

THE ICI POLYURETHANES BOOK

SECOND EDITION

GEORGE WOODS



Polyurethanes



THE ICI POLYURETHANES BOOK

SECOND EDITION

GEORGE WOODS



Published jointly by



Polyurethanes

and



JOHN WILEY & SONS

Chichester - New York - Brisbane - Toronto - Singapore

Copyright © 1990 by ICI Polyurethanes

All rights reserved.

Reproduction, transmission, or storage of any part of this publication by any means is prohibited without the prior written consent of the Managing Editor, Robert Genge.

Library of Congress Cataloguing-in-Publication Data:

Woods, George

The ICI Polyurethanes book / George Woods. – 2nd ed.
p. cm.

Includes bibliographical references and index.

ISBN 0-471-92658-2 (cloth)

1. Polyurethanes. I. ICI Polyurethanes (Firm) II. Title.

TP1180.P8W66 1990

668.4'239–dc20

90-43732

CIP

British Library Cataloguing-in-Publication Data

Woods, George

The ICI Polyurethanes Book. – 2nd ed.

1. Bioengineering. Use of materials. Polyurethane

I. Title

668.4239

ISBN 0 471 92658 2

Introduction

Polyurethanes make a varied and increasing contribution to our daily lives – from foam insulation to shoe soles, car seats to abrasion-resistant coatings. I hope that this book will reflect the versatility of these materials, and convey to the reader an understanding of their production, properties and the considerable potential they still have to fulfil.

In preparing this book we have held a number of different readers in mind. Foremost are those who wish to obtain a better understanding of polyurethanes – without necessarily having to study the subtleties of the chemistry and physics involved. Designers may learn of the opportunities offered by polyurethanes for the manufacture of complex composites, students and teachers should find this a helpful introduction to an important family of materials, and users of polyurethanes will have an easily accessible source of important information on processing, safety and the properties of polyurethanes. We believe a significant section of the readership of the book will be found in the Third World, where polyurethanes are set to make a genuine contribution to development and the enhancement of the quality of life.

In the two years following the publication of the first edition of this book, in 1987, it became clear that the entire print run would sell by 1990. Therefore a second edition was put in hand. This was timely as in this period much progress and many changes have taken place. The most obvious are the change in use of CFCs, and the advent of polyurea elastomers.

A new chapter has been written – within ICI Polyurethanes – cross referenced to the original text, and bringing these important aspects fully up to date. It is printed at the end of the book.

The *ICI Polyurethanes Book* should prove of great value to all who are engaged in product design, development and manufacture. By promoting a better understanding and broader knowledge of polyurethanes, I hope it will make a genuinely worthwhile contribution to the exciting future of polyurethanes in the decade to come.

David Sparrow
Research Manager ICI Polyurethanes
Everberg, Belgium
July 1990

Acknowledgements

In the production of a book such as this, a great deal of behind-the-scenes work goes on and a number of people have been involved. Thanks are due in particular to Paul Chapon of ICI France who sowed the seed for the enterprise, and Roger Natan and Judith Dobbs in Belgium for suggestions and advice in the early stages. We would like to thank Dr. Dennis Allport who, as technical editor, brought his wide experience of polyurethanes to assist George Woods in the major task of planning and writing this book. Dr. Allport also guided the late John Barrett who, as editorial consultant, assisted in the presentation of George's work. We are indebted to Jim Pattison and the staff of Dunholm Publicity in England for nurturing the manuscript over many months.

Many members of the ICI Polyurethanes staff have helped with contributions and particularly with thorough checking of the drafts. Dr. David Sparrow, Dr. Arun Watts, Mr. Bill Green and Dr. Mike Jeffs and their teams assisted greatly particularly David Thorpe and Graham Carroll. Much of the data on physical testing has been revised and completely updated by John Partington and Benoit Fraeys de Veubeke. Final editorial guidance has been provided by Clare Hunt and Graham Look of Communication Systems in Brussels.

The design and layout of the book, typesetting and print production supervision has been carried out by Aad Schram in Holland.

Second edition

In this second edition George Woods and the technical editor David Sparrow have completely reviewed the book and prepared a detailed update which is printed as Chapter 13. We are extremely grateful to them for the considerable effort they have made.

Again we are indebted to Jim Pattison at Dunholm Publicity for progressing the whole project and shepherding it through its many stages, also to Graham Look of Communication Systems for editorial assistance.

Robert Genge
Managing Editor

1 **An introduction to polyurethanes**

Polyurethanes are all around us, playing a vital role in many industries – from shipbuilding to footwear; construction to cars. They appear in an astonishing variety of forms, a variety that is continuously increasing.

Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from buildings to the modest domestic refrigerator. Comfortable and durable mattresses and car and domestic seating are manufactured from flexible foam. Items such as shoe soles, sports equipment, car bumpers and ‘soft front ends’ are produced from different forms of polyurethane elastomers. And many of us rely on polyurethanes – elastic threads of the material are found in underwear and other clothing.

All polyurethanes are based on the exothermic reaction of polyisocyanates with polyol molecules, containing hydroxyl groups. Relatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Additionally several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate-based plastic materials. The chemically efficient polymer reaction may be catalysed, allowing extremely fast cycle times and quantity production. No unwanted by-products are given off and, because the raw materials react completely, no ‘after cure’ treatment is necessary.

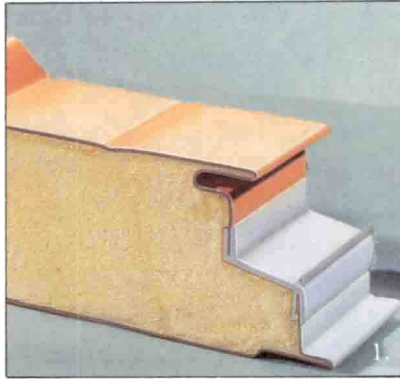
Cost and processing advantages

Although the unique advantage of using polyurethanes lies in the wide variety of high performance plastics that can be produced, polyurethanes may often compete with low cost polymers. This is because raw material costs are not the only considerations in the total costs of producing an article.

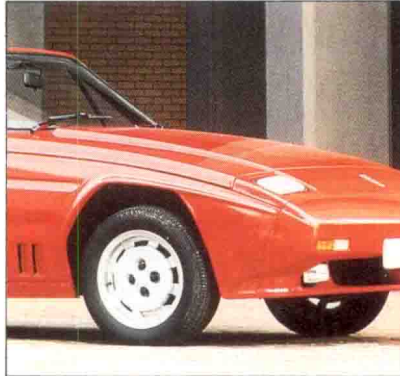
Factors of at least equal importance are cycle times, the cost of tooling and finishing as well as reject rates and opportunities for recycling. As polyurethane reaction moulding requires only low pressures, moulds can be made of less expensive materials. This allows the simple production of inexpensive prototypes for the development of new products or the refinement of established ones.

Figures 1-1 to 1-8
Polyurethanes are used for a variety
of applications

1. Metal faced building panels
2. Shoe and boot soles



3. Car exterior panels
4. Car seating



5. Housings for electronic equipment
6. Buoyancy in boats



7. Refrigerator insulation
8. Structural foam furniture

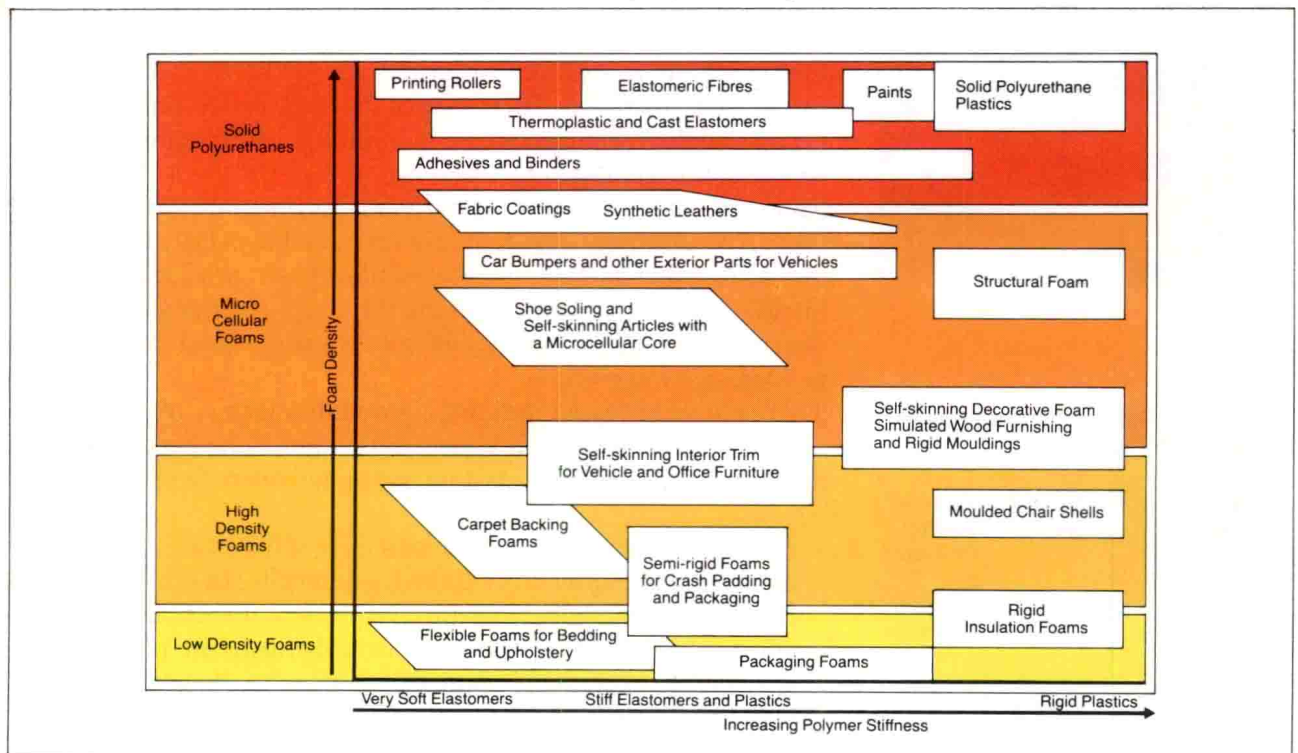


Polyurethanes also differ from most other plastic materials because they allow the processor to control the nature and the properties of the final product. This is possible because most polyurethanes are made using reactive processing machines. These mix together the polyurethane chemicals which then react to make the polymer required. The polymer is usually formed into the final article during this polymerisation reaction. This accounts for much of the versatility of polyurethanes: they can be tailored with remarkable accuracy to meet the needs of a particular application.

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 1220 kg/m^3 and polymer stiffnesses 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.

Figure 1-9 Property matrix of polyurethanes



Polyurethane reaction mixtures have another important property – they are powerful adhesives. This enables simple manufacture of strong composites such as building panels and laminates, complete housings for refrigerators and freezers, crash padding for vehicles and reinforced structures in boats and aircraft.

Types 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.

Figure 1-10 Photomicrograph showing the open cells of a flexible foam

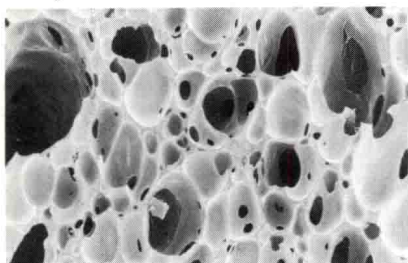


Figure 1-11 Photomicrograph showing the closed cells of a rigid foam

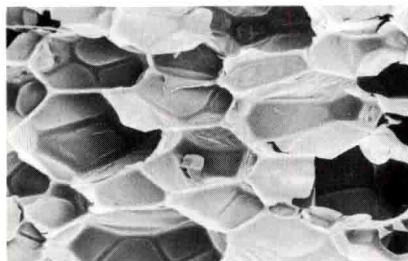


Table 1-1 Relative importance of three foams types.

Foam type	Density kg/m ³	Approx. usage (millions of tonnes/year)
Low density flexible	10–80	2
Low density rigid	30–80	0.9
Self-skinning foams Microcellular elastomers	400–800	0.6

Foams

By itself the polymerisation reaction produces a solid polyurethane. Foams are made by forming gas bubbles in the polymerising mixture. This is called ‘blowing’.

Foam manufacture can be carried out continuously, to produce continuous laminates or slabstock, or discontinuously, to produce moulded items or free-rise blocks.

Flexible foams can be produced easily in a variety of shapes by cutting or moulding. They are used in most upholstered furniture and mattresses. Flexible foam moulding processes are used to make comfortable, durable, seating cushions for many types of seats and chairs. The economy and cleanliness of flexible polyurethane foams are important in all upholstery and bedding applications. Strong, low density rigid foams can be made and, when ‘blown’ using fluorocarbons, closed-cell structures are produced that have low thermal conductivity. Their superb thermal insulation properties have led to their widespread use in buildings, refrigerated transport vehicles, refrigerators and freezers.

Rigid and flexible foam articles having an integral-skin that is both decorative and wear-resistant, are produced by a fast, simple, moulding process. Fine surface detail can be reproduced by the integral skin of the foam, allowing the simple manufacture of instrument housings, articles with a simulated wood finish and padded steering wheels.

There are three foam types that, in quantity terms, are particularly significant: low density flexible foams, rigid foams, self-skinning foams and microcellular elastomers (high density flexible foams).

- *Low density flexible foams* are materials of densities 10-80 kg/m³, composed of lightly cross-linked, open-cells. In other words, air may flow through the structure very easily. Essentially flexible and resilient padding materials, flexible foams are produced as slabstock or individually moulded cushions and pads. 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 the 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. A chlorofluoromethane gas is usually contained within the cells, and

as these substances have a much lower thermal conductivity than air, such closed-cell foams have a significantly lower thermal conductivity than any open-celled foam. However, if this low thermal conductivity is to be retained, the chlorofluoromethane gas must not leak away. Consequently, rigid polyurethane foam insulation must have at least 90 percent of closed cells and a density above about 30 kg/m^3 .

- *High density flexible foams* are defined as those having densities above 100 kg/m^3 . The range includes moulded self-skinning foams and microcellular elastomers. Self-skinning foam systems are used to make moulded parts having a cellular core and a relatively dense, decorative skin. There are two types, those with an open-cell core and an overall density in the range up to about 450 kg/m^3 and those with a largely closed cell or microcellular core and an overall density above about 500 kg/m^3 . Microcellular elastomers have a substantially uniform density in the range from about $400\text{--}800 \text{ kg/m}^3$ and mostly closed cells which are so small that they are difficult to see with the naked eye. The biggest applications of self-skinning foams and microcellular elastomers are in moulded parts for upholstery and vehicle trim and for shoe-soleing. Microporous elastomers are microcellular foam foils or sheets having a proportion of open, communicating cells. Chapters five and six describe self-skinning and microcellular foams, the former concentrating on high density flexible foams while the latter describes the RIM (Reaction Injection Moulding) process – a commonly used and growing method of moulding microcellular elastomers and self-skinning foams. RIM is used for other types of polyurethanes such as structural foam and substantially solid elastomers.

Solid polyurethanes

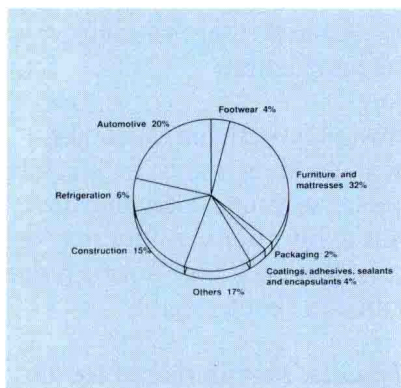
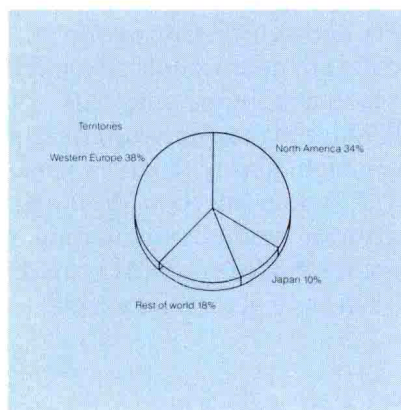
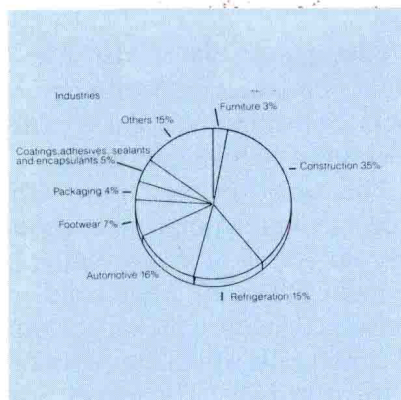
Although foamed polyurethanes form some 90% by weight of the total market for polyurethanes, there is a wide range of solid polyurethanes used in many, diverse applications.

Solid polyurethane 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 or hard, of high or low resilience, solid or cellular. A wide range of polyurethane elastomers is described in chapter eight.

Adhesives, binders, coatings and paints. Polyurethanes are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Polyurethane paints and coatings give the highest wear resistance to surfaces such as floors and the outer skins of aircraft. They are also becoming widely used for high quality finishes on automobiles.

Applications of polyurethanes

Figure 1-12 World polyurethane markets.



Top: World MDI polyurethane market by industry.

Centre: World polyurethane market by territory.

Bottom: Total world polyurethane market by industry.

A detailed breakdown of the polyurethanes industry by application is shown in figure 1-12. The versatility of polyurethanes is demonstrated by a summary of their applications in five important areas.

Automotive

In recent years, polyurethanes have found increasing use in this area, to the benefit of both the manufacturer and customer. Applications include seating, interior padding, exterior body panels, complete soft front ends, components mounted in the engine space and accessories such as mirror surrounds and spoilers. This is a particularly exacting market as materials are carefully selected to meet tough specifications.

Furniture

The market for cushioning materials is dominated by polyurethane flexible foams. And where strong – tough but decorative – integral-skinned flexible or rigid foam structures are needed, polyurethanes are also ideal. Polyurethanes compete with rubber latex foam, cotton, horsehair, polyester fibre, metal springs, wood, expanded polystyrene, polypropylene and PVC.

Construction

When sandwiched between metal, paper, plastics or wood, polyurethane rigid foam plays an important role in the construction industry. Such composites can replace conventional structures of brick, cement, wood or metal, particularly when these latter materials are used in combination with other insulating materials such as polystyrene foam, glass fibre or mineral wool.

Thermal insulation

Rigid polyurethane foams offer unrivalled technical advantages in the thermal insulation of buildings, refrigerators and other domestic appliances, and refrigerated transport. Competitive materials include cork, wood, glass fibre, mineral wool, foamed (expanded) polystyrene, urea formaldehyde and phenol formaldehyde.

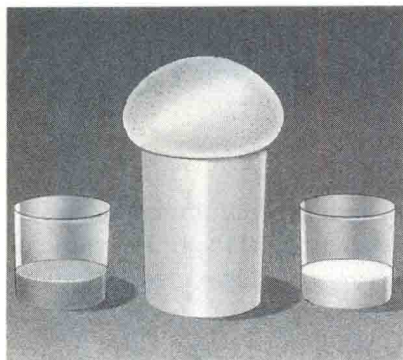
Footwear

Soles and some synthetic uppers for many types of footwear are produced from polyurethanes. These compete with traditional leather and rubber, polyvinyl chloride and poly(ethylene-vinyl acetate). Polyurethane adhesives are widely used in shoe and slipper manufacture. Polyurethane coatings are used to improve the appearance and wear resistance of shoe uppers made from both real leather and from PVC leathercloth.

2 Making Polyurethanes

In this chapter the basic principles and methods of manufacture of the wide variety of polyurethane materials are described. Those readers requiring a detailed discussion of polyurethane chemistry should also read Chapter 3. Other readers can pass directly from this chapter to Chapter 4.

Figure 2-1 A polyurethane is formed when two liquid chemicals, an isocyanate and a polyol, react on being mixed together in the presence of suitable catalysts and additives.



There is a fundamental difference between the manufacture of polyurethanes and many other plastics materials. The majority of thermoplastics, unlike most polyurethanes, are polymerised in large chemical factories and then sold to the user as polymer granules or powders. These are then converted to useful articles by one of the thermoplastic processing techniques which involve heating, shaping the melted polymer under pressure, and cooling. The properties of articles made in this way are almost entirely dependent upon the properties of the thermoplastic polymer purchased from the manufacturer. The polymerisation of most polyurethanes, however, is carried out by the converter and not by the chemical manufacturer. The latter sells polyurethane chemical components, usually in the form of liquids, and provides advice and information to enable the customer to make the polyurethane he requires by mixing the chemical components in specified proportions.

Specially blended polyurethane chemical components are also sold by chemical manufacturers to make polyurethanes for particular applications. The purchase of such pre-blended chemical components or 'systems' enables the customer to make polyurethanes by a simple mixing process, but nevertheless it is the customer who makes the polyurethane polymer in addition to shaping it into a useful article. The exceptions are some polyurethane elastomers which are made by the chemical manufacturers. These include elastomeric polyurethane fibres (spandex fibres), which are sold directly to textile manufacturers, and thermoplastic polyurethane elastomers, which are supplied in granular or sheet form for conversion into articles by injection moulding, extrusion, blow-moulding, calendering, lamination or some other established thermoplastic conversion process.

Table 2-1 Some highlights in the development of polyurethanes

1937-40	Otto Bayer and co-workers made polymers by polyaddition processes from various diisocyanates with glycols and/or diamines.	1960	ICI introduces the first polymeric MDI-based semi-rigid energy absorbing foam for vehicles.
1940-5	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).	1960-5	Rigid foam blowing by chlorofluoromethanes.
1945-7	Manufacture of millable polyurethane elastomers, coatings and adhesives.	1962	First production line moulded 'deep seat' flexible polyurethane car cushions at Austin-Morris (U.K.).
1950	Cast elastomers from polyester diols, diisocyanate prepolymers and chain extenders.	1963	ICI demonstrates production line manufacture of refrigerators using MDI-based polyurethane foam.
1953	First flexible polyurethane foam manufacture with a Bayer system using a high pressure machine, a polyester polyol and TDI.	1963	First cold-store built entirely from metal-faced polyurethane rigid foam laminate made continuously (Australia).
1956	First manufacture of polyether-based flexible polyurethane foam in the U.S.A. using a two stage or 'pre-polymer' process.	1964	ICI inverse- and floating-platen systems for the continuous manufacture of rigid polyurethane foam-cored building boards in production.
1957	ICI introduces the first commercially available polymeric MDI composition for rigid polyurethane foam manufacture.	1965	First commercial production of self-skinning flexible foam (Soc. Quillery, France).
1959	ICI introduces the first rigid foam system based on polymeric MDI and a polyether polyol.	1968	ICI introduces isocyanurate rigid foams.
1959	'One-shot' system for flexible polyether-based foam introduced in the U.S.A.	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.

The chemicals

A urethane group is formed by the chemical reaction between an alcohol and an isocyanate. 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.

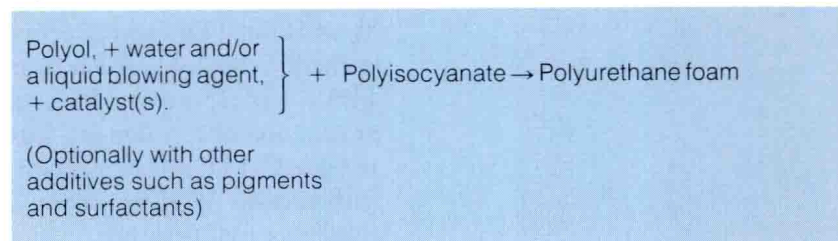
The urethane-producing reaction was well known in the nineteenth century, but only as a laboratory curiosity. It was not until the late 1930s that the commercial potential of polyurethanes as fibres, adhesives, coatings and foams began to be recognised by Otto Bayer, his co-workers, and others. In fact, most polyurethanes' applications have been developed during the past 30 years. Table 2-1 illustrates that progress.

Most polyols and polyisocyanates used in the manufacture of polyurethanes are liquid at ambient temperatures (ca. 18°C) and are easily handled. The reactions which produce a solid polymer are rapid and substantially complete within two minutes. The solid product can generally be handled within five minutes from the start of mixing, although rates can be varied enormously by the choice of

catalyst and its concentration. The reactions are exothermic – the heat generated may be used to vaporise a liquid ‘blowing agent’ such as a fluorocarbon, when the reacting chemicals will polymerise and expand to produce a polyurethane foam. Alternatively, some water may be incorporated in the polyol so that it reacts with the polyisocyanate to release carbon dioxide gas.

The reactions which produce polyurethane foam may be summarised as figure 2-2 below.

Figure 2-2 The polyurethane foam reaction



Polyols

Some 90 percent of the polyols used in making polyurethanes are polyethers with terminal hydroxyl groups. Hydroxyl-terminated polyesters are also used to obtain polyurethanes with special properties. Polyesters are usually more expensive than polyethers, but competitively priced polyesters (made from recovered diacids), have been developed, particularly for use in making rigid foams. The polyols that are used to make polyurethanes have been developed to have the required reactivity with commercially available isocyanates and to produce polyurethanes with specific properties. The choice of polyol, especially the size and flexibility of its molecular structure and its functionality (the number of isocyanate-reactive hydroxyl groups per molecule of polyol) controls, to a large extent, the degree of cross-linking achieved in the polymer that is formed in the reaction with the polyisocyanate. That degree of cross-linking has a dominant effect on the stiffness of the polymer: to obtain a rigid foam there must be a stiff polymer network and, hence, a high degree of cross-linking; for flexible foam a proportionally lesser degree of cross-linking is needed.

The characteristics of the polyols to make the two principal classes of polyurethanes are:

Table 2-2 Characteristics of polyols

Characteristic	Flexible foams and elastomers	Rigid foams, rigid solids, and stiff coatings
Molecular weight range	1,000 to 6,500	400 to 1,200
Functionality range	2.0 to 3.0	3.0 to 8.0

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.

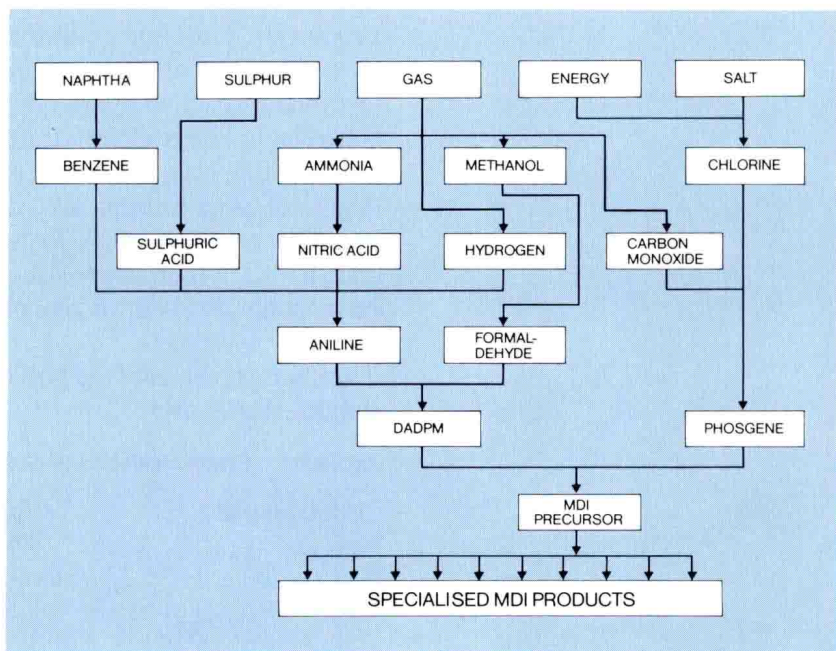
Several aromatic and aliphatic isocyanates are available, but about 95 percent of all polyurethanes are based on two of them. These are toluene diisocyanate (TDI), and diisocyanato-diphenylmethane (MDI) and its derivatives. Both materials are derived from readily-available petrochemical intermediates and are manufactured by well understood and closely defined chemical processes.

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 (known as 80:20 TDI). A 65:35 mix is also available. TDI is used mainly in the production of low density foams for cushioning, generally 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.

Development of MDI was necessary as the volatility of TDI caused severe problems when TDI-based rigid foams were sprayed in enclosed spaces, such as the holds of ships. The production chemistry of MDI is considerable more complex than that of TDI. However, this complexity confers a significant degree of freedom on the chemical manufacturer to modify and optimise grades of MDI to meet specific user needs.

MDI is produced from aniline and formaldehyde, reacted together using hydrochloric acid as a catalyst. This condensation

Figure 2-3 Manufacturing route to MDI



reaction produces a complex mixture of polyamines which are phosgenated to obtain a polyisocyanate mixture. The product, known as polymeric MDI, is principally used for manufacture of rigid foams.

Such polyisocyanate mixtures can be processed further to give a variety of compositions, known as MDI variants, which have a wide range of applications.

Pure MDI is a solid of melting point 38°C which is produced by separation from a polymeric MDI precursor. It can be used in its basic form or modified chemically to give a composition that is liquid at ambient temperatures.

To make polyurethanes as cost-effective as possible, producers of isocyanates have developed processes for tailoring the MDI composition to the requirements of the end-product. The polyisocyanate mixtures are formulated to offer a range of differing functionalities. Functionality is defined as the average number of chemically-reactive groups on each individual molecule present.

Table 2-3 Range of MDI variants

Average functionality	Product description	Polyurethane type	Main applications
2.0	Pure MDI	High performance elastomers	Shoe-soleing. Spandex fibres. Flexible coatings. Thermoplastics.
2.01 - 2.1	Modified, liquid pure MDI	High performance elastomers. Microcellular elastomers.	Shoe-soleing. 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 foundry sand binders.
2.8 - 3.1	High functionality polymeric MDI.	Rigid polyurethane and isocyanurate foams.	Continuous lamination of rigid foam and rigid foam slabstock.

Table 2-3 shows that the functionalities of the products available range from 2.0 to about 3.0.

Diisocyanate products are required for making elastomers, whilst high functionality MDI – rich in polyisocyanates – is desirable for the manufacture of rigid foams and binding materials. Within the latter group, wide variation in molecular weight distribution and

functionality is possible, giving considerable control over reactivity, viscosity, and application properties.

Between these two extremes of functionality lie several MDI variants specially selected to meet the needs of a variety of polyurethane products – structural foam, integral-skin foam and semi-rigid foam. It is this tailoring of the isocyanate component that enables the polyurethanes producer to choose optimum properties of handling, processing and polymer characteristics for a particular application. In addition to TDI and MDI, speciality isocyanates are produced, but in much smaller quantities. Other aromatic diisocyanates 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.

Polyurethanes based on aromatic diisocyanates tend to yellow gradually on exposure to daylight, a process that can be slowed down – but not prevented completely – by the use of additives.

Aliphatic diisocyanates, which are much less reactive than the aromatic diisocyanates, are therefore used for applications requiring high resistance to yellowing. Those most widely available are 1-isocyanato-3-isocyanatomethyl-3,5,5,-trimethylcyclohexane (isophorone diisocyanate or IPDI), 1,6-diisocyanato-hexane (hexamethylene diisocyanate or HDI) and 4,4-diisocyanato-dicyclohexylmethane (hydrogenated MDI or HMDI). The isomeric diisocyanates, 1,4- and 1,3-di(isocyanato-dimethyl-methyl)-benzene (*m*- and *p*-tetramethyl xylene diisocyanate or *m*- and *p*-TMXDI), which behave like aliphatic diisocyanates, are also available.

Figure 2-4 Annual sale of MDI and TDI

