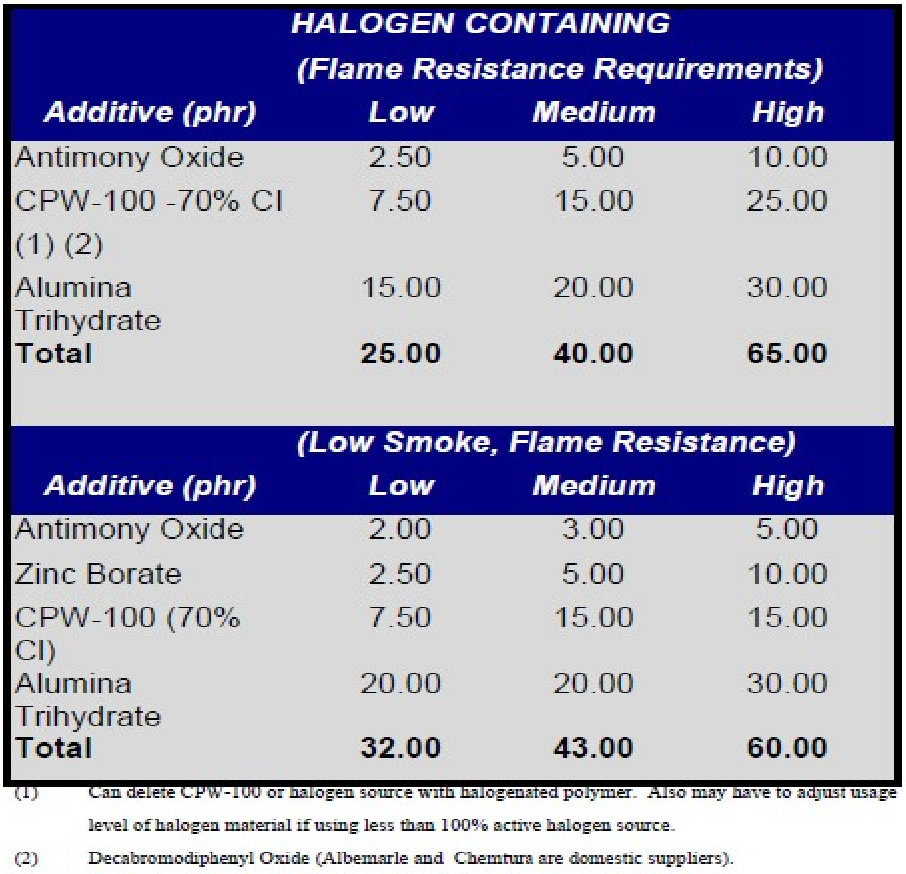
Boric acid or orthoboric acid (commercially known as OptiborR) is a white triclinic crystal that is soluble in water (5.46 wt.%), alcohols, and glycerin. It is a weak acid and has a pH of 4 (saturated solution at room temperature). Upon heating in air to above 75°C, it loses part of its water of hydration to form metaboric acid (HBO_2) at around 120°C–130°C. The metaboric acid can be further dehydrated to boric oxide at around 260°C–270°C.

$2H_3BO_3 \rightarrow 2HBO_2 + 2H_2O \rightarrow B_2O_3 + H_2O$

Due to their low dehydration temperatures and water solubilities, boric acid and sodium borates (borax pentahydrate and borax decahydrate) are mostly used as fire retardants in wood/cellulosic products such as timbers, plywood, particle board, wood fiber, paper products, and cotton products. In recent years, boric acid has also been used as fire retardant in epoxy intumescent coating, phenolics, urethane foam, and so on. When necessary, boric acid can be coated with silicone oil such as silicone to alleviate its water solubility in water-based coating.

2.3.1.6 Zinc borate and ammonium pentaborate

Zinc borate and ammonium pentaborates are going to be reviewed in details in this thesis [6]. A summary of flame resistance requirements table are shown in figure 2.2



HALOGEN CONTAINING

(Flame Resistance Requirements)

Additive (phr)	***Low***	***Medium***	***High***
Antimony Oxide	2.50	5.00	10.00
CPW-100 -70% Cl (1) (2)	7.50	15.00	25.00
Alumina Trihydrate	15.00	20.00	30.00
Total	**25.00**	**40.00**	**65.00**

(Low Smoke, Flame Resistance)

Additive (phr)	***Low***	***Medium***	***High***
Antimony Oxide	2.00	3.00	5.00
Zinc Borate	2.50	5.00	10.00
CPW-100 (70% Cl)	7.50	15.00	15.00
Alumina Trihydrate	20.00	20.00	30.00
Total	**32.00**	**43.00**	**60.00**

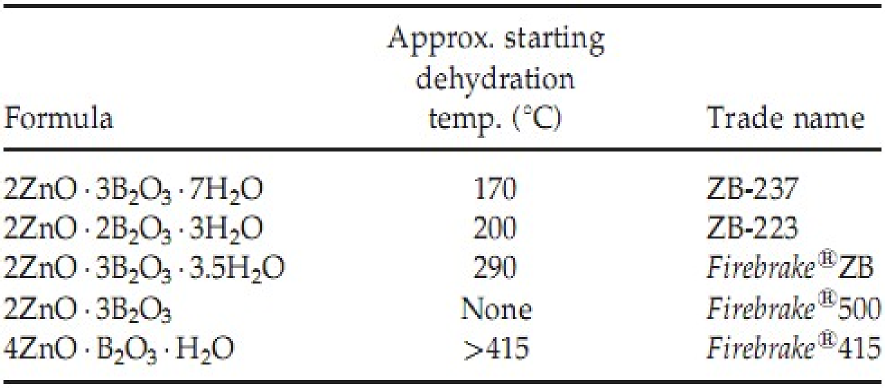
(1) Can delete CPW-100 or halogen source with halogenated polymer. Also may have to adjust usage level of halogen material if using less than 100% active halogen source.

(2) Decabromodiphenyl Oxide (Albemarle and Chemtura are domestic suppliers).

Figure 2.2 : Flame resistance requirements for different fire retardants [6]

2.4 Zinc Borate

Among all of the boron containing fire retardants used in polymers, zinc borate has the most commercial importance. Depending on the reaction conditions, a host of zinc borates can be produced. In figure 2.3 all types of zinc borates are shown: Zinc borate(2 $ZnO.3B_2O_3.3.5H_2O$) which is called as Firebrake ZB , is the most widely used among all of the known zinc borates has been widely used extensively in PVC, polyamide, polyolefin, epoxy, phenolics, and various elastomers.And stable to 290^0 C-300^0 C. Due to the demand of high production throughput and thin-walled electrical parts, engineering plastics are processed at increasingly higher temperatures. Also Firebrake 500 ($2ZnO.3B_2O_3$) – an anhydrous zinc borate- is stable to at least 500 ^{0}C and Firebrake 415 ($4ZnO.\ B_2O_{3.}\ H_2O$) is stable to > 415 ^{0}C [7].



Formula	Approx. starting dehydration temp. (°C)	Trade name
$2ZnO \cdot 3B_2O_3 \cdot 7H_2O$	170	ZB-237
$2ZnO \cdot 2B_2O_3 \cdot 3H_2O$	200	ZB-223
$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$	290	*Firebrake*®ZB
$2ZnO \cdot 3B_2O_3$	None	*Firebrake*®500
$4ZnO \cdot B_2O_3 \cdot H_2O$	>415	*Firebrake*®415

Figure 2.3 : Types of zinc borate [7]

The zinc borate functions as a flame retardant, smoke suppressant, afterglow suppressant, and anti-tracking agent. It is a synergist of chlorine and bromine-containing flame retardants of polymers. The zinc borate can generally display synergistic effects with antimony oxide in fire retardancy. This synergy can be more dramatic when used in conjunction alumina trihydrate (ATH) or magnesium hydroxide (MDH).

Since mid-1990s, the market demand for fire retardant polymers that are halogen free has been increasing steadily in wire and cable, transportation, electrical/electronics, and construction products. In wire and cable, for example, ATH and MDH have been used extensively in halogen-free, fire retardant polyolefins [8].

2.4.1 General properties of zinc borate

The most common used zinc borate is $2ZnO.3B_2O_3.3.5H_2O$, however there is also 9 types of zinc borates are used: $4ZnO.B_2O_3.H_2O$, $ZnO.B_2O_3.1.12H_2O$, $ZnO.B_2O_3.2H_2O$, $6ZnO.5B_2O_3.3H_2O$, $2ZnO.3B_2O_3.7H_2O$, $2ZnO.3B_2O_3.3H_2O$, $3ZnO.5B_2O_3.14H_2O$, $ZnO.5B_2O_3.4.5H_2O$. Worldwide consumption of these zinc borate salts is several thousand metric tons per year. In figure 2.4 main structure of zinc borate is defined:

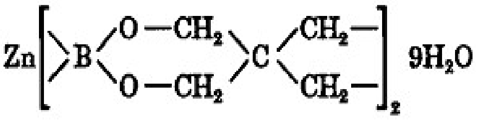


Figure 2.4 : Main structure of zinc borate

Zinc borate is often used with various compounds such as ATH, Sb_2O_3, $Mg(OH)_2$... but in this case in many countries using Sb_2O_3 and halogen containing flame retardant additives are banned due to the harmful effects of these compounds [9]. Also in figure 2.5 and table 2.2 Firebrake ZB is given in details.

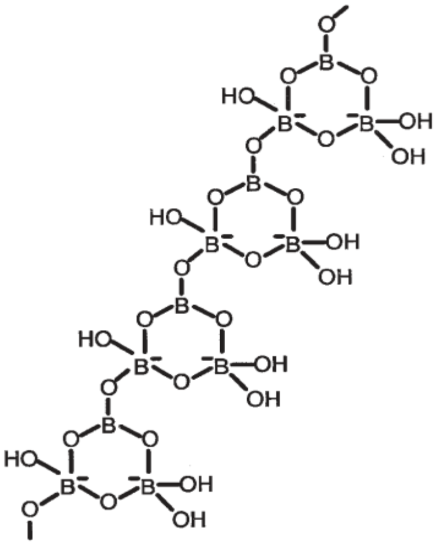


Figure 2.5 : Molecular structure of Firebrake ZB (zinc atoms that complex with oxygens are not displayed)

Table 2.2 : The theoretical composition and physical properties of zinc borate [10]

B_2O_3, %	48.05
ZnO, %	37.45
Crystal water, %	14.50
Refractive index	1.58
Average particle size, micro	7-12
Solubility(at room temperature),%	0.28
Specific gravity, g/cc	2.77

2.4.2 Types of zincborates

2.4.2.1 Firebrake ZB

This zinc borate can normally be prepared either by reacting boric acid with zinc oxide or by reacting borax pentahydrate with zinc sulfate. A recent single cyrstal x-ray crystallography study showed that it has a structure of $Zn[B_3O_4(OH)_3]$. It has been used extensively in PVC, polyamide, polyolefin, epoxy, phenolics, and various elastomers. (2ZnO.3B2O3.3.5H2O)

This zinc borate functions as a flame-retardant, smoke suppressant, and anti-arcing agent. In halogen-containing polymers, its efficacy depends on the type of halogen and base polymer used. In contrast to antimony-oxide, zinc borate is a smoke suppressant in halogen-containing polymers.

2.4.2.2 Firebrake 500

This anhydrous zinc borate is recommended for use in engineering plastics processed at temperatures higher than 300 0C which is the upper limit of Firebrake ZB (2ZnO.3B2O3) processing temperature. It is reported to be an effective smoke suppressant in chlorofluoropolymers for plenum cable applications. Recently it was claimed that this anhydrous zinc borate can replace antimony oxide (or sodium anitomonate) completely in high temperature polyamide applications. Like its anhydrited analog, this anhydrous zinc borate can also improve CTI, thermal stability, and the color stability of polyamide containing halogen sources.

This anhydrous zinc borate was also claimed to improve the stability of a halogen-free polyamide containing aluminium diethylphosphinate. For aircraft applications, this zinc borate alone is also reported to be effectice in reducing the HRR of polyetherketones and polysulfones.

2.4.2.3 Firebrake 415

This zinc borate has an unusually high onset of dehydration temperature (>415 ^{0}C). This type is recommended for use as a synergist of a halogen sources in engineering plastics such as polyamides. (4ZnO.B2O3.H2O)

2.4.2.4 Zinc borate

Zinc borate 2ZnO.3B2O3.7H2O is formed when borax is added to aqueous solution of soluble zinc salts at temperatures below about 70 0C. An x-ray structure determination has indicated that this compound is orthorhombic and has a zinc triborate monohydrate structure. Zinc borate 2ZnO.3B2O3.7H2O lose water of hydration when heated from 130 to 250 0C. [10]

2.4.2.5 Other zinc borates:

Zinc borate 3ZnO.2B2O3 forms a white amorphous powder or triclinic crystals depending on the method of preparation, specific gravity 3.64(amorphous), 4.22 (crystalline) and melting point 980oC. The amorphous form is slightly soluble in water and hydrochloric acid, the crystalline is insoluble in chloric acid. The heat stability of hydration water of zinc borate is between 290-300oC, which enables the polymer processibility. Because the refractive index of zinc borate is nearly the same to the refractive indices of many polymers, it enables the pigment load to below. The teoretical composition and physical properties of zinc borate having 3.5 hydration water [8].

2.4.3 Production of zinc borate

Zinc borate (2ZnO.3B2O3.3.5H2O) in general is produced with the reaction between zinc oxide and boric acid. Boric acid is solved in water between temperatures 95oC and 98oC and zinc oxide and seed crystal of 2ZnO.3B2O3.3.5H2O is added to this solution at a certain stoichometric ratio. The reaction continues for a while by mixing and the zinc borate format is filtered, dried and ground. The boric acid solution is fed to the system as reflux [11]. A basic production chart takes place in figure 2.6.

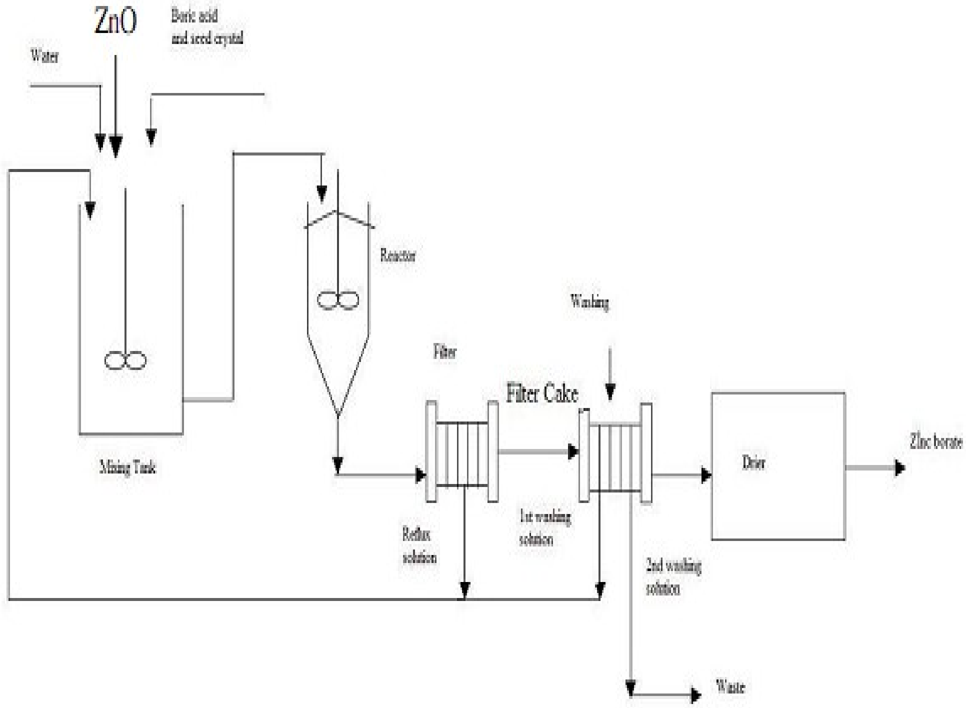


Figure 2.6: Flow sheet of a general production system of zinc borate [8]

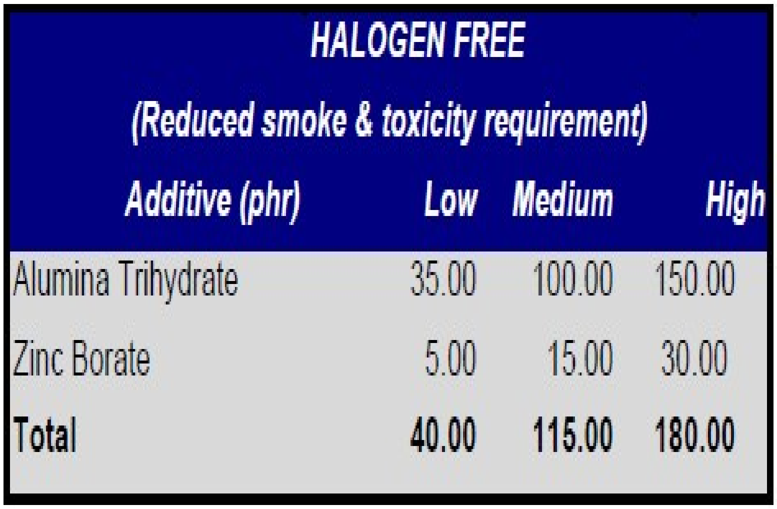
2.4.4 Fire retardance and smoke suppressant application of zinc borate

Among all of the boron-containing retardants used in polymers, zinc borate has the most commercial importance. Depending on the reaction conditions, a host of zinc borates can be produced. Around 1970, RTM/U.S. Borax patented and commercialized a unique form of zinc borate with a molecular formula of 2ZnO•3B O•3.5HO.44,45 In contrast to previously known zinc borates, this zinc borate (known in the trade as Firebrake® ZB)46 is stable to 290°C–300°C.

Due to the demand of high production throughput and thin-walled electrical parts, engineering plastics are processed at increasingly higher temperatures. To meet this market demand, RTM/U.S. Borax also developed an anhydrous zinc borate, Firebrake 500 (2ZnO• 3B O), that is stable to at least 500°C and Firebrake 415 (4ZnO• B_2O_3 • H_2O) that is stable to >415°C.

2.4.5 Synergy of zinc borate-ATH mixture

ATH decomposition is an endothermic reaction, which, 300°C, which means that the reaction is absorbing RTM6/ATH/ZB system at dif-degradation temperature level of most polymers. Another important aspect of the reaction is release of water vapour formed from the hydroxyl with ZB+ATH group bonded with aluminium. This water is different concentrations released into the flame hindering the combustion process by diluting the concentration of flammable neat evolving gases and restricting the access of oxygen through the composite surface. An added benefit of the decomposition reaction is that no toxic or corrosive gases are produced unlike some other flame retardant compounds are present. ATH also operates as a heat sink extending the time to reach the as expected. Different observations can be made by polymer decomposition temperature. ATH has analysing the TGA results of RTM6 and a combi-higher heat capacity than most organic resins [11]. In figure 2.7 ATH and zinc borate synergy is easily seen:



HALOGEN FREE

(Reduced smoke & toxicity requirement)

Additive (phr)	Low	Medium	High
Alumina Trihydrate	35.00	100.00	150.00
Zinc Borate	5.00	15.00	30.00
Total	**40.00**	**115.00**	**180.00**

Figure 2.7: ATH and zinc borate synergy [11]

2.5 Ammonium Pentaborate

Ammonium pentaborate (APB) is produced from the reaction between ammonia and boric acid in water. It has a water solubility of 10.9 wt.% at 25 0C. Upon thermal decomposition

APB first gives off a large amount of water starting at about 120 0C. At about 200 0C, it starts to give off ammonia and, at about 450 0C, it is all converted to boric oxide which is a glass former. APB functions such as both an inorganic blowing agent and a glass-forming fire retardant:

$(NH_4)_2O.5B_2O_3.8H_2O \rightarrow 2NH_3\uparrow + 8H_2O\uparrow + 5B_2O_3$APB solution can be sprayed on paper or the paper can be dipped into the solution to yield fire retardant products. In additon to the cellulose, it has also been used as a flame retardant in polyurethane foam and epoxy intumescent coatings.

It is reported that, partially dehydrated APB is an effective intumescent flame retardant in thermoplastic polyurethane. APB at 5-10 phr loading in TPU can provide 7- to 10-fold improvement in burn-through test. It is believed that in the temperature range of 230 ^{0}C – 450 ^{0}C, the dehydrated APB and its released boric oxide/boric acid may react with the diol and/or isocyanate, the decomposed fragmants from TPU, to produce a highly cross-linked borate ester and possibly boron-nitrogen polymer that can reduce the rate of formation of flammable volatiles and result in intumescent char. $B_2O_3 + 6ROH \rightarrow 2B(OR)_3 + 3H_2O$

$H_3BO_3 + 3RNCO \rightarrow B(NHR)_3 + 3CO_2$

Its usage in polymers, however, is limited by its high water solubulity (10.9) and low dehydration temperature. PPG reported the use of APB in conjunction with APP, zinc borate, silica, talc and so on, in a flame-retardant intumescent coating for protection against hydrocarbon fires. [12]

2.6 Flame Retardancy of Polyurethane

2.6.1 Main properties and uses of polyurethane

Polyurethanes are one of the most versatile classes of materials today and their demand as a high performance industrial material continues to grow. The wide application of PUs necessitates understanding the chemistry and structural elements that improve the thermal stability and flame retardancy as these are important prerequisites to obtain tailor-made

products for high performance applications such as in aggressive environments. Polyurethanes (PUs) represent a wide class of polymers made by reacting diisocyanates or polyisocyanates with diols or polyols [9].

Nowadays, more and more attention is being paid to improving the flame retardant properties of PUs as it is an essential requirement for applications such as in wire and cables, PU foams in different household stuffs such as upholstered furniture and mattresses, aircraft interiors, fire resistant coatings and clothes, sandwich panels, insulating boards, construction metals etc.

Rigid PU foam has a number of particular advantages:

- It can be produced in a wide range of densities.

- It adheres to various facings without the use of adhesives.

- It can also be produces in comples cavities [13].

In figure 2.8 polyurethane usage is demonstrated:

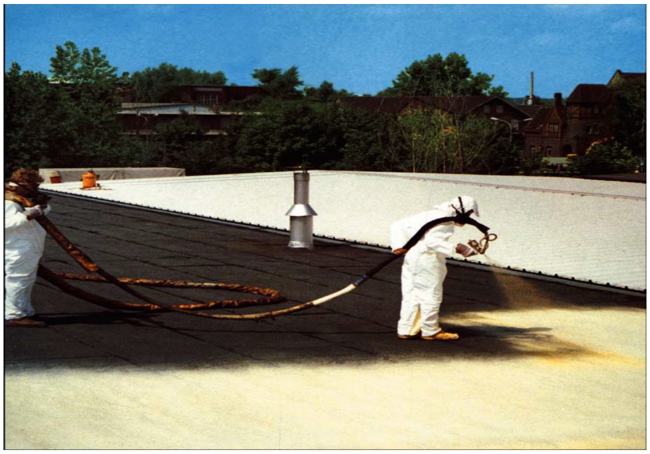


Figure 2.8 : Thermal insulation and sealing in one operation [13]

2.6.2 Structure of polyurethane

The common reactions of iscocyanates can be put into two main classes: (1) the reactions of isocyanates with compounds containing reactive hydrogen to give addition products and (2) the polymerization of isocyanates, i.e., self-addition. Isocyanates react with hydroxyl compounds to give urethanes and with amines to give ureas.[8] Basic reaction schme for urethane is shown in figure 2.9

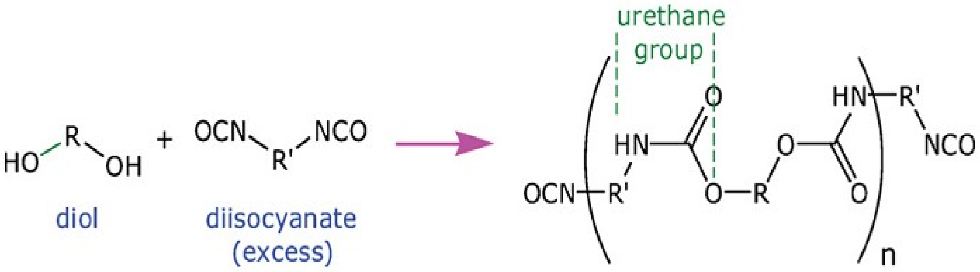


Figure 2.9 : Basic reaction scheme for urethane formation [8]

Similar reactions (in figure 2.10) occur with water, initially with the formation of an unstable carbamic acid, and with carboxylic acids, with formation of mixed acid anhydrides.

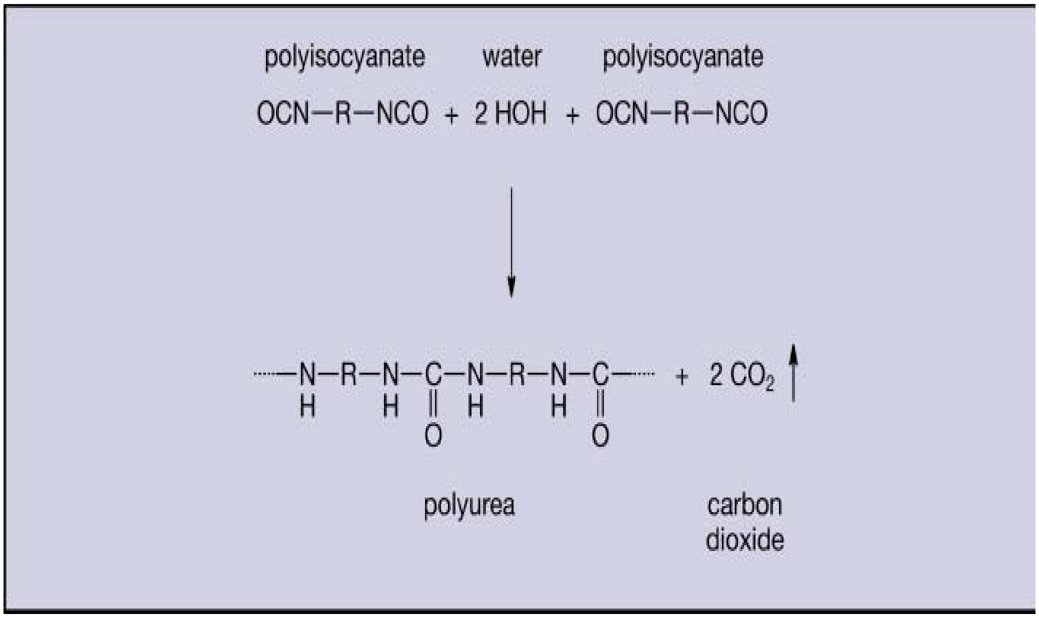


Figure 2.10 : Polyurethane/water reaction [10]

However, in both of these cases the intermediates thus formed then break down; in the case of water, with the formation of an amine which reacts further with more isocyanate to give a urea.

Addition to the polyurethane formation; in the case of the carboxylic acids,the mixed anhydrides break down to form amide groups. [10]

2.6.3 Production of rigid polyurethane foam

The production of rigid PU foam require two main liguid components – a polyol and a polyisocyanate- and a blowing agent.

During the reaction a considerable amount of heat is released which is used partly to evaporate readily volatile liquids (blowing agents). As a result, the reaction mix is expanded to form a foam.

2.6.4 Combustion of polyurethane

Polyurethanes are very combustible plastics. The Oxygen Index (OI) of PU foams is in the range of 16-18. Also the flammability of polyurethanes, especially PU foams, strongly depends on the structure of the polyol and the isocyanurate index. The density of the foam is another very important factor for the flame-spread. According to the scientific researches the effect of foam density and addition of flame retardant to the foams provided the major contributions to combustion performance test results. Changes in polymer morphology and calculated percent of polyureas did not show any significant effect on flammability [10].

2.6.4.1 Intumescent and non-intumescent systems

Based on the flame retardant mechanism PUs can be classifed into either intumescent or nonintomescent types. The use of intumescent flame-retardant PUs is one of the easiest, economical and the most efficient ways to protect materials against fire. Intumescent flame retardants swell, bubble and char on exposure to a flame and carbonaceous porous foamed mass acts as a barrier to heat, air/O_2 and pyrolysis products. At high temperature, the formed char layer on the surface provides resistance to heat and mass transfer, giving good heat insulation to the underlying binder. Therefore, an intumescent system shields the underlying PU from heat and fire. This lowers the temperature of the surface beneath the char and causes a lag in the surface temperature rise. Additionally, the char layer hinders the diffusion of oxygen to the PU site, i.e., the site of combustion.

The intumescent fire retardant/PU system has several advantages such as low smoke, low toxicity, low corrosion, long life, and are halogen free. The physical structure of the char layer plays a very important role in the performance of the flame retardant. On the other hand, the intumescent systems do not swell and char during exposure to flame.

Zincborate acts with ATH as intumescent agents as in the case of figure 2.11

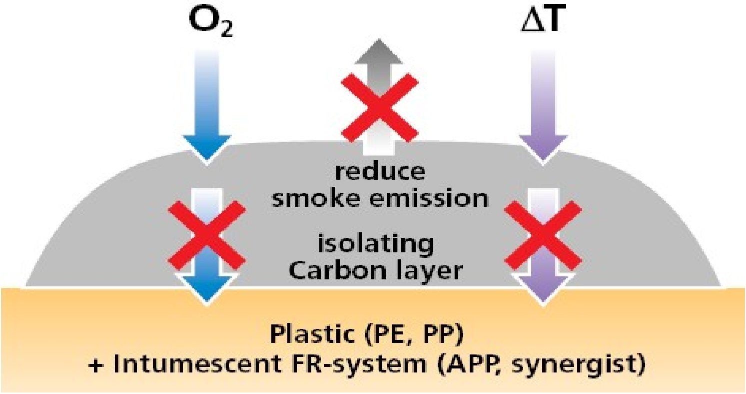


Figure 2.11: The mechanism of intumescent flame retardant systems which are typically a combination of phosphorus and nitrogen compounds [14]

2.6.5 Fire retardants in flexible and rigid polyurethane

In flexible PUs several fire retardants are used: (1):Inorganic fire retardants: ATH,ZB;(2):Intumescent systems: Ammonium polyphosphate(PPP);(3):Phosphoruc-containing fire-retardants:Aromatic polyphosphonate and bisphenol A polycarbonate, polybispropoxyphosphazene,polydimethylsiloxane.(4):Iron-containing fireretardants:In rigid PU foams here are the fire retardants(1):ATH, ammonium polyphosponate (APP) in combination with Firebrake ZB.(2):Expandable graphite.(3):Phosphorus containing fire-retardant additives.(3)Halogen containing fire-retardants: aliphatic bromine,aliphatic chlorine.(4):Boron-containing fire-retardants:Boric acid with 1,2-propanediol [14].

2.6.6 Flame retardance mechanism in polyurethane

Flame retardant PUs are combustible materials that prevent or delay flashover from the surface of combustibles. A flame retardant is not designed to prevent the material from ignition but to keep the flame spread rate to a minimum and prevent sustained burning. Therefore, flame retardants tend to keep the flame from spreading by increasing the resistance of the polymer to ignition

The flame retardance mechanism – the interference with the combustion process – can function either in the condensed phase(solid phase) or in the vapor phase(flame zone) through a physical mechanism, a chemical mechanism or a combination of these mechanisms. Combustion is a complex process and different mechanisms may be involved in the presence of different types of flame retardants. Therefore, the substitution of one type of flame retardant may result in a change in the flame retardance mechanism. Flame retardants interfere with combustion during specific stages of processes such as heating, decomposition, ignition, or flame spread. For example, the incorporation of inorganic fillers dilute the polymer, produce a stable organic-inorganic interface, reduce the concentration of decomposition gases and increase the diffution path barrier of the volatiles produced during the degradation process.

2.6.6.1 Condensed-phase

Flame retardants accelerate the breakdown of the polymer and cause a layer of carbon (char) on the polymer surface. The char layer protects the PU material, and itsprotective property depends on the physical and chemical structure of the char layer. The char formation at surface often produces a foamed matrix in a process known as intumescence. Intumescent systems containing phosporus and nitrogen genreally flow the condensed phase flame retardant mechanism.

2.6.6.2 Vapor-phase

Radical mechanism of the combustion process is stopped by aflame retardant in the gas phase. The exothermic processes that occur in the flame are therefore stopped and the system cools down due to the reduced concentration of the formation of flammable gases.

The reactive radicals such as HO. and H. Can react in the gas phase with radicals like X. (halogenated radicals) or others that result from flame retardant degradation. Halogen-type flame retardants usually follow the vapor phase flame retardant mechanism. In figure 2.12 there is a sum of combustion mechanism in polyurethane can be seen.

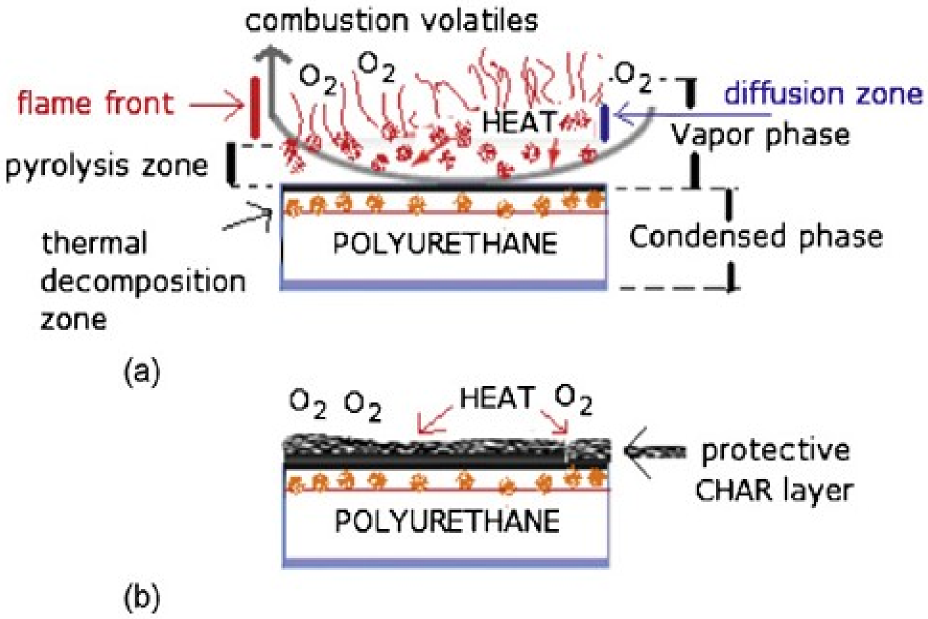


Figure 2.12: PU with and without flame retardant-resulting l heat release a) and with flame retardant-resulting low heat release b) showing the process occuring during combustion. A low-density, high porosity char produces better flame retardancy [10]

Therefore, an ideal flame retardant might have propertiessuch that (a) it should be resistant towards flame and reduce the flammability up to a certain point, (b) it should be thermally stable at processing temperatures, (c) it should be compatible with the PU binder, (d) it should at least maintain or improve the mechanical properties of the PU, (e) it should be free of health hazards, and finally ,(f) it should be cost effective.[10].

Halogen-free polymers

Zinc borate in conjunction with ATH or MDH is used in many halogen-free polymers. The mode of action of this zinc borate and metal hydroxide is summarized as follows:

$2\ ZnO.3B_2O_3.3.5H_2O + Al(OH)_3 \rightarrow xAl_2O_3.yZnO.zB_2O_3 + B_2O_3\uparrow$

$$2\ ZnO.3B_2O_3.3.5H_2O + Mg(OH)_2 \rightarrow xMgO.yZnO.zB_2O_3 + B_2O_3\uparrow$$

Zinc borate and alumina oxide forms a porous and ceramic-like residue at temperatures above 600 ^{0}C. [15]

2.7 Flame Retardancy of PVC

2.7.1 Main properties and uses of PVC

PVC is never used alone. It is always mixed with heat stabilizers, lubricants, plasticizers, fillers, and other additives to make processing possible, all of which can influence its physical and mechanical properties. PVC has extremely good chemical resistance but low molecular mass chlorinated solvents. Therefore PVC is widely used in the construction and lining of chemical plants and is formulated as $(\text{-}CH_2\text{–}CHCl\text{-})_n$.

PVC can be divided into two main classes as rigid PVC and flexible PVC.

Major uses of flexible PVC include wire and cable jacketing and primary insulation, window gaskets, flooring based on plastisol-derived sheet goods and calendered tiles, calendered film and sheet for upholstery, wall coverings, roofing membranes, pond and pool liners, shower curtains, apparel, and geo-membranes.

PVC is also used in various systems where flexibility and isolation is needed. This situation results in PVC use especially in electrical cables.

Electrical systems are estimated to be the cause of around one fifth of all fires. Cables can contribute significantly not only to the cause of fires, to the spread of fire and to heat emission in the case of fire, they also can result in three ways:

- Increased smoke production
- Increased carbon monoxide production
- Release of irritant gases (depending on the materials used)

The situation is made worse in many office and shop buildings, because new cables are added.. for these reasons fire testing methods and building safety standards define specific fire safety requirements applicable to cables for upgraded IT networks or new electrical security standards [16]. In figure 2.13 synergy of ZB and SB_2O_3 is shown.

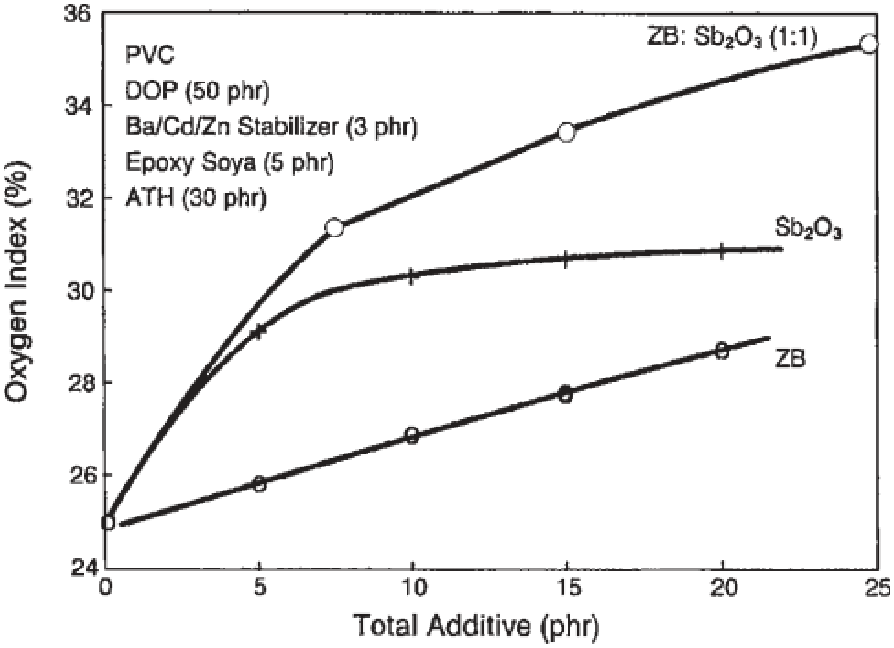


Figure 2.13: Oxygen index of flexible PVC formulations (all contain 30 phr ATH) [16]

2.7.2 Mechanism of fire retardants in PVC

The flammability performance of PVC plays a significant role in itsselection for many applications. Its relatively high chlorine content(56.8%) makes it more resistant to ignition and burning than most organic polymers. In the case of flexible PVC, the plasticizers can contribute more flexibility in most instances detract from its resistance to fire.

To meet specifications such as oxygen index, heat release, smoke evolution or extent of burning in cable tests, flame-retardant (FR) and smoke suppressant (SS) additives are often incorporated. Synergistic combinations of FR and SS additives help PVC formulations meet many stringent FR specifications cost effectively.

In flexible PVC, the partial replacement of antimony oxide with the zinc borate can not only display synergy in flammability test performance but also results in dramatic smoke reduction. This synergy can be more dramatic when used in conjunction with ATH or magnesium hydroxide (MDH). A recent cone calorimeter study showed that, in flexible PVC, the partial replacement of antimony with the zinc borate could reduce both the HRR and carbon monoxide production drastically at a heat flux of 35 kW/m^2. In certain PVC formulations, the zinc borate can replace antimony oxide completely.

In contrast to flexible PVC, this zinc borate alone improves both fire retardancy and smoke suppression in rigid PVC. [4]

2.7.3 Fire retardants used in PVC

PVC if flame retardant tends to burn in place under the heat flux from an early stage fire, forming char; it does not melt into a burning pool which spreads the fire. Under moderate heat flux,such as occurs in the early stages of real-world fires. Limiting Oxygen Index (LOI) of chlorinated PVC is 60-70. Antimony oxide (Sb_2O_3) is the FR additive for PVC and other chlorine-containing polymers. Sb_2O_3 itself is relatively inert in early stage fire situations because the temperature at whict it sublimes is 1550^{0}C. However it reacts with HCl and atomic chlorine produced by the degradation of PVC and with oxygen to form more volatile species such as $SbCl_3$ (b.p. 223^{0}C), SbOCl (170^{0}C) or other antimony oxychlorides which act as radical-scavenging flame poisons in the vapor phase.

Another widely used FR additive for PVC is aluminum trihydrate (ALT), which works in both vapor and solid phases. Its mechanism of action is to vaporize water of hydration whose latent of heat of evaporation cools the solid phase while smiltaneously the evolved vapor dilutes the flame. The evaporation of water vapor from ALT starts at a temperature about 240^{0}C and progresses as the temperature increases.

Magnesium hydroxide [$Mg(OH)_2$] is another FR additive with a mechanism similar to ALT. This one however starts losing water of hydration at a temğerature of about 300^{0}C. Combinations of ALT and magnesium hydroxide are used to provide long-acting FR performance where this is needed to pass particular specifications.

Zinc borate, including U.S. Borax, is effective as aflame retarding smoke suppressant. It is generally used in combination with other FR and SSadditives. A high level of zinc borate reduces the heat stability of PVC unless special stabilizing means are used.

Also as seen in figure 2.14 alkylaryl and triaryl phospate esters, chlorinated paraffins, copper compounds are also used as FR additives [16].

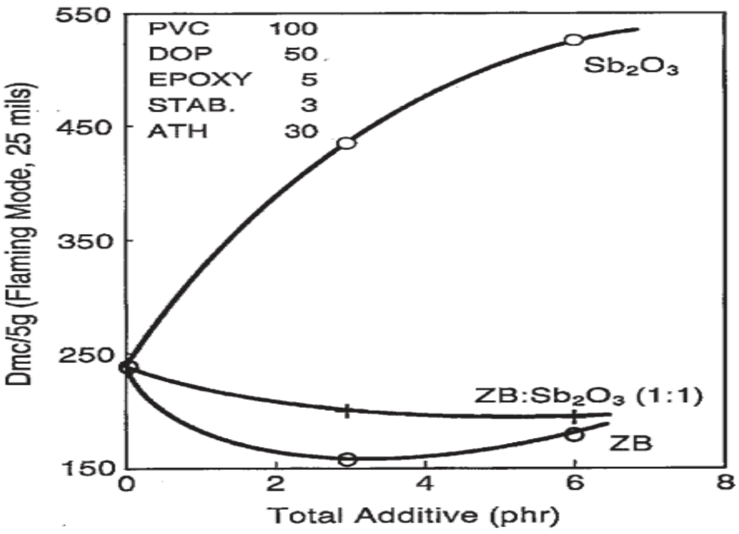


Figure 2.14 : Smoke test of flexible PVC (all formulations contain ATH) [16]

2.7.4 Zinc borates used in PVC

Zinc borates are a predominately a condensed phase fire retardant. In a halogenated system such as flexible PVC,it is known to markedly increase the amount of char formed during polymer combuston, whereas the addition of antimony trioxide, a vapor-phase flame retardant has little effect on char formation. Analyses of the char formation show that about 80%-95% of the antimony is volatilized, whereas the majority of the boron remains in the condensed phase is in agreement with the fact that boric oxide is a good afterglow suppressant.

- Firebreak ZB reacts with HCl released from PVC degradation to form zinc chloride, zinc hydroxychloride, boric oxide, water, and boron trichloride

- The zinc species (such as zinc chloride, and zinc hyrdoxychloride) in the condensed phase can alter the pyrolisis chemistry by catalyzing the dehydrohalogenation and promoting cross-linking, resulting in increased char formation and a decrease in both smoke production and flaming combustion

- It is believed that a portion of the zinc can be volatilized to the gas phase in the form of zinc chloride, which colud function as a gas-phase flame retardant similar to that of $SbCl_3$.

- The relased boric oxide is a low melting-glass that can stabilize the charand inhibit afterglow.

- The water relased can promote the formation of a foamy char that is a good barrier. In addition, the released water can absorb 503 J/g of heat. [10]

Also in figure 2.15 the effect of different fire retardants on PVC formulation is taken in consideration:

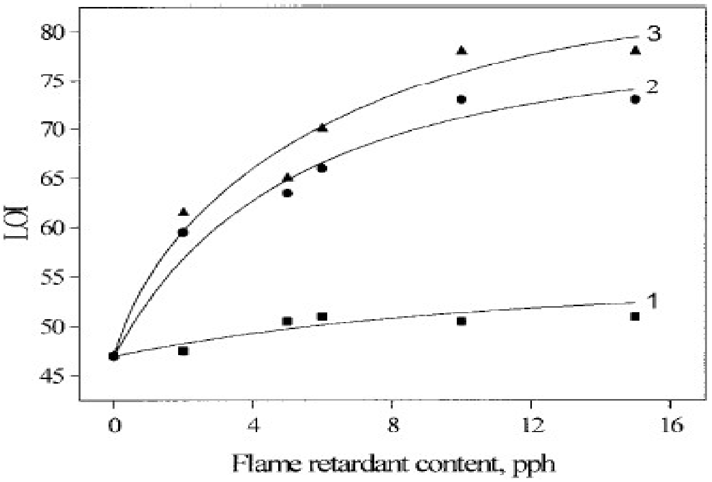


Figure 2.15: Effects of ATH, ZB, and ZB-ATH contents on LOI of PVC **[17]**

2.8 Burning Tests Used for Polymers

In this part cone calorimetry, limiting oxygen index (LOI) and UL-94 Analysis analysis will be reviewed. The cone calorimeter test is widely used to examine the performance of fire retardant polymers and it is at present the one of the most advanced method for assesing the fire behavior of materials. The test apparatus contains an electric heater, an ignition source and a gas collection system. In cone calorimetry, the thermal response of a sample depend on the applied radiation intensity. The principle of cone calorimeter experiments is based on the measurement of the decreasing O^2 concentration in the combustion gases of a sample subjected to a given heat flux. Typically, the subject material is irradiated with a heat intensity similar to that experienced in a fire sitation (25-75 kW/m^2) and the ignition, heat release and smoke release characteristics of the materials are measured.

The limiting oxygen index (LOI) or oxygen index (OI) is a method for evaluation of the flammability of materials. LOI is defined as the minimum concentration of oxygen in an oxygen-nitrogen mixture, required to sustain burning of a vertically mounted specimen. Thus, the more oxygen required (higher LOI), the stronger the flame retardancy effect. The oxygen index was described as follows:

$$\text{oxygen index} = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

Hence, higher LOI values represent better flame retardancy and a smaller LOI represents a more flammable material.

UL-94 horizontal (ASTM D365, IEC 60695-11-10, IEC 60707, ISO 1210) and vertical (ASTM D365-77, ASTM D3801, IEC 60695-11-10, IEC 60707, ISO 1210) burning tests are the standardapplied by the American Underwriters Laboratories for testing the flammability and fire safety of plastic materials used in devices and appliances. UL-94 tests contain test procedures for both horizontally and vertically positioned test specimens in the forms of rods. In the UL-94HB (Horizontal burning) test, the burning of a horizontal specimen is tested. Specifications are; slow burning on a horizontal specimen; burning rate < 76 mm/min for thickness < 3 mm. In UL-94VB (Vertical Burning) tests, the test specimen is vertical and ignited by a Bunsen burner to be classified according to self extinguishing characteristics as V-0, V-1 or V-2. These tests are more rigorous than the HB test since the verticals specimens are burned by their lower ends, thus preheating material above it, and the samples must extinguish themselves. The top class, V-0, is achieved if the mean inter-flame time o five samples after 10 applications flame does not exceed 5 s. The material is placed in class V-1 if the mean after flame is less than 25 s. If flaming drippings occur, the material is classifed in V-2; the ignition of surgical cotton placed below the specimen serves as a criterion. [9]

3. EXPERIMENTAL PART

3.1 Materials

For the preparation of flexible PVC; $Al(OH)_3$, Zinc borate, $CaCO_3$, H.Talcid, Sb_2O_3, heat stabilizer, DOP were added different amounts in flexible PVC and tested.

PVC: A commercial production provided from PETKİM.

$Al(OH)_3$:A commercial white powder used to provide synergytic effect with zinc borate.

$CaCO_3$: A commercial coated filler.

Hidro Talcite ($Mg_6Al_2(OH)_{16}.CO_3.4H_2O$): A commercial filler.

Zinc borate ($3ZnO.3BO_3.3.5H_2O$): A commercial production (obtained from Melos A.Ş.) used as a flame retardant additive.

Sb_2O_3: A commercial fire retardant.

Calcium aluminum phosphite(CaAlP) (Ca_6Al_2 $(HPO_3)_2(OH)_{14}.4H_2O$): A commercial fire retardant.

3.2 Equipments

Single Screw Extruder

3.3 Production of PVC Samples for Fire Test

PVC powder, liquid DOP and heat stabilizer were put together and CaCO3 powder, Al(OH)3, zinc borate, h.talcit were mixed in a container and then extruded from a laboratory extruder containing single screw and and cut into small pieces. This mixture was extruded as 2 mm thick profile from an extruder profile.

This experiment was carried out by 6 times with different fire retardant additives.In the table 3.1 the materials used for fire retardant PVC formulation is shown.

Table 3.1 : The materials used for fire retardant PVC formulation

	$CaCO_3$(%)	$Al(OH)_3$(%)	Zinc borate(%)	H.Talcit(%)	Sb_2O_3(%)	CaAIP
Exp.1	90	4	8	8		
Exp.2	110					
Exp.3	102				8	
Exp.4	94	18	8			
Exp.5	94		8			8
Exp.6	94		8	8		

3.3 Application of UL Flame Rating – UL 84

3.3.1 Horizontal testing (HB)

Procedure: A specimen is supported in a horizontal position and is tilted at 45 ^{0}C. A flam is applied to the end of the specimen for 30 seconds or until the flame reaches the 1 inch mark as in figure 3.1. If the specimen continues to burn after the removal of the flame, the time for the specimen to burn between the 1 and 4 inch marks are recorded. If the specimen stops burning before the flame spreads to the 4 inch mark, the time of combustion and damaged length between the two marks is recorded. Three specimens are tested for each thickness.

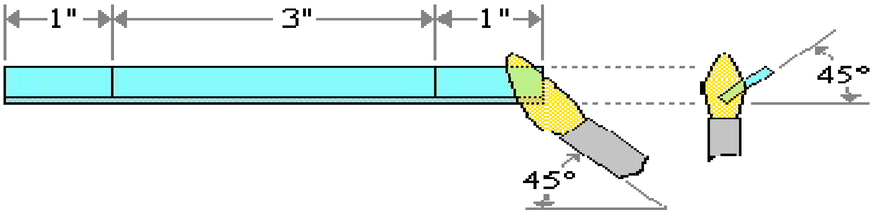


Figure 3.1: Horizontal flame test [8]

3.3.1.2 Requirements

Specimens must not have a burning rate greater than 1.5 inches/minute for thicknesses between 0.120 and 0.500 inches and 3 inches/minute for thicknesses less than 0.120 inches.

Specimens must stop burning before the flame reaches the 4 inch mark.

3.3.2 Vertical testing (V-0, V-1, V-2)

Procedure is a specimen is supported in a vertical position and a flame is applied to the bottom of the specimen.the flame is applied for ten seconds and then removed until flaming stops at which time the flame is reapplied for another ten seconds and then removed. Two setsof five specimens are tested. The two sets are conditioned under different conditions. In figure 3.2 the application of test method is seen:

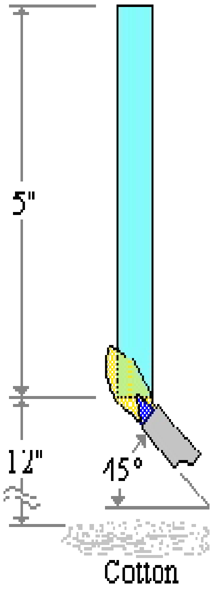


Figure 3.2 : Vertical flame test [8]

3.3.2.1 Requirements

V-0

Specimens must not burn with flaming combustion for more than 10 seconds after either test flame application.

Total flaming combustion time must not exceed 50 seconds for each set of 5 specimens.

Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.

Specimens must not drip flaming particles that ignite the cotton.

No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame.

V-1

Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application.

Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens.

Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.

Specimens must not drip flaming particles that ignite the cotton.

No specimen can have glowing combustion remain for longer than 60 seconds after removal of the test flame.

V-2

Specimens must not burn with flaming combustion for more than 30 seconds after either test flame application.

Total flaming combustion time must not exceed 250 seconds for each set of 5 specimens.

Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp.

Specimens can drip flaming particles that ignite the cotton.

No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame [8].

3.3.3 Preparation of samples for UL-94 tests

After PVC with flame retardant additive sample has been prepared, PVC stripes of each experiment (2 mm thick) were cut according to the requirements of the UL-94 vertical tests.

3.4 Experimental-2 for Polyurethane

3.4.1 Sample-1 ammonium borate synthesis

3.4.1.1 Materials

Boric acid (orthoboric acid), 25% aqueous ammonia

3.4.1.2 Ammonium borate production

100 gms of boric acid(orthoboric acid) are heated to 100 ^{0}C to 125 ^{0}C to dehydrate about 1 mol of water per molecule of the boric acid thereby producing metaboric acid (HBO_2) for one day. Then it is slowly added to 100 gms of aqueous ammonia, containing 25% ammonia, at ambient temperature and pressure.

The mixture is cooled to keep the temperature to below the boiling point wherein the ammonia escapes from the water. The mixture is allowed to react for 1-4 hours thereby producing ammonia salt of metaboric acid (NH4)BO3 then the excess water is evaporated off by heating or spray drying thereby producing a powdered polyammonium diborate with the general formula (NH2)HvBxOy wherein n is a number 2-4, v is a number 0-3, x is a number 2-4 and y is a number 57.

3.4.1.3 Calculation

First, ammonium-boric acid dried in the oven at 125 0C. Then the amount of the water evaporated from H_3BO_3 was calculated by weighing the new material. New formed metaboric and boric acid amount can be calculated according to the given equation:

H_3BO_3→ H_2O + HBO_2 (metaboric acid)

1 mole boric acid= 62 grams

1 mole water= 18 grams

First weight of the H_3BO_3= 100 gr

Weight after 24 hours H_3BO_3= 88 gr

62 grams H_3BO_3 release→ 18 gr H_2O (water)

100 grams H_3BO_3 should release→ 29 grams of H_2O (water)

This result showed that boric acid should be kept more than 24 hours to release all water in the structure.

After second 24 hours, the sample was again weighed. Total amount of water evaporated was 29 grams- this was what is expected. Then this metaboric acid and 100 grams of 25% aqueous ammonium solution were together taken into a beaker and heated to 50^0C and stirred for 24 hours.

After stirring the mixture was left for drying in the oven and 24 hours later the sample was taken and turned into powder.

3.4.2 Sample-2 ammonium borate production

100 gms of boric acid(orthoboric acid) are heated to 140oC to until five mols of water per molecule are removed thereby producing tetraboric acid (H2B4O7) then it is slowly added to 100 gms of aqueous ammonia containing 25% ammonia while agitating. The mixture is allowed to react for 12 hours thereby reducing the tetraboron oxyacid to diboron oxyacid and boric acid, and reacting it with the ammonia thereby producing ammonia salt of boric acid and polyammonium salt of polyboron oxyacid. The mixture is then dried by heat or spray drying and two mols of the ammonia salt of boric acid react to produce a powdered polyammonium diborate(NH2)H2B2O3).

3.4.2.1 Calculation

4H3BO3→H22B4O7 + 5H2O

4H3BO3→ 248 gram

5H2O→ 90 grams

248 grams boric acid release 90 grams of water

100 grams boric acid release 36.3 grams of water

After 36.3 grams of water evaporation, tetraboric acid (H2B4O7) was obtained. 25% of 100 grams ammonium borate was added onto 63.7 grams of tetraboric acid. They were stirred in a beaker at 80 0C for 10-15 minutes. After 15 minutes, the temperature was set at 45 0C and the mixture was stirred for 12 hours. Next day, the ammonium exit from the beaker. After this the tetraboric acid and ammonium complex put in the oven and dry for 24 hours at 1100C. Turn into powder.

3.4.3 Sample-3 modified zinc borate production

About 50 gr by weight of powdered zinc borate are added to about 50 parts by weight of concentrated ammonia containing 25% ammonia while agitating. The mixture is allowed to react for 12 hours to the boiling point of ammoniac and the zinc borate is hydrolyzed, split into smaller molecules and reacted with ammonia radicals thereby producing ammonium zinc salts of polyboron oxyacid and polyammonium zinc salt of polyboron oxyacid. It is then dried at 115 ^{0}C and pulverized into a fine powder.

3.4.4 Sample-4 pentaerithyritol-boric acid production

The required amounts of pentaerythritol (1.0 mol) and boric acid (1.0 mol) and water (2 L) were taken in a round-bottom flask equipped with stirrer, condenser, thermometer pocket, and gas bubbler and reacted at reflux temperature under nitrogen atmosphere and slow stirring. After 45 min, metal acetate solution in water was added slowly. The mixture was again heated to reflux temperature for $ h with slow stirring. On cooling to room temperature, a solid complex precipitated, which was washed with water and dried at 60°C for 48 h. These complexes were ground to a fine powder, sieved through (200 BSS) , and again dried at 100°C for 24 h. The yield of these salts was = 80-85 %.

3.5 General Procedure for Polyurethane Foam

3.5.1 Materials

Polyol: Viscous liquid, the characteristic chemical feature of which is hydroxyl groups based on oxygen and hydrogen, a commercial polyester polyol, blowing agent was added.

Isocyanate: chemical compounds with isocyanate groups (-NCO) as functional groups are known as isocyanates. Isocyanates based on MDI (methylene diphenylene diisocyanate) are used for producing polyurethane foam. A commercial aromatic polyisocyanate (the weight ratio of isocyanate/polyol=1,15)

In figure 3.3 forming of a MDI polymer is shown whereas the difference of 4,4'- MDI and 2,4' MDI also shown.

Sb_2O_3: A commercial fire retardant

ATH: A commercial fire retardant

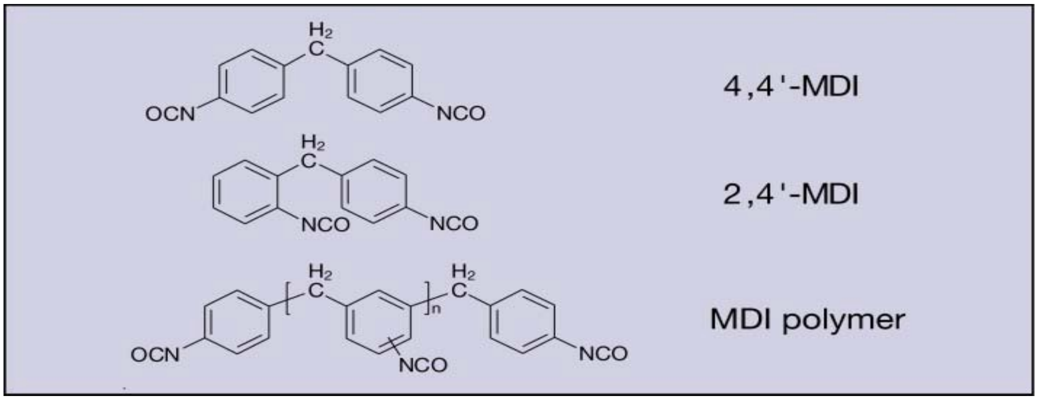


Figure 3.3 : MDI polymer

Sample 1: Ammonium borate synthesized at 125 ^{0}C.

Sample 2: Ammonium borate synthesized at 140 ^{0}C.

Sample 4: Pentaerithyritol synthesis with boric acid

$ZnBO_3$ zinc borate ($3ZnO.3BO_3.3.5H_2O$): A commercial product (MELOS A.Ş.) fire retardant

TCPP (Tris(chloroisopropyl)phosphate): A commercial liquid fire retardant.

TCP (Tricresyl phosphate) : A commercial liquid fire retardant which can be used instead of TCPP.

Hydroxy stearic acid $ZnBO_3$:

3.5.2 Equipments

Mechanical stirrer

The flame test (adapted from UL-94)

3.5.3 Synthesis of flame retardant polyurethane

Polyol and certain amont of the flame retardant materials(following table3) were stirred (according to the recipes of experiments) with a mechanical stirrer at 1500-2000 rpm for 5 minutes. Then the necessary amount of isocyanate (always taken as 1,15 times of polyol) was added onto this mixture and again stirred with a mechanical stirrer about 5 minutes (the plastic cup starts to heat). The mixture starts to blow to form foam while reaction occurs. In 15 minutes growing of the foam stops and the foam was left to get cold and take it the last shape. In figure 3.4 a classic rigid polyurethane foam formation is shown.

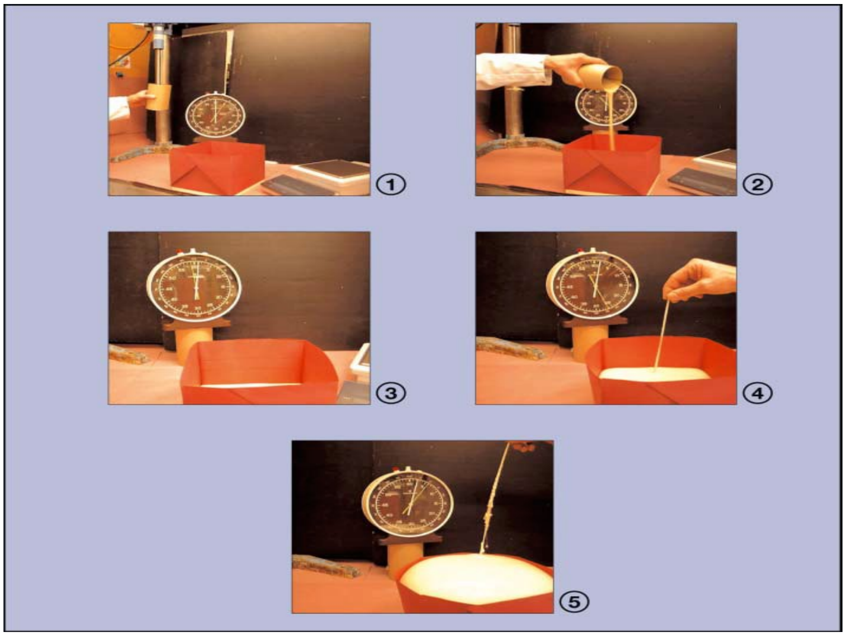


Figure 3.4: Preparation of polyurethane foam

1st and 2nd pictures: Adding polyol and isocyanate.

3rd picture: Blowing og polyurethane foam

4th picture: Cream control

5th picture: Tack-free control

3.5.4 Density test of specimens:

All polyurethane foams were prepared in polyethylene glasses thus for calculating the density of samples, smooth square pieces of all the foams were cut and then dimensions were measured and the pieces were weighed.

4. RESULTS AND DISCUSSION

4.1. Fire Retardant PVC

Flexible PVC formulations contain PVC, DOP, heat stabilizer and filler such as $CaCO_3$. Fire resistance PVC formulations are prepared by adding fire retardant powder in replace of some $CaCO_3$ filler. By doing this, the physical properties of fire resistance flexible PVC material are not very different from original flexible PVC material.

Used fire retardant compounds were a mixture of zinc borate and $Al(OH)_3$, Sb_2O_3, $CaAlPO_3$ and hidro talcite. The results are summarized in the table 4.1.

Table 4.1: The efficiency of fire retardants in PVC

	$CaCO_3$(%)	$Al(OH)_3$(%)	Zinc borate(%)	H.Talcit(%)	Sb_2O_3(%)	Phospate	Vertical Test
Exp.1	90	4	8	8			Burned
Exp.2	110						Burned
Exp.3	102				8		6 sn
Exp.4	94	18	8				8 sn
Exp.5	94		8			8	Burned
Exp.6	94		8	8			Burned

P.S. All the additives were taken as % of total weight of polyol and isocyanate components.

As seen from the table Sb_2O_3 alone is very effective fire retardant additive for PVC that contains chlorine. Adding 8% Sb_2O_3 to the formulation resulted V-0 fire retardant rating value by UL 94 method. V-0 value could be achieved by adding a mixture of 8% zinc borate and 18% ATH keeping total filler value as 110%.

4.2 Fire Retardant Polyurethane

Rigid polyurethane foam was prepared by mixing polyester type polyol and polyisocyanate components. Foam formation has started in a very short time, approximately 2-3 minutes at room temperature. In the case of fire resistance polyurethane formulation, certain amount of fire retardants were mixed with polyol component with a mechanical stirrer for at least 5 minutes in order to disperse the powder homogeneously in polyol. Viscosity of the polol has increased after the mixing. TCPP was used in the fire resistance polyurethane formulation as both viscosity reducer and fire retardant component. Sb_2O_3 was added to the system of a number of formulations as fire retardant since TCPP contains some chlorine. In talbe 4.2 the efficiency of different fire retardants are shown.

Table 4.2: The efficiency of fire retardants in polyurethane

	$ZnBO_3$(%)	Sample 1	Sample 2	ATH(%)	Sb_2O_3(%)	TCPP(%)	Horizontal Test
Exp.5	15	0	0	0	0	10	Burned
Exp.6	20	0	0	0	3	10	Burned
Exp.7	35	0	0	0	3	10	8 sn, V-0
Exp.8	15	0	0	50	3	10	1 sn, V-0
Exp.9	15	0	0	50	0	10	0 sn, V-0
Exp.10	0	10	0	50	0	10	0 sn, V-0
Exp.11	0	0	20	50	0	20	1 sn, V-0
Exp.12	5	0	5	40	0	8	5 sn, V-0
Exp.13	15	0	0	40	0	8	1 sn, V-0

As seen in the table 4.2. Zinc borate is effective in the amount of about 15-35%. The mixture of zinc borate and other fire retardant compounds gave V-0 value in UL-94 test. An optimum formulation of zinc borate: 15%, ATH: 50% and 10% TCPP is effective for fire retardant properties of V-0.

In addition to the experimentals with $ZnBO_3$, TCPP, boric acid and ATH; new experimental were carried out with stearic acid modified $ZnBO_3$, hydroxy stearic acid modified $ZnBO_3$, H_3BO_3 and TCP were used. Also in table 4.3 the effect of different fire retardants in polyurethane can be seen.

Table 4.3: Effect of different fire retardants in polyurethane

	Modif. ZnBO3(%)	ZnBO3(%)	Sample 1 (%)	Boric acid(%)	ATH(%)	TCPP(%)	TCP(%)	Horizontal Test
Control	0	0	0	0	0	0	0	Burned
Exp.14	30	0	0	0	0	3	0	Burned
Exp.15	15	0	0	0	50	0	0	7 sn
Exp.16	15	0	0	0	50	8	0	8 sn
Exp.17	15	0	0	0	40	8	0	4 sn
Exp.18	15	0	0	0	40	5	0	5 sn
Exp.19	10	0	5	0	50	10	0	3 sn
Exp.20	15	0	5	0	40	5	0	5 sn
Exp.21	15	0	10	0	30	10	0	5 sn
Exp.22	0	0	0	10	30	10	0	3 sn
Exp.23	15	0	0	0	40	10	0	7 sn
Exp.24	15	0	0	0	50	8	0	4 sn
Exp.25	15	0	5	0	30	10	0	6 sn
Exp.26	15	0	10	0	30	5	0	4 sn
Exp.27	0	10	0	0	40	0	8	3 sn
Exp.28	10	0	0	0	40	0	0	4 sn
Exp.29	10	0	0	0	40	8	0	5 sn
Exp.30	10	0	0	0	40	0	10	6 sn
Exp.31	0	0	0	10	30	10	0	2 sn

According to the results in the table, nearly all the formules provide the flammability. Control sample was no flame retardant added Polyurethane.

Experimental 22 and 31 have the same percentage additive but the difference between two samples in the 22, boric acid was first added to polyol and then mixed with isocyanate.

From 14^{th} samples to 22th samples stearic acid modified $ZnBO_3$ was used and from exp. 23 to exp. 30 hydroxy stearic acid modified $ZnBO_3$ was used.

Actually, according to UL-94 standart test, it can be said that the specimens which were burn out in 10 seconds are already successful because 4 inches of the sample did not burn in this time as seen in table 4.4.

Table 4.4: Results of polyurethane samples

	Fire retardancy	Dispersibility	Density(g/m^3)	Dimensional Stability
Control	Burned	Good	35	Stable
Exp.5	Burned	Good	85	Stable
Exp.6	Burned	Good	92	Stable
Exp.7	V-0	Good	96	Stable
Exp.8	V-0	Good	100	Stable
Exp.9	V-0	Good	102	Stable
Exp.10	V-0	Good	97	Stable
Exp.11	V-0	Good	87	Stable
Exp.12	V-0	Good	89	Stable
Exp.13	V-0	Good	93	Stable
Exp.14	Burned	Good	95	Stable
Exp.15	V-0	Very Viscos	117	Stable
Exp.16	V-0	Good	67	Stable
Exp.17	V-0	Good	67	Stable
Exp.18	V-0	Good	72	Stable
Exp.19	V-0	Good	92	Stable
Exp.20	V-0	Good	79	Stable
Exp.21	V-0	Good	98	Stable
Exp.22	V-0	Good	87	Stable
Exp.23	V-0	Good	89	Stable
Exp.24	V-0	Good	82	Stable
Exp.25	V-0	Good	63	Stable
Exp.26	V-0	Good	68	Stable
Exp.27	V-0	Good	65	Stable
Exp.28	V-0	Good	72	Stable
Exp.29	V-0	Good	59	Unstable
Exp.30	V-0	Good	93	Unstable
Exp.31	V-0	Good	72	Stable

According to the table 4.4, following results were observed:

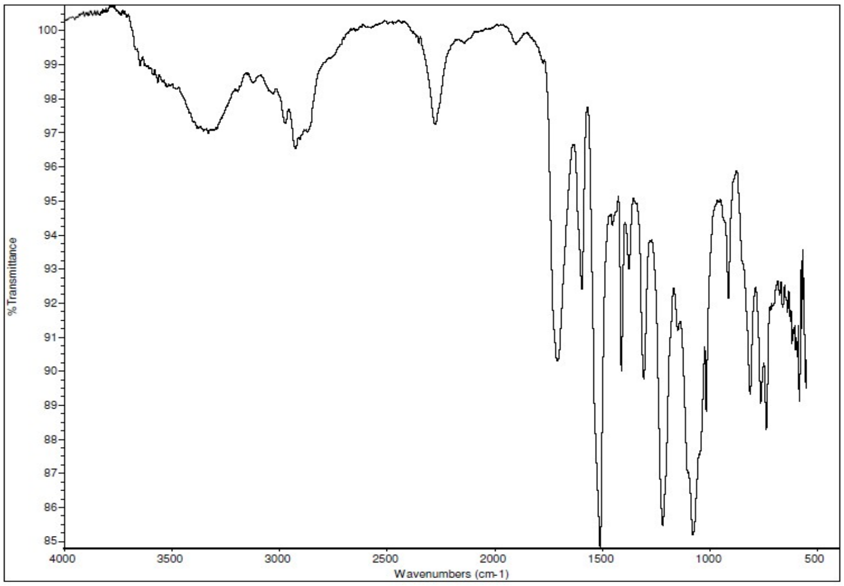
- TCP can be replaced with TCPP because TCPP is environmentally not accepted. Besides, TCPP evaporates fast from the product and is a toxic fire retardant. TCP is not as volatile as TCPP and in terms of flre retardancy TCP gives the same as result as TCPP.

-When hydroxy stearic acid modified $ZnBO_3$ is used as flame retardant TCPP or TCP should not be used due to dimensional instability of formed foam.

-H_3BO_3 is also a very successful fire retardant in the PU formulation where water is not present during usage of PU foam since H_3BO_3 dissolves water in slowly.

- Surface modified $ZnBO_3$ is dispersed in polyol much easier than $ZnBO_3$ during the preparation of PU formulation.

In figure 4.1, 4.2 and 4.3 FTIR spectrums of control sample, sample 13 and sample 28 is shown respectively.



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- **Figure 4.1 :** FTIR spectrum of control sample

Control sample: No flame retardant added polyurethane, same time called as sade in graphics.

The contents of Sample 13 and Sample 28 formules were explained in page 60, 61 in details.

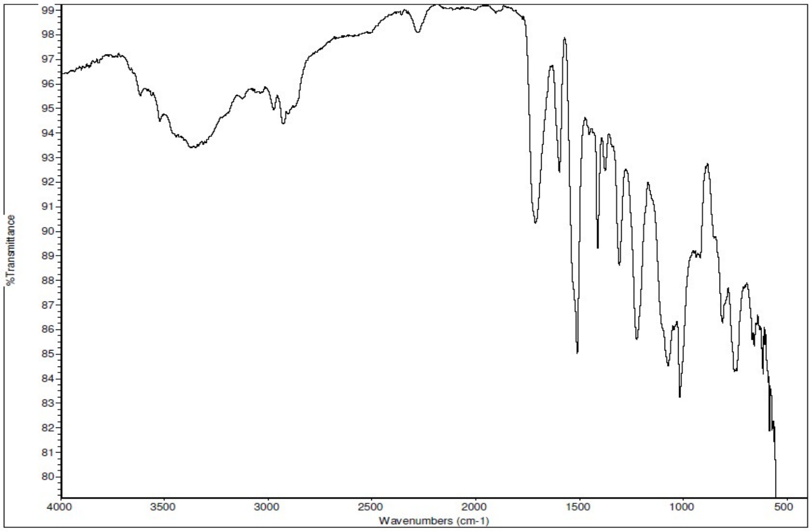

Figure 4.2: FTIR spectrum of sample 13

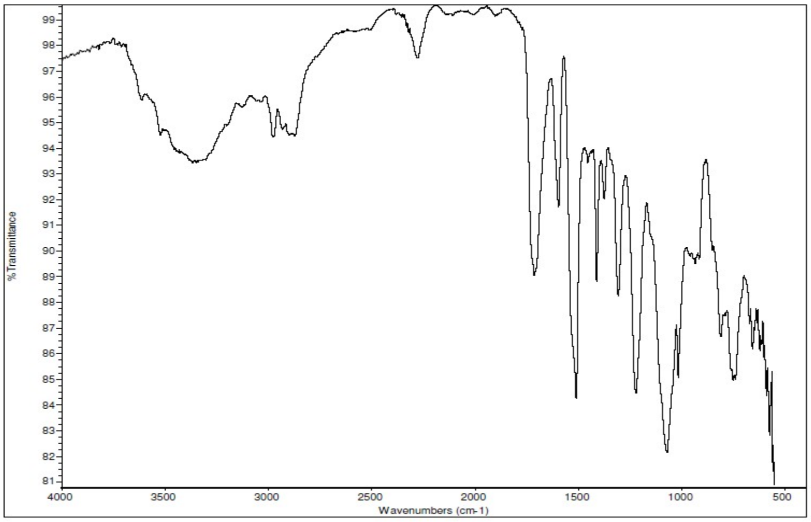

Figure 4.3: FTIR spectrum of sample 28

4.3 FTIR Study of Self Estinguished Polyurethane

ATR-FTIR spectrum of some polyurethanes are shown in figure 4.1, 4.2, 4.3. The general apperance of spectrum of ordinary PU and Self Estinguished Polyurethane samples are not very different. This suggest that insoluble FR materials use in this work (zinc borate, ATH and others) are captured by PU foamcells. This results that only PU part of samples are effective in obtaining ATR spectrum. Infrared light probably comes to directly PU foamcell and reflecting from it and insoluble FRs in the cell not be observed or determined. Obviously slight difference between spectrums are present but about sixty wieght percent of FR additives does not give any FTIR signal. In figure 4.4 TGA thermogram of samples are shown

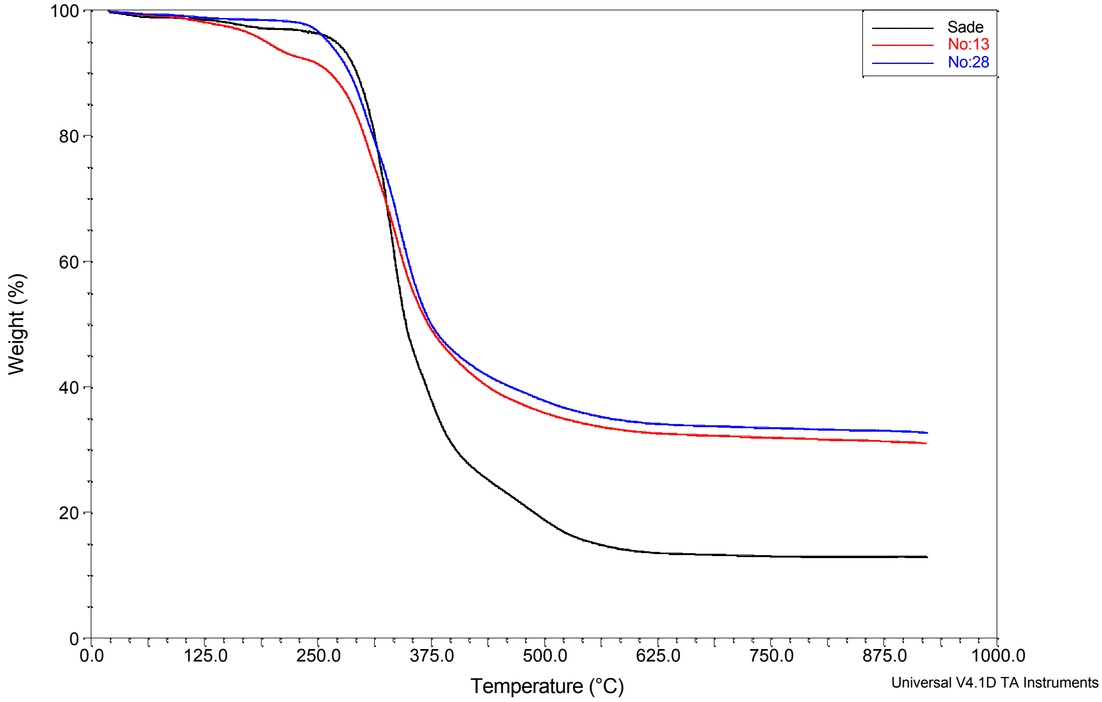

Figure 4.4 TGA thermogram of samples control (sade), no 13 and no 28

4.4 TGA Study of PU

Thermograms of three PU samples are shown in figure 4.4

As seen in fig.4.4, PU without any FR materials (sade) ,the composition temperature starts at about 210 ^{0}C and reaches to 330 ^{0}C at higher value. At about 450 ^{0}C, another type of decomposition starts and decomposition finishes at about 600 ^{0}C living ten percent residue.

As seen in fig 4.4, PU containing TCPP (no 13), gives about 200 ^{0}C, a maximum weigt loss that will be probably due to evaporation of TCPP at this temperature.

At about 230 ^{0}C, decomposition starts and completes about 700 ^{0}C leaving about 32 percent residue.

Total inorganic FR additives is about 45 percent. This shows that some weight loss of inorganic FRS due to water eliination occured (200-700 C) during this period.

As seen in figure 4.4 (no:28), the decomposition temp starts at about 240 ^{0}C and reached to max. value 330 ^{0}C. finishes about 700 ^{0}C leaving 34 percent residue. Similar weight loss of inorganic additives is also observed in this TGA.

5. CONCLUSION

The aim of this study was to improve the flame retardant and smoke suppressant properties of flexible PVC and rigid Polyurethane where at this time the other properties of materials should not be effected so much: Preparation (dispersibility) and processing of FR materials and fillers are easily combined in PU and PVC, secondly density, thirdly diomensional stability at least should be conserved as the original material. [14] This was trying to be achieved by using zinc borate and synthetic boron compounds but in order to obtain better results, new experiments should be carried out. The high amounts of the fire retardants that used in PVC and Polyurethane should be decreased. What is more, in rigid Polyurethane samples, compression strength tests also should be carried out to figure out if the existing formules are appropriate all of the aspects. Also this study gave an idea that boric acid –alone- can be a good fire retardant.

In the case of fire retardancy of PVC, the optimum formules can be experimental 3 and 4 where adding 8% Sb_2O_3 , 102% $CaCO_3$ to the formulation or a mixture of 8% zinc borate and 18% ATH and 94% $CaCO_3$ keeping total filler as %110 but nowadays Sb_2O_3 is not preferrible for the environment thus it would be better to use zinc borate compounds.

In the case of fire retardancy and other properties of Polyurethane, experimentals 16, 17, 18, 20, 25, 26, 27, 28 and 31 give the best results. The best formules re listed in table 4.5

Table 5.1: Best formules of polyurethane

	Modif. $ZnBO_3$(%)	$ZnBO_3$(%)	Sample 1(%)	Boric acid(%)	ATH(%)	TCPP(%)	TCP(%)
Exp.16	15				50	8	
Exp.17	15				40	8	
Exp.18	15				40	5	
Exp.20	15		5		40	5	
Exp.25	15		5		30	10	
Exp.26	15		10		30	5	
Exp.27		10			40		8
Exp.28	10				40		
Exp.31				10	30	10	

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