

CHAPTER II



THEORY AND LITERATURE REVIEW

2.1 Reaction

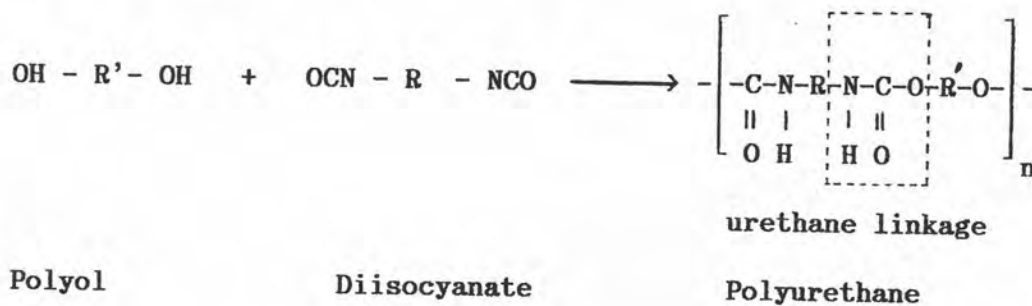
Of all the new polymeric materials developed during the century, polyurethanes have probably had the most impact on every day life. During the last 20 years, there has been a rapid growth in the production and consumption on polyurethanes, which is largely due to their versatility of the reactions of the isocyanate group ($-NCO$) and the ingenuity of polymer scientists in tailoring polymer structures to provide required physical properties.

In term of tonnage, the polyurethanes are the most important of the thermosetting resins. They do not approach the output of the major thermoplastic polymer but polyurethanes find their way into a far wider range of application types. They are used in the form of light weight the flexible foams, rigid foams, elastomers, coatings and adhesives, and have found a number of applications in the furniture and bedding, automotive, building, refrigeration, textile, coating, footwear and also used as thermoplastic materials (2).

The chemistry of polyurethane formation is complicated.

Polyurethanes result from the reaction between alcohols with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate). This type of polymerisation is called *addition polymerisation*.

Figure 2-1 Polyurethane addition reaction



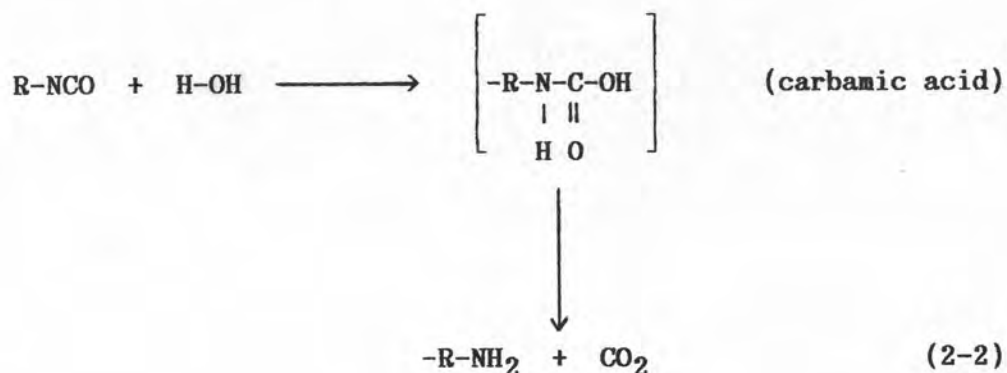
The reaction is *exothermic* (5). The rate of the polymerisation reaction depends upon the structure of both the isocyanates and the polyols. Certain groups of chemicals which are themselves at least difunctional reactant ($f > 2$) are used, then a cross-linked product may be formed. The polyfunctionality may be provided by the isocyanate compound, the reactant chemical or both. The reaction mechanism can be classified as a *nucleophilic reaction* on an activated carbonyl group and the formation of the polymer is by a step-wise process (2).

The nucleophilic groups which react with the isocyanate

The product of the above equation is the average structure. Step-wise theory predicts that the product will be a mixture with a distribution of sizes which will include some unreacted monomeric diisocyanate. Similarly, if twice as much diol is used, the same arguments will apply. In the production of polyurethanes, these intermediate (or prepolymer) products can be used as reactants to form the final product by further reaction.

An important feature of the reaction is that no by-product of a small molecule is formed. The reactants can be mixed together and placed in a mould where they will be transformed into solid products with the evolution of heat (about 80 kJmol^{-1}) This is the basis for the production of polyurethane products.

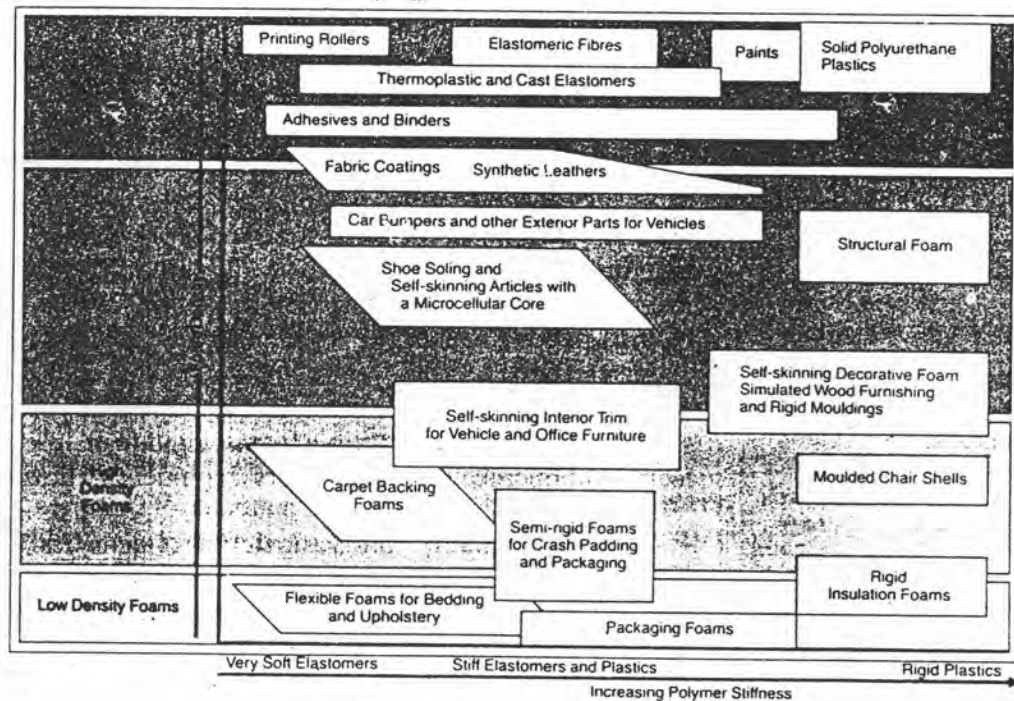
Other relevant reactants are water and amines, both primary and secondary. The water acts as a nucleophile like other hydroxyl compounds and leads to an unstable product which decomposes to give carbon dioxide and an amine (eq. 2-2) :



2.2 Summary of the properties of polyurethanes

Polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 kg/m^3 to $1,220 \text{ kg/m}^3$ and polymer stiffness from very flexible elastomers to rigid, hard plastics. Although an oversimplification, the following chart illustrates the broad range of polyurethanes, with reference to density and polymer stiffness (5).

Figure 2-3 Property matrix of polyurethanes.



2.3 Type of polyurethanes

A consideration of particular properties of certain grades of polyurethanes and the way in which these are used will serve to demonstrate their versatility.

2.3.1 Foams

By itself the polymerisation reaction produces a solid polyurethanes. Foams are made by forming gas bubbles in the polymerising mixture. Flexible foams can be produced easily in a variety of shapes by cutting or moulding. They are used in most upholstered furniture and mattresses. Strong, low density rigid foams can be made, when blown, using fluorocarbons, closed-cell structures are produced that have low conductivity.

Figure 2-4 Photomicrograph showing the open cells of flexible foam

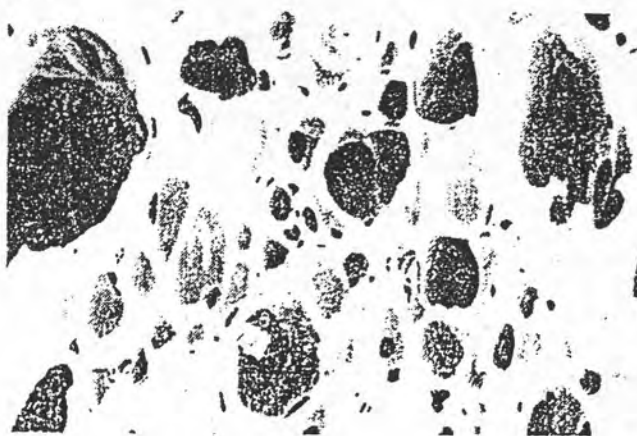
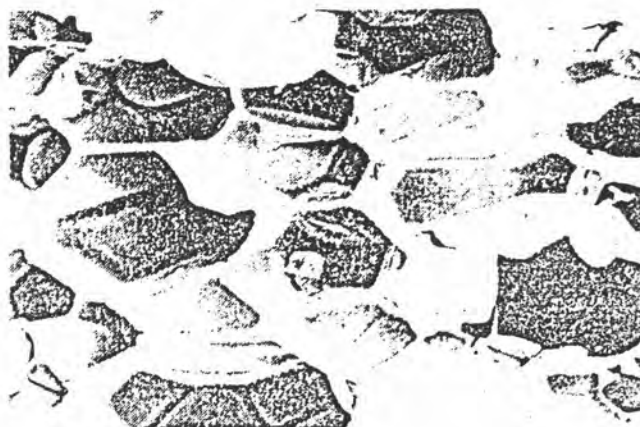


Figure 2-5 Photomicrograph showing the closed cells of a rigid foam.



Flexible polyurethanes, and many elastomers have segmented structures consisting of long flexible chains (eg. of polyether or polyester oligomers) jointed by the reactively rigid aromatic polyurethane - polyurea segments. Their characteristic properties depend largely upon secondary or hydrogen bonding of polar groups in the polymer chains. Hydrogen bonding occurs readily between the NH-group (proton donor) and the carbonyl groups (electron donor) of the urethane and urea linkages. Hydrogen bonds are also formed between the NH-groups of the urethane and urea linkages and the carbonyl oxygen atoms of polyester chains. The oxygens of polyether chains also tend to align by hydrogen - bonding with the NH-groups, but these bonds are much weaker and more labile than those formed with carbonyl oxygen atoms. The hard segments and especially the stiff polyurea hard segments, display strong secondary bonding, and tend to agglomerate into hard segment domains in structures having long flexible chains.

Rigid polyurethane polymers, in contrast, have a high density of covalent cross-linking. This results from the use of branched starting materials such as polyfunctional alcohols, amines and isocyanates.

There are three foam types that are particularly significant :

- *Low density flexible foams* are materials of densities 10-80 kg/m³, composed of lightly cross-linked, open-cells. Air may go through the structure very easily. Semi-rigid variants also have an open-cell structure but different chemical formulations.
- *Low density rigid foams* are highly cross-linked polymers with a closed-cell structure - each bubble within material has unbroken walls so that gas movement is impossible. These materials offer good structural strength in relation to their weight, combined with outstanding thermal insulation properties.
- *High density flexible foams* are defined as those having densities above 100 kg/m³. The range includes moulded self-skinning foams and microcellular elastomers.



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2.3.2 Solid polyurethanes elastomers

Most polyurethane elastomers have excellent abrasion resistance with good resistance to attack by oil, petrol and many common non-polar solvents. They may be tailored to meet the needs of specific applications, as they may be soft and hard, of high or low resilience, solid or cellular.

2.3.3 Adhesives, binders, coatings and paints

Polyurethane are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Polyurethane paints and coatings gives the highest wear resistance to surfaces and the outer skins of aircraft. They are also becoming widely used for high quality finishes on automobiles.

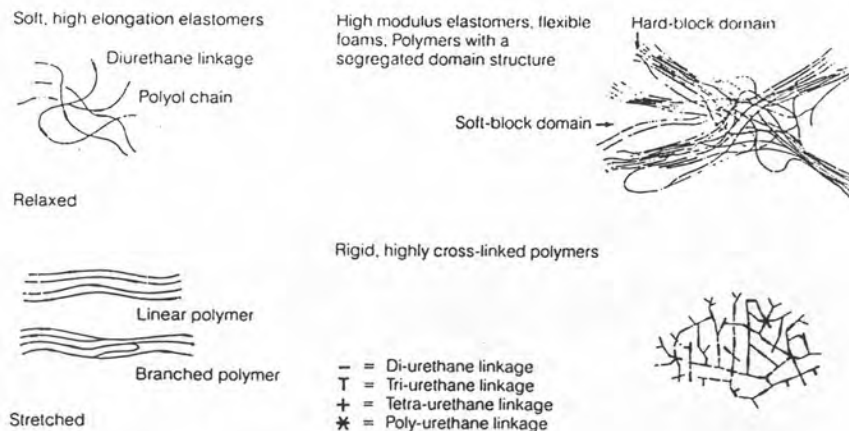
2.3.4 Cross-linking in Polyurethanes

The molecular structures of polyurethane polymers vary from rigid cross-linked polymer to linear, highly - extensible elastomers all inllustrated diagrammatically in figure 2-6

2.4 Raw materials for urethane polymers

A urethane group is formed by the chemical reaction between an alcohol and an isocyanate. Most polyols and polyisocyanates used in the manufacture of polyurethanes are liquid at ambient temperatures. Polymerisation rates can be

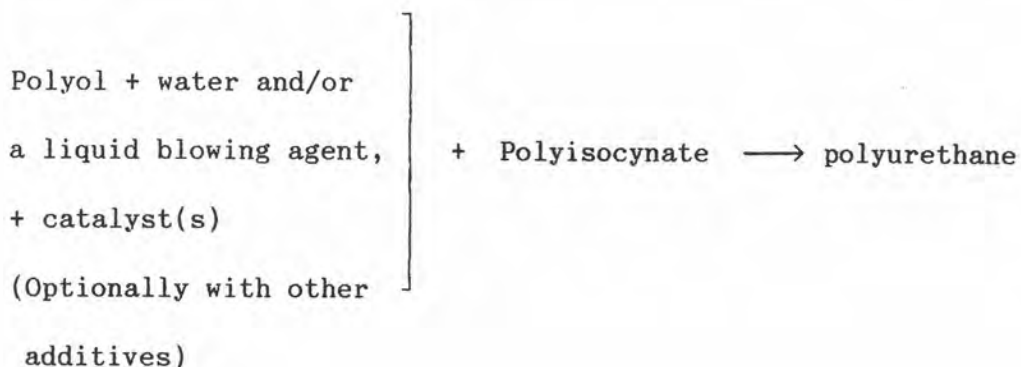
Figure 2-6 Polyurethane polymer structure



varied enormously by the choice of catalyst and its concentration. The reactions are exothermic - the heat generated may be used to vapourise a liquid blowing agent when the reacting

chemicals polymerise and expand to produce a polyurethane foam. Alternately, some water may be incorporated in the polyol so that it reacts with the polyisocyanate to release carbon dioxide gas.

The reaction which produced polyurethane foam may be summarised below



2.4.1 Polyol

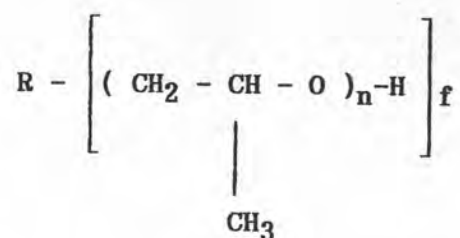
These materials are compounds or mixtures of compounds containing the hydroxy group with functionalities equal to or greater than two. These are two main groups of polyols which in general lead to different properties. These are the polyether polyols and the polyester polyols. Polyester are usually more expensive than polyether, and the characteristics of polyols used to make the two main classes of flexible and rigid polyurethanes as shown in table 2-1

Table 2-1 Polyols for polyurethane manufacture.

Characteristic	Flexible foams and elastomers	Rigid foams, rigid plastics and stiff coatings
Molecular weight range	1,000 to 6,500	150 to 1,600
Functionality range	2.0 to 3.0	3 to 8
Hydroxyl value range (mg KOH/g)	28 to 160	250 to 1,000

The choice of polyol, especially the molecular weight and functionality of its molecular structure and its functionality (the number of isocyanate-reactive hydroxy groups per molecule of polyol) controls, to a large extent, the degree of cross-linked structure formed in the polymer that is formed in reaction with the isocyanates.

Polyether polyols are low molecular weight polymers with terminal hydroxyl group and are mostly derived from propylene oxide. A general formula for polyether polyol is :



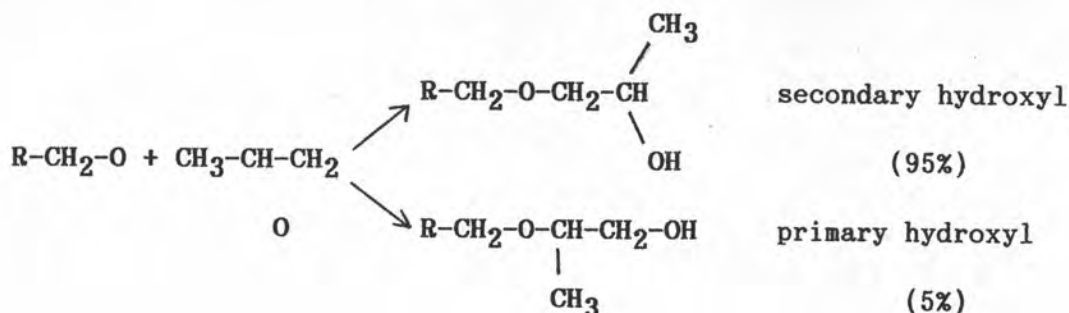
where R is an initiator fragment and f is the functionality

of the initiator and therefore the polyol. This indicates that the terminal groups are secondary hydroxyl. These are sometimes tipped with ethylene oxide units in order to give primary hydroxyl terminal group which are more reactive. In general, a high molecular weight, low functionality polyol will give flexibility in the final polyurethane product.

Most of the polyether polyols used to make flexible polyurethane foams and elastomer are triols based on trifunctional initiators, mainly glycerol or trimethylpropane

Initiator	+	Alkylene oxide	—————>	Polyether polyol
Polyfunctional alcohol or amine		Propylene oxide alone or copolymerised with ethylene oxide		Polyether polyol with both primary and secondary hydroxyl end-group

Figure 2-7 The manufacture of polyether polyol



Polyester polyols are produced from polyesterification of acids with excess of diols, triols and so on. In the case where triols or high functionality compounds are used with diacids, then a complex product is obtained with degrees of branching leading to polyfunctionality which depends on component types and proportions.

The "hydroxy value" is used as a measure of the concentration of isocyanate-reactive hydroxyl group per unit weight of polyol and is expressed as mg KOH/g. The measured hydroxyl value of the polyol is related to its molecular weight and functionality.

Hydroxyl value = number of milligram of KOH which is equivalent to 1 g. of polyol

$$\text{Hydroxyl value} = \frac{56.1 \times \text{functionality}}{\text{molecular weight}} \times 1000$$

For the purpose of formulating compositions, it is necessary to know the hydroxyl value provided that the type of polyol is known. In order to achieve the desired balance of hydroxyl to iso-cyanate groups in a formulation, the isocyanate index is specified.

$$\text{Isocyanate index} = \frac{\text{number of mole equivalents of isocyanate} \times 100}{\text{number of mole equivalents of polyol}}$$

A comparison of polyurethane product properties gives an indication of the differences between polyether and polyester polyols. Polyether polyol gives products with better hydrolytic stability and resilience and lower hysteresis losses. They also lead to better low temperature performance and lower viscosity mix for processing. Polyester polyols give products with better cut resistance and oil resistance.

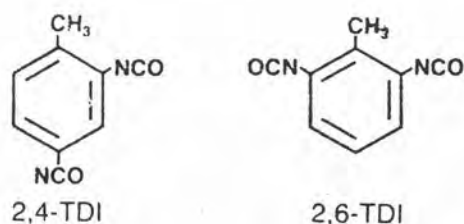
2.4.2 Isocyanates

Another major method of varying the properties of the final polyurethane is by varying the type of isocyanate used. Isocyanates may be modified in many ways to give products with differing physical and chemical properties.

Several aromatic and aliphatic isocyanates are available, about 95% of all polyurethanes are based on two of them. These are toluene diisocyanate (TDI), and diisocyanato-diphenyl methane (MDI) and its derivatives. Most of the TDI used is a mixture of two molecular forms called isomers - the 2,4 and 2,6 isomers in an 80:20 mix. A 65:35 mix is also available. TDI is used mainly in the production of low density foams for cushioning, general as slabstock. TDI is also used for moulded cushions, sometimes mixed

with various MDI products. The pure 2,4 isomer is used in some elastomer manufacture.

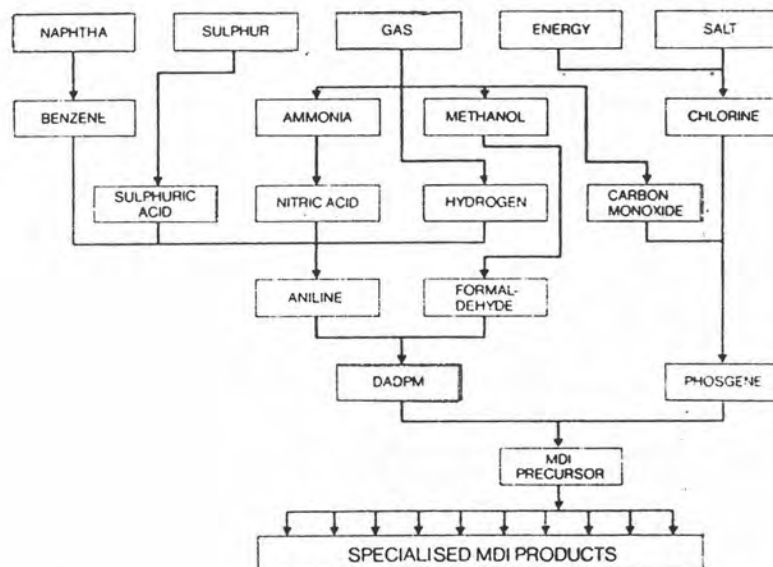
Figure 2-8 TDI isomer



Development of MDI is necessary as the volatility of TDI cause severe problems. The production of MDI is considerable more complex than that of TDI. MDI is produced from aniline and formaldehyde, react together using hydrochloric acid as a catalyst. This condensation reaction produced a complex mixture of polyamines which are phosgenated to obtain a polyiso-cynate mixture. Pure MDI is substantially 4,4'- diisocyanato diphenyl methane (4,4'-MDI). The polyisocynate mixtures are formulated to offer a range of differing functionality. The product, known as the polymeric MDI, is principally used for manufacture of rigid foams.

Such MDI is a solid (melting point 38 ° C) which is produced by separation from a polymeric MDI precursor. To make polyurethanes as cost-effective as possible, producers of isocyanates have developed processes for tailoring the MDI

Figure 2-9 Manufacturing route of MDI



composition to the requirements of the end-product. The polyisocyanate mixtures are formulated to offer a range of differing functionalities. Functionalities defined as the average number of chemically-reactive groups present on each individual molecule. Table 2-2 show that the functionalities of the products available range from 2.0 to about 3.0

MDI is available in several forms based on two types of product, purified monomeric MDI and polymeric MDI. Pure MDI is substantially 4,4-diisocyanato-diphenylmethane (4,4'-MDI). It usually contains small amount of the 2,4-isomer.

Table 2-2 Range of MDI variants



Average functionality	Product description	Polyurethane type	Main applications
2.0	Pure MDI	High performance elastomers	Shoe-sole Spandex fibres Flexible coatings Thermoplastics
2.01 - 2.1	Modified, liquid pure MDI	High performance elastomers Microcellular elastomers	Shoe-sole Flexible coatings RIM and RRIM Cast elastomers
2.1 - 2.3	Liquid, low functionality polyisocyanates	Flexible, semi-rigid and rigid (structural) foams. One-component froth.	Automotive parts Cabinets for electronic equipment Insulating sealants Cast elastomers
2.5	Low viscosity liquid polyisocyanates	High density flexible foams. Structural foams	Foam-backs for carpets vinyls Computer cabinets and other moulded articles
2.7	Low viscosity polymeric MDI	Low density rigid foams. Semi-rigid foams. Isocyanurate foams. Particle binders	Insulating foams Energy absorbing foams Isocyanurate foam building panels Mine-face consolidation Chipboard and laundry sand binders
2.8 - 3.1	High functionality polymeric MDI	Rigid polyurethane and isocyanurate foams	Continuous lamination of rigid foam and rigid foam slabstock

Figure 2-10 Pure MDI

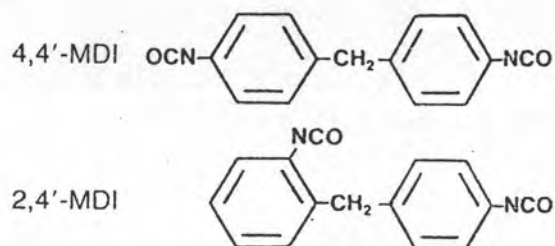
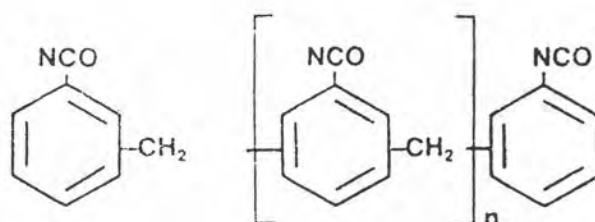


Figure 2-11 Polymeric MDI



Polymeric MDIs are undistilled MDI compositions made by phosgenation of polyamine mixtures. Polymeric MDI composition are available with effective mean functionalities from about 2.5-3.0 and characterised by their content of reactive isocyanate groups. The viscosity increases with increasing mean molecular weight and polymeric isocyanate content.

Diisocyanates produced are required for making elastomers, whilst high functionality MDI-rich in polyisocyanates - is desirable for manufacture of rigid foams and binding materials. Other aromatic diisocyanate include 1,5 -diisocyanato-naphthalene (naphthalene diisocyanate or NDI), and 1,4-diisocyanato-benzene (p-phenylene diisocyanate or PPDI) which are used to make polyurethane elastomers.

2.4.3 Additives

Apart from polyisocyanates and polyols - the basic materials for polyurethane production - a wide variety of auxiliary chemicals may be added in order to control and modify both the polyurethane reaction itself and the properties of final polymer. These additives include catalysts, cross-linking agents, chain extending agents, blowing agents, surfactants, colouring materials, fillers, smoke suppressants and flame retardants. All practical polyurethane systems include at least some of these auxiliary chemicals, table 2-3

2.4.3 (a) Catalyst

Catalysis plays a vital role in the preparation of urethane because it not only affects the rate of chemical reactions, responsible for chain propagation, extension, and cross-linking but also affects the ultimate properties of the resulting polymers. Catalysts are employed whose functions are not only to bring about faster rates of reaction but also to establish a proper balance between the chain-propagating reaction (primarily the hydroxyl-isocyanate reaction) and the foaming reaction (isocyanate-water reaction). A balance has to be established between polymer growth and gas formation in order to entrap the gas (CO_2) efficiently and to develop sufficient strength in the cell walls at the end of foaming reaction to

Table 2-3 Reasons for using additives

Additive	Type of material	Purpose
Catalysts	Tertiary amines Organometallic compounds	To speed up the reaction of isocyanate and polyol
Cross-linking chain-extending agents	Polyols Polyamines	To give polymer cross-linking or to introduce specialised polymer segments
Blowing agents	Water (reacts with isocyanate giving carbon dioxide gas). Chlorofluoromethanes	To produce foamed structures
Surfactants	Silicone fluids	To aid and help foam-forming processes
Colours	Various pigments Carbon black	To identify different foam grades and for aesthetic reasons
Fillers	Particulate inorganic materials Fibres (chopped, milled or as continuous fibres, nets or scrim)	To modify properties (stiffness, fire performance etc.)
Flame retardants	Phosphorus or halogen-containing molecules	To reduce flammability
Smoke suppressants	Particulate inorganic and/or organic materials. (polycarboxylates, hydrated oxides, borates, etc.)	To reduce the amount of smoke or to slow down the rate of smoke production on burning.

maintain their structure without shrinkage or collapse. The catalysts most commonly employed are tertiary amines and metal catalysts, especially tin catalysts. Tertiary amines are catalyst for both isocyanate-hydroxyl and the isocyanate-water reactions. The efficiency of tertiary amines catalysts increases as the basicity of the amine increases and the steric shielding of the amino nitrogen decreases.

Organotin compounds are extremely effective catalysts for the isocyanate-hydroxyl reaction (1). Water-blown flexible polyurethane foams are usually catalyzed with a synergistic mixture of one or more tertiary amines and an organotin catalyst.

Table 2-4 Reactivity of catalysts in isocyanate-hydroxy reaction.

Catalyst*	Concentration, %	Order of activity
Uncatalyzed	—	1
TMBDA	0.1	56
DABCO	0.1	130
TMBDA	0.5	160
DBTDL	0.1	210
DABCO	0.2	260
DABCO	0.3	330
SnOct	0.1	540
DBTDL	0.5	670
DBTDL + TMBDA	0.1 + 0.2	700
SnOct + TMBDA	0.1 + 0.2	1000
DBTDL + DABCO	0.1 + 0.2	1000
SnOct + TMBDA	0.1 + 0.5	1410
SnOct + DABCO	0.1 + 0.5	1510
SnOct	0.3	3500
SnOct + DABCO	0.3 + 0.3	4250

* TMBDA = tetramethylbutanediamine, DABCO = 1,4-diaza[2,2,2]bicyclo-octane, DBTDL = dibutyltin dilaurate, and SnOct = stannous octoate.

Table 2-5 Reactivity of catalysts in isocyanate-water reaction.

Catalyst*	Order of activity
Stannous octoate	1.0
<i>N</i> -Ethyl morpholine	1.1
Dibutyltin dilaurate	1.3
Triethylamine	1.5
<i>N,N,N',N'</i> -Tetramethyl-1,3-butanediamine	1.6
1,4-Diaza[2.2.2]bicyclooctane (DABCO)	2.7

* Ratio: 0.1 part catalyst per 100 parts resin.

Table 2-6 Some commercially available organo-metallic catalysis.

Catalyst	Principal applications
Stannous octoate	Slabstock polyether-based flexible foams, moulded flexible foams.
Dibutyltin dilaurate	Microcellular foams, RIM, two-pot moulding systems, elastomers.
Dibutyltin mercaptide	Hydrolysis resistant catalyst for storage stable two-pot systems.
Dibutyltin thiocarboxylates	Delayed action (hindered) catalysts for RIM and high resilience foams.
Diocetylthiothiocarboxylates	
Phenylmercuric propionate	In glycol solution for potting compounds, as a powder for delayed action catalysis.
Lead octoate	Urethane chain extension catalyst
Alkali-metal salts, e.g. CH_3COOK , K_2CO_3 NaHCO_3 and Na_2CO_3	General catalysts for the urethane reaction and for isocyanate polymerisation
Calcium carbonate	A common filler with a catalytic effect on the urethane reaction and on the cure rate of polyurethanes.
Ferric acetylacetonate	Catalyst for cast elastomer systems, especially those based on TDI.

Table 2-8 Chain-extending agents, cross-linking agents and curing agents and their isocyanate equivalents.

Additive	Functionality	Mole weight	OH value (mg KOH/g)	Weight of diisocyanate (g per 100 g of required additive)	
				TDI	MDI
Ethylene glycol $C_2H_4(OH)_2$	2	62.07	1801	280	401
Diethylene glycol $O(C_2H_4OH)_2$	2	106.12	1057	164	235
Propylene glycol $C_3H_6(OH)_2$	2	76.11	1474	229	329
Dipropylene glycol $O(C_3H_6OH)_2$	2	134.18	836	130	186
1,4-Butane diol $C_4H_8(OH)_2$	2	90.12	1245	193	278
Polypropylene glycol 400	2	400	280	42.5	62
<i>m</i> -Phenylene diamine $C_6H_4(NH_2)_2$	2	108.15	1037	161	231
Diethyl toluene diamine $C_6HCH_3(C_2H_5)_2(NH_2)_2$	2	178.27	629	97.7	140
Dimethylthio toluene diamine $C_6HCH_3(SCH_3)_2(NH_2)_2$	2	214.34	523	81.2	116
Water HOH	2	18.01	6230	968	1389

2.4.3 (c) Blowing agents

Flexible polyurethane foams are usually made using the carbon dioxide formed in the reaction of water and diisocyanate (water blowing) either as the sole blowing agent or as the principal blowing agent in association with trichloromonofluoromethane or methylene chloride, or a mixture of both. Blowing agent is an excellent compounding component for softness and density control of resilient one-shot polyether foams.

Table 2-9 Non-reactive blowing agents for polyurethanes.

Blowing agent	Trichloro- monofluoro- methane (CFM-11)	Dichlorodi- fluoro- methane (CFM-12)	Methylene- chloride
Molecular weight	137.38	120.92	84.94
Density at 20°C (g/ml)	1.488	1.486	1.336
Boiling point at 1 atm. (°C)	23.8	-29.8	40.1
Freezing point (°C)	-111	-160	-96.7
Threshold Limit Value (TLV*, ppm)	1000 ppm	1000 ppm	50 ppm A ₂
Solubility (g/100 g solvent at 20°C)			
Water	Insoluble	Insoluble	2
Ethanol	∞	∞	∞
Polyethers	Adequately soluble for all applications		

* From TLVs, Threshold Limit Values for Chemical Substances in the Work Environment Adopted by ACGIH for 1986-87. (A₂ notation indicates a substance suspect of inducing cancer in man.)

2.4.3 (d) Surfactants

Selected surfactants, or mixtures of surfactants, help in mixing incompatible components of the reaction mixture. They are particularly useful in foam making where they help to control the size of the foam cells by stabilising the gas bubbles formed during nucleation and may stabilise the rising foam by reducing stress concentrations in the thinning cell-walls. In flexible foam, surfactants also help to control the degree of cell opening and increase the operating margin between the extreme collapse, when cell opening occurs before the reaction mixture has sufficiently polymerised, and a high content of closed cells which results from cell opening being too long delayed.

2.4.3 (e) Fillers

Particulate fillers are used in flexible polyurethane foam to reduce their flammability and to increase the weight of seat cushions for furniture and to increase their resistance to compression. Fibrous fillers are reinforcing : they give increased stiffness and they increase the range of operating temperature of rigid foams. Mineral fillers are used to reduce costs and to increase the compressive strength of the rigid foams used in composite building panels.

Table 2-10 Some fillers and their application in polyurethanes

Filler	Typical applications
Calcium carbonate. (Ground chalk, ground limestone, whiting)	Flexible foams, semi-rigid foams, binder compositions, rigid self-skinning mouldings.
Barium sulphate. (Barytes)	Flexible foams, semi-rigid foams, especially for sound-absorbing.
Clays (China clay, kaolins, etc.)	Flexible systems
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers
Clay balls, vermiculite, expanded mica, etc.	Rigid foams
Glass micro-spheres	Flexible, microcellular foams, RIM
Glass flakes	Elastomeric RIM
Silicates, cements	Rigid foams, sealants, grouting compounds
Short fibres, milled and chopped glass-fibre, Aramid fibres, carbon fibres, conducting fibres, (aluminium, coated glass, steel)	Elastomeric RIM, rigid foams
Glass cloths and scrimms, wire mesh, organic fibres, etc.	Encapsulation in rigid foams, reinforcement of low density flexible foam mouldings.



Table 2-11 Some high modulus reinforcing fibres

Fibre	Young's modulus (ϵ)	Specific gravity (s.g.)	ϵ /s.g.
E'-glass fibre	70	2.55	27
Aluminium	70	2.7	26
Aramid fibre 'Kevlar' 29	80	1.3	61
'Kevlar' 49	120	1.4	86
Carbon fibre (PAN)	250-400	1.8-1.9	140-210
Carbon fibre (Pitch)	200	1.9	105
Steel	200	7.8	26
Alumina fibres	350	4.0	88
Polyethylene fibres	30-70	0.96	31-73
Boron fibres	400	2.5	160

2.4.3 (f) Retardants

Polyurethanes, in common with all other organic materials, will burn given the application of sufficient heat in the presence of oxygen. The physical state of the polymer is also extremely important. Both the ignitability and the burning rate of polyurethanes may be reduced by the addition of flame retardants which operate through one or more of the following mechanism

- Provision of a heat sink by filling with incombustible materials to delay ignition and reduce the rate of burning.

- Provision of an energy sink and means of diluting the combustion gases by filling with substances that decompose on heating to give incombustible products such as water and carbon dioxide.
- Modification of the mechanism of burning by filling with materials, such as halogenated flame-retardants, that react with the polymer or that produce a gas that decomposes to yield free radicals.
- Induced char formation by the used of additives.

Table 2-12 lists examples of flame retardants in three classes : non-reactive liquid flame retardants; compounds that react with isocyanates to become bound into the polymer network; and some other materials that reduce the rate of burning.

Table 2-12 Some flame retardants for polyurethanes.

Additive	Typical application
A. Non-reactive liquids	
Tris (2-chloropropyl) phosphate, 'Daltogard' F	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.
Dimethyl methyl phosphonate	Rigid foams.
B. Isocyanate-reactive additives	
Tris (polyoxyalkyleneglycol)-phosphonates and phosphite esters.	Flexible and semi-rigid foams.
Tris (halogenated polyol)-phosphonates.	Flexible and rigid foams.
Dibromoneopentyl glycol. 'FR' 1138	Polyether-based polyurethanes.
Brominated polyester and polyether diols. 'Saytech' RB-79 and 42-43	Rigid polyurethane and polyisocyanurate foams.
Tetrabromobisphenol A Tetrabromophthalic anhydride	Rigid polyurethane and polyisocyanurate foams.
C. Fillers	
Ammonium salts, sulphate, polyphosphate, etc.	Together with halogenated additives in rigid polyurethanes.
Aluminium hydroxide. Melamine.	All polyurethanes but especially in low density flexible foams for ignition and smoke suppression.
Calcium carbonate	Heat absorbing filler.

2.5 Burning mechanism of plastics

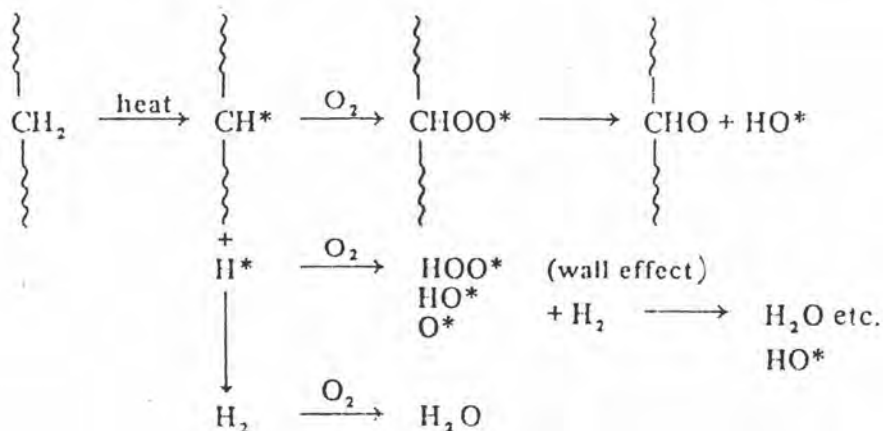
If plastic materials are therefore exposed to heat in air, degradation reactions will take place and the volatiles formed may leave behind a porous residue, this will ease the penetration of oxygen from surrounding air and cause further oxidation reactions in the solid substrate. The residues often consist of a carbonaceous char, which increases the amount of heat absorbed from surrounding radiations, and promotes further pyrolysis of the material beneath. There will be therefore a cumulative rise in temperature and eventually the vapours will ignite to form a flame. Ignition may be induced by an external flame (flash-ignition) or may occur spontaneously (self-ignition). The heat generated by combustion may sustain the ignition by continually providing the necessary thermal energy for the pyrolysis of the substrate material. In these case the material is said to be *flammable*. Such heat of combustion may not sufficient on the other hand, to provide the necessary thermal energy to cause the material to pyrolyse and produce volatiles at a sufficient rate to sustain ignition, and consequently the flame will eventually extinguish. In this case the material is said to be *self-extinguishing* (6).

The temperature at which volatiles produced from pyrolysis will ignite and the subsequent combustion rate depend on their chemical combustion and on the relative proportions of

combustible volatiles and oxygen present. Ignition will not take place nor will the flame be sustained if the concentration of combustible volatiles is below or above their flammability limits.

2.6 Chemistry of combustion of volatiles

Volatiles from thermal degradation of polymers invariably contain C-C and/or C-H groupings which constitute sites for free radical formation and oxygen attack.

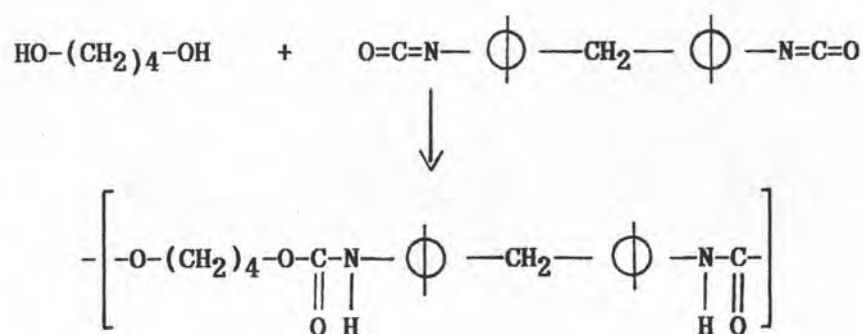


It appears that the ignition susceptibility and the rate of flame propagation are related to the ease and the rate of formation of OH^* radical. The reactions leading to the formation of CO_2 and H_2O are highly exothermic and the heat developed provides an autoaccelerative effect on the oxidative reactions and on the final rate of combustion. The presence of solid particles in the gas phase, however, can reduce to some extent the excitation energy for the oxidative process by the so-called 'wall effect', so that larger amounts of the less active $^*\text{OOH}$ radicals are produced. There may also be some contribution

from charred residues which may burn by glowing and generate more heat.

The flammability characteristics depend, therefore, on (i) their basic chemical structure, (ii) the intrinsic flammability of volatiles and (iii) the ratio of combustible matter in the gas phase. Non-combustible products of pyrolysis such as halogen halides, amines, CO₂, fluorocarbons, etc. have the effect of raising the ignition temperature, increasing the oxygen demand for sustained ignition, and may cause self extinction of the burning products.

Products and mechanisms of thermal degradation of polyurethane are of particular interest to focus attention upon the degradation of the polyurethane link and the polymer prepared from 1,4-butane diol and methylene bis-(4-phenyl diisocyanate) has been used to this purpose (2).



A TVA trace for this polyurethane of shown in Figure 2-12.

This broad low temperature peak is due to evolution of solvent

and this high temperature peak, which show a maximum rate about 300°C can be attributed to genuine degradation products. A large cold ring fraction is also formed which is in two parts - a liquid and solid whose IR spectra prove that they are the two monomers. A SATVA trace of the more volatile products is shown in Figure 2-13. The materials in each peak were identified by a combination of IR spectrometry, mass spectrometry and GLC as 1, CO₂; 2. butadiene ; 3. tetrahydrofuran; 4. dihydrofuran and 5. water. Carbon monoxide is also formed and a trace of HCN if large sample is degraded.

The variety of products formed immediately suggests that the mechanism of thermal degradation of polyurethane is very complicated. In fact it can be shown spectroscopically that at about 210 ° C the polyurethane linkage disappears without any of the other products being formed. Thus the overall reaction which is the exact reverse of the polymerisation process in which the polyurethane is formed. Thus the two monomers are primarily formed and all the other products are formed from these monomers while they are diffusing from the hot polymer. The overall reaction is presented by the mechanism shown in Figure 2-14 which accounts for all the observed products.

Figure 2-12 TVA trace for a polyurethane. Trap temperature :
 0°C ; -45°C ; -75°C ; -100°C ; -196°C

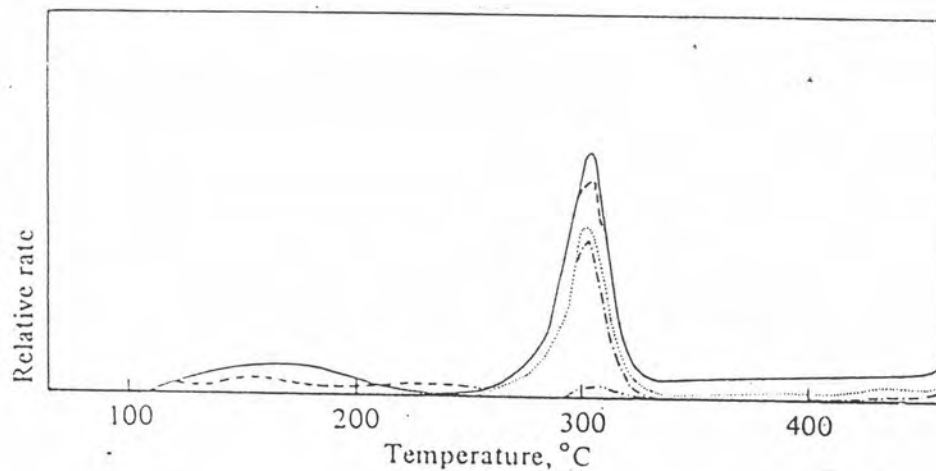


Figure 2-13 SATVA trace for volatile products of degradation of polyurethane.

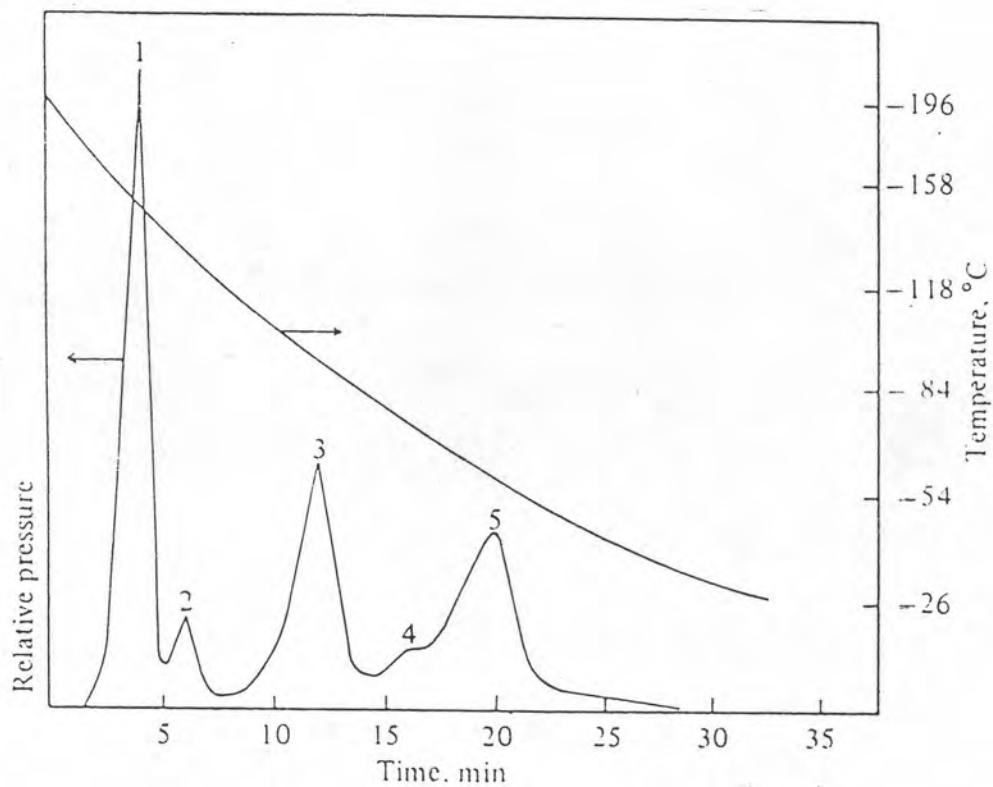
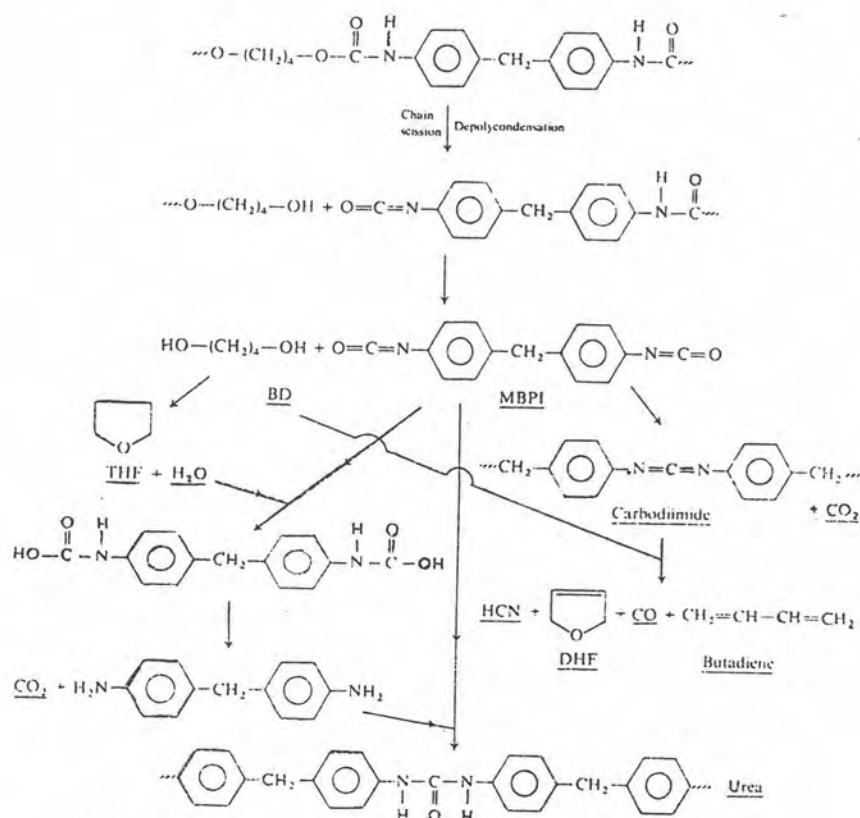


Figure 2-14 Mechanism of thermal degradation of a polyurethane



2.7 The combustion process

The burning of polyurethane foams may be considered as occurring in five stages (3), as follows.

Stage I Heating from an external source is applied to the material, progressively raising its temperature. The rate

of temperature rise decrease with specific heat and with thermal conductivity. The excellent thermal insulation properties of polyurethane foams promote a rapid temperature rise at the exposed surface, because heat cannot be easily transmitted to the layers of foam or to a substrate. Higher-density foams heat more slowly than lower-density foams, because they have a higher specific heat per unit volume and dissipate heat more rapidly.

Stage II The polyurethane foam reaches its temperature of initial decomposition and begins to form four types of product: combustible gases, noncombustible gases, entrained solid particles (polymer fragments), and carbonaceous char. The evolution of gases results in expansion of the system into adjacent air space or into the lower layers of foam, or both. Thus combustible and noncombustible gases both can cause difficulty by disrupting the chemical and physical structure of the foam, exposing new surfaces to destructive temperatures. The carbonaceous char is useful as an insulating layer that protects the lower layers of foam from exposure to heat.

The decomposition products vary with polymer composition, temperature level, rate of temperature rise, endotherms and exotherms, and rate of volatiles evolution. Differential thermal analysis, thermogravimetric analysis, and time-of-flight mass spectrometer analysis indicate that relatively small differences in chemical composition, temperature, and heating rate can



volatilized toluene diisocyanate and are favored when flame resistance is important.

Stage III The combustible gases ignite in the presence of sufficient oxygen or oxidizing agent, and combustion begins. The conditions of ignition depend on the presence of and external source of ignition and the temperature and composition of the gas phase.

Stage IV The heat of combustion raises the temperature of the gaseous products of combustion and of the noncombustible gases, increasing heat transfer by conduction; the expansion of the heated gases increases heat transfer by convection; the heating of the entrained solid particles and solid products of combustion to incandescence increases heat transfer by radiation.

Stage V The heat transferred from the combustion zone to adjacent material produces further decomposition and ignition, resulting in flame propagation. Slow combustion of the porous carbonaceous residue by progressing glowing and charring can contribute to propagation.

2.8 Flame retardant polyurethane foams

Flame retardance requires the disruption of the burning

in to carbon, which form char, and water vapour, which is noncombustible. Since the urethane or carbamate group has been found to decompose at temperatures between 200 and 300 ° c, the polymer itself cannot be redesigned to obtain greater resistance to high temperature without being removed from the class of polyurethane foams.

With this class of materials, therefore, improvement in flame retardance by influencing the phenomena in stage II is generally achieved by incorporating flame retardants such as phosphorus and halogen compounds. Boron and antimony compounds are known to impart flame retardance but are not as widely used, partly because they are less effective and partly because they are generally available in the form of nonreactive and often solid additives, whereas phosphorus and halogen can be incorporated into the liquid basic materials. Phosphorus compounds are believed to favor char formation by catalyzing reaction that produced carbon. Halogen compounds are believed to inhibit the free-radical chain reactions involved in decomposing the polymer in to combustible gases besides diluting the evolved volatiles with non combustible hydrogen halides.

The behavior of polyurethane foam in stage III is largely to determine the composition of the gas phase. Ammonium carbonate additive whose principal function is the evolution of noncombustible gases. If the content of combustible gases can be

kept below flammable limits until mixture with the atmosphere produces dilution and cooling ignition will not occur. Physical restraint on the rate of volatile evolution, such as the use of an installed coating or covering or the formation of the strong char coat, can reduce the probability of ignition.

Flame behavior in stage IV, since the heat of combustion is a function of gas evolved. The presence of noncombustible gases with significant specific heats reduces temperature rise through heat absorption and make less heat available to promote flame propagation. Catalysis reactions favoring formation of solid carbon (soot) substantially reduces the available heat of combustion, and combustion to carbon monoxide rather than carbon dioxide represents a major reduction in combustion heat. Hydrogen halides are believed to influence combustion reactions in the gas phase, besides serving as diluents for heat absorption.

Flame propagation cannot occur without the heat transfer in stage V, to produce further decomposition and ignition. The presence of installed coating or covering or the formation of an insulating layer of carbonaceous residue can prevent heat from reaching underlying foam. Bromine compounds are believed to be effective when conditions favor their forming an insulating blanket of heavy gases between the zone and the combustion zone.

2.9 Type of flame retardants

The flame retardants employed in polyurethane foam can be divided into three groups of chemicals (7) :

- inorganics,
- nonreactive organics, and
- reactive organics.

The application of nonreactive flame retardants, both inorganic and organic, depends upon effectiveness, cost, and ease of compounding in a particular polymer. The ideal flame retardant will cause only minimal deterioration of other polymer properties such as impact strength, tensile strength and heat and lighth stability. Reactive flame retardants are incorporated in the polymer during its polymerization. They are substituted for all or part of the monomer. As such, they become part of the polymer matrix, and provide a high degree of flame retardancy.

Chemicals designated as flame retardants for plastics and resins have demonstrated the ability to alter some phase of the combustion procession at least one of the numerous test available to determine flame retardancy.

The properties of a particular flame retardant dictate its use and compatibility with polymers. Many flame

retardants, particularly the nonreactive organic type, and mixtures of chemicals with unspecified compositions. The viscosity, particle size, and specific gravity have a strong influence upon the compounding and final properties of the flame retarded polymer. These are included with solubility characteristics which may affect compounding or the tendency of the additive to be extracted from the plastic.

Application of flame retardants to plastics accounts for 87 % of the total market. Table 2-13 present consumption for the various flame retardants.

Table 2-13 U.S. consumption of flame retardants in plastics
(1989)

<i>Type</i>	<i>Consumption (tonnes)</i>
Organobromine compounds	29,000
Organochlorine compounds	15,000
Chlorophosphates	13,000
Phosphate esters	20,000
Antimony oxides	18,500
Alumina trihydrate	177,000
Total	272,500

2.9.1 Inorganic Flame Retardants

Inorganic flame retardants are largely used as synergists with halogenated organics or to release water with cools a flame. Two inorganic materials, alumina trihydrate and antimony oxide , constitute over 50 % of the flame retardant market. High loadings of these materials are used, in part, because they act as fillers in addition to their function as flame retardants.

Alumina trihydrate has the highest usage of all flame retardants. This additive is used in products where demands for physical properties of the polymer and flame retardancy are not stringent. Heating of alumina trihydrate above 250 °C forms water an alumina. The water, approximately 35 weight percent of the additive, absorbs heat,cools the flame, and dilutes flammable gases and oxidant in the flame. The alumina is an excellent conductor, and removes heat from the flame zone. Aluminar trihydrate may be use as the sole flame retardant, or may be applied in combination with more efficient chemicals.

Halogen synergists enable formulators to use less additive without impairing the flame retardancy of the plastic. They are believed to work by capture of free radicals generated in a flame. The brominated and chlorinated flame retardants form hydrochloric and hydrobromic acids upon thermal decomposition. The inorganic flame retardants react with the halogen to form a

metal chloride or bromide which interferes with chain branching reactions.

The most widely used synergistic flame retardant is antimony oxide. This chemical forms antimony trichloride and antimony oxychloride upon thermal decomposition of chlorinated organics. Volatile antimony trichloride (b.p. 280 ° c) participates directly in flame quenching by reaction with flame-propagating free radicals. Antimony trioxide react directly with hydrocarbons to give water and molecular hydrogen instead of free radicals which propagate the flame. In some polymers antimony trioxide tends to retain heat after flaming has ceased (afterglow). The heated inorganic may then serve as a source for reignition for some components.

Boron compounds, led by zinc borate, act in both the flame and condensed phases to promote char formation, inhibit the release of combustible gas, and suppress. They generally form boron trihalides. Other boron compounds, used as flame retardants include ammonium fluoroborate, barium metaborate, boric acid, borax, ammonium pentaborate, and disodium octaborate.

2.9.2 Nonreactive Organic Flame Retardants

The nonreactive organic flame retardants are additives which are not chemically bound to the polymer chain. They are

generally added to the plastic following the polymerisation. Three general groups of chemicals are used as organic nonreactive flame retardants : chlorinated compounds, brominated compounds, and phosphorus compounds. The organic flame retardants may act in either the vapor or condensed phase. The halogenated organics are thought to function as flame retardants by inhibiting free radical formation in the flame. The phosphorus-containing additives are believed to act in the condensed phase to decrease the amount of combustible gas and enhance char. In the vapor phase, the phosphate ester are thought to degrade to relatively nonvolatile acids which inhibit flaming by promoting conversion of the organic to water and char.

Chlorinated organics such as chlorinated paraffins are usually used in combination with a synergist. These are largely straight-chain, saturated, $C_{10} - C_{30}$ paraffins with chlorine contents from 20 to 70 %. They act as secondary plasticizers, but have limited heat stability ($<220^{\circ}C$).

The brominated flame retardants include a variety of aromatic and aliphatic compounds. These flame retardants have high heat stability and tend to be more effective than chlorine compounds on a weight basis such as decabromodiphenyl oxide, pentabromocyclohexane and hexabromocyclodecane.

The organic phosphorus-containing flame retardants are

largely liquid at room temperature. They include phosphates $((RO)_3PO)$, phosphites $((RO)_3P)$, phosphonates $((RO)_2R'PO)$, phosphine oxide (R_3PO) , and phosphine (R_3P) .

2.9.3 Reactive Organic Flame Retardants

The reactive flame retardants contain many of the same fire retarding components as the additive types; however, these additives are chemically bound to the polymer backbone. They eliminate many of the problems associated with the nonreactive types; for example, migration of the additives and loss of flame retardancy during extended life uses are virtually eliminated. The reactive flame retardants tend to be more expensive than the nonreactive types, and they may have a deleterious effect on processing characteristics. Unsaturated polyesters, epoxy resins, and polyurethane have the highest use for these additives.

Chlorinated, brominated, and phosphorus-containing compounds are used as reactive flame retardants. The mechanism by which they impart flame retardancy is thought to be similar to that of the nonreactive organics. Tetrabromobisphenol-A and dibromophenyl glycol are most popular. Other flame retardants have alcoholic, acidic, phenolic, oxirane, and vinyl functional groups which allow them to polymerize and be incorporated in the polymer backbone.

Halogen-free compositions are generally made flame-retardant by incorporation of inorganic fillers, particularly alumina trihydrate (ATH) or, in the case of polymer which are processed at temperature above about 180 ° C, magnesium hydroxide. Although such compounds are essentially non-toxic and relatively inexpensive, the high loadings required for effective flame retardancy lead to processing difficulties and a marked deterioration in the mechanical properties of the host polymer.

2.10 Development of tin-based fire retardants

Despite the fact that tin salts have been known as fire retardants since the mid-nineteenth century, until very recently their industrial use has been limited to specialised treatments for woolen sheepskins and rugs. In view of the increasing demand for novel, non-toxic, fire-retardant additives for synthetic polymers, the programme research was initiated in I.T.R.I laboratories during the mid-1980s, to develop tin chemicals as flame retardants and smoke suppressants for plastics, elastomers and related materials. Preliminary studies demonstrated the effectiveness of tin(IV) oxide, SnO_2 , both in its anhydrous and hydrous forms, as a flame and smoke-inhibitor for halogen-containing polymer formulations such as PVC, halogenated polyester resins and polychloroprene. Subsequent work was aimed at developing tin additives with improved activity compared to tin (IV) oxide. This led to the conclusion that, of a series of metal

hydroxystannates and stannates, MSn(OH)_6 and MSnO_3 effective with regard to flame-retardant and smoke-suppressant performance.



Table 2-14 Properties of zinc hydroxystannate and zinc stannate

	ZHS	ZS
Chemical formula CAS No. Appearance	ZnSn(OH)_6 12027-96-2 white powder	ZnSnO_3 12036-37-2 white powder
Analysis (approx.): Sn Zn Cl free H_2O	41% 23% <0.1% <1%	51% 28% <0.1% <1%
Specific gravity Decomposition temperature ($^{\circ}\text{C}$) Toxicity	3.3 >180 very low†	3.9 >570 very low†

†Acute oral toxicity, LD_{50} (rats): >5000 mg/kg.

In flexible foams the incorporation of flame retardants has been found detrimental to indentation load deflection (ILD) and compression set properties, and in rigid foams the used of flame retardants has been found to decrease dimensional stability. In both areas flame retardance is achieved at a significant increase in material costs. The incorporation of flame retardants sometimes necessitates extensive formulation work to obtain the desire reactivity and storage stability.

The effectiveness of a particular flame retardant is highly dependent on the form in which it is available and on the composition of the basic polymer. The incorporation of phosphorus is effective until its concentration reaches 1.0-1.5 wt-% in the total formulation, and further increase seems to produce no further benefit. Aromatic chlorine additives have been found to be less effective than other compounds with equivalent chlorine content.

2.11 Aspects of flammability

The flammability of polyurethane foams may be considered from three viewpoints (3):

- fire hazard or the extent to which the material represents a danger to life and property
- fire damage or the extent to which the behavior of the material in a fire contributes to financial loss
- fire protection or the extent to which the material reduces hazard and damage to other material reduces hazard and damage to other materials in the system.

Aromatic-based polyethers sometimes reduce ease of ignition, but they have been found to increase smoke density. Polymeric polyaryl isocyanates tend to favor char formation, but they have been found to produce more smoke than toluene

diisocyanate. Phosphorus and halogen flame retardants have been successful in reducing surface flame spread, but they have been found to reduce resistance to high temperature and to increase development of smoke and toxic products. Materials that give better performance in tests involving application of flame to an exposed, cut surface may prove inferior when protected from directed flame impingement by a coating or covering. In certain cases a foams that presents less fire hazard may also result in more fire damage and less fire protection. To meet flammability standards and reduce the toxicity of gaseous combustion products, federal, state and local requirements, insurance underwriters, and other codes have forced the use of flame retardants and increased research and development of new additives.

2.12 Smoke and toxic substances

Combustion products that are toxic to human are produced by burning both natural and synthetic materials. The commonest combustion products are

- Carbon monoxide (CO). Burning polyurethane foam will produced about the same amount of CO as an equal weight of natural products but it may burn much faster thus producing the CO more quickly.

- Smoke from the fire is a significant toxic hazard but

an important effect of smoke is the loss of vision which hinders escape and rescue. Polyurethane is the especially materials which melt easily and drop away from the flame. Such materials tend to give low smoke figures compared with non-melting materials in small scale test.

- Carbon dioxide (CO_2). It is not itself toxic but in high concentrations, it dilutes and reduces the available oxygen level in the air. It also stimulates the rate of breathing thus increasing the hazard from more toxic combustion products which are also present.

- Hydrogen cyanide (HCN) is highly toxic and produced on burning all nitrogen-containing organic compounds. Polyurethane foams produce less HCN than the wool, nylon and polyacrylonitrile textiles commonly used in furnishings.

- Acrolein is highly toxic but it is not formed in significant amounts on burning polyurethane.

Table 2-15 Toxic gases from polyurethane foam and wood.

Material	Concentration of gas (ppm).			
	CO	CO ₂	HCN	NO
Beech	6516	127300	29	75
Plywood	19090	52090	875	5
Hardboard	7400	104540	30	54
Polyisocyanurate rigid foam	3145	4990	380	0.6
Polyurethane rigid foam	2910	5700	300	0.55

2.13 Literature review

One of the major areas of concern in recent years has been the use of polyurethane foams in upholstered furniture. In particular, relatively few efficient commercial flame retardants have been designed for flexible foams, although some work involving partial substitution of antimony trioxide in flexible foams has been carried out by Pitts (6). Several metal oxides, including SnO₂ and SnO, have been incorporated into a chlorinated polyurethane composition, at the level 5 phr, along with 10 phr of Sb₂O₃, going a self-extinguishing foam, comparable in performance to a composition which contained 15 phr of Sb₂O₃ alone. However, neither SnO₂ nor SnO were effective at a level of 15 phr without the presence of Sb₂O₃ (8).

Cusack, Monk, Pearce and Reynold (9) investigated that zinc hydroxy stannate and zinc stannate impart beneficial

properties to the polyesters in terms of flame retardancy and smoke / carbon monoxide suppression, and the improvements performance are, in general, superior to those exhibited by tin(IV) oxide or antimony (III) oxide. The surface area and degree of dispersion of the fire-retardant additive has been shown to have a marked effect on its efficiency and, in this connection, colloidal tin(IV) oxide is found to exhibit significantly improve flame-retardant properties compared to powder SnO_2 . Simultaneous tin additives markedly increase amount of char formed during combustion whereas Sb_2O_3 , a vapour-phase flame retardant, has little on char formation.

Pearson, P.G.(10) examined that the use of **alumina trihydrate** as a fire retardant additive in rigid polyurethane foams and compares its effectiveness against conventional flame retardant additives such as halogens and phosphorus compounds with particular reference to reducing toxicity and smoke propagation.

Studnicki, Szylwanski, Walczyk and Zabski (11) studied on the synthesis of **polyhydroxyl alkyl esters** and **chloroalkyl esters of phosphoric acid**. The process involves a simultaneous reaction of phosphorus trichloride, ethanol, epichlorohydrin, subsequent isomerization reactions, and a transferification by means of glycerine besides a reaction with epichlorohydrin. The product of these reactions, containing 5 to 7% of phosphorus, 20

to 24 % of chlorine, its hydroxyl number being 520 to 560 mg KOH/g was need as a fire retardant of burning in the production of self-extinguishing rigid polyurethane foams to be applied as thermoinsulating materials.

Cusack, Smith and Arthur (12) investigated metal stannates as smoke suppressants in glass-reinforced polyester. It has been found that the smoke suppressancy results for the metal stannates incorporated into the GRP panels at a level of 2 phr are the largest smoke reduction (46%) is given by $\text{Na}_2\text{Sn}(\text{OH})_6$ and ZnSnO_3 .

Ashida and Kaneyoshi (13) studied the ammonium sulfate as fire-retardant for isocyanate-based foams. They described that ammonium sulfate powder is employed alone or in conjunction with a weakly basic powder to neutralize the acidity of the sulfate (50%), as a flame retardant for isocyanate-based foams and in particular, rigid and flexible polyurethane foams.

Cusack, Heer and Monk (14) studied the efficiency of inorganic tin compound - zinc hydroxy stannate (ZHS) and zinc stannate (ZS) as fire-retardant and smoke suppressant in halogenated polyesters. They found that a low level of ZHS (< 5phr) incorporated into halogenated polyester resins imparts good flame retardancy. The degree of flame-retardant synergism is found to depend on the chemical nature of the halogen source and its level in the resin. ZHS is particularly effective in

resins based on either the chlorinated compound chlorendic anhydride (CA) or the brominated derivative dibromoneopentyl glycol (DBNPG), and exceptionally good smoke-, carbon monoxide-, and carbon dioxide-suppression is found in polyester resins containing these compounds. The flame-retardant action of ZHS in the brominated resin involves both condense and vapour phase reactions, its action in the chlorinated polymer appears to be almost exclusively in the vapour phase. The observed smoke- and CO-suppressant effects in the halogenated resins may arise from two independent mechanisms: (a) char formation, leading to a reduction in the supply of flammable volatiles to the flame, and (b) gas phase oxidation of the soot and aromatic tars produced during polymer pyrolysis.

Hornsby, Mitchell and Cusack (15) studied about flame retardance and smoke-suppression of polychloroprene containing inorganic tin compounds and show that polychloroprene is of relatively low flammability compared to many other elastomers has demanded increased flammability resistance and reduced smoke emission on combustion. It is found that both anhydrous tin dioxide and ZHS are effective retardants and smoke-suppressants at low addition levels (1 to 5 phr), and that a flame-retardant (and possibly smoke-suppressant) synergism exists between tin additives and chlorinated paraffin wax in polychloroprene. (Chlorinated paraffin wax is an effective flame-retardant.) They suggested that tin acts predominantly in the condensed phase by a

char promotion mechanism. However, at high Cl/Sn ratios, extensive volatilization of tin (chloride or oxychlorides) may occur, giving rise to a vapour phase mechanism similar to that known to operate in combined antimony trioxide/halogen systems.