CHAPTER 2

THEORY

The original discovery leading to the world-wide interested in all class of polyurethane was made by Otter Bayer and his co-workers of I.G. Farbenindustric at Leverkusen, Germany in 1937 that commercial potential of polyurethanes as fibres, adhesives, coating and foams began to be recognized. In fact, most polyurethanes application have been developed during the past 30 years. Table 2.1 shows progressive of polyurethanes.

2.1 Reaction of isocyanate

Reaction with polyols : G. woods(1987) described that polyurethanes contain carbonate groups in their backbone structure. They are obtained by the reaction between isocyanate with more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate) and alcohols that have two or more reactive hydroxyl groups per molecule (diols or polyols). This kind of polymerization is called addition polymerization. All polyurethanes are based on exothermic reaction of diisocyanate or polyisocyanate with polyols molecules. The rate of reaction is influenced by the structure and functionality of both isocyanate groups and polyols, including the location of substituents in proximity to the reactive isocyanate group (steric hindrance) and the nature of the hydroxyl group (primary or secondary). Relative few basic isocyanates and a range of polyols of different molecular weight and functionalities are used to produced various kinds of polyurethane products in an extremely wide range of grade that is stiffness from very flexible elastomer to rigid, hard plastics. The range of end products which is derived from polyurethanes is shown in Figure 2.1.

The reaction of diisocyanate with polyol is shown in Equation (2.1).

$$\underset{\text{Polyol}}{n\ \mathrm{OH\text{-}R\text{-}OH}} + \underset{\text{Diisocyanate}}{n\ \mathrm{OCN\text{-}R'\text{-}NCO}} \longrightarrow \underset{\text{Urethane linking Polyurethane}}{\left[\mathrm{O\text{-}R\text{-}}\boxed{\mathrm{O\text{-}CO\text{-}NH\text{-}}}\mathrm{R'\text{-}NH\text{-}CO}\right]_n} \quad \text{.......(2.1)}$$

Table 2.1 Illustrates some highlights in the development of polyurethanes (Wood G.,1987)

1937-40 Otto Bayer and co-Workers made polymers by polyaddition processes from various diisocyanates with glycols and/or diamine.

1940-45 Development of millable polyurethane elastomers and adhesives in Germany (I.G. Farben), U.K. (ICI) and the U.S.A. (Du Pont). Polyurethane coatings for barrage balloons (ICI), synthetic polyurethane bristles (I.G.Farben).

1945-47 Manufacture of millable polyurethane elastomers, coatings and adhesives.

1950 Cast elastomers from polyester diols, diisocyanate prepolymer and chain-extenders.

1953 First flexible polyurethane foam manufacture with a Bayer system using a high pressure machine, a polyester polyol and TDI.

1956 First manufacture of polyether-based flexible plyurethane foam in the U.S.A. using a two stage or 'pre-polymer' process.

1957 ICI introduces the first commercially available polymeric MDI composition for rigid polyurethane foam manufacture.

1959 ICI introduces the first rigid foam system based on polymeric MDI and a polyether polyol.

1959 'One-shot' system for flexible polyether-based foam introduced in the U.S.A.

1960 ICI introduces the first polymeric MDI-based semi-rigid energy absorbing foam for vehicles.

1960-5 Rigid foam blowing by chlorofluoromethanes.

1962 First production line moulded 'deep seat' flexible polyurethane car cushions at Austin-Morris (U.K.).

1963 ICI demonstrates production line manufacture of refrigerators using MDI-based polyurethane foam.

1963 First cold-store built entirely from metal-faced polyurethane rigid foam laminate made continuously (Australia).

1964 ICI inverse- and floating-platen systems for the continuous manufacture of rigid polyurethane foam-cored building boards in production.

1965 First commercial production of self-skinning flexible foam (Soc. Quillery,France).

1968 ICI introduces isocyanurate rigid foams.

1968 General Motors make the first polyurethane microcellular bumper for the Pontiac G.T.O.

1973 MDI based 'soft-face' bumpers made by RIM system for Chevrolet taxis.

1979 ICI introduces wholly-MDI-based systems for flexible foam moulding.

1983 ICI introduces system to make dual-hardness, moulded seating from MDI-based, flexible foam.

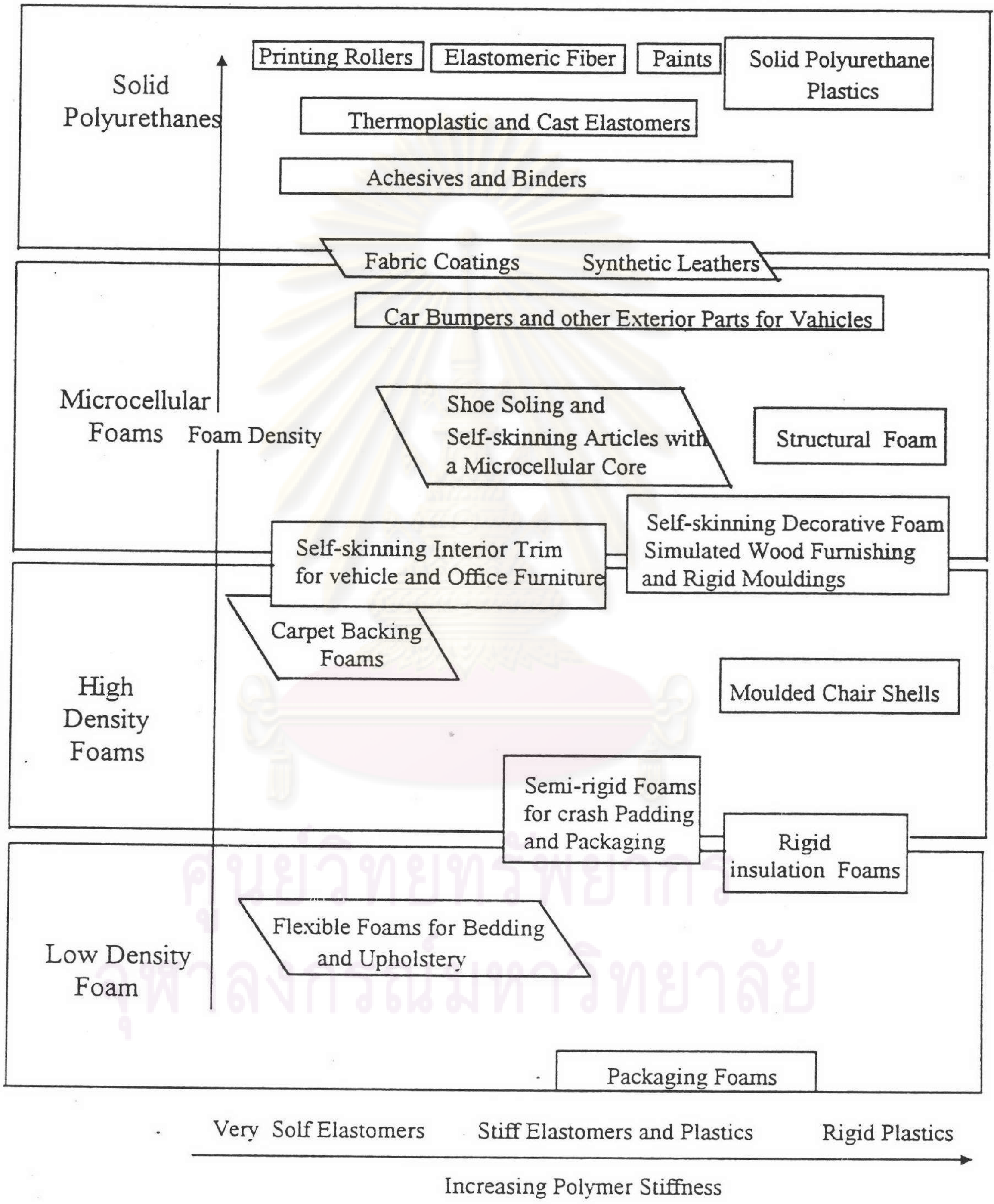
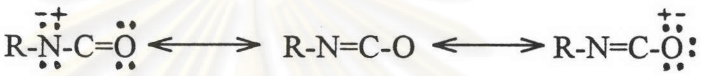


Figure 2.1 Properties metrix of Polyurethane
(Wood G., 1987)

The key to the manufacturing of polyurethane is the unique reactivity of the heterocumulene groups in diisocyanate toward nucleophilic addition which reactive hydrogen atom is transferred to the nitrogen of the isocyanate and the remainer is attached to the carbonyl. The formation of the polymer is by a step-wise process (G. norman and S. Gerald,1985). The polymerization of the isocyanate group enhances the addition across the carbon-nitrogen double bond which allows rapid formation of addition polymer from diisocyanate and macroglycols (O.Kirk,1983).



$$\text{R-}\overset{-+}{\ddot{\underset{..}{\text{N}}}}\text{-C=}\ddot{\underset{..}{\text{O}}} \longleftrightarrow \text{R-N=C-O} \longleftrightarrow \text{R-N=C-}\overset{+-}{\ddot{\underset{..}{\text{O}}}}\text{:}$$

The important characteristic of reaction is giving no by-product of a small molecule is formed.

The reaction of isocyanates with compounds containing active hydrogen atoms i.e. amine, water etc. was capable of much wider application in polymer formation.

Reation with amines : diamines are used as chain-extending and curing agent in polyurethane manufacturing. It can increase the potential for both primary (covalent) and secondary, or hydrogen-bonded, crossliking and resulting urea segments in polymer as shown in Equation 2.2.

$$\text{R-NCO} + \text{R}'\text{-NH}_2 \longrightarrow \underset{\text{Urea}}{\text{R-NH-CO-NH-R}'} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

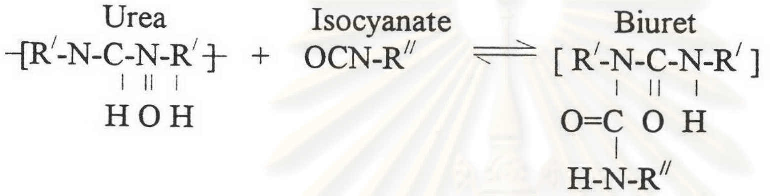
Reaction with water : the reaction of isocyanates and water leads to substituted carbamic acid (unstable product) which decomposes to give amine and carbondioxide that acts as blowing agent in the manufacturing of low density flexible foams.

$$\underset{\text{Isocyanate}}{\text{R}'\text{-NCO}} + \underset{\text{Water}}{\text{H-O-H}} \longrightarrow \underset{\text{Substituted carbamic acid}}{[\,\text{R}'\text{-NH-COOH}\,]} \longrightarrow \underset{\text{Amine}}{\text{R-NH}_2} + \underset{\text{Carbondioxide}}{\text{CO}_{2(g)}} \quad \ldots\ldots(2.3)$$

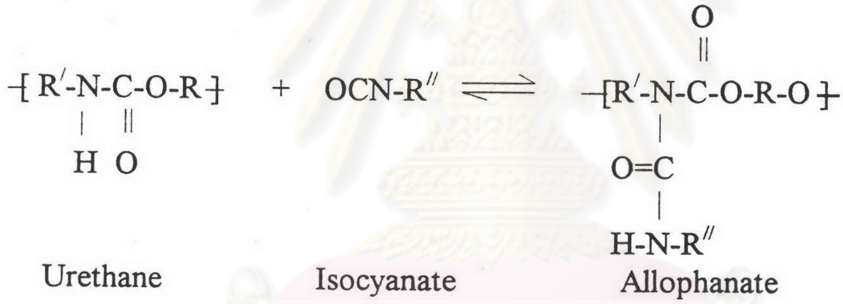
$$\underset{\text{Isocyanate}}{\text{R}'\text{-NCO}} + \underset{\text{Carboxylic acid}}{\text{R-COOH}} \longrightarrow \underset{\text{Amide}}{\text{R}'\text{-NH-CO-R}} + \underset{\text{Carbondioxide}}{\text{CO}_{2(g)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.4)$$

Secondary reaction of isocyanate

Isocyanates may react, under suitable conditions, with the active hydrogen atoms of the urethane and urea linkages to form biuret and allophanate linkages, respectively. Both reactions are cross-linking reactions. The reaction of isocyanates with urea groups is significantly faster and occers at lower temperature than that with urethane groups.



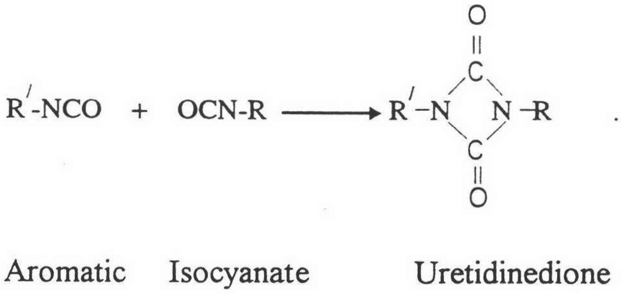
$$-[R'-\underset{H}{N}-\underset{O}{\overset{\|}{C}}-\underset{H}{N}-R']- + OCN-R'' \rightleftharpoons [R'-\underset{\underset{H-N-R''}{|}}{\underset{O=C}{N}}-\underset{O}{\overset{\|}{C}}-\underset{H}{N}-R']$$ ....(2.5)



$$-[R'-\underset{H}{N}-\underset{O}{\overset{\|}{C}}-O-R]- + OCN-R'' \rightleftharpoons -[R'-\underset{\underset{H-N-R''}{|}}{\underset{O=C}{N}}-\overset{O}{\overset{\|}{C}}-O-R-O]-$$ ....(2.6)

Isocyanate polymerization reactions

Isocyanates form oligomers, especially in the presence of basic catalysts, giving uretidinediones (commonly called dimers), and isocyanurates (commonly called trimers).Dimer formation arises only from aromatic isocyanates and it is inhibited by ortho substituents. Thus 2,4- and 2,6- TDI do not form dimers at normal temperatures but 4,4$'$- diphenylmethane diisocanate (MDI) dimerises slowly when left standing at room temperature. At higher temperatures insoluble polymeric materials are formed.



................................(2.7)

2.2 Raw material for polyurethanes

The starting materials for produce polyurethane are the two main participants, namely isocyanate and polyol. In additive to the isocyanate and polyol, auxiliary materials(additives) are added to control the process of reaction and to obtain particular characteristics of final polymer.

2.2.1 Isocyanate

Isocyanates are made by phosgenation of primary amine or amine hydrochlorides in an inert medium (O-dichlorobenzene). The reaction proceeds in two stages : first at room or higher temperature to generate the carbamyl chloride and HCl; further treatment with phosgene at temperature of the order of 150-170°C, then forms the isocyanate according to Equation 2.8 and 2.9.

$$RNH_2 \xrightarrow{COCl_2} \underset{\text{Carbamyl Chloride}}{RNHCOCl} + HCl \xrightarrow{RNH_2} RNH_2Cl + RNCO \quad \text{................}(2.8)$$

$$RNH_2HCl \xrightarrow{COCl_2} RNCO + HCl \quad \text{..}(2.9)$$

The structural formula of diisocyanate are given in Figure 2.2 which includes TDI, MDI, NDI, HDI, H_{12}MDI, XDI, IPDI, TMDI, PPDI, CHDI, TODI, but about 95% of all polyurethanes are based on toluene diisocyanate (TDI), 4,4′-Diphenylmethane diisocyanate (MDI) and its derivatives. Both of them are derived from petrochemical intermediates.

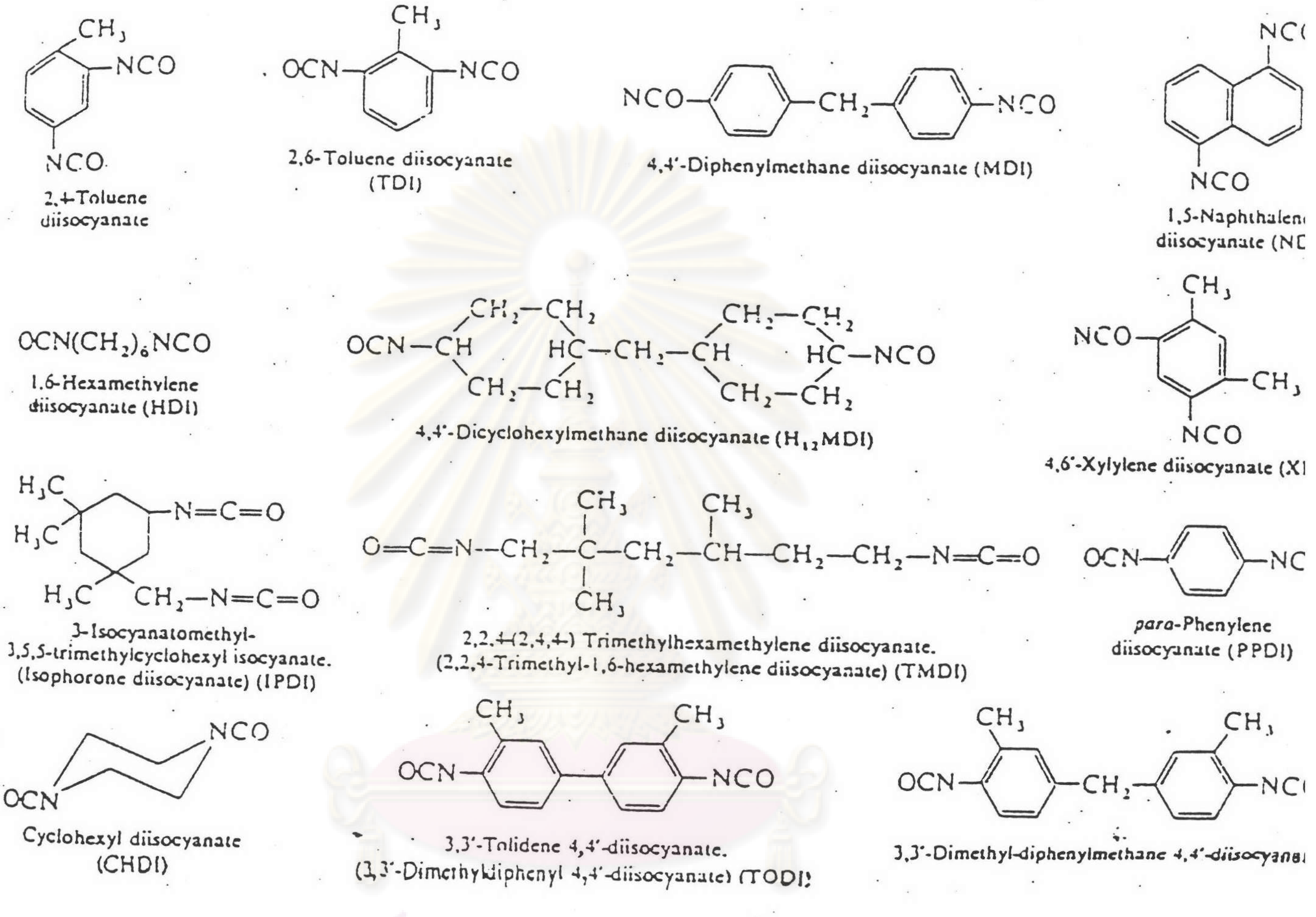
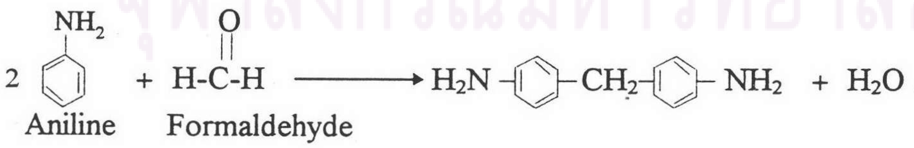


Figure 2.2 Structural formula of diisocyanates
(Hepburn C., 1982)

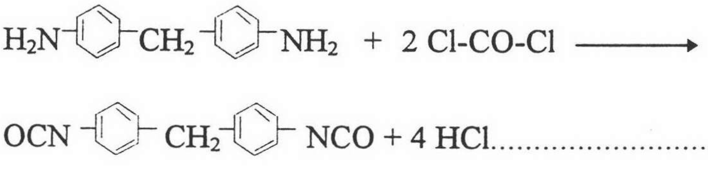
TDI is prepared by direct nitration of toluene to give 80:20 mixture of 2,4- and 2,6-dinitroderivatives, followed by hydrogenation to diaminotoluenes. The diamine mixture are treated with phosgene at temperature up to 140°C and the derived diisocyanare mixture is isolated and purified by distillation. Flowsheet and diisocyanate preparation route for production TDI are detailed in Figure 2.3 and Figure 2.4, respectively.

TDI mixtures can occured a serious toxic hazard in use, having a marked effect on the respiratory system and the skin, and care is very necessary in handling if damage to health is to be avoided. On the other hand, the diisocyanate MDI based on diaminodiphenylmethane is considerable safer to use, having as much lower volatile but it is manufacturing is more complex than that of TDI. Otherwise, the disadvantage is less easily purified and consequently MDI is often used in the crude (undistilled form). The manufacture of MDI is shown in Figure 2.5.

MDI is produced from aniline and formaldehyde by using hydrochloric acid as a catalyst. This condensation reaction produced a complex mixture of polyamide which are phosgenated to obtain a polyisocyanate mixture as shown in Equation 2.10 and 2.11. The product, known as the polymeric MDI as shown in Figure 2.6 (L.F. Hatch and S.Matar, 1981).



.............(2.10)



....(2.11)

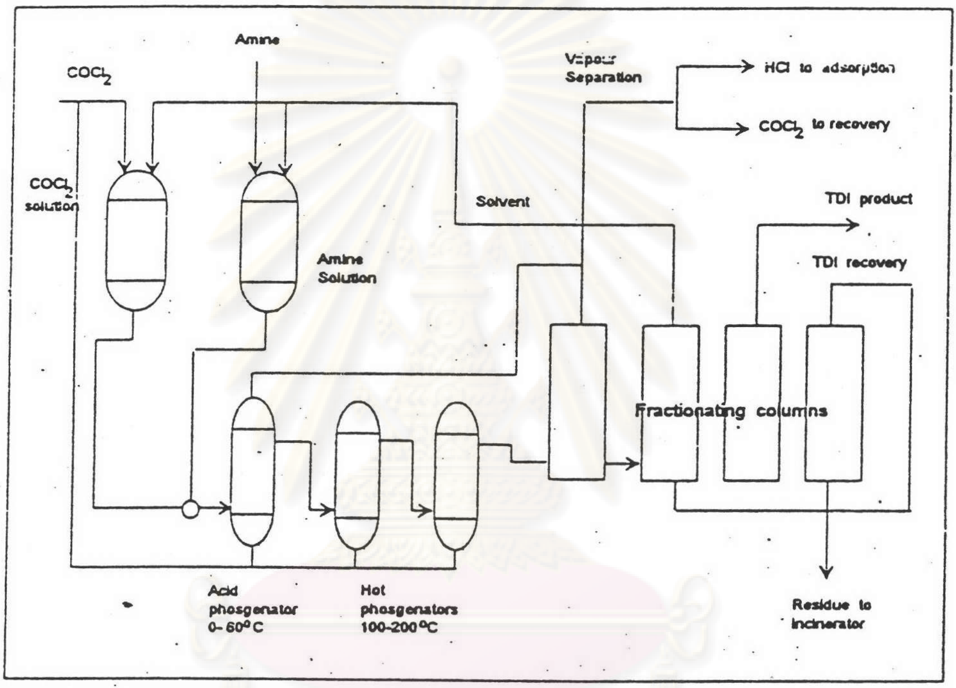


Figure 2.3 Flowsheet for the production of toluene diisocyanate

(P. Wright and A.P. Cumming, 1969)

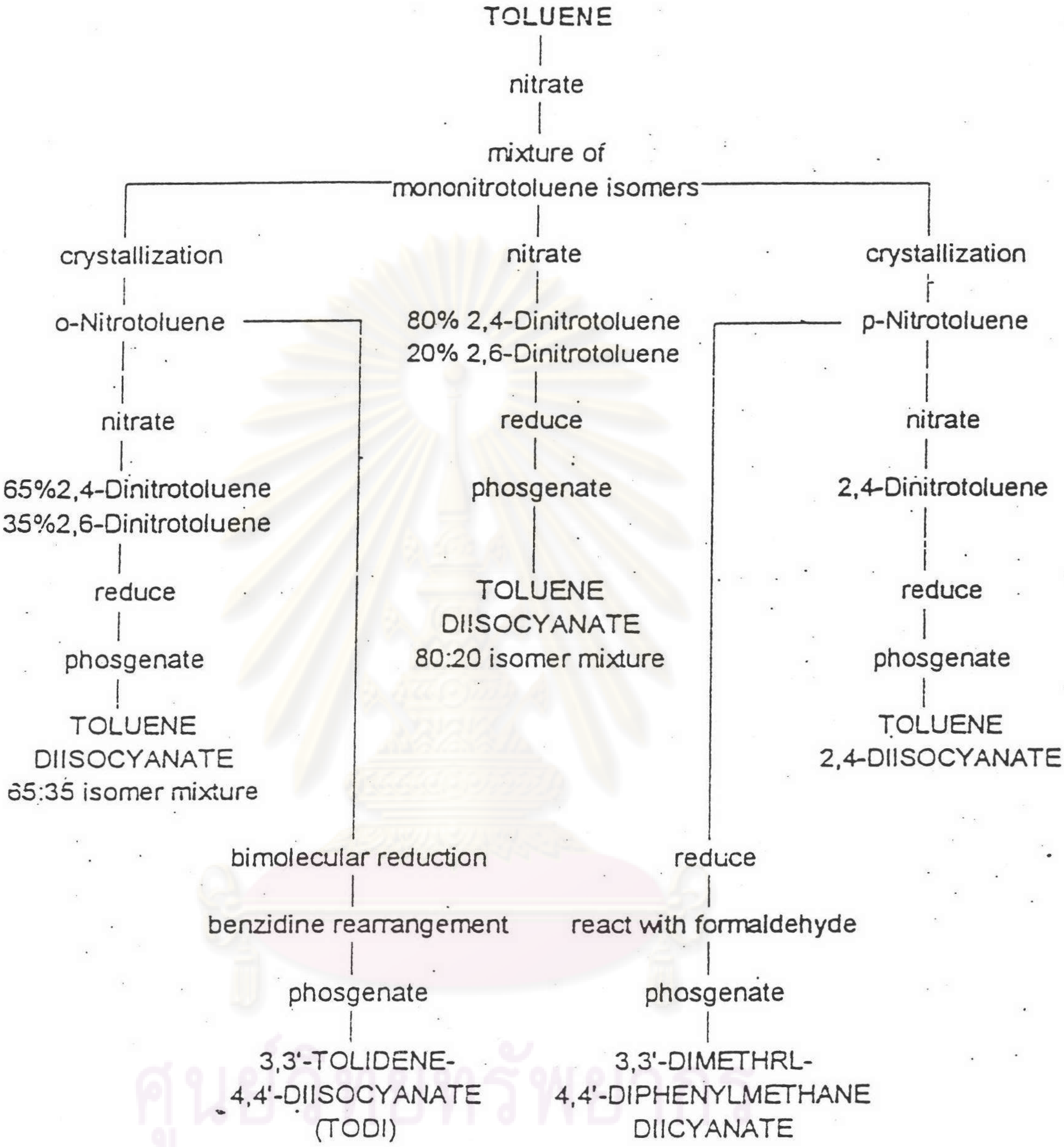


Figure 2.4 Diisocyanate preparation routes for production of TDI
(Hepburn C., 1982)

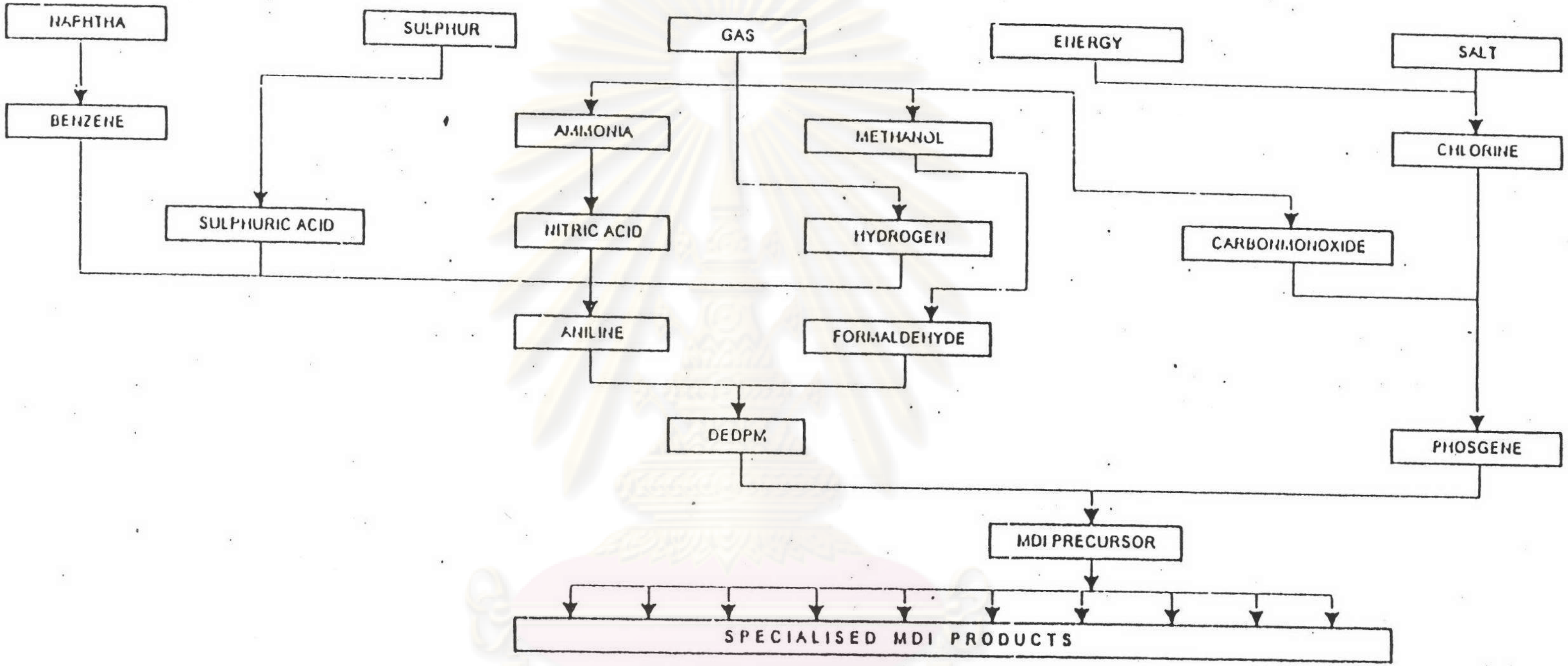


Figure 2.5 The manufacture of MDI
(Wood G., 1987)

Polymeric MDI may contain 55% of the $4,4'$- and $2,4'$-Diisocyanate and 20-25% of triisocyanates and the remainder being polyisocyanates. Another form of MDI is pure MDI, a low melting solid (m.p. 38°C) is available and is produced by seperation from a polymeric MDI precursor. It usually contains a small amount of the $2,4'$ isomer.

Because of different range of functionality, structure and compositions, the selection of MDI may obtain the differnt kinds of polyurethane. Table 2.2 shown the suitible applications which are effect on properties of polyurethane.

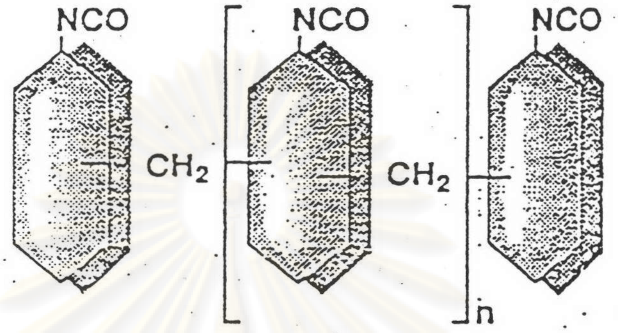


Figure 2.6 Structure of polymeric MDI
(Wood G., 1987)

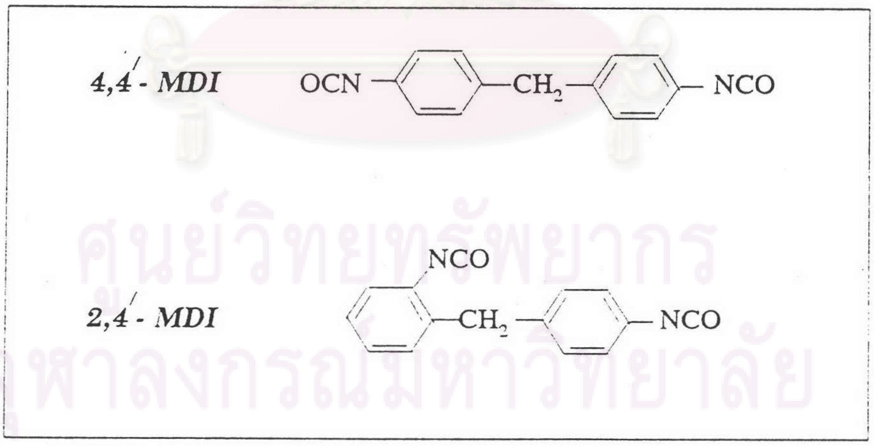


Figure 2.7 Structures of pure MDI
(Wood G., 1987)

Table 2.2 Range of MDI variants
(Wood G., 1987)

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

2.2.2 Polyols

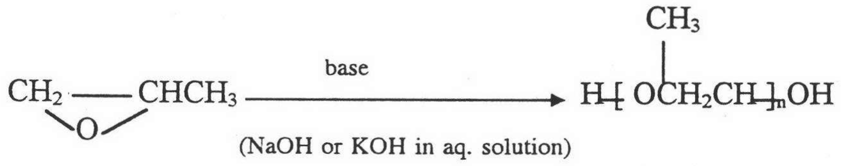
Most of the polyols used in making polyurethanes are classified in two types :hydroxyl-terminateed polyethers and hydroxyl-terminated polyester. The structure of polyol influences on the properties of the final urethane polymer.

2.2.2.1 Polyether polyols

Polyether polyols are high molecular weight polyols that range from viscous liquid to waxy solids, depending on structure and molecular weight. Commercial polyether polyols are shown in Table 2.3. Most polyether polyols used in polyurethane manufacturing are polypropylene glycols which are derived from propylene oxide.

Table 2.3 Commercial Polyether Polyols (M. Morton, 1987)

Common Chemical Name	Type	Structure
Poly(tetramethylene adipate)glycol	polyester	$HO[(CH_2)_4OCO(CH_2)_4COO]_n(CH_2)_4OH$
Poly(ε-caprolactone)glycol	polyester	$H[O(CH_2)_5CO]_XORO[CO(CH_2)_5O]_vH$
Poly(hexamethylene carbonate)glycol	polyester	$HO[(CH_2)_6OCOO]_n(CH_2)_6OH$
Poly(oxytetramethylene)glycol	polyether	$HO[(CH_2)_4O]_nH$
Poly(1,2-oxypropylene)glycol	polyether	$HO[CH(CH_3)CH_2O]nCH_2CH(CH_3)]OH$
Poly(butadiene)glycol	polyhydro-carbon	$HO(CH_2CH=CHCH_2)_XOH$



Propylene oxide

Polypropylene glycol

Propylene oxide is produced from propylene via a chlorohydrin intermediate and polymerized by basic catalysts.

The manufacturing of propylene glycol uses ethylene glycol or propylene glycol or diethylene glycol as initiator and uses catalyst in a common solvent. Then pump into a catalyzing vessel heated to 80-100°C under vacuum where the solvent is removed and the alcoholate formed, and transferred to the reactor vessel at 90-120°C. Propylene oxide is pumped into a pressure of 10-50 psi which is maintained until the desired molecular weight is reached, when any excess propylene oxide is distilled off and the polyether mixture transferred to a neutralized vessel and neutralized by sulfuric acid. Then the mixture is filtered and remaining water reduced to 0.05% maximum. Antioxidants are added to prevent storage stability. Polypropylene glycol flowsheet is given in Figure 2.8 and Figure 2.9, respectively.

Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups.

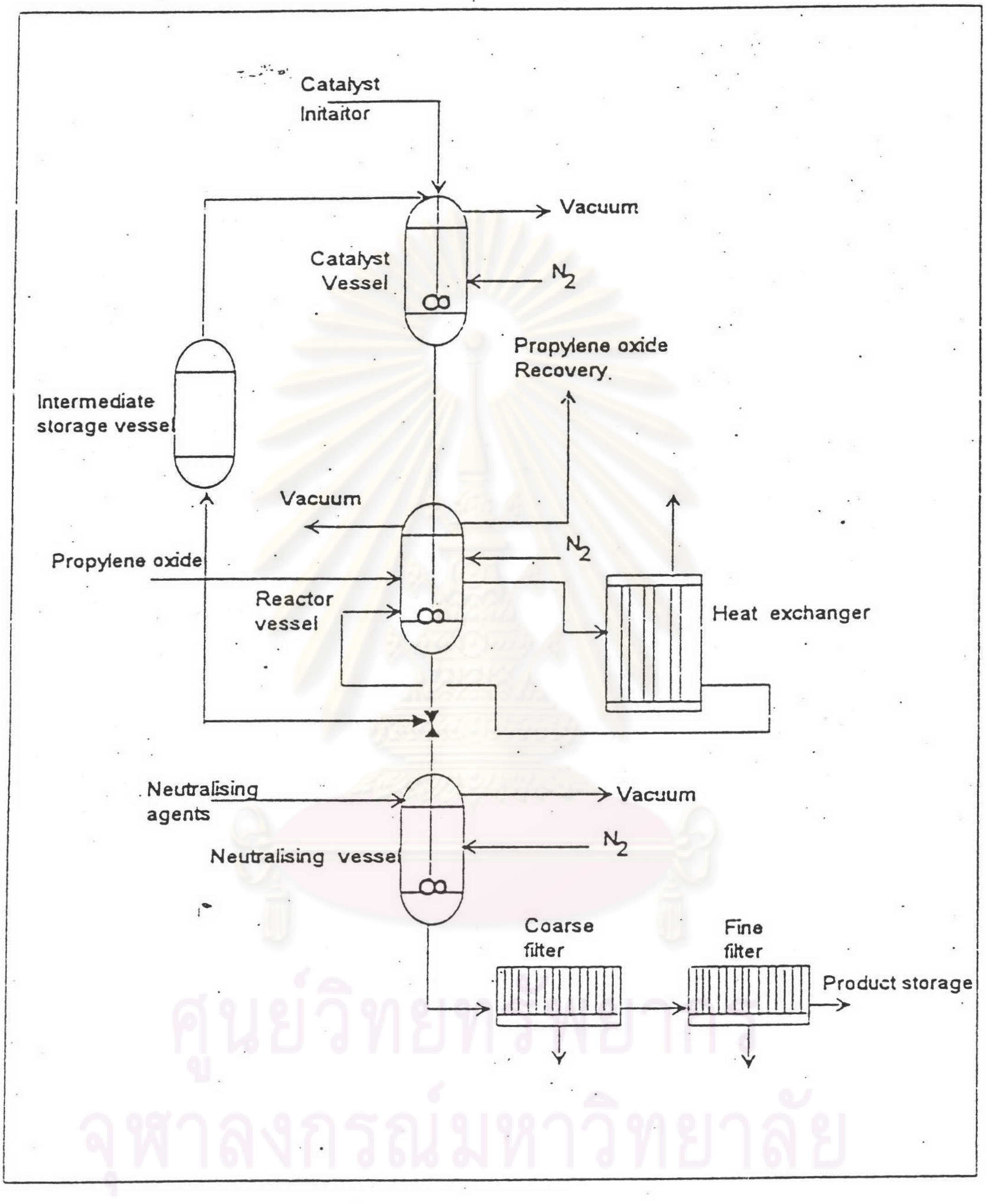


Figure 2.8 Polyether(polypropylene)glycol manufacture flowsheet
(Hepburn C., 1982)

Initiator +	Alkylene oxide →	Polyether polyol
Polyfunctional alcohol or amine	Propylene oxide alone or copolymerized with ethylene oxide	polyether polyol with both primary and secondary hydroxyl end-groups

The polymerization of Propylene oxide and Ethylene oxide

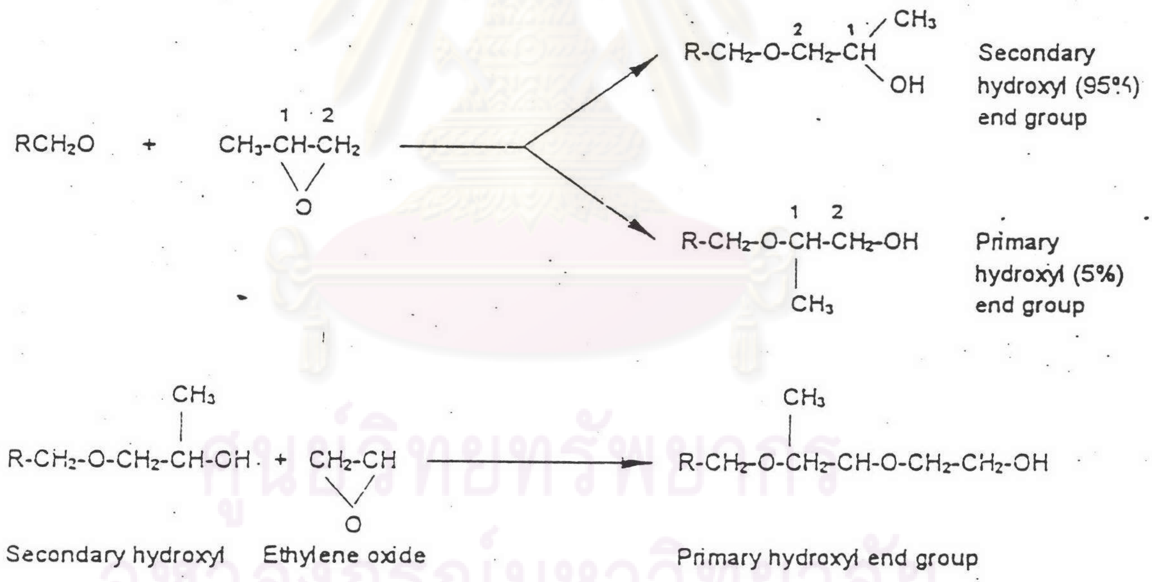


Figure 2.9 The manufacture of polyether polyols
(Wood G., 1987)

Table 2.4 Advantage and disadvantage of polyester polyols compare with polyether polyols

Type of Polyols	Advantage	Disadvantage
Polyester polyols	-Greater mechanical strength -Oil resistance and dry cleaning solvent resistance -Stable to oxidation and higher temperature resistance	-Higher cost -More difficult to handle (more viscous) -Sensitive to hydrolysis
Polyether polyols	-Lower cost -Hydrolysis resistance	-Inferior mechanical strength -Sensitive to oxidation

For preparation of polyesters, conventional methods of polyesterification, i.e. reaction between acid and diol or polyol, are used, the water of condensation being removed by distillation and the reaction help by use of vacuum or an azeotrope. The molecular weight can be controlled by the molar ratio of the reactants and the reaction conditions, but it is essential that the terminal groups should be hydroxyl terminated so as to react an excess of the stoichiometric amount of the difunctional glycol with the dibasic acid as shown in Equation 2.12.

$$(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \longrightarrow H[OROOCR'CO\ ]_nOROH\ + 2n\ H_2O ......(\ 2.12\ )$$

Condensation polymerization manufacturing of polyester polyols is shown in Figure 2.10.

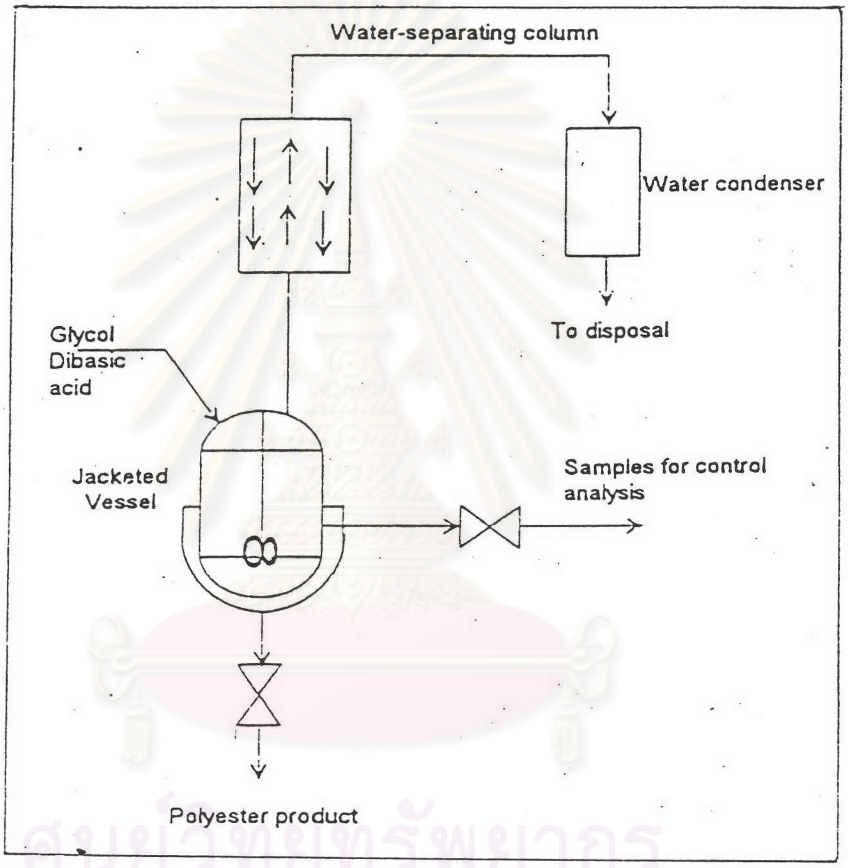
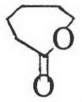


Figure 2.10 Condensation polymerization equipment
for manufacture of polyesters
(Hepburn C., 1982)

A molar excess of glycol over acid in the range of 5-20% is required to be heated to 200-500°C under vacuum to prevent oxidation discoloration. Water is removed during the reaction and any glycol evaporated returned by the use of a fractionating column.

Polyester polyols is used in production of specialty polyurethane flexible foam and thermoplastic polyurethane elastomers and fibres. Polyester polyols are also made by the reaction of caprolactone with suitable glycols. The reduction of ester groups in the macromolecule improves the hydrolytic stability of the products.



$+ \ \text{HOROH} \longrightarrow \text{HOR}\!\left[\text{OC(CH}_2\text{)}_5\text{O}\right]_n\!\text{H}$ ....(2.13)

Polycarprolactone

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

$$\text{Hydroxyl Value (mg KOH/g)} = \frac{56.1 \times (\text{functionality})}{\text{Molecular Weight}} \times 100$$

Hydroxyl Value is convenient for calculation of the stoichiometric formulation of manufacturing polyurethane. In order to achieve the chemically stoichiometric equivalents of hydroxyl to isocyanate group, the isocyanate index is specified.

Isocyanate index is defined as the amout of isocyanate used relative to the theoretical equivalent amout of isocyanate required.

$$\text{Isocyanate index} = \frac{\text{Actual amout of isocyanate used}}{\text{Theoretical amout of isocyanate required}} \times 100$$

$$\text{Isocyanate Value} = \%\ \text{NCO groups} = \frac{42 \times (\text{functionality}) \times 100}{\text{Molecular weight}}$$

$$= \frac{4200}{\text{Equivalent weight}}$$

Calculating the ratio of the components required for polyurethane manufacturing is to calculate the number of parts by weight of the isocyanate that are required to read with parts by weight (pbw) of the polyol and proportionate amounts of additives.

2.2.3 Auxiliary material (additives)

In addition to isocyanates and polyols - the basic materials for making polyurethanes - a wide range of auxiliary chemical may be added to control and modify both the polyurethane reaction and the properties of the final polymer.

These additives include catalyst, chain extenders, cross-linking agents, flame retardants, colouring material and fillers which are shown in Table 2.5.

2.2.3.1 Catalyst

In urethane technology catalysts are widely used to give desired balance of reaction rate between compound of differing active hydrogen activity. The important role of catalyst is not only affects the rate of chemical reaction, responsible for chain propagation, extension, and cross-linking but also influence the ultimate properties of the final polymers.

Choice of the catalyst depend on catalyst activity, odour, vapour pressure, toxicity, solubility, processing, cost etc.

The commonly used catalyst canbe devided into two categories

1. Tertiary amines (see Table 2.6) which promote OH/NCO reaction (blowing).

The mechanism of this catalyst involve the donation by the tertiary nitrogen to the carbonyl carbon of the isocyanate group, then formation of a complex intermediate. The efficiency of tertiary amine increase with the basicity of the amine, and decrease with increasing steric shielding of the amino nitrogen.

2. Organometallic compounds (see Table 2.7) which promote OH/NCO reactions (polymer forming).

Organometallic compounds are much more efficient catalysts than the amines, especcially for the hydroxyl/isocyanate reaction (S.J. Blunden, 1976).

Table 2.5 Reasons for using aadditive
(Wood G., 1987)

Additives	Type of material	Purpose
Catalyst	Tertiary amines Organometallic compounds	To speed up the reaction of isocyanate and polyol
Cross-linking chain-extending agents	Polyols Polamines	To give polymer cross-linkink 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	Vasious 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 scrims)	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 slowdown the rate of smoke production on burning.

Table 2.6 Some tertiary-amine catalysts
(Wood G., 1987)

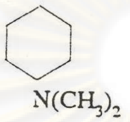
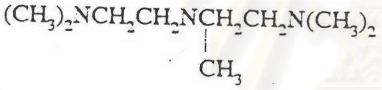
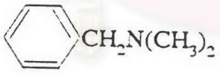
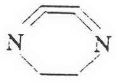
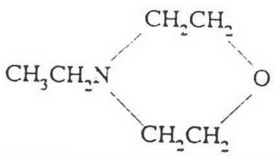
Catalyst	Application
1 N,N-Dimethylaminoethanol $(CH_3)_2NCH_2CH_2OH$	Inexpevsive, low-odour, isocyanate reactive, mobile liquid catalyst used in polyether-based flexible foams.
2 N,N-Dimethylcyclohexylamine, (Catalyst SFC) 	Liquid with an intense odour. Rigid foams, polyester-based flexible foams and some semi-rigid foams.
3 Bis-(2-dimethylaminoethyl)ether $(CH_3)_2NCH_2CH_2OCH_2CH_2N(CH_3)_2$	Low-odour, mobile liquid used in high resilience and cold-cure flexible foams.
4 N,N,N',N',N''-Pentamethyl-diethylene-triamine  $(CH_3)_2NCH_2CH_2\underset{\substack{\vert\\ CH_3}}{N}CH_2CH_2N(CH_3)_2$	Flexible foams and semi-rigid foams.
5 N,N-Dimethylbenzylamine, (Catalyst SFB) 	Liquid with characteristic smell used in polyester-based flexible foams, semi-rigid foams and for prepolymer making.
6 N,N-Dimethylcetylamine $CH_3(CH_2)_{14}CH_2N(CH_3)_2$	Viscous liquid with a low odour used in polyester-based flexible foams and some potting compounds.
7 Diaminobicyclooctane(DABCO) 	Solid, soluble in water, glycols and polyethers. May be used in most types of polyurethanes.
8 N-Ethylmorpholine 	Volatile, low viscosity liquid with characteristic odour. Used as synergistic catalyst in flexible foams and in prepolymer preparation.

Table 2.7 Some commercially available organometallic catalysts (Wood G., 1987)

Catalyst	Principal application
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 Dioctyltin thiocarboxylates	Delayed action (hindered) catalysts for RIM and high resilience foams.
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.

This allows the polymer -formation polyol/isocyanate reaction to proceed at a sufficient rate to increase viscosity rapidly to a state where gas is effectively trapped, as well as to developed enough gel strength to prevent the foam from collapsing after gas evolution has ceased.

2.2.3.2 Chain- extenders and crosslinking agents

Chain- extenders are difunctional substances, glycols, diamines or hydroxy amines which a diamine chain extender give more excellent physical properties results than if a diol were used, probably due to the introduction of urea linkages which enter strong hydrogen bonded interaction as shown in Figure 2.11 and Figure 2.12. Chain-extenders are used in flexible polyurethanes such as flexible foams; microcellular elastomer, cast elastomer and RIM systems. Some chain-extending agents and cross-linking agent are shown in Table 2.8.

Crosslinking agents having a functionality of three or more are used to increase the level of covalent bonding in rigid polyurethane foam.

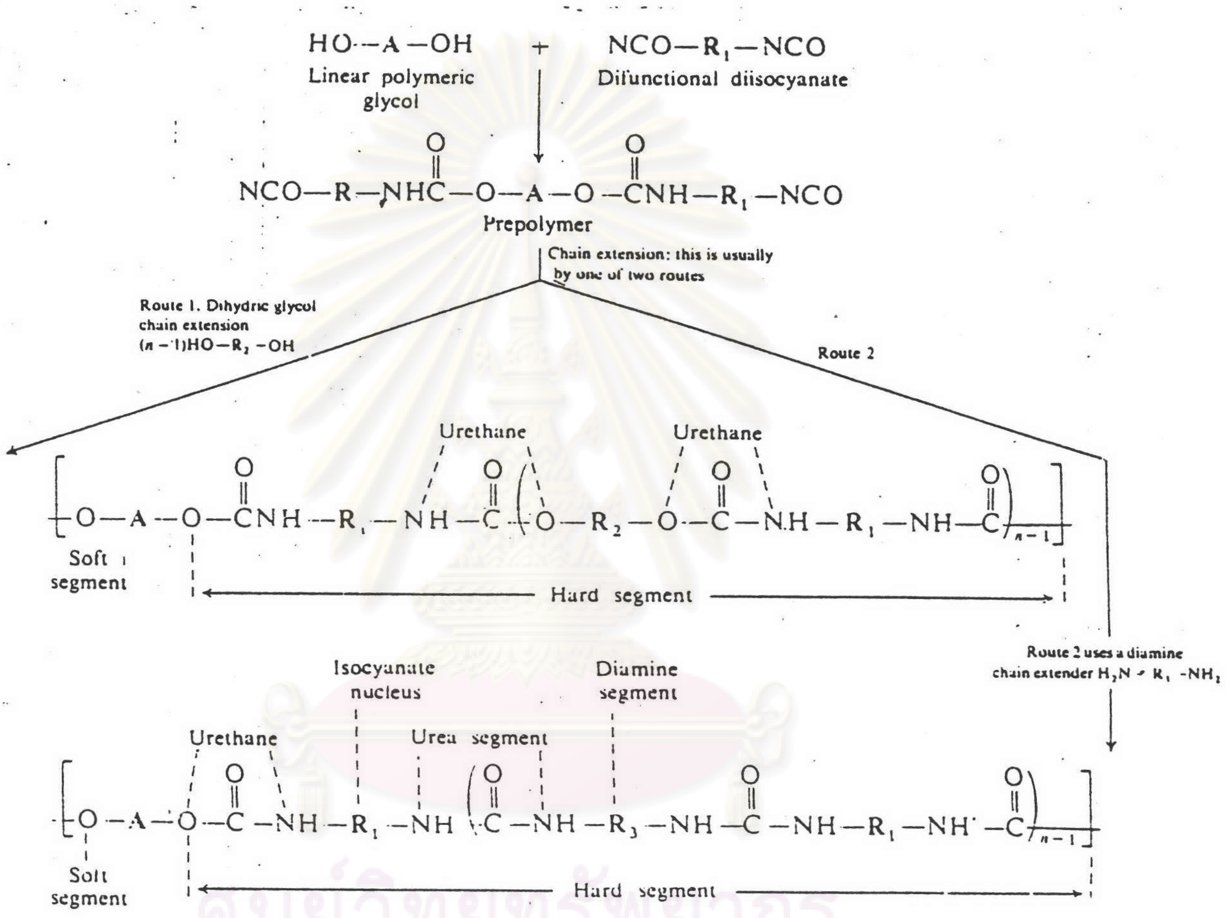


Figure 2.11 Prepolymer reaction sequence for elastomer synthesis (Hepburn C.,1982)

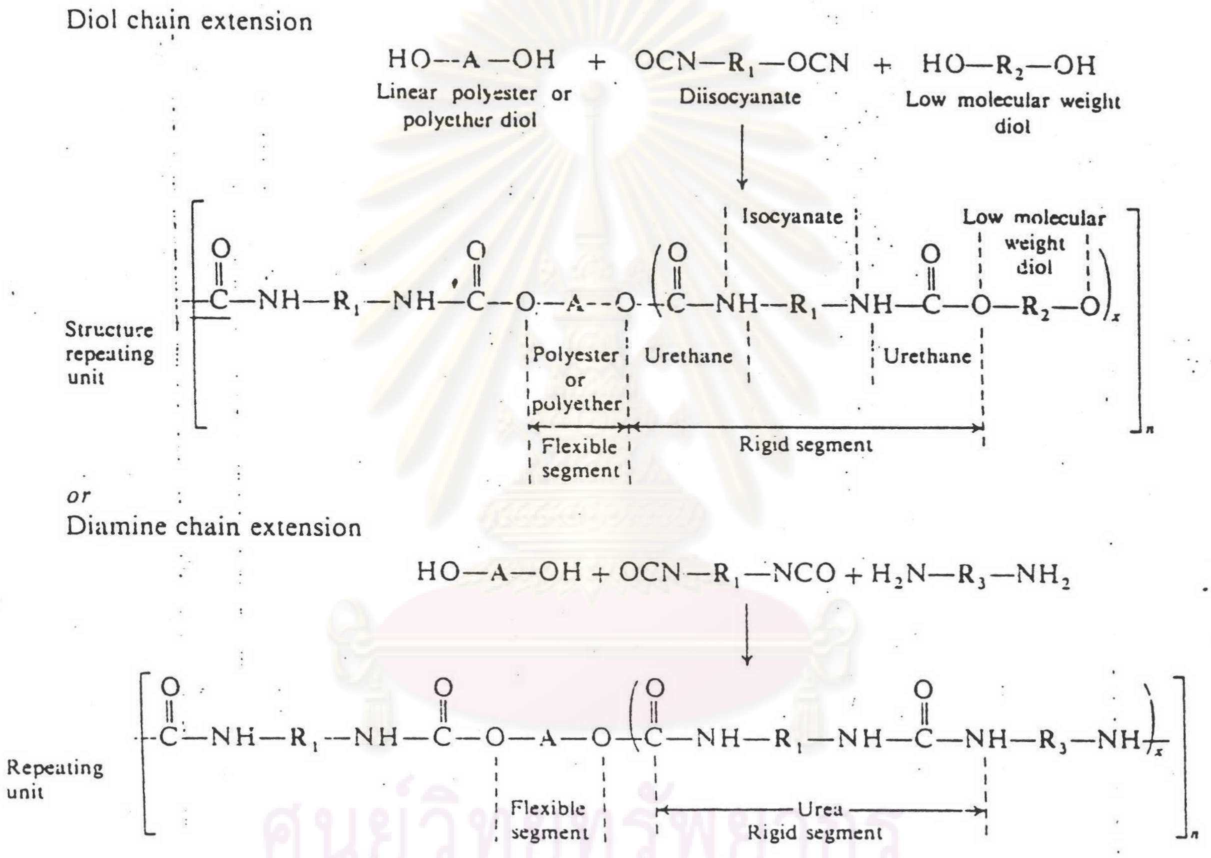


Figure 2.12 One shot reaction sequence for elastomer synthesis (Hepburn C., 1982)

Table 2.8 Chain-extending agents, cross-linking agents and curing agents and their diisocyanate equivalents

(Wood G., 1987)

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	43.5	62
m-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 (H_2O)	2	18.01	6230	968	1389
Diethanolamine $HN(CH_2CH_2OH)_2$	3	105.14	1601	248	357
Triethanolamine $N(CH_2CH_2OH)_3$	3	149.19	1128	175	252
Glycerol $CH_2OHCHOHCH_2OH$	3	92.11	1827	284	407
‘Daltolac’ C 5	3	150	1125	175	251
‘Daltolac’ 50	4	468	480	75	107
‘Uropol’ G 790	4	280	800	124	178

2.2.3.3 Blowing agents

Cellular polyurethanes are manufactured by using blowing agents to form gas bubbles in the polymerizing reaction mixture. Blowing agents may be considerd in two types as physical and chemical blowing agent.

Water can react with diisocyanate to generate carbondioxide as gas bubbles in “flexible foam”. In addition to generating carbondioxide, the water/isocyanate reaction produces not only polyureas, an essential part of polymer hard segment, but also the exothermic heat required to complete the polymerization and vaporise any non-reactive blowing agent used. Physical blowing has no effect upon the hard segment of polymer chain but tend to reduce the stiffness of polymer. On the other hand, chemical blowing stiffness the polymer by increasing the polyurea content of the polymer structure and the degree of the secondary bonding between polymer chains. Some non-reactive blowing agents are given in the Table 2.9.

2.2.3.4 Flame Retardant

Polyurethane will burn given the application of sufficient heat in the presence of oxygen. Flame retardants are added to polyurethanes to reduce the flammability, ignitability and the burning rate of polyurethanes which operate through one or more of the following mechanisms:

- 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 carbondioxide.
- 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.
- Including char formation by the use of additives.

The most widely used flame-retardants in both flexible and rigid foam systems are chlorinated phosphate ester. The common flame-retardants are shown in Table 2.10.

Table 2.9 Non-reactive blowing agents for polyurethane
(Wood G., 1987)

Blowing agent	Trichloro-monofluoro-methane (CFM-11)	Dichloro-difluoro-methane (CFM-12)	Methylene chloride
Molecular weight	137.38	120.92	84.94
Density at 20^0C(g/ml)	1.488	1.486	1.366
Boiling point at 1 atm (°C)	23.8	-29.8	40.1
Freezing point (°C)	-111	-160	-96.7
Threshold limit value (TVL*,ppm)	1000 ppm	1000 ppm	50 ppm A_2
Solubility (g/100 g solvent at 20°C)			
Water	Insoluble	Insoluble	Insoluble
Ethanol	∝	∝	∝
Polyethers	Adequately soluble for all applications		

Table 2.10 Some flame retardants for polyurethane
(Wood G., 1987)

Addtive	Typical application
A. Non-reactive liquids	
Tris(2-chloropropyl)phosphate, ‘Daltogard’ F	All polyurethanefoams including polyester-based foams and microcellular elastomer.
Tris(2-chloroethyl)phosphate, (T.C.E.P.)	Polyether-based flexible and rigid foams.
Tris(2,3-dichloropropyl)phosphate, ‘Fyrol’ FR2 ‘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.
Dibromoneopentyl glycol ‘FR’1138	Polyether-based polyurethanes.
Tetrabromobisphenol A Tetrabromophthalic anhydride	Rigid polyurethane and polycyanurate foams.
C.Fillers	
Ammonium salts, sulphate, polyphosphate, etc.	Together with halogenated additives in rigid polyurethanes.
Aluminium hydroxide. Melamine.	Alll polyurethanes but especially in low density flexible foams for ignition and smoke supression.
Calcium carbonate	Heat absorbing filler.

2.2.3.5 Colouring materials

During manufacturing low density flexible foam, it usually add pigment pastes in order to identify the grade and the density of the foam. The pigment are also used in both organic and inorganic pigments. The characteristic of pigment used must not react with isocyanates and must be stable at the high curing temperatures reached in the manufacture of low-density foams. The most widely useed colouring material is carbon black which gives some protection against surface discolouration of foam cause by UV. light. Polyurethane foam is easily coloured by dyeing but its disadvantage is high cost.

2.2.3.6 Fillers

Particulate and fibrous fillers may be used in most kinds of polyurethanes. Particulate fillers are used in flexible polyurethane foams to reduce their flammability and increased stiffness and they increase the range of operating temperature of rigid foams, self-skinning foams and flexible RIM products. Mineral fillers are sometimes used to reduce costs and to increase the compressive strength of rigid foam. R. Gachter et.al (1987) introduced and guided for the selection and usage of fillers. Some fillers and their application are listed in Table 2.11 and 2.12, respectively.

Table 2.11 Some fillers and their application in polyurethanes
(Wood G., 1987)

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, (aluminum, coated glass, steel)	Elastomeric RIM, rigid foams
Glass cloths ans scrims, wire mesh, organic fibres, etc.	Encapsulating in rigid foams, reinforcement of low density flexible foam mouldings.

Table 2.12 Some high modulus reinforcing fibres
(Wood G.,1987)

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)	250-40	1.8-1.9	140-210
Carbon fibre (Pitch)	200	1.9	105
Steel	200	7.8	26
Alumina fibre	350	4.0	88
Polyethlene fibre	30-70	0.96	31-73
Boron fibres	400	2.5	160

2.3 Static Mixers

Static mixers, often refered to as motionless mixers, are in-line mixing devices which consist of mixing elements inserted in a length of pipe line (Tube). ther are a variety of element designs available from the various manufactures but alll are stationary in use. The energy for mixing is derived from the pressure loss incurred as the process fluids flow through the mixing elements and additional pumping energy is necessary over and above that normally needed forpumping requirements. The number of elements required in any application is dependent on the difficulty of the mixing duty, more elements being necessary for difficult tasks. Normally mixer sizes from 3/8 in. to 10 inch. in diameter (25.4 cm.) are of metallic construction. The length of each element is 1.5 times its diameter.

2.3.1 Basic principle of mixing

Nowaday, static mixers have many type for used in many mixing applications. Figure 2.12 shows the type of static mixers. Another type of static mixers have same basic principle of mixing as well as Kenics type which designs for low pressure drop. This designs also consists of a series of mixing elements aligned at 90°, each element being a short helix of one and a half tube diameter in length. Each element has a twist of 180° and rigth-hand and left-hand elements are arranged alternately in a pipe-line. The basic principle is increased interfacial of fluids which mixing in the tube.

Assume two fluids, which the color of the first fluid is white and the other is black, are followed in the first ribbon (element). The white fluid is over the black fluid. While the two fluid are flowed, the white fluid have been controled to the bottom and the black fluid have been controled to the top of the ribbon (element). When the black and the white fluid have gone to the second ribbon, each fluid have seperated two sections because of the second ribbon aligned at 90° with the first ribbon. While the fluid leaved from the second ribbon, the fluid have seperated four sections and have seperated eight sections when gone out from the third ribbon.

The number of sections have been calculated from the formular

$N = 2^n$ when

N is the number of sections

n is the number of ribbons or elements

2.3.2 Radial Mixing

As fluid follow the curves of elements, they are rotated rapidly toward the pipe wall or rotated back to the conner.

Figure 2.13 Flow pattern in left-element and right-element

(Oldshue J.Y., 1983)

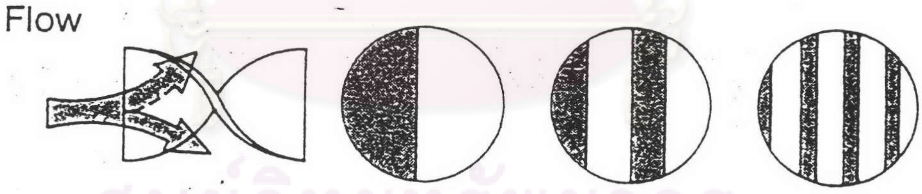


Figure 2.14 Division of flow in Kenics static mixers

(Oldshue J.Y., 1983)

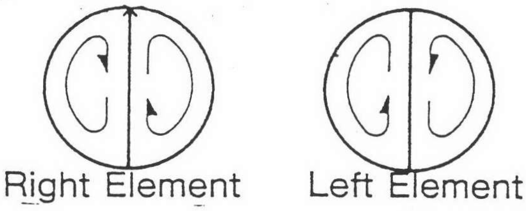


Figure 2.15 Radial mixing in Kenics static mixers

(Oldshue J.Y., 1983)