MDI and TDI: Safety, Health and the Environment.

A Source Book and Practical Guide

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1 MDI, TDI and the polyurethane industry

MDI and TDI are high tonnage products, which comprise about 90 % of the total diisocyanate market. The predominant use of MDI and TDI is in the manufacture of polyurethanes. Polyurethanes are produced by reacting diisocyanates with polyols and other chemicals. The range of polyurethane types, from flexible or rigid lightweight foams to tough, stiff elastomers, allows them to be used in a wide diversity of consumer and industrial applications. Some examples are:

Rigid foam

- thermal insulation of buildings, refrigerators, deep freeze equipment, pipelines and storage tanks;
- buoyancy aids in boats and flotation equipment;
- packaging;
- furniture;
- equipment housings.

Flexible foam

- household furniture including bedding;
- automotive seating;
- cushioning for diverse industrial applications;
- textile laminates.

Integral skin, semi-rigid and low density structural foams

- steering wheels, headrests and other automotive interior trim components;
- furniture elements;
- sports goods such as skis and surf boards.

Elastomers

- shoe soles;
- vehicle body panels;
- rollers and gear wheels;
- conveyors;
- sealants for the construction and automotive industries;
- fibres.

Figure 1.1 shows the areas of application as a function of stiffness and density of each polyurethane product (Woods, 1990).

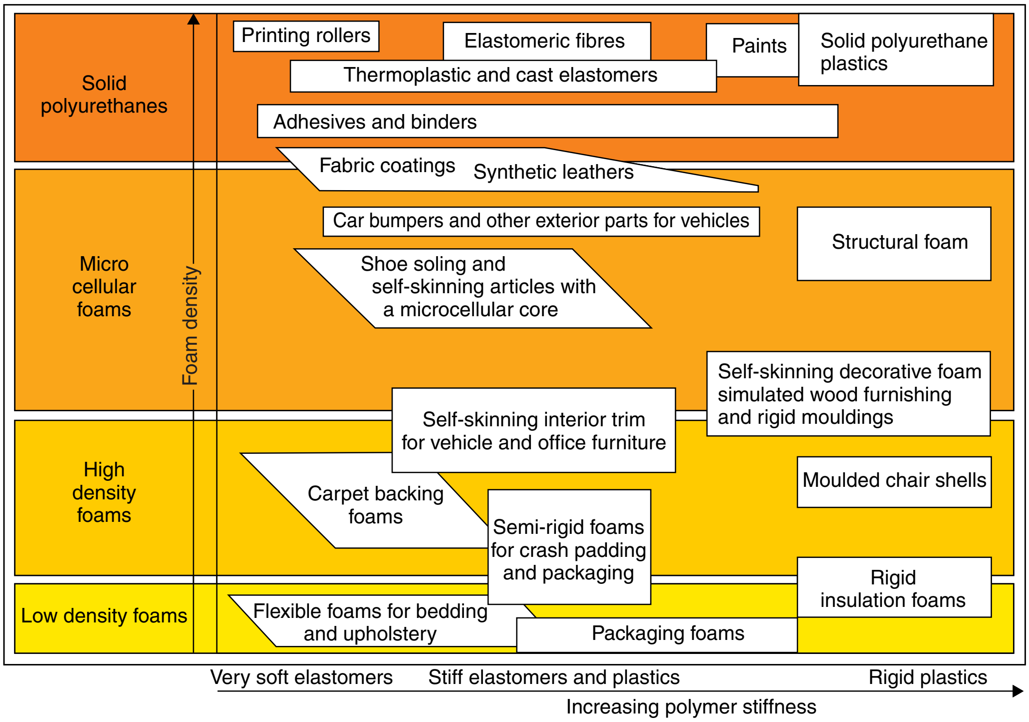

Figure 1.1 **Property matrix of polyurethanes (figure by courtesy of Huntsman Polyurethanes)**

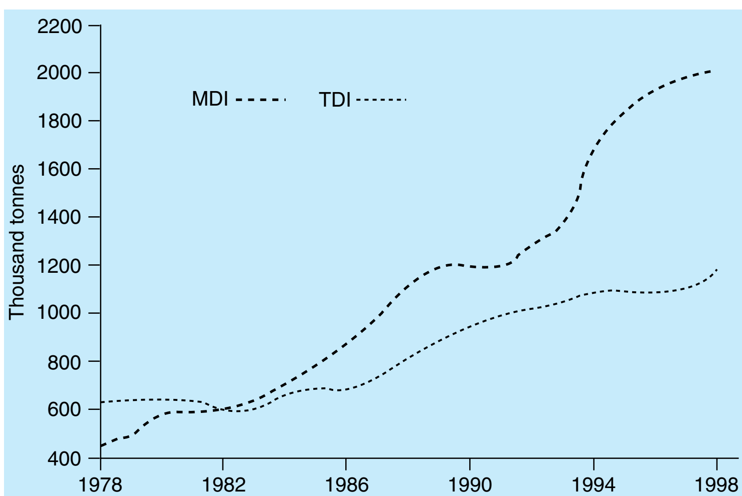

Figure 1.2 **Global tonnages of MDI and TDI from 1978 to 1998**

References about MDI and TDI production levels
CW (1998); Petersen (1999); ECN (1999); UT (2000).

By 2003 the global production of MDI and TDI together will approach 4 million tonnes. Over more than 40 years the tonnages of MDI and TDI have increased year upon year as new markets and new applications have been found (Figure 1.2). It is estimated that this growth trend is likely to continue at a high level as indicated by the statistics of market development around the world, especially in the Pacific Rim and in Latin America, and as there evolve high tonnage applications, such as the use of MDI as a particle board binder. Continuing vigilance in the safety of handling of MDI and TDI will be needed during this period of geographical and applicational expansion. The rapidly expanding product stewardship movement, in which MDI and TDI producers and the polyurethane industry have been collaborating closely for many years, will support this.

Types of MDI

The acronym *MDI* was devised from one of the chemical's many names, *methylene diphenyl diisocyanate*. Common synonyms are diphenylmethane diisocyanate and diisocyanatodiphenylmethane. The generic term MDI is often used for pure MDI and for the technical grade of MDI commonly known as polymeric MDI. In Table 1.1 is given basic information about these types of MDI and modified MDIs, which can be made from both pure MDI and polymeric MDI.

Table 1.1 **Types of MDI used in industry.**

Type of MDI	Description	Form at 25 °C
MDI	Generic term for any type of unmodified MDI.	–
Polymeric MDI	Comprises mixed monomeric MDI and higher molecular weight species. Formerly also called crude MDI or technical grade MDI.	Translucent brown liquid
Pure MDI	Commercial monomeric MDI. It is also known as monomeric MDI, 4,4′-MDI or MMDI. It comprises about 98 % 4,4′-MDI, with 2,4′- and 2,2′-MDI constituting most of the remainder.	White solid (fused or flake)
Modified MDIs also known as **MDI derivatives**. Some are known as **MDI prepolymers**. Others are known as **MDI variants**.	These terms represent either pure or polymeric MDI as modified to make handling easier or to increase the diversity of final polymer properties. Producers have wide ranges of products tailored to specific applications.	Whitish brown solids or liquids, depending on formulation

The term *Polymeric MDI* is a misnomer: it is not a polymer. It is a liquid mixture containing monomeric MDI isomers and oligoisocyanates: the latter are sometimes referred as oligomers, which is incorrect usage. For certain applications it is necessary to refine the mixture by distillation and/or crystallization to form pure MDI, a solid at ambient temperature. Currently, the ratio of production levels of polymeric MDI to pure MDI that is manufactured is about 4:1. This ratio, and particularly the relative tonnages of modified MDIs

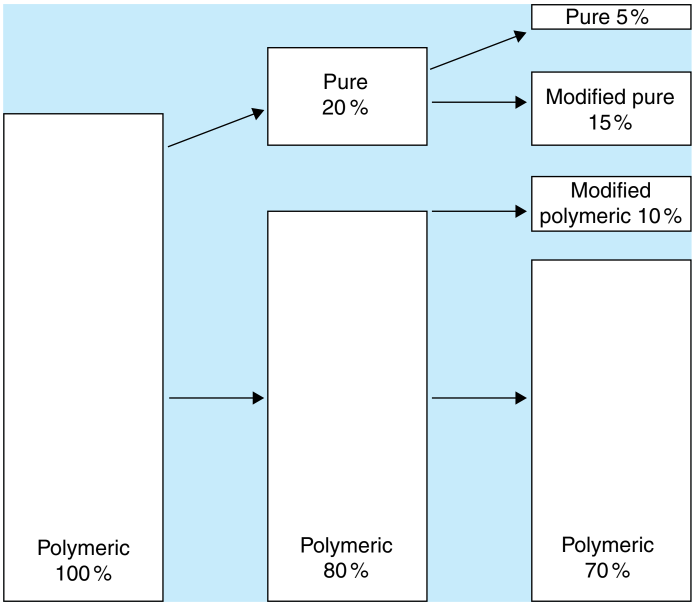

Figure 1.3 **Production of MDI types**

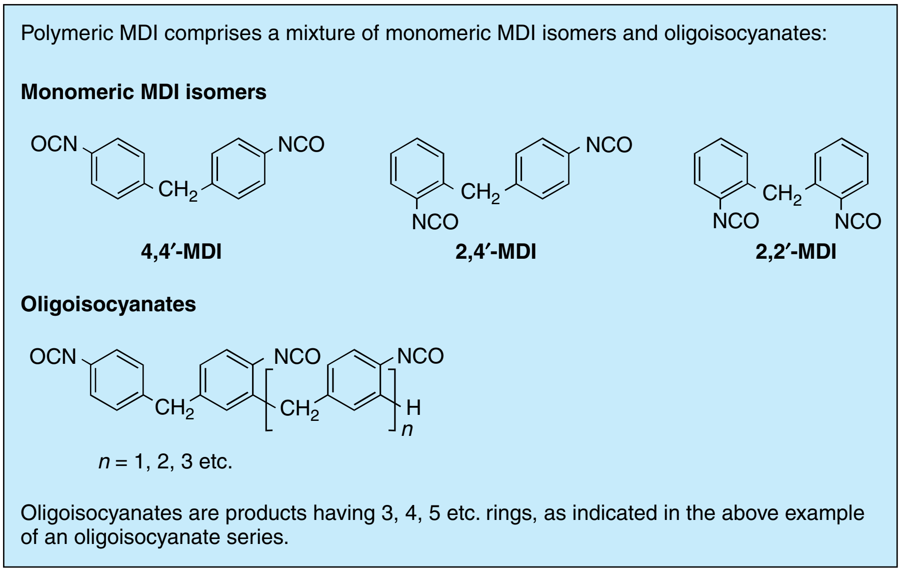

Figure 1.4 **Chemical structures of MDI species**

produced, will depend on the prevailing applications into which they are sold. A very approximate indication of the relative production levels of MDI types is shown in Figure 1.3.

Pure MDI is predominantly 4,4′-MDI monomer with a very small percentage of 2,4′-MDI and 2,2′-MDI isomers. Pure MDI is also known as monomeric MDI or as 4,4′-MDI (see Figure 1.4). Both pure MDI and polymeric MDI may be partially reacted to form modified MDIs, also called MDI derivatives, which include MDI variants and MDI prepolymers. There are solvent grades of some of these materials for applications which demand an even distribution of the diisocyanates. The pre-reacted types of MDI give improved chemical handling properties and allow more precise control of the nature of the polymer produced in the polyurethane reaction. For example, solid pure MDI can be partially reacted to form modified MDIs which are liquid at ambient temperatures. Conversion of pure MDI or polymeric MDI to the respective modified products is carried out by the original manufacturers or by specialist formulators. *Parts 5.1* and *5.2* give details of the manufacture and of the nomenclature of MDI, including structures and Chemical Abstract Registry numbers.

Types of TDI

The mixture of TDI isomers contains at least 99 % monomeric TDI; there is no equivalent of polymeric MDI, which contains a range of higher molecular weight species.

The acronym *TDI* comes from several synonyms for TDI, the commonest of which is *toluene diisocyanate*: other widely used synonyms are toluylene diisocyanate and tolylene diisocyanate. TDI is produced as a single isomer, as mixtures of isomers (Figure 1.5) and as modified TDIs. In Table 1.2 are given the types of TDI used on an industrial scale. TDI is manufactured very predominantly as 80/20 TDI. The pure 2,4-TDI isomer is used in industrial quantities for special applications associated with elastomers. The pure 2,6-TDI isomer is synthesized only for use as a laboratory chemical.

There are two TDI isomers in industrial TDI mixtures:

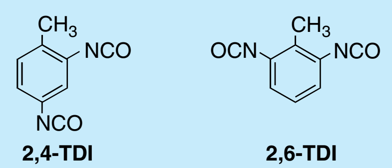

Figure 1.5 **Structures of TDI isomers**

Table 1.2 **Types of TDI used in industry.**

Type of TDI	Description	Form at 25 °C
TDI	Generic term for all unmodified types of TDI.	–
2,4-TDI	An isomer produced in mixed isomers of TDI.	Colourless liquid
80/20 TDI	A mixture of 80 % 2,4-TDI with 20 % 2,6-TDI. Also known as 80:20 TDI.	Colourless liquid
65/35 TDI	A mixture of 65 % 2,4-TDI with 35 % 2,6-TDI. Also known as 65:35 TDI.	Colourless liquid
Modified TDIs Some are **TDI prepolymers**	Isomers of TDI which are partially reacted to give versatility in handling or in final polymer properties.	Colourless liquids

Test substances

Ultimately, it is important to understand how MDI and TDI interact with humans, with other species and with the physical environment. An extensive range of studies has been undertaken, largely by industry. However, there are limitations to the types of real life study which can be undertaken, both for ethical reasons and because of the complexity of the situations. Accordingly, many of the studies have been completed in research laboratories. One example is the study of laboratory biological systems to predict the effect of diisocyanates on humans. Another example is the use of precisely controlled laboratory pond studies to investigate the possible effects of diisocyanates in standing water such as canals and lakes. The choice of test substance for such research studies is important. Both MDI and TDI are hydrophobic and insoluble in water. In some cases solvents such as dimethylsulphoxide or dimethylformamide have been used to introduce MDI and TDI into water. The use of such solvents, which does not represent real-life situations, may give misleading results.

Of the various types of MDI, only polymeric MDI has been used widely as a test substance: pure MDI is unsuitable for many types of study because it is a waxy solid, which cannot be dispersed finely in water. Modified MDIs have not been reported widely as test substances because there are many proprietary variations and they are often reformulated. The individual solid isomers, 2,2′-MDI and 2,4′-MDI, have rarely been used as test substances in biological studies. The individual oligoisocyanates of MDI are very difficult to isolate and have not been used in studies. Even when polymeric MDI is used as a laboratory test substance there are problems in mixing it with water or aqueous biological systems.

Most studies of the effects of TDI have been carried out with the predominant commercial product, 80/20 TDI. However, individual isomers can be isolated readily and studies have also been carried out with 2,6-TDI as well as with the commercial 2,4-TDI and 65/35 TDI. All of these isomers and isomer mixtures are liquids under most test conditions. Where researchers fail to specify precisely what type of TDI has been employed, it is usually assumed that they have used 80/20 TDI.

Diisocyanates and amines

It is important to recognize that MDI or TDI or related species may be converted very easily to the diamines MDA and TDA in some test systems or in analytical work-up procedures, especially when solvents are used. This can give rise to misleading results, since the chemical and biochemical reactions of the diisocyanates and diamines differ considerably. Examples of this have arisen with TDI in the Ames Test (Gahlmann *et al.*, 1993; Seel *et al.*, 1999) and in the analysis of airborne TDI using solvents in impingers (Nutt *et al.*, 1979).

Misapprehensions

Misinformed commentators on the safety, health and environmental scenes commonly make mistakes because of a similarity of sound of chemical terms or similarity of chemical structure. The following are corrections of common errors:

Diisocyanates are *not* cyanides

Although the two chemical names are similar, no cyanide is used to make isocyanates or is present in isocyanate products. In addition, no cyanide is released during the normal use of isocyanate-based polyurethane products. As with any nitrogen-containing organic substance (for example wood and some fabrics), polyurethanes liberate hydrogen cyanide under some burning conditions.

MDI is *not* methyl isocyanate

One particularly important misconception is that MDI is methyl isocyanate (MIC), the substance released in Bhopal, India, in 1984. The chemical structures, as well as the physical and toxicological effects of the two substances differ very considerably. MIC is highly volatile, whereas MDI has very low volatility. The ratio *MIC volatility: MDI volatility* at ambient temperature is approximately 35 000 000:1. MIC can form a blanket of dense, high concentration vapour, affecting a large area, as it did in Bhopal. This cannot arise with MDI because it is of such low volatility that MDI-saturated air has almost exactly the same density as air over a wide temperature range.

Diisocyanates are *not* isothiocyanates

There is occasional confusion between these two types of compound, which are quite different in their chemistry and biochemistry. Health problems associated with crops such as rape seed have been associated with the naturally occurring isothiocyanates, which are characterized by the –NCS group. Diisocyanates, which have reactive –NCO groups, are not naturally occurring.

'Urethane' (ethyl carbamate) is *not* polyurethane

Polyurethane is not a polymer of urethane (urethan), as might be expected from its name. Urethane is a chemical, also known as ethyl carbamate ($NH_2COOC_2H_5$), of molecular weight 89 and is an animal carcinogen. Polyurethanes are polymers of high molecular weight, which are biochemically inert. Urethane and polyurethanes differ very significantly in their chemistry and biochemistry.

Polyurethanes made from MDI and TDI

MDI and TDI are used almost entirely for the production of polyurethane polymers. Accordingly, most references to the *use* of MDI and TDI in this book are related to polyurethane production. In 1998 the global tonnage of polyurethanes was 7.5 million tonnes. It is expected that about 10 million tonnes of polyurethanes per annum will be manufactured by 2002. At that time production levels for Americas, Europe and Asia Pacific will all be about the same (Petersen, 1999).

Polyurethane is sometimes abbreviated to *PU* or *PUR*. A further term, *PIR*, is commonly used for polyisocyanurates which are diisocyanate-based products with high thermal stability. The information given on diisocyanates in this book is, however, equally relevant both to polyurethane and to polyisocyanurate production.

Production and usage of polyurethanes

Production based on region

Figure 1.6 shows regional production of polyurethanes in 1998. Regions of high growth are Asia Pacific, which already has a very high per capita usage of polyurethanes, and Latin America.

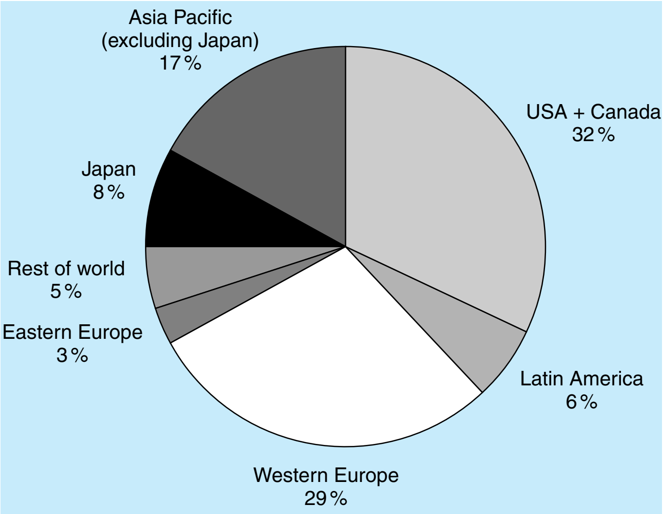

Figure 1.6 **Regional production of polyurethanes**

Production based on application

Figure 1.7 shows percentage consumption of polyurethanes in 1998 according to the type of application. Furniture, mattresses and automotive seating are made predominantly from flexible foams and semi-rigid foams. Shoe applications relate to elastomers; construction and insulation are of rigid foams. Other applications include coatings, adhesives, artificial leather, fibres, and electronic applications.

Production based on types of polyurethane

In Figure 1.8 is given a breakdown of polyurethane usage in 1998 according to types of polyurethane. Furniture applications are predominantly related to TDI-based flexible foams. Insulation and construction are almost entirely related to MDI-based rigid foams, and footwear is largely modified MDI-based

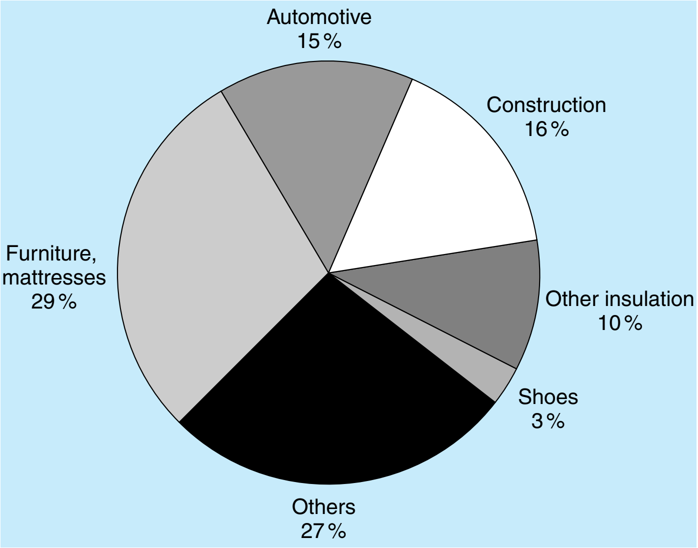

Figure 1.7 **Polyurethane production based on application**

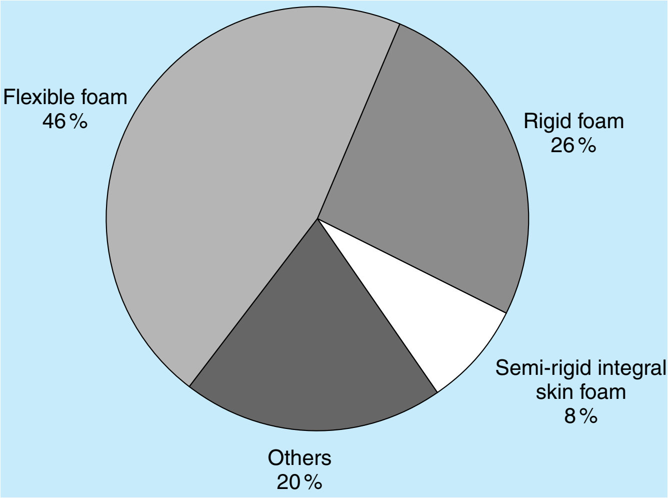

Figure 1.8 **Polyurethane production based on type of polyurethane**

elastomers. The large sector of other applications comprises a very wide diversity including elastomers, thermoplastic polyurethanes, wood products (e.g. particle board) and coatings. The automotive sector includes rigid body parts, seating, interior trim and paints.

The components of polyurethanes

The basic reaction between a diisocyanate and a polyol produces a polyurethane addition polymer with the liberation of heat.

$$\text{diisocyanate} + \text{polyol} \longrightarrow \text{polyurethane polymer} + \text{heat}$$

Details of the chemistry of the reactions are given in *Part 5.3.*

However, a number of ancillary chemicals and processing aids are usually required to allow sufficient control to produce useful commercial products. Catalysts are needed to allow the reaction to progress at a speed compatible with production processes. Surfactants are used to control the interaction between nonhomogeneous components of the reacting system. The properties of the polymer structures may be modified by the use of chain extenders or by cross-linkers. Fire retardants, fillers and pigments may also be added.

Blowing agents can be added to the reacting systems to cause foaming. Blowing agents may be nonreactive or reactive. Nonreactive blowing agents act by evaporating within the foaming mix. Water, a reactive agent, causes blowing by reacting with MDI or TDI to form carbon dioxide gas within the polyurethane reaction mixture. According to the type of blowing agent and the concentration in the reacting mix, it is possible to produce polyurethane polymers of different densities, and of different thicknesses of skin. Water and other blowing agents are used together in formulations to achieve the required balance of density and physical properties. In Table 1.3 is given a list of typical components of polyurethane formulations. The most important reactant with MDI or TDI is the polyol, as indicated above.

Polyurethanes: thermosets and thermoplastics

Thermosets

Polyurethanes are produced predominantly as thermosets. This means that once the reactions have ceased the polyurethane is cured and it cannot be heat-shaped without degradation. This thermal stability results from the degree of cross-linking of polymer chains (the cross-link density) and/or the nature and frequency of repeating units within the polymer chains.

Thermoplastics

A wide range of formulations may be used to produce thermoplastic polyurethanes (TPUs), based on pure MDI or modified MDI. TPUs are normally supplied in the form of pellets as feedstock for the production of polyurethane components. Unlike thermosetting materials, these can be thermoformed, usually by high temperature injection moulding or extrusion. The market for thermoplastic polyurethanes includes high performance footwear such as ski boots, automotive parts such as high performance elastomeric components, and hoses and electrical cabling.

Processing of MDI and TDI to form polyurethanes

The versatility of polyurethanes is such that they are manufactured not only with a wide diversity of properties and forms, but also in a range of production situations from small workshops through to highly automated production lines. It must be emphasized that whatever degree of automation is used chemical reactions are being carried out in a factory with a workforce which has very largely not received an education in chemistry. Therefore a sound education in safety procedures is essential. Some processes for manufacturing polyurethanes are listed below:

Table 1.3 **Typical components of polyurethane formulations.**

Chemical type	Reactivity to diisocyanates	Example
Polyol	Reactive	• Hydroxyl-terminated reaction products of ethylene oxide and propylene oxide, with an initiator such as glycerol
Chain extender	Reactive	• Bifunctional short chain reactive molecules such as butane diol
Cross-linker	Reactive	• Polyfunctional low molecular weight amines or alcohols such as triethanolamine
Blowing agent[a]	Reactive	• Water (producing carbon dioxide from the isocyanate–water reaction)
	Nonreactive	• Carbon dioxide (as gas or liquid)
	Nonreactive	• Pentane
	Nonreactive	• Methylene chloride
Catalyst	Reactive	• Hydroxyl-terminated tertiary aliphatic amines such as triethanolamine
	Nonreactive	• Tertiary aliphatic amines such as dimethyl cyclohexylamine, diazabicyclooctane, *N*-ethyl morpholine
	Nonreactive	• Stannous octoate
	Nonreactive	• Dibutyl tin dilaurate
Surfactant	Nonreactive	• Silicone liquids
Fire retardant	Nonreactive	• Tris(beta-chloropropyl) phosphate (TCPP)
	Reactive	• Propoxy brominated bisphenol A
Filler	Usually nonreactive	• Glass fibre
	Nonreactive	• Calcium carbonate
	Reactive, but insoluble	• Melamine

[a]Formerly, CFCs were used very widely, but have now been replaced by other materials: see *Part 2, Releases to atmosphere from polyurethane manufacturing sites.*

- continuous foaming of slabstock for making blocks of rigid or flexible foam;
- reaction moulding of items such as car seating cushions or vehicle panels;
- spraying of insulation or paints;
- continuous production of polyurethane insulation board with metal or paper facings.

There are different ways in which the chemicals used to make polyurethanes are supplied and brought together during processing. MDI and TDI are almost invariably supplied without the incorporation of other polyurethane chemicals.

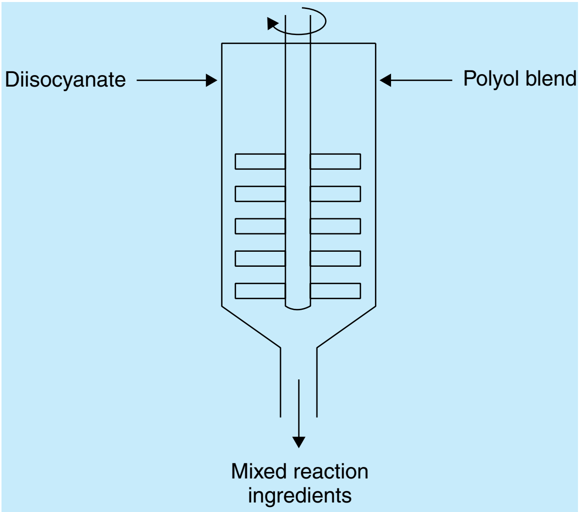

Figure 1.9 **Two-stream processing**

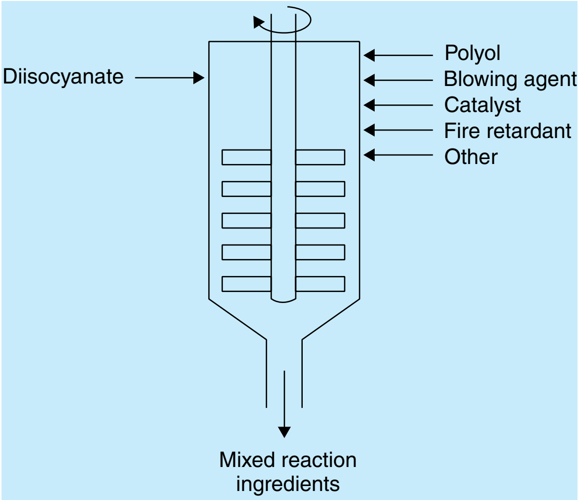

Figure 1.10 **Multi-stream processing**

This is because they react with many products, including water which is often found in polyurethane formulations. A polyurethane system may be supplied as two components, which are the diisocyanate and a complete blend of all the other materials. This allows processing with two-stream metering to the mixing head (see Figure 1.9). This approach is very simple, but inflexible as regards formulation and hence final product properties. It is appropriate for long production runs of the same polyurethane product.

The ultimate in flexibility is the individual supply and metering of each polyurethane component, using a multi-stream mixing head (see Figure 1.10). With this approach, variations in formulation can be used to produce polyurethanes of different specifications without interrupting continuous processes.

The formulation can even be changed during the dispensing of a shot of reacting mix into a mould. For example, composite cushioning with two hardness sectors can be produced in one shot.

Non polyurethane applications of MDI and TDI

MDI and TDI may be used in processes without polyols, chain extenders or cross-linkers: however, the products are not polyurethanes. For example, MDI alone is used as a binder in particle board. In this process MDI and wood chips (or other substrate) are mixed and fed into a continuous hot press. The resulting board is bound as a result of the MDI reacting with the wood and with the water in the wood. Other examples of the use of MDI are as a binder in the production of sand-based foundry moulds and for the production of very low density polyurea foams for packaging. The precautions needed to handle MDI and TDI still apply to these non polyurethane processes.

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