

CHAPTER II

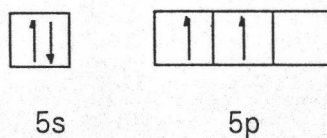
LITERATURE SURVEY

2.1 Theoretical background

2.1.1 Introduction

Tin, a group IVB element, has an outer electron configuration $5s^2 5p^2$ and like carbon, silicon, germanium, and lead, can form compounds in both the +2 and +4 oxidation states depending upon the in which its valence electron shell are used in the bonding.

Tin atom (ground state)



If the two 5s electrons remain as a pair, the oxidation state is +2, whereas promotion of one of these electrons to the vacant 5p orbital produces the electronic configuration characteristic of the +4 oxidation state.

Tin compounds may be divided into two main classes;

1. Inorganic tin compounds in which tin, with a valency of +2 or +4, is chemically associated with an element other than carbon or with an ionic radical.
2. Organotin compounds which possess one or more direct tin-carbon bonds and have the general formula R_4SnX_{4-n} , where R is an alkyl or aryl group, X is an anionic species,

chloride, oxide, hydroxide or other functional groups, and n is 1 to 4. Hence, these compounds can be conveniently divided into four classes:

- a) monoorganotin compounds, $R\text{SnX}_3$
- b) diorganotin compounds, $R_2\text{SnX}_2$
- c) triorganotin compounds, $R_3\text{SnX}$
- d) tetraorganotin compound, $R_4\text{Sn}$

2.1.2 Manufacture of organotin compounds.

Manufacture of organotin compounds usually comprise two principle steps; the first step consists of making direct tin-carbon bonds in compounds such as $R_4\text{Sn}$; the second stage is one of comproportionation in which $R_4\text{Sn}$ is reacted with stannic chloride to produce compounds of the type $R_3\text{SnCl}$, $R_2\text{SnCl}_2$ and $R\text{SnCl}_3$. Other derivatives may then be simply produced from these chlorides, for industrial and other uses.

Reaction schemes are shown in figure 2-1.

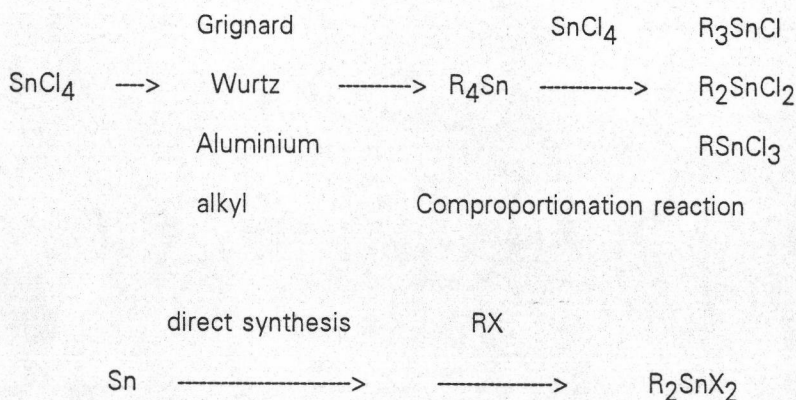


Figure 2-1 Manufacturing routes of organotin compounds.

The Grignard route for the industrial production of tetraorganotin is flexible and produces high yields. It is used to manufacture tetraphenyl tin, tetrapropyl tin, tetraoctyl tin and tetrabutyl tin compounds.

In the Wurtz synthesis, sodium is used in place of magnesium. To date this process does not appear to have been readily used because the competing side reactions are a problem. The aluminium alkyl route has advantages in that it can be operated continuously and no solvents are needed. There is also a direct synthesis route which involves reaction between tin and alkyl halides.

Starting from a tetraorganotin, comproportionation reactions with tin(IV) chloride can be used to produce tri-, di-, and mono-organotin compounds as shown in figure 2-2

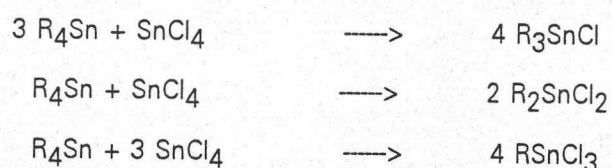


Figure 2-2 Comproportionation reaction of organotin compounds.

2.1.3 Chemical properties and application.

The tin-carbon bond is more polar than carbon bonds to carbon, silicon or germanium in group(IV)B. However, the tin-carbon bond is stable to water and atmospheric oxygen at normal temperatures and is quite stable to heat (many organotins can be distilled under reduced pressure with little decomposition).

The number and nature of the organic group, attached to the tin atom dramatically affect the properties of the compound, and this has resulted in wide range of applications (table 2-1).

Table 2-1 Principal industrial uses of organotin compounds 12.

Application	Function	Principal compounds used
PVC stabilisation	Stabilisation against effects of heat and light	dialkyltin di-isooctylthioglycolate (alkyl = methyl, butyl, octyl ,2-butoxy-carbonylethyl) dialkyltin maleate (alkyl = methyl, butyl,) mono-alkyltin triisooctylthioglycolate (alkyl = methyl, butyl, octyl ,2-butoxy-carbonylethyl)
Polyurethane foamsR IV silicones	Homogeneous catalysis	dibutyltin diacetate dibutyltin dioctoate, dibutyltin dilaurate
Esterification	Homogeneous catalysis	butanestanonic acid dibutyltin diacetate, dibutyltin oxide
Glass treatment	Precursor for tin(IV) oxide films on glass	dimethyltin dichloride, butyltin trichloride methyltin trichloride
Wood preservation	Fungicide	bis(tributyltin)oxide, tributyltin napthenate tributyltin phosphate
Agricultural chemicals	Fungicide Insecticide Miticide Antifeedant	triphenyltin acetate triphenyltin hydroxide tricyclohexyltin hydroxide bis(trineophyltin) oxide 1-tricyclohexylstannyl-1,2,4-triazole
Antifouling	Biocide	triphenyltin chloride, triphenyltin fluoride bis(tributyltin) oxide, tributyltin fluoride tributyltin chloride, tributyltin acrylate polymers
Material Protection (leather,paper, etc.)	Fungicide	bis(tributyltin) oxide
Moth proofing of textiles	Insecticide Antifeedant	triphenyltin chloride triphenyltin hydroxide
Disinfection	Bacteriostat	tributyltin benzoate

Tetraorgantins R_4Sn are usually colourless liquids which are thermally stable to 200 °C. Although these compounds are toxic to mammals, they do not possess significant biological activity. They were used as precursors for other organotin compounds because they are readily degraded under environmental conditions to tri-, di-, mono-organotin, and ultimately, inorganic tin compounds. Maximum biological activity occurs in triorganotin series. They are used commercially as biocides in a number of areas.

Dialkyltin compounds R_2SnX_2 , are powerful stabilisers for PVC. The most effective heat stabilisers are those containing Sn-S bonds. Monoorganotin compounds exhibit low mammalian toxicity and are thus desirable industrial compounds. Today their main use has been as synergistic additives for stabilising PVC and, to a lesser extent, as esterification catalysts. There are indications that they may have a place as waterproofing agents for cellulosic materials such as cotton textiles, paper and wood and as flame retardants for woolen fabrics.

Before discussing the flame retardant and smoke suppressant properties of tin compounds in detail, it is important to outline the factors influencing polymer combustion.

2.1.4 The burning of polymeric materials.

A burning polymer is a complex combustion system. To create a basis for fire retardant research, it is important to clarify the combustion mechanisms of polymers. The process by which a polymer burns can be summarised in a combustion cycle which are shown below;

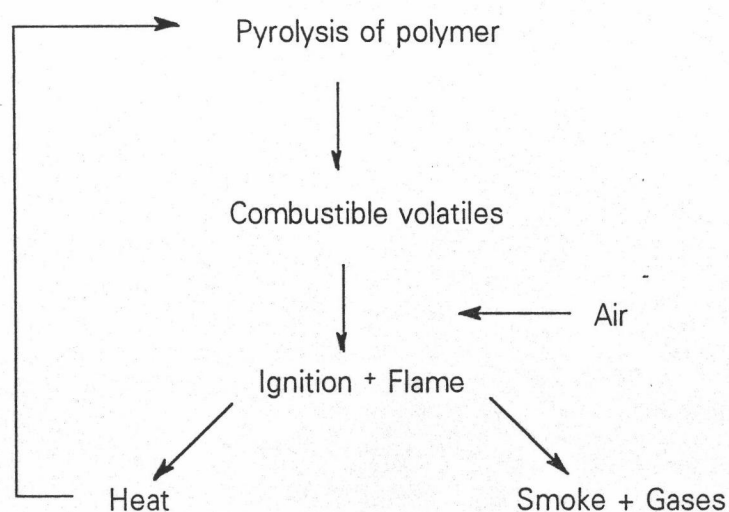


Figure 2-3 Pyrolysis of polymer.

Polymers ignite and burn in a three-step process. The first step is fuel production in which heat from an outside source causes a temperature rise in the fuel, with subsequent breaking of chemical bonds and production of volatile flammable gases which diffuse into the surrounding air environment. The second step is the ignition of these flammable gases. Ignition cannot be achieved until interdiffusion of the flammable gases with air has produced a flammable mixture of some minimum volume. Then, this mixture must be heated, by the external heat source, to its ignition temperature. In this time, the combustion which is an exothermic reaction is initiated. The third step is that of flaming combustion, a strictly gas-phase process, but one that is coupled with the fuel in that heat is transferred from the flame back to the condensed phase to continue the process of gaseous fuel production. While the ignition step must be accomplished in a flammable premixed volume of fuel vapour and air, flaming combustion of solid or liquid fuels continues by a process that is a diffusion flame. Hence, polymer combustion may be retarded or prevented if flame retardant affects the equilibrium of combustion, i.e. in the rate of evolution of pyrolytic gases, the rate of mixing with oxygen in air, ignition, the rate of reaction with oxygen and/or the rate of heat flow back to the polymer.

The reactions occurring in a burning polymer may be classified according to the site of action, i.e. in the condensed phase or in the gas phase.

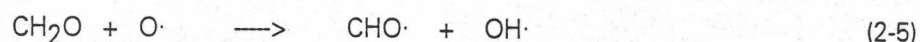
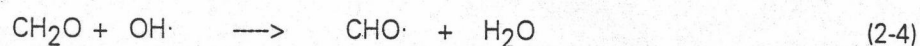
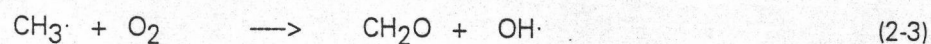
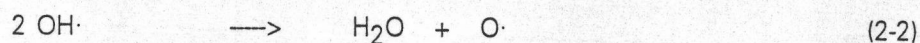
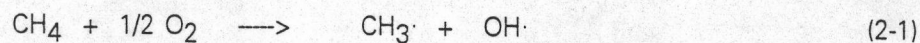
2.1.4.1 Condensed phase reactions.

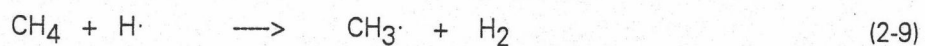
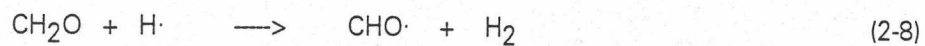
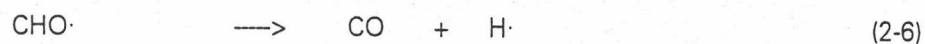
On the combustion, high molecular weight polymers decompose before vaporisation. Sufficient thermal energy (typically, 200-400 kJ/mole) is required to rupture a C-C or C-X bond and although, once initiated, the cleavage process proceeds rapidly, because of propagating chain reaction. Each bond rupture produces two radicals which react with a low activation energy (20-40 kJ/mol), with other polymer chains. As a result, polymer breaks down to give the gaseous monomer or cross-linking in order to give an involatile char, according to the nature of the polymer being burnt.

2.1.4.2 Gas phase reactions.

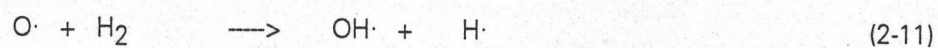
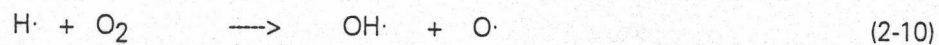
The processes involved in the flames of burning polymer systems are complex and are not well understood. The mechanism of combustion of methane involves several radical reactions which are shown below;

Chain propagations.

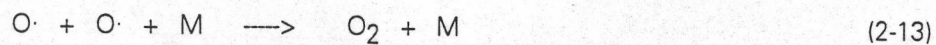
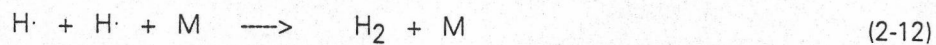




Chain branching.

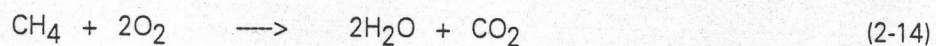


Termination (three-body reaction).



Where M is a solid catalyst.

Overall reaction.



In more complex fuel-rich flames, initially attacked by atom rather than OH radical probably occur since the concentration of the latter species are low, thus resulting in the formulation of CO, H₂, H₂O and solid carbon as the major product.

The reaction occurring in a burning polyurethane prepared from toluene diisocyanate, hexamethylene isocyanate or diphenyl-methane-p,p-diisocyanate with poly-1,4-butanediol adipate, poly-1,6-hexanediol adipate or polydiethylene glycol adipate has been shown ¹³ in Figure 2-4.

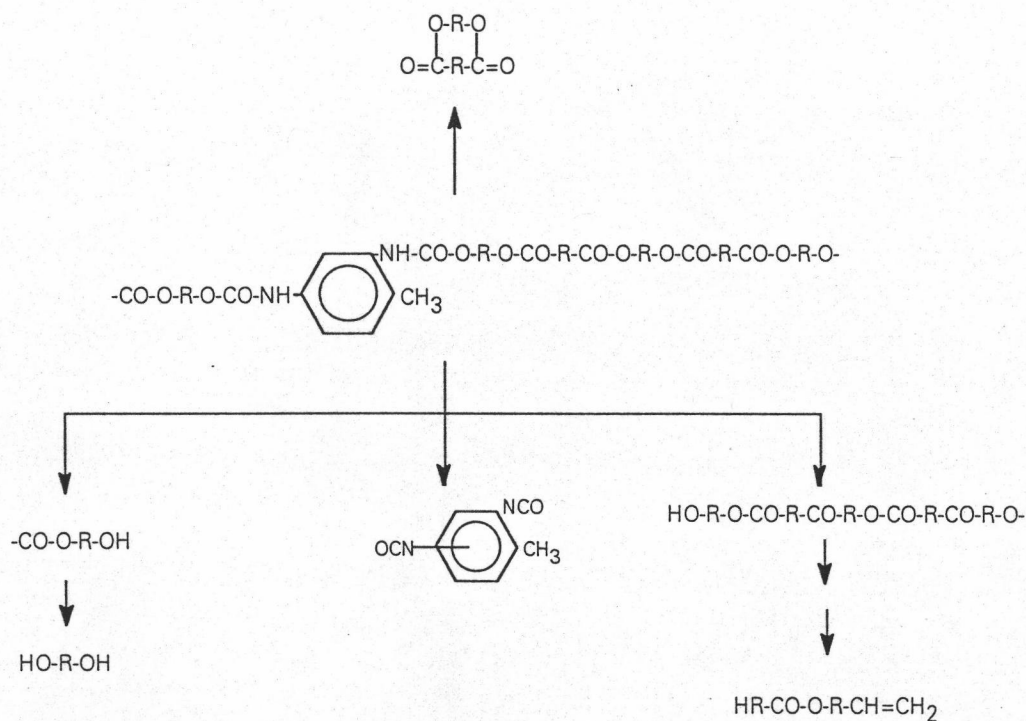


Figure 2-4 Mechanism of thermal degradation of a polyurethane.

2.1.5 Flame retardants.

Flame retardants may be divided into two types;

a) Additive retardants are incorporated into polymers by being physically mixed with polymer, normally after the polymerisation is completed. They do not affect the chemical structure of the monomeric units.

b) Reactive flame retardants appear to be most versatile in thermosetting materials, in which substitution of compounds can be effected at a stage much closer to end use than might be the case with thermoplastics. Additive type flame retardants appear to be most versatile in thermoplastics.

Flame retardants may act in many different ways, often simultaneously.

2.1.5.1 Solid phase retardation.

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

i) Diversion of pyrolysis towards char formation, instead of volatile, flammable compounds, results in a reduction of flammability. The formation of a thermally stable barrier during combustion at the polymer surface reduces the amount of fuel fed to the flame. However, char formation can only occur if the degradation path of the polymer involves extensive cross-linking and, consequently, polymers which were depolymerised easily do not leave carbonaceous chars.

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

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

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

In wool, certain metal complex (eg. ZrF_6^{2-} , SnF_6^{2-}) are used to inhibit pyrolysis by direct complexing with the proteinaceous substrate or by yielding involatile derivatives of the low molecular weight pyrolysis products.

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

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

2.1.5.2 Gas Phase Retardation.

Whereas condensed-phase reactions leading to a change in primary pyrolysis patterns are mostly heterolytic (ionic) in character, vapor phase inhibition involves homolytic (free radical) processes.

Halogenated retardants yield HCl or HBr, which break the chain of reactions in the flame by scavenging highly active radicals¹⁴⁻¹⁶.

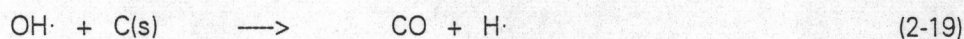
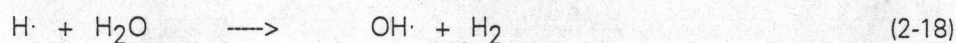
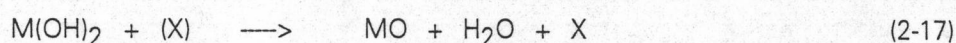
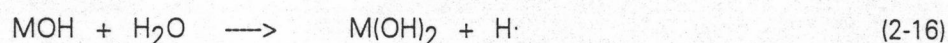
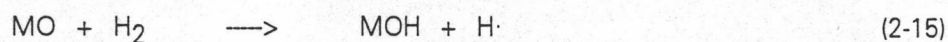
In general, brominated compounds are better than chlorinated compounds, since they break down more readily. The compounds used for this purpose must, however, be stable up to the pyrolysis temperature to prevent halogen loss before pyrolysis occurs.

A second gas-phase mechanism involves the catalysis of radical recombination. The introduction of heterogeneous, finely divided metal or metal oxide particles into the flame is a very effective way of inhibiting flame reaction. The free radicals in the flame recombine on the metal oxide surface, giving up a fraction of the collision energy to this third-body intermediate. This type of mechanism is found in the antimony oxide/chlorine retardants where, through the formation of volatile $SbCl_3$ or $SbOCl$, finely divided antimony or antimony oxide is released in the flame.

2.1.6 Smoke suppression and mechanism.

Among the combustion gases, carbon monoxide, has commonly been of chief concern. Other toxic gases which can be formed in fire include hydrogen cyanide, nitrogen oxide, hydrogen chloride, and sulfur oxide. Visible smoke from the burning polymer is generally thought to result from incomplete combustion. Since polymer flames are diffusion flames, stoichiometric mixing for complete burning does not readily occur. The visible smoke can consist of liquids or solids. Carbonaceous or aqueous components are probably most commonly encountered in polymer smokes.

Early work on smoke suppressants has shown that the predominant class of these additives for fuel are metal salts and complexes¹⁷. Other classes include sulfur and nitrogen oxide precursors. The metal appears to function as smoke suppressants through the gas phase destruction or the prevention of the formation of soot particles. A general mechanism for destruction of solid carbon in the dispersed phase has been proposed as shown below.



In this mechanism, oxides or hydroxides of the metal catalyse the decomposition of hydrogen or water vapour producing hydroxyl radicals which will oxidise solid carbon. Certain compounds are believed to perform their smoke retardant function in the solid or condensed phase, by promoting char formation, diluting the polymer content, dissipating heat, and altering

the chemical reactions in the condensed phase. This type of mechanism may be identified by an increase in the char residue.

Theoretically, a flame retardant which is effective in the condensed phase would be expected to perform a smoke retardant function, because increased retention of material in the solid phase or char would result in a reduction in combustible compounds and a reduction in compounds in the gaseous phase which would appear as smoke.

However, a flame retardant may succeed only in preventing oxidation which produces heat and flame and unoxidised material may escape into the gas phase as soot and tar forming smoke. A flame retardant which acts primarily in the gaseous phase would not prevent decomposition of the material and, by inhibiting ignition or combustion, may ensure that the decomposition products are more likely to be visible as smoke.

2.1.7 Example of flame retardant and/or smoke suppressant in polymers.

2.1.7.1 Phosphorus ¹⁸.

Phosphorus is believed to perform most of its flame retardant function in the condensed phase. The effect of phosphorus on the surface characteristics of the char may involve the formation of nonvolatile oxide of phosphorus which act as a flux for the carbonaceous residue. On the chemical reactions, these compounds may involve partial oxidation followed by dehydration to yield water, a noncombustible gas with relatively low heat of formation, and carbon. Thus phosphorus may not be effective as smoke retardant.

2.1.7.2 Bromine and chlorine.

Bromine is believed to perform most of its flame retardant function in the gaseous phase whereas the flame retardant function of chlorine is in both the gaseous and condensed phases. The chemical reaction may involve halogenation followed by dehydrohalogenation to yield a polymeric residue rich in double bonds which is then converted to carbon.

Aliphatic chlorine is more effective than aromatic chlorine in both polyesters and polyurethanes. Similarly aliphatic and alicyclic bromine compounds have been found to be more effective than aromatic bromine compounds in flame retarding polystyrene. This difference is attributed to the higher bond energy of aromatic halogen, which makes it less readily available for flame retardant action.

2.1.7.3 Antimony.

Antimony appears to be ineffective when used by itself. It is principally used as a synergist with the halogens, particularly bromine and chlorine. Where polyesters containing no other flame retardants require about 17 percent bromine for self-extinguishing behavior, similar results can be obtained with 13 percent bromine and 1 percent antimony trioxide, or a percent bromine and 2 percent antimony trioxide.

The increased effectiveness is probably due to the longer residence time of bromide as antimony tribromide, relative to bromide as hydrogen bromide. The greater effectiveness of bromide compared to chlorine is also observed. For polyester containing halogen with 5 percent antimony trioxide, 6 percent bromide produces the same level of flame retardance as 24 to 25 percent chlorine. Unfortunately, antimony trioxide-halogen system tends to increase smoke production during combustion of the associated polymer, and also result in undesirable rigidity and/or brittleness, in addition to a strong pigmentation. Furthermore, recent health and environmental issues have focused attention on the possible toxicity/carcinogenicity of Sb_2O_3 , and consequently, its use as a flame retardant has been subject to intense scrutiny.

2.1.7.4 Aluminium.

Aluminium is believed to perform most of its flame and smoke retardant function in the condensed phase. Hydrated aluminium compounds, such as hydrated aluminium oxide, appear to be generally more effective than the anhydrous compounds at equal aluminium

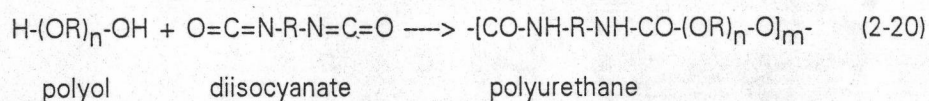
concentration. This is believed to be due to the removal of heat required to effect dehydration.

2.1.7.5 Tin.

Tin is believed to perform most of its flame retardant function in the condensed phase. It may be effective as smoke retardant. The tin compounds which have been used include tin oxide, sodium stannate, calcium stannate and zinc stannate. Other metal elements which appear to have some effect in the condensed phase, as flame retardant or both, are lead in group IVA, zinc and cadmium in group IIB, copper in group IB, iron, cobalt, and nickel in group VIII, manganese in group VIIB, chromium and molybdenum in group VIB, vanadium in group VB, and titanium in group IVB.

2.1.8 Polyurethane foam.

Polyurethane foams are prepared by the reaction of a polyol or polyester compound with a di- or polyisocyanate ¹⁹ as shown in equation 2-20.



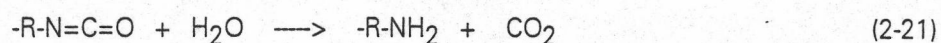
The reaction is exothermic. The rate of the polymerisation reaction depends upon the structure of both the isocyanates and the polyols. The reaction mechanism can be classified as a nucleophilic reaction on an activated carbonyl group and the formation of polymer is by a step-wise process ²⁰.

The nucleophilic groups react with the isocyanate group, containing hydrogen atoms bonded to oxygen, nitrogen, sulphur and other less likely high electron density atoms. However, the significant group cannot react with the carbon-hydrogen bond system.

In the route of the reaction, the reactive hydrogen atom is transferred to the nitrogen of the isocyanate and then, the remainder is attached to the carbonyl.

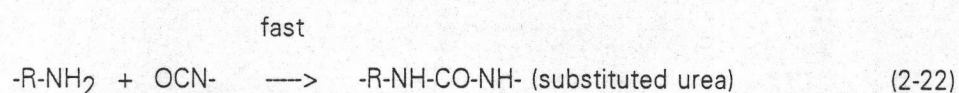
Variation in the composition of the diol group R can produce flexible product if R is long and has easily rotatable group. Otherwise, short and rigid R group gives a more rigid product. If the reactants are polyfunctional, the occurred cross-linking will impart other variations in physical properties.

Other relevant reactants are water and amines, both primary and secondary. The water acts as a nucleophile like other hydroxy compounds and leads to an unstable product generating carbon dioxide, which functions as a blowing agent and an amine as shown in equation (2-21).



Quite often a volatile organic compound, e.g. a chloro-fluorocarbon (CFC), is added to the reaction mixture to assist in the blowing of the foam. Other additives include catalysts to increase reaction rates, and surfactants to control the structure.

Analogously, the amines react with isocyanate groups to produce substituted urea as shown in equation (2-22).



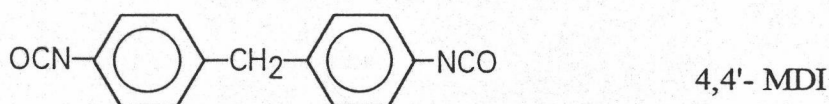
Polyurethane foams can be divided into three main classes;

	average molecular weight per branch
1. flexible	2500 - 20000
2. semi-flexible or semi-rigid	700 - 2500
3. rigid	400 - 700

According to the polyurethane synthesis, foam contained many fundamental components which were described below.

2.1.8.1 Isocyanate.

The most important isocyanates used in polyurethane manufacture are the 2,4- and 2,6-toluene diisocyanate(TDI), 4,4-diphenylmethane diisocyanate (MDI) containing small amount of the 2,4-isomer and its aliphatic analogue.



Unfortunately, TDI mixtures can represent a serious toxic hazard in use, affecting the respiratory system and the skin, so their usage are limited. On the other hand, the diisocyanate MDI based on diaminodiphenylmethane is considerably safer to use, having a much lower volatility. Hence, the MDI is mainly used for manufacture of polyurethanes.

2.1.8.2 Polyol.

There are two main groups of polyols which in general lead to different properties. These are the polyester and polyether polyols. Polyether polyol gives products with better hydrolytic stability and resilience. It also lead to better low temperature performance and lower viscosity mix for processing. Polyester gives products with better cut resistance and oil resistance. Polyester polyol is usually more expensive than polyether polyol.

The choice of polyol, especially the molecular weight and functionality of its molecular structure and functionality (the number of isocyanate-reactive hydroxy groups per molecule of polyol), controls the degree of cross-linked activity in the polymer.

2.1.8.3 Catalysts.

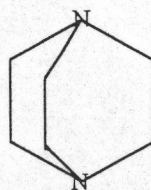
The catalyst most widely used commercially in polyurethane processes are tertiary amines and organotin compounds.

In the case of the amines, promotion of urethane links is related to the strength of the base but structure effects can also be important, as shown in table 2-2 ;

Table 2-2 Base strength and catalyst activity.

Amine	pKa	Relative rate of butanol/ phenyl isocyanate reaction
NMe ₃	9.9	2.2
NMe ₂ Et	10.2	1.6
NMeEt ₂	10.4	1.0
NEt ₃	10.8	0.9
Triethylene diamine	8.2	3.3

The relatively weakly basic triethylene diamine, where there is little or no steric hindrance, is an extremely powerful catalyst compared with triethylamine.



Triethylene diamine

While the organotins show remarkable activity, promoting reactions of NCO with OH groups in preference to reaction with water. They are readily soluble in the reaction mixtures and have the advantage of low volatility and little odour, dibutyl tin dilaurate and tin octoate are widely used.

2.1.8.4 Surfactants

Surfactants are added to the foam formulation to decrease the surface tension of the system and facilitate the dispersion of water in the hydrophobic medium, aid in nucleation stabilize the foam, and regulate all structure. The choice of surfactant depends on the type of foam preparation. Both ionic and non-ionic surfactants have been employed.

a) Ionic surfactants.

Anionic surfactants, such as alkali salts of fatty sulphonates or salts of fatty acid or sulphonic acids with amine, have been used for the preparation of polyester and polyether prepolymer foams. In contrast, cationic surfactants are not widely used.

b) Non-ionic surfactants.

These surfactants have been recommended for use in polyester and polyether prepolymer foams. Silicone oils (polydimethyl or methyl phenyl siloxanes) at very low concentrations are very good nucleating agents for polyurethane foam.

With the addition of silicone three basic problems are overcome:

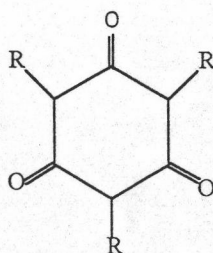
- 1) irregular gas bubble formation and growth;
- 2) incompatibility of polyol and isocyanate (especially crude MDI) which means that the polyol and isocyanate tend to separate after mixing;
- 3) instability of the foaming reaction mixture.

It is clear that silicones influence the cell structure and consequently the physical properties of the foam. However, adding too much silicone does not give any further improvements. The optimum quantity is dependent on the constituents, foaming conditions, mixing efficiency, etc.

The important component in determining the properties of polyurethanes are polyol(s) and isocyanate. Their physical properties, including flammability, of polyurethane foams are dependent on the isocyanate number, hydroxy number, and functionality of the polyol(s) used in the formulation. Hence, foams are characterised by defining an NCO/OH index:

$$I = \frac{56100 \times K_{\text{NCO}} \times [\text{NCO}]}{42 \{ (K_{\text{OH}} \times [\text{OH}]) + (K_{\text{OH}'}) \times [\text{OH}'] \}}$$

When K_{NCO} is the "isocyanate value", It is defined as the amount of the NCO available in 1 g isocyanate. K_{OH} and $K_{\text{OH}'}$ are the "polyol values". These values are defined as the number of the hydroxy content of 1 g polyol and 56100 are average molecular weight of isocyanate and polyol. $[\text{NCO}]$, $[\text{OH}]$ and $[\text{OH}']$ are the amounts of each component used in the foam formulation. The most common types of rigid foam have indices, I , of about 100 (polyurethane foams) or 400 (polyisocyanurate foams). The latter being significantly less flammable, due to the formation of the thermally stable isocyanurate ring as presented below;



Other additives in polyurethane are blowing agents, fillers and flame retardant. Examples of flame retardants are shown in table 2-3.

Table 2-3 Some flame retardants for polyurethanes.

Additives	Typical Application
Tris(2-chloroethyl)phosphate, Daltogard	All polyurethane foams including polyester-based foams and microcellular elastomers
Tris(2-chloroethyl)phosphate, T.C.E.P.	Polyether-based flexible and rigid foams
Tris(2,3-dichloropropyl)phosphate, Fyrol FR-2, Celluflex FR-2	polyether-based rigid and flexible foams
Tetrakis(2-chloroethyl)-2,2-bis(chloromethyl) propylene phosphate, Phosgard 2XC20	Low volatility material for flexible and rigid foams.
Dimethoxy methyl phosphate	Rigid foams
Tris(halogenated polyol) phosphonate	Flexible and rigid foams
Aluminium hydroxide, Melamine	All polyurethanes but especially in low density flexible foams for ignition and smoke suppression

2.2 Research works.

Due to the concern about fire hazard of polyurethane in recent years, there is considerable interest in developing novel flame retardants for these polymer.

Pitts²¹ investigated the effects of SnO_2 and SnO , in combination with Sb_2O_3 , on flexible chlorinated foam. These showed that neither SnO_2 nor SnO were effective at a level of 5 parts per hundred resin (phr) without the presence of Sb_2O_3 . However, the tin oxides used at 5 phr with 10 phr of Sb_2O_3 gave a self-extinguishing foam, comparable in performance to a composition which contained 15 phr of Sb_2O_3 alone.

Cusack, Smith and Kroenke¹⁰ investigated Tin (IV) oxide, either alone or in combination with melaminium betaoctamolybdate or molybdenum(VI) oxide was an effective flame retardant and smoke suppressant for rigid PVC. Elemental analysis of the char residues indicated that a proportion of the tin and molybdenum is lost from the polymer possibly as volatile metallic

chlorides or oxychlorides and it is suggested that these metals can operate as fire retardants in both the condensed and vapour phases.

Tasher, Shenkov, Troev, Borissov, Zabski and Edlinski¹⁸ investigated that phosphorus-containing compound, obtained by alkylation of aminoalcohol with dimethyl phosphite, may be used as flame retardants in rigid polyurethane foams.

Cusack, Monk, Pearce and Reynold⁷ indicated that zinc hydroxystannate and zinc stannate; at incorporation levels of 1-10 phr; impart flame, smoke and carbon monoxide suppressant properties of brominated polyester. These improvements in performance are superior to those exhibited by tin (IV) oxide or antimony (III) oxide.

In addition, these investigators examined that the surface area and degree of dispersion of the additive affect on its fire retardant efficiency. Hence, colloidal SnO_2 has been found to be more effective as flame retardant than powder SnO_2 .

Asiha and Kaneyoshi²² investigated the ammonium sulfate as fire-retardant for isocyanate-based foams particularly in rigid and flexible polyurethane ammonium sulfate powder is employed alone or in conjunction with a weakly basic powder neutralising the acidity of the sulfate.

Bains, Cusack and Monk⁶ carried on the retardant properties of zinc hydroxystannate, relative to those of antimonytrioxide in brominated polyester resin containing various inorganic fillers. The effectiveness of ZnSn(OH)_6 and ZnSnO_3 as flame retardants depended on several factors including incorporation level of the additives and fillers, and, bromine content of the resin. In general, Sb_2O_3 gave optimum performance in alumina trihydrate-filled resin, whereas ZnSn(OH)_6 exhibited a flame retardant synergism with anhydrous Al_2O_3 . Furthermore, $\text{ZnSn(OH)}_6\text{-Al}_2\text{O}_3$ combination inhibited the evolution of carbon monoxide from burning polymers and was clearly an excellent overall fire retardant system for this type of polymer.

Cusack, Heer and Monk⁵ examined zinc hydroxystannate exhibited flame-, smoke- and toxic gas-retardant properties in unsaturated polyesters based on the halogenated compounds, chlorendic anhydride (CA) or dibromoneopentylglycol (DBNPG). In addition, they suggested that the fire-retardant action of the tin additive involved both the condensed and vapour phase in

the DBNPG resin, whereas its effects in the CA system appear to be almost exclusively due to vapour phase activity.

Hornsby, Mitchell and Cusack⁴ suggested that tin(IV) oxide and zinc hydroxystannate increased flame retardancy and reduced rates of smoke evolution particularly when used with chlorinated paraffin wax. It was apparent that tin acted mainly in the condensed phase by a char formation. However, at high Cl/Sn ratios, volatilisation of tin chloride or oxychloride might occur, resulting in a vapour phase flame retardation.