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The present package was prepared to respond to the growing interest on polyurethanes production shown by INTIB users in developing countries.

Relevant and technical information on the subject published within the last ten years is enclosed. However, taking into consideration the broad scope of Polyurethane materials such as fibres, foams, coatings, elastomers, etc., on which there is an enormous amount of published information throughout the world. This package is devoted to recover information specifically on polyurethanes foams more specifically, polyurethane foams.

As no annotated bibliography was found that covered this period, a retrospective information search was carried out. 120 abstracts were selected from more than 500 relevant journal articles, patent documents, reports, etc. Bibliographies (1.2, 34-36) covering the 1977-1981 period, already exist.

An information package is intended as a time-saving tool for people involved in chemical industries since it supplies them with primary information selected from a wide variety of existing sources, which usually is not readily accessible to developing countries.
CONTENTS

1. RETROSPECTIVE INFORMATION SEARCH 1980-1991
   1.1 abstracts Index
   1.2 abstracts
   1.3 references

2. AVAILABLE BOOKS AND JOURNALS FOR POLYURETHANES
   PRODUCTS AND RELATED SUBJECTS

3. SOME WORLDWIDE POLYURETHANES PRODUCERS

4. SOME EQUIPMENT SUPPLIERS AND CONSULTANCY SERVICES

5. SOME R & D INSTITUTES

6. INTERNATIONAL PROJECT REVIEW

7. BIBLIOGRAPHY

8. RELEVANT TECHNICAL AND PAPERS ENCLOSED
   8.1 MDI flexibility leads ICI's Polyurethane thrust
   8.2 Polyurethanes: The Learning Curve
   8.3 Recent Developments in Polyurethanes-IV. Flexible Foams
   8.4 Recent Developments in Polyurethanes-IV. Rigid Foams
   8.5 Recent Developments in Polyurethane-IV. The Applications of Isocyanates to Polymer Technology
   8.6 Rational and Flexible PUR Processing
   8.7 Optimising a PU Formulation by the Taguchi Method
   8.8 PU Processing-Modular Design Plant
   8.9 Standards for Polyurethanes
INTRODUCTION

According to the existing literature, the polymers known as polyurethanes (PUs) are nowadays, considered the most versatile of the plastic materials. Their applications spanning the whole range of polymer products as PU elastomers, PC fibres, flexible, semi-rigid and rigid PU foams, solid plastics, coatings and adhesives. In general, they compete in various applications with metals, plastics and rubbers. Urethane polymers serve basic human needs in many diverse applications ranging from plastics in automobiles to artificial hearts.

World consumption PUs in 1990 was approximately 4.5 million tons and it is expected to reach 5 million tons by 1995. According to (4.1.11), eight manufacturers share seventy percent of the world PUs manufacturing capacity. Major manufacturers of PUs raw materials include ICI, Bayer, Dow Chemical, Basf, Olin and Arco. About 80% of all PU chemicals are used in flexible and rigid foams.

World PUs is concentrated in North America (34%), Japan (10%), Western Europe (38%), and rest of the world (18%).

Even though the chemical reaction which produces an urethane was first discovered by Wurtz (1860), the patent issued to Bayer AG, in 1937 is considered the starting point for the development of this polymer. However, the commercial exploitation of polyurethanes, as with so many other polymers did not progress until the 1950, with the ending of the world war II.

PUs contain carbamate groups (—NHCOO—), also referred to as urethane groups in their backbone structure. Frequently other functional groups as ester, ether, amide or urea groups are present. This is often the case in PUs of commercial interest. PUs are produced by exothermic(heat-producing) reaction of polyisocyanates with polyols, essentially, liquid components which react together to form a solid. Polymerization of this type (where no small molecule is eliminated) is usually called polyaddition or rearrangement polymerization.

The true foundation of the PU industry is the isocyanate. This organic functional group is capable of an enormously diverse range of chemical reactions. The rate of the reaction depends on the structure of the components and can be very rapid. This can be an advantage, but it is also presents control problems for the chemist and the equipment manufacturer (8.1.5).

The polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic or polycyclic in structure and can be used directly as produced or modified. Aliphatic isocyanates tend to form more flexible PUs. Diisocyanates are used in preparing the more flexible, resilient types of urethane foams and elastomers. Polyfunctional isocyanates provide higher cross-link densities in rigid urethane foams and solid polymers. Aliphatic and alycyclic isocyanates are most often used in coatings. The main isocyanates used in PUs manufacture are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). The latter is now the most widely used form. Other diisocyanates are used for spandex fibres, surface coatings, and special elastomers.

Polyols used with polyisocyanates can be classified as polyether polyols, polyester polyols and natural products. Initially, polyester polyols were the preferred raw material for PUs. At present polyester polyols are used in the greatest volume because of low cost and a wide choice of types. Most commercial polyester polyols are based on the less expensive propilen or ethylene oxides or are a combination of the two.

The chemical suppliers have made available a wide range of isocyanates, polyols and additives.
Prs are normally sold as reactive chemicals to the final processors who convert them by a multitude of reactive processing techniques into the end products. The processor may need to be educated or trained to maximise the potential of the process.

The foam outlets of PUs have certainly a major success story from its whole range of polymer products. Depending on its mechanical behaviour, a PU foam or urethane foam as they are often called, is described as being a flexible, a rigid or a semi-rigid PU foam.

Foam formulation contain the two major chemical components, polyol and isocyanate with suitable catalysts, surfactants for stabilization of foam structure and blowing agents which produces gas for expansion. The foam are made using both polyester and polyether polyols, although usually the latter is used, especially for rigid foams.

Catalysts as amines, tin soaps, organic tin compounds are used in PUs manufacture.

In the production of flexible PU foams the reaction between isocyanate and polyol is exothermic and this heat can be used to evaporate a volatile liquid mixed into the reactants, thus forming a foam. The gas for expansion is primarily carbon dioxide. For rigid PU foam the blowing agent is a halocarbon, such as chlorofluoromethane, trifluoromethane, or other similar volatile material. Flexible foams are based on polyoxypropylene diols of 2000 molecular weight and triols up to 4000. Rigid foams are based on polyether made from sorbitol, methyl glucoside or sucrose.

Foam machines appear to be complex but actually are based on a few simple principles. There are some common elements needed for effective production: Feed tanks, metering units, mixers, temperature control systems, process control systems and other requirements like conveying systems, double belt lamination lines, molds and mold carriers.

Molding is one of the most fundamental operations in the PU industry. Virtually, any isocyanate-derived polymeric solid or foam can be molded in some way.

Most urethane foams are produced by one-shot processes, in which all raw materials are combined in a single step. In some specialized applications there are advantages in prereacting the isocyanate and part of the polyol to form a prepolymer, which is then combined with the remaining reactants.

The main applications sectors for PUs are flexible foams in furniture and mattresses. In the transportation industry(seat cushions, back cushions, bucket-seat padding). It is also used in carpeting(Virgin and bonded industry). 51 of flexible foam production is used in specialty applications.

PU foams (rigid) is known as an optimal heat insulation material in building and refrigeration applications. Other uses include tank and pipe insulation. Flotation and packaging are specialty applications for rigid foams.

In practical applications the flammability of PUs must be taken into consideration. The fire behaviour of these materials can be modified by flame retardants.

The industrial application in the form of elastomers (PU rubber, urethane rubber) has been relatively small compared with foams.

The term covers a very wide range of PUs, classified according to the method of manufacture. The elastomers can be thermoplastic or thermo-setting. The main types are cast PU elastomers, millable PU and thermoplastic PU.
while methods of processing are different, all of the elastomers exhibit some or all combination of desirable physical properties which add up to make urethanes completely unique (8.1.5):

- high abrasion resistance
- high tear strength
- excellent resistance to oils, solvents, ozone and radiation
- excellent low temperature flexibility
- good electrical properties
- high tensile strength over a wide range of hardness
- high resistance to impact

PU elastomers have found applications in practically all industries. Castable urethanes have extraordinary physical properties. They are actually engineering materials and are chosen for use on the basis of these properties. Thermoplastic PUs can be processed by most of the common fabrication methods including injection moulding, calendering, extrusion, etc.

RIH process has become almost synonymous with PU. The term has been applied to the chemical systems, but only the PU system is of commercial significance. RIH process is used to produce high-quality PU-reaction injection molding of the sort used in automotive exterior applications. These products are cost competitive with other rubbers and plastics and which also possess superior properties.

It is expected the large-series automobile models of the late 1980s and early 1990s will have an increasing numbers of external body work panels produced by RIH or reinforced RIH (KRHN).

Other applications for thermoplastic PUs are: wire and cable jacketing, calendered film and adhesives, shoe soles, agricultural and medical applications.

Fillable gums can be processed on rubber-processing machinery, and are cured by rubber-curing agents. The overall usage of these is relatively small compared with total PU elastomers applications.

PU surface coatings are successfully used because of their abrasion resistance, skin flexibility, fast curing, good adhesion and chemical resistance. Applications include varnishes and paints usually used on furniture, wire coatings, tank lines, etc.

As with most materials, PUs have their limitations such as low resistance to steam, fuel ketones, esters, strong acids and basis and they are not high temperature materials (maximum service temperature up to 250 F).

In general, fully cured PUs can be considered as safe for human use. However, exposure to dust generated in finishing operations should be avoided. Since PUs are combustible they have to be applied in a safe and responsible manner. At no time should exposed foam be used in building construction.

Experts (8.1.5) agree that PUs with their enormous and varied properties, will be with no doubt, materials of great potential. They are not only products of modern chemistry but they also contribute greatly to social needs: economy of energy, conservation of heat, preservation of foodstuffs, reduction of fuel, and improvement of personal safety, surely, an excellent prospectus for any industrial material.
1. Retrospective Search of Information Sources for the period 1980-1991 (*)

1.1 ABSTRACTS INDEX

| 1. Generalities | 9,11,13,14,18,20-23,30,33 |
| 2. Raw materials: | |
| 2.1 Isocyanates | 8,10,13 |
| 2.2 Polyols | 13 |
| 2.3 Selection | 19 |
| 3. Manufacturing Processes: | |
| 3.1 Flexible foams | 6 |
| 3.2 Rigid foams | 7,15,25,30 |
| 3.3 Formulation: | |
| 3.3.1 Compounding, and | 17 |
| 3.3.2 Optimizing, method for | 1,2 |
| 3.3.3 Calculations, equations for | 26 |
| 3.4 Flame retardants | 31 |
| 3.5 Polymerization, studies of | 16 |
| 3.6 Kinetics | 32 |
| 4. Equipment: | |
| 4.1 Mixing process | 3,24,27 |
| 4.2 Cellular foams | 4,5,28 |
| 4.3 Non cellular foams | 4 |
| 4.4 Coating on textiles | 4 |
| 5. Modular design plant | 5 |
| 6. Applications | 9,15 |
| 7. Wastes and recycling | 12,29 |
| 8. Health and safety factors | 33 |
| 9. Bibliography | 34-36 |

*Information sources: Chemical abstracts, Engineering index
1.2 ABSTRACTS*:

1. - Polyurethane finishing formulation by
     the Japanese method. K. Sogome, Masaaki, Masaaki
     Chem. 1979, 1, 257-260. A review of methods for poly-
     urethane finishing with a special emphasis on the
     Japanese methods. A classification chart is
     presented giving a general classification of
     polyurethane finishing machines. The paper
talks about the availability of polyurethane finishing
     machines in Japan. The modular design of the
     machines is also discussed. See p.51

2. - Polyurethane processing plants and machinery
     based on polyether-based raw materials. S. Koide
     May. A review of polyurethane processing plants
     and machinery based on polyether-based raw
     materials. The modular design of the
     machinery is discussed. See p.52

3. - Polyurethane processing plants and machinery
     based on polyether-based raw materials. S. Koide
     May. A review of polyurethane processing plants
     and machinery based on polyether-based raw
     materials. The modular design of the
     machinery is discussed. See p.52

4. - Polyurethane processing plants and machinery
     based on polyether-based raw materials. S. Koide
     May. A review of polyurethane processing plants
     and machinery based on polyether-based raw
     materials. The modular design of the
     machinery is discussed. See p.52

5. - Polyurethane processing plants and machinery
     based on polyether-based raw materials. S. Koide
     May. A review of polyurethane processing plants
     and machinery based on polyether-based raw
     materials. The modular design of the
     machinery is discussed. See p.52

6. - Polyurethane processing plants and machinery
     based on polyether-based raw materials. S. Koide
     May. A review of polyurethane processing plants
     and machinery based on polyether-based raw
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*Complete documents can be obtained from: British Library Lending Div.
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United Kingdom, LS23 7BQ
7. - Recent developments in polyurethanes XV. S. B. Sasmal. J. Plast. Film. Tapes (Engl. Transl. Text India 1968, 11110, 44-9, 466 (Engl. The green of color polyurethane foams from polyesters or polyethers and disocyanates is discussed. The effects of comonomers, catalysts, and volatile monomers on the product foams are discussed. Some green of poly foam is also discussed.)

8. - Recent developments in polyurethanes XVI. J. V. Lynn. S. H. Sasmal. (India Plast. Fab. Text. India 1969, 384-6. Engr. The science of polyurethane foams and the chemical and physical reactions with various monomers and cellulose are described. Some results in the application of polyurethane foams are given.)


11. - Plastics in high tech industries by 301 A.D. Kranasamurthy. H. (Hindustan Org. Chem. Ltd, India). Chem. Age India 1968, 149-56 (Engl.): Developments in engineering plastics, e.g. polyamides, polycarbonate, polyesters, PET, and polyurethanes, their processing technol., and current and future applications in India are discussed.


14. - 083733 POLYURETHANES (PLR). Since their discovery fifty years ago, polyurethanes have clearly demonstrated their versatility and ability to stimulate new areas of demand. Today, despite more modest growth prospects, the polyurethane industry is continuing the process of innovation both in terms of technology and markets. Following the outlook for polyurethane by major segment, recent developments and implications in terms of polyurethane raw materials are reviewed and the structural changes which are taking place in the industry are described.


15. - 083668 VERSATILITY OF IN-SITU POLYURETHANE FOAM. The use of rigid, low density polyurethane foam for insulation purposes is widespread throughout the world with approximately one million tons of raw materials being sold for this purpose. The principal reasons for the continued growth of polyurethanes are insulation efficiency, ease and versatility of fabrication and long term aging properties. The advantage of on-site application is that it allows the insulation of non-regular surfaces as well as the facility to insulate areas where access is difficult, particularly paperwork and narrow cavities. The article highlights some of the important trends in in-situ foaming, covering both spray-applied and liquid-dispersed molecules.


17. - 092567 GUIDE TO FORMULATING AND COLD-POUNDED POLYURETHANES. Various polymer materials obtained from reacting isocyanates and polyols. Polyurethanes can be formulated to make a variety of products, from furniture to decorative ceiling beams.

(Author abstract)


19. - 092629 RAW MATERIAL SYSTEMS FOR RIGID POLYURETHANE FOAM. Various end-use dependent methods of producing rigid polyurethane foam require the raw materials with controlled reaction profiles and expansion characteristics. This control is achieved by selecting the polyols according to functionality and reactivity, the catalysts according to their differing influence on urethane formation and blowing reaction, and the foaming stabilizers according to their effects on the expansion behaviour of the reaction mix and on cell structure. The raw material systems can be characterized by determining the volume increase, the temperature, the viscosity and the expansion pressure as a function of time. (Edited author abstract)

20. -

089261 POLYURETHANES (PUR). The consumption of polyurethanes experienced a healthy growth rate even during the period 1980-83, when other material groups had to suffer considerable set-backs at times. This report describes the development in the various sectors for PUR-applications. New developments in raw materials and additives as well as optimization of products for new areas are described. Advances in processing technology, mostly concerned with the PUR-sector, have contributed significantly to the above average success in the market. Such pressing subjects as health and safety at work and promotion of the environment are also briefly discussed. 44 refs.


21. -

089342 PROGRESSIVA TECNOLOGIA DEGLI ESPANSI POLIURETANI (Advances in the Technology of Expanded Polyurethanes). This article describes new methods and new materials in production of foamed polyurethanes of high strength and low energy consumption. It is shown how these innovations result in shorter manufacturing cycles, better fire resistance, higher dimension stability and other advantages.

The discussion focuses on polyurethane foams based on methylene diisocyanate. In Italian.


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102: 1222 Apparatus for mixing at least two chemically reactive plastic compositions. Werner, Eric J. (Red. Maschinenbau GmbH und Co, Ger. Offen. DE 3,324,375 (Cl B29B1/06), 11 Apr 1983, App. 13 Sep 1982, 10 pp. The apparatus, exp. useful for polyurethane foaming, comprises a mixing chamber, inlet for introducing reactive resin compositions to the mixing chamber, an outlet for the mixture, an outlet for returning the components to a storage chamber which has therein air channels, and a means for maintaining a constant pressure on the components during return to the storage chamber, and mixing in the mixing chamber. The apparatus is designed to, in particular,...

25. -

102: 267733 Continuous production of plastic foam. Griffiths, Anthony. Charles. Murray (Armstrong International Ltd): Brit. UK Pat. appl. GB 2,128,723 A (Cl C08D2/02) 04 Apr 1983, 11 Oct 1984, GB Appl. 1,733, 21 Jan 1983; 1985; ..., ... p. Polyurethane foam having uniform properties is prepared by feeding reactants to the bottom of a vertical pipe through a hop into a diverging area while the foam is removed at the top by means of a conveyor. Thus, a mix of polyether polyol, water 4.3, silicone surfactant 0.5, amine catalyst 0.2, and water 0.3, as well as catalyst 0.3, are forced through a hop into the hop, then through a mixer into a diverging area where the foam is formed. The apparatus is designed to form a constant mixture in the hop, and the gas flow through the hop is 100 kg/m. net throughput 20.4 m. and vertical velocity 0.6 m. min.
10.1117/1 Polyurethane formulation calculations. Liu, Houjun (Shanxi Prov. Inst. Chem Ind. Peco. Rep. China). Hefeng Xiangxiu Gongye 1984, 7(3), 185-6 (Ch). Equations are given for calculating polyols and polyisocyanates or isocyanate prepolymer. The isocyanate comp.-OH compn. equiv. ratio was maintained at 0.97-1.03 to obtain theor. wt. >25,000.

10.12255a Mixing method and apparatus for polyurethane synthesis. Nakaj S.P.H. (cm. Kokei Tohkyo sho) J 15,412 [64 15,423] (Ch. C. 1968(68), 73 Jan Nov., 1) pp. 87/92-394, 06 Apr 1982, 2 pp. A simple and efficient mixing of the reactants in the mixing process involves feeding the reactants into a mixing chamber, while a non-reacting and non-moment test, colors, release, etc., is fed in the direction vertical to the consumer fees, and the direction of the 3rd component is the direction intended for the material.

09792 RATIONELLE UND FLEXIBLE PUR-VERARBEITUNG. (Rational and Flexible PUR-Processing). This paper is concerned with the apparatus and automation used in the processing of polyurethanes, particularly of polyurethane foams. Details are given of the dosing equipment, means of transport for material and products, moulds and mould carriers, auxiliary transport equipment, hand tools for specific purposes, cost analysis. In German.

09753 RECYCLING FLEXIBLE FOAM: A NOVEL TECHNOLOGY PRODUCES A QUALITY PRODUCT WITH IMPROVED ECONOMICS. Air Products' polyurethane foam scrap recycle technology offers several incentives to foam manufacturers. It is a new option for scrap utilization which offers economic rewards greater than most current alternatives. Although one could consider ground foam as a filler, since the particles are chemically bound within the product and since the particles have essentially the same physical properties as the end product, the foam is nearly identical to virgin foam. Finally, no significant changes are required for the production equipment or process.

099807 POLYURETHANE, STAND DER TECHN. UND KUENSTIGE ENTWICKLUNG. (Polyurethanes - Technological Status and Future Development). This review paper discusses the chemistry, polymerization mechanism, properties and applications of polyurethanes which are obtained by additional polymerization of specially selected monomers. Polyurethane-POLYURETHANES - Research - Contd. these are either flexible (elastomers) or stiff (plastics). The description of polyurethane technology, particularly in the production of foamed products, is followed by an extensive review of application fields. Forecasts for the future developments is included. In German.
31. - 074999 POLIURETANO ESPANSO RIGIDO. (Rigid Foamed Polyurethane). Foamed polyurethane is known as an optimal heat insulating material for buildings. However, in practical applications the flammability of polyurethanes must be taken into consideration. The fire behavior of these materials can be modified by flame retardants. These aspects of rigid polyurethane foams are examined in this article. In Italian.

Orsini Pietro; Amano, Massimo. Mater Plast Elastomers 9 Sep 1982 p 522-528.

32. - 96: 4884x A kinetic study of reactions between polymers. Rasor, A.; Walsh, D. J. (Lab. Synth. Org., Univ. Maine, 72017 Le Man, Fr.). Eur. Polym. J. 1981, 17(10), 1057-9 (Eng). The rate of reaction of polymers contg. different reactive groups was studied. Isocyanate-terminated poly(ethylene oxide) was treated with hydroxyl-terminated poly(ethylene oxide). Polymers with higher mol. wts. gave lower rates of reaction. It was not possible to find an analogous low mol. wt. compd. which gave a reasonable rate of reaction compared with the polymers. Thus, the rate of reaction is very dependent on the environment of the reacting groups and brings a possibility of ambiguity into the conclusions.


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25.- 09178 POLIURETANI FLESSIBILI A BASE DI MDF [MDI Base Flexible Polyurethanes]. New and unusual ones are forming in the United States for these polyurethanes, already well-known in Europe; form absorbent products to contraceptives, foams for medical use in small packs used for plant protection. The annual growth rate until 1990 could be about 10 percent. (Author abstract) in Italian.


32. - 091282: AUMENTA LA PRODUTTIVITA DELLE MACCHINE PER POLIURETANI. (Increase in productivity for polyurethane machines). Improvement in the system of feeding and in the mixing head and an ever increasing use of dispersions and products which are opening the way to maintenance of productions with higher and more rapid cycles also for large components. (Abstract) in Italian.

33. - 102: 75674: Research in the field of polyurethanes in Romania. 


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51. - 96: 96586y Results of 15 years of rigid polyurethane foam 
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211-20 (Eng). A review with 9 refs.

52. - 96: 965777 The search for low-smoke polyurethane foams. 
Murch, Robert M.; Kehr, Clifton L. (W. R. Grace & Co., 
Columbia, MD 21228 USA). Proc. Int. Conf. Fire Saf. 1982, 7, 
23-33 (Eng). A review with 24 refs. esp. concerning variations in 
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polyurethane foams.

53. - 96: 5136j Step growth polymerization. Part II. Developments 
in polyurethanes. Sparrow, D. J.; Walton, I. G. (Org. Div. ICI 
(Eng). A review with 94 refs.

(USSR). Plast. Massy 11,4 (9), 31-4 (Russ). A review with no refs. of prep., properties, and uses of elastic, semirigid, 
and rigid polyurethane foams.

55. - 97: 182356o Studies of the formation and properties of 
polyurethanes suitable for reaction injection molding. 
Molding Fast Polym. React., 51-34 (Eng). A review with 30 
refs.

56. - 97: 72867r Preparation and study of isocyanate polymers. 
III. Infrared spectroscopic study of the reaction kinetics 
of polyurethane formation. Farkas, Ferenc (Graboplast. 

57. - 97: 7576x Current status and trends in the production 
and use of polyurethanes outside the USSR. Murashov, Yu. 
4, 43-60 (Russ). A review with 41 refs. is given dealing with 
the manuf. and uses of polyurethanes and urethane rubbers 
outside the USSR.

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Chem. reactive components (e.g. polyisocyanates and polyols) are 
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USSR. A review with 49 refs.

61.- 95: 151593h Optimization of selected ingredients of foaming solutions for polyurethanes. Kopel, Pavel; Bebeza, Frantisek; Turcany, Josef; Solo, Stefan (Partisovske, Czech). Korazit 1981, 31(5), 122-6 (Slav).


I. Akaboshi


I. Akaboshi


** Complete list of abstracts can be obtained from UNIDO-INTIB
2. AVAILABLE BOOKS AND JOURNALS FOR POLYURETHANES AND RELATED SUBJECTS

2.1 Fundamentals of Reaction Injection Moulding

2.2 The ICI Polyurethanes Book

2.3 Polyurethanes in Medicine
Leah, W.D., CRC Press, 1986, 240pp., £39.00

2.4 Equipment for Processing Plastics and Rubber, Series KHM-2 Equipment for the Production of Moulding Polyurethanes. Review Information.
Befedov, A.S., Apanasenko, E.E., Kondurazov, A.P., 1986. 46pp., (Russ) rub 0.73.

2.5 Polyurethane Handbook

2.6 Organosilicon Polyurethanes
Kurnetova, V.P. et.al., 1984, 221pp, (Russ) rub 2.90.

2.7 Plastic Handbook, Vol.7: Polyurethanes. 2nd Ed.

2.8 Modified Polyurethanes

2.9 Polyurethane: Kunststoff Handbook
Becker/Braun

2.10 Polyurethane-Based Composite Materials

2.11 Physical Chemistry of Polyurethanes

2.12 Synthesis of Polyurethanes

2.13 Advances in Urethane Science and Technology

2.14 International Progress In Urethanes

2.16 International Progress in Urethanes

2.17 Developments in Polyurethanes

2.18 Urethane abstracts
1971, m. $115. Technomic Publishing Co., Inc.

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MODERN PLASTICS ENCYCLOPEDIA

A PLASTICS PRIMER 4

KEY WORD INDEX 12

TEXTBOOK 17

Basics and compounds 17
Acetal 19
Acrylic 20
Alloys & blends 23
Allyl 139
Bismaleimides 140
Cellulosics 24
Epoxy 140
Fluoroplastics 26
Ketone-based resins 27
Liquid crystal polymers 45
M amine-formaldehyde 154
Nitrile 30
Nylon 30
Phenoic 143
Polyamide-imide 33
Polyarylate 34
Polybenzimidazole 41
Polybutylene 42
Poly carbonate 44
Polyester, thermoplastic 45
Polyethylene 55
Polyethylene terephthalate (PET) 49
Polycyclohexylenedimethylene terephthalate (PCT) 49
Polyethylene terephthalate (PET) engineering grades 50
Polyethylene terephthalate (PET) standard grades 52
Polyester, thermoset 144
Polyetherimide 54
Polypropylene 55
Branch polypropylene 67
Ethylene acid copolymer 70
Ethylene-ethyl acrylate 70
Ethylene-methyl acrylate 72
Ethylene-vinyl acetate 72
Ethylene-vinyl alcohol 73
High-density polyethylene 62
HMW high-density polyethylene 65
Ionomer 74
Linear low-density polyethylene 56
Linear polyethylene 55
Low-density polyethylene 68
UHMW polyethylene 66
Very low-density polyethylene 61
Polypmide, thermoplastic 75
Polyamide, thermoset 146
Polymethylpentene 81
Polyphenylene oxide, modified 82
Polyphenylene sulfide 83
Polypropylene 84
Polypropylene homopolymer 86
Polypropylene impact copolymers 88
Polypropylene random copolymers 89
Polyurethane 147
Silicones 150
Styrene resins 90
ABS 90
ACS 91
Acrylic-styrene-acrylonitrile 92
Crystal polystyrene 94
Expandable polystyrene 101
Impact polystyrene 96
Olefins modified SAN 102
Polystyrene 92
Styrene-acrylonitrile (SAN) 101
Styrene-butyadiene 104
Styrene-maleic anhydride 105
Sulfone-based resins 106
Polyarylsulfone 106
Polyethersulfone 106
Polyethylene 108
Thermoplastic elastomers (TPEs) 109
Elastomeric alloy TPEs 110
Engineering TPEs 112
Olefinc TPEs 113
Polyurethane TPEs 114
Styrene TPEs 116
Urea 154
Vinyl-based resins 133
Chlorinated PVC 134
Dispersion PVC 136
PVC 133
Suspension PVC 137
Vinylidene chloride 138

Chemicals and additives 157
Antifogging agents 159
Antimicrobials 159
Antioxidants 161
Antistats 164
Colorants 167
Color concentrates 170
Special colorants 172
Coupling agents 175
Silanes 175
Titanates 177
Degradability additives 178
Flame retardants 182
Foaming agents 184
Fragrances 188
Lubricants 190
Modifiers 192
Mold release agents 196
Organic peroxides 199
Plasticizers 202
Polyurethane foam catalysts 208
Smoke suppressants 210
Stabilizers 212
Heat stabilizers 212
UV stabilizers 216
Surface-active agents 220

Reinforced plastics and composites (including fillers) 223
Composite raw materials 225
Bulk molding compounds (BMC) 225
Prepregs 225
Reinforced thermoplastics 228
Sheet molding compounds (SMC) 229
Stampable thermoplastics 230
Thick molding compounds (TMC) 232

Fibrous reinforcements 237
Aramid hybrids 238
Aramids 237
Carbon fibers 239
Carbon/glass hybrids 240
Ceramic fibers 241
Glass fibers 242
Metallic fibers 246
Thermoplastic fibers 247

Fillers 248
Glass fillers 248
Mineral fillers 248

Primary processing 253
Blow molding 255
Blow molds 261
Extrusion-blow molding 255
Injection-blow molding 258
Multilayer-blow molding 260

Calendering 262
Casting of acrylic 264
Casting of film 269
Casting of nylon 270

Compression and transfer molding 271
Extrusion 275
Blown film extrusion 281
Extruder screen changers 283
Extrusion compounding 275
Extrusion dies 284
Extrusion gear pumps 286
Extrusion processing 278

Gravimetric extrusion control 288
Foam processing 290
Expandable PS foam molding 290
Foam extrusion 291
Polyurethane foam processing 292
Thermoplastic structural foam molding 296

Injection molding 298
Hot runner molds 308
Injection molding thermoplastics 298
Injection molding thermostets 302
Injection molds 307
Multi-injection molding 306
Reaction injection molding 311

Reinforced plastics/composites processing 312
Compression molding RP 312
Continuous RP laminating 315
Filament winding 316
Open mold processing 318
Pultrusion and pulforming 321
Resin transfer molding 325
Tape and fiber placement 326
Rotational molding 331
Becker/Braun
Kunststoff
Handbuch

Polyurethane
Herausgegeben von Günter Oertel
3. Some worldwide Polyurethanes Producers

3.1 U.S. Producers

**5484000 POLYURETHANE**

<table>
<thead>
<tr>
<th>Company</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ares Industries, Inc.</td>
<td>P.O. Box 327, Chanhassen, MN 55317</td>
</tr>
<tr>
<td>Alpha Foam Systems, Inc.</td>
<td>5300 Main Street, Cleveland, OH 44122</td>
</tr>
<tr>
<td>Corcoran Mfg Co. Inc.</td>
<td>1725 S. Mission St, Anaheim, CA 92803</td>
</tr>
<tr>
<td>Purolight Inc.</td>
<td>P.O. Box 15245, Sarasota, FL 34279</td>
</tr>
<tr>
<td>Gallagher Corp</td>
<td>3266 Morrison Dr, Sun Prairie, WI 53132</td>
</tr>
<tr>
<td>Molded Dimensions Inc.</td>
<td>101 Sunset Rd, Packwaukee, WI 53074</td>
</tr>
<tr>
<td>Newage Industries Inc.</td>
<td>18300 Progress Dr, Willow Grove, PA 18996</td>
</tr>
<tr>
<td>Pazz-O-Matic Inc.</td>
<td>21200 General Dr, Vancerson, MN 55440</td>
</tr>
<tr>
<td>Rubber Masters, Inc.</td>
<td>709 S. Colony Ave, Baltimore, MD 21229</td>
</tr>
<tr>
<td>Urethane Products Industries Inc.</td>
<td>4500 Hudson-Snake Dr, Sylva, OH 44224</td>
</tr>
</tbody>
</table>

**5484000 POLYURETHANE FOAM**

<table>
<thead>
<tr>
<th>Company</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accurate Foam Co.</td>
<td>P.O. Box 512, Le Ponte, IN 46350</td>
</tr>
<tr>
<td>Carpenter Packaging Co.</td>
<td>3611 Manhudd Ave, Richmond, VA 23230</td>
</tr>
<tr>
<td>Gan Midwest</td>
<td>3500 E 97th Place, Chicago, IL 60628</td>
</tr>
<tr>
<td>Ethyl Corporation, Inc.</td>
<td>9200 Zionsville Rd, Indianapolis, IN 46268</td>
</tr>
<tr>
<td>Foam Enterprises</td>
<td>18300 Waterfront Circle, Minneapolis, MN 55441</td>
</tr>
<tr>
<td>Hunt Co.</td>
<td>Rubber Fabrication Div., 1724 New Brighton Blvd. P.O. Box 1421, Minneapolis, MN 55440</td>
</tr>
<tr>
<td>Ohio Rubber Co.</td>
<td>Ortho Div., Interstate 35W, Dept U, Canton, TX 76101</td>
</tr>
<tr>
<td>Presto Manufacturing Co.</td>
<td>34 Franklin Ave, Brooklyn, NY 11211</td>
</tr>
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</table>

3.2 U.S. Producers: Supplementary and Tentative List

<table>
<thead>
<tr>
<th>Company</th>
<th>Address</th>
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<tbody>
<tr>
<td>Air Products and Chemicals Inc.</td>
<td>P.O. Box 538, Allentown, PA 18105 ph.215-481-4911</td>
</tr>
</tbody>
</table>
<pre><code>                    |                                   |                                   |
</code></pre>
<p>| Akro, Chemical Div.            | 300 S. Riverside plaza           |
| Chicago, IL 60606 ph.312-906-7500 |
| Anderson Development Co.       | 1415 E, Michigan,               |
| St. Adrian, MI 49221 ph. 517-263-2121 |
|                                   |                                   |
| Atochem North America, Inc.    | 266 Barristow Rd.                |
| Glen Rock, NJ 07452 ph. 201-447-3300 |
|                                   |                                   |
| Dow Chemical                   | 2020 Dow Center Midland          |
| MI 48640                         |
|                                   |                                   |
| Ferro Corp, Bedford Chemical Div. | 7050 Krick Rd. Bedford,        |
| OH 44146 ph. 216-641-8580        |
| Formulated Resins Inc.         | Spragueville Rd.                 |
| P.O. Box 508, Grenville, RI 02828 ph.401-949-2060 |</p>
W.R. Grace & Co,
Organic Chemical Div.
Specialty Chemicals Unit (pp)
Hardman Incorporated

ICI Polyurethanes Group,
ICI Polyurethanes Group, PU Div. (pp)

MO Chemicals, Inc.

Olin Corp. Chemicals Group

Perma-Flex Mold Co.

Sartomer Company Div. of Pony Industries Inc.

Texaco Chemical Co.
(c)

Toyomenka (America) Inc. (pp)

Union Carbide Chemicals and Plastics Co.Inc. Specialty Chemicals Div. (c,i)

E.F. Whitmore & Co. (p)

Witco Corp. Organics Div.

55 Hayden Ave.Lexington, MA 02173
ph. 617-861-6600

600 Cortland
St.Belleville, NJ 07109
ph. 201-751-3000

Mobay Rd, Pittsburgh,
15205-9741 ph. 412-777-2000

P.O.Box 700,
Ridgewood, NJ 08520

120 Long Ridge Rd.
Stamford, CT 06904
ph.203-356-2000

1919 E. Livingston ave.
Columbus OH 43209
ph. 614-252-8034

Marshall building,
W.Chester, PA 19382
ph. 215-430-2200

P.O.Box 430, Bellaire
ph. 713-666-8000

39 Old Ridgebury Rd.
ph. 800-243-8160

520 Madison Ave.,
New York, NY 10022
ph. 212-605-3655

a = additives, c = catalysts, f = foam, i = intermediates, p = poliols, pp = prepolymer
3.4 European Producers: Supplementary and tentative list

**GERMANY**

Ashland Südchemie Kornfest GmbH
Postfach 440-D-4010
Hilden

BP Goodrich Chemical (Deutschland) GmbH
Görlitzer-Str. 1/6
D-4040 Neuss 1

Eberhard-Chemie GmbH
Postfach 930131
D-5000 Köln 91

Fomo Schaumstoff GmbH & Co. KG.
Werkstr. 6
D-4353 Oer Ermenschwick

EMW Betriebe Zumerling & Weyl GmbH Siemenstr. 9 and Co. Werner
D-6252

Geier + Voss GmbH
8204 Kolbermoor/Rosenheim
Postfach 1260

Häger & Kassner GmbH
Postfach 449-D-4730 Ahlen Westf.

Hefela GmbH
Postfach 1180,
D-5227
Windeck/Kosbach

Iromer Chemie GmbH
Hafenringstr. 1-3
D-4500 Osbrück

Vosschemie GmbH Chemische
Postfach 1355
D-2082 Vettersen

U.K.

Akro Chemie UK Ltd
1-5 Queens Rd., Birsham
Surrey KT12 5NL,
ph. 9322-47891

Baxenden Chemicals Ltd.
Paragon Works, Baxenden,
Accrington, Lancashire,
BB5 2SL
ph.0254-872278

Bridgetown Industries Ltd.
Green Lane, Bridgetown,
Cannock, Staffordshire,
WS11 3JW

CEP Marine Ltd.
15-20 Greemhey Place,
East Gillibrands,
Skelmersdale, Lancashire,
WN8 9SA

Lankro
P.O.Box 1, Eccles
Manchester M30 0EH
ph. 61-789-7300

Durham Chemicals Ltd
Wedgewood Way, Stevenage
Berts. SG1 4QH
Asia producers:

**ITALY:**
- Ausind S.p.A.
  - 13 Corso Sempione
  - 21053 Castellanza
  - ph.331-501100
- Latì S.p.A
  - 21040 Vedano Olona

**AUSTRIA:**
- Vianova Kunstharz A.G.
  - 104 Altmannsoeferstr.
  - 1120 Vienna
  - ph. 1-85050

**FRANCE:**
- Electra-Unic-Industri
- Plastibel
- Somplethane

**SWITZERLAND:**
- Crisco AG
  - Sevelen
  - ph. 085-5643132
- Haag Technic AG
  - Derendingen
  - ph. 065-423313

3.5 Asia Producers:

**JAPAN**
- Bridgestone Tire Co Ltd.
  - 1-10-1 Kyobashi, Chuo-Ku
  - Tokyo 104
  - ph.234-0304
- Harima Chemicals Inc.
  - 4-21 Dosho-Hashi,
  - Higashi-Ku Osaka
  - ph.6-201-2461
- Hodoqaya Chemical Co Ltd.
  - 4-2 Toranomon,
  - 1-Chome, Minato-Ku
  - Tokyo 105
  - ph.03-504-8631
<table>
<thead>
<tr>
<th>Company Name</th>
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<th>Phone/Ext</th>
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<tbody>
<tr>
<td>Kamatsuya Kaqaku KK</td>
<td>890 Oqiwara, Hidaka-Machi, Hidaka Gun Wakayama Pref.649-12 ph. 73-863-2007</td>
<td></td>
</tr>
<tr>
<td>Mitsui Toatsu Chemicals</td>
<td>3-2-5, Kasumigaseki, Chiyoda-Ku, Tokyo ph. 2223622</td>
<td></td>
</tr>
<tr>
<td>Sumitomo Bayer Urethane Co., Ltd</td>
<td>3 Souke, 1 Chome, Kukuchi, Amagasaki City, Hyogo Pref. 661 ph. 06499-2401</td>
<td></td>
</tr>
<tr>
<td>Takeda Chemical Industries</td>
<td>2-3-6, Dosho-Nashi, Chuo-Ku Osaka 541</td>
<td></td>
</tr>
<tr>
<td>Toyo Tire &amp; Rubber Co. Ltd</td>
<td>1-17-18 Edobori, Nishi-Ku Osaka ph. 6-441-8801</td>
<td></td>
</tr>
<tr>
<td><strong>INDIA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hindustan</td>
<td>81 Maharshi Karve Marg. Bombay 400.002 ph. 22-314271</td>
<td></td>
</tr>
<tr>
<td>Sasmira</td>
<td>Bombay</td>
<td></td>
</tr>
<tr>
<td><strong>ISRAEL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thio-Atim International</td>
<td>6 Hazorfim Street, (1986) Ltd Ramon Yam, Bat Yam 59605 Israel</td>
<td></td>
</tr>
<tr>
<td><strong>SINGAPORE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geneplast Private Limited</td>
<td>18, Meythal Rd. SG 2262 ph. 2652177</td>
<td></td>
</tr>
<tr>
<td>Industrial Engineering Suppliers</td>
<td>98, Owen Rd SG 082-Sing.</td>
<td></td>
</tr>
<tr>
<td>Insutech Thermal &amp; Engineering(S) Pte Ltd</td>
<td>50 Pal Crescent SG-1232 Sing.</td>
<td></td>
</tr>
<tr>
<td><strong>TAIWAN</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nan Pao Resins Chemical Co., Ltd</td>
<td>12 Nan Hai Village Shee Kang Shiang Tainan, Taiwan ph. 6-795-2801</td>
<td></td>
</tr>
</tbody>
</table>
3.6 **Australian, Canadian and African Producers:**

**AUSTRALIA**

Barbman-Quinn PTV.Ltd

P.O.Box 113
Artarmon N.S.W 2064
ph. 2-430259

Prambston Manufacturing Co. PTV.Ltd

Hallam Rd.
Hallam, Vic. 3803
ph. 3-703-1175

AC Matrick Chemicals PTV.Ltd

P.O.Box 59
Botany, N.S.W 2919
ph. 2-666-0331

**CANADA**

Dural Products Ltd

550 Marshall Ave.
Dorval, P.Q H9P 1C9,
Canada, ph. 514-636-6230

Uniroyal Ltd,
Uniroyal Chemical Div.

ERB Street
Elmira, Ont. N3B 3A3,
Canada, ph. 519-669-1671

**SOUTH AFRICA**

Industrialis Grethanes (PTY) Ltd

P.O.Box 411
Edenvale 1610 S.A.
ph. 11-690-1186

3.7 **Latin American Producers:**

**BRAZIL**

3M Do Brasil Ltd

Caixa Postal 123
13100 Campinas Brasil
ph. 192-641700

**CHILE**

Industrias Quimicas Solor
Chilena ltda

Manchester 2838, Santiago
ph. 513452-516679

**COLOMBIA**

Anhidridos y Derivados de Colombia S.A. (Andercol)

Carrera 64-CH 95-84
Autopista Norte, Medellin
Ph. 2370083

BASF Quimica Colombiana

Calle 37, n 7-43 Piso 5
Bogota
ph. 2326080

**ARGENTINA**

Dyneon Argentina S.A.

Av. Corrientes 3247, 1120 Buenos Aires
ph. 4330340
4. Some Equipment Suppliers and Consultancy Services:

**GERMANY**

Battenfeld Maschinen Fabriken GmbH
Postfach 1164-65
D-5882 Heinerzhagen

Cannon Deutschland GmbH
Postfach 1162
D-6053 Mühlheim/Main

Didier Engineering GmbH
Alfredstr.28,
P.O.Box 100945,
D-4300, Essen 1
ph. 0201-72450

Elastogran Maschinenbau GmbH
Mitterstrassweg
D-8021
Strasslach bei München

Glas Hate Kunststoffver-
arbeitungsanlagen GmbH
Otto-Scheugenpflug-Str.16
D-6050 Offenbach-Bieber

Grenzebach Maschinenbau GmbH
Postfach 11 55,
8854 Asbach-Bäumenheim
(Hamlar)

Gusmer-Guscraft GmbH
Liebigstr.8,
D-6054 Rodgau 6

Hennecke GmbH Maschinenfabrik
Postfach 1180
5205 Sankt Augustin 1
(OT Birlinghoven)
<table>
<thead>
<tr>
<th>Company Name</th>
<th>Address</th>
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<tbody>
<tr>
<td>Hermann Jennert KG Maschinen und Anlagenbau</td>
<td>Lindenplatz 62</td>
</tr>
<tr>
<td></td>
<td>5900 Siegen (Geisweid)</td>
</tr>
<tr>
<td>D.J. Keil KG Ing.Büro</td>
<td>Freiburg von Stein Str.2</td>
</tr>
<tr>
<td></td>
<td>D-6107 Reinheim</td>
</tr>
<tr>
<td>Kern-Liebers</td>
<td>D-723 Schramberg</td>
</tr>
<tr>
<td>Klöckner Ferromatic Desma GmbH</td>
<td>Postfach 1140</td>
</tr>
<tr>
<td></td>
<td>D-2807 Achim</td>
</tr>
<tr>
<td></td>
<td>ph. 04202-50-0</td>
</tr>
<tr>
<td>Krauss-Maffei Aktiengesellschaft</td>
<td>Postfach 50 03 40</td>
</tr>
<tr>
<td></td>
<td>8000 München 50</td>
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<tr>
<td>Lackfa Isolierstoffe GmbH &amp; Co.</td>
<td>Industriestr.2</td>
</tr>
<tr>
<td></td>
<td>D-2084 Kellingen 2</td>
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<tr>
<td>Lotsch und Partner Modelbau GmbH &amp; Co.</td>
<td>Flügelstr.7</td>
</tr>
<tr>
<td></td>
<td>D-4600 Dortmund 41</td>
</tr>
<tr>
<td></td>
<td>ph. 0231-402410</td>
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<tr>
<td>Puroll K-H-E GmbH &amp; Co. KG.</td>
<td>Rudolf-Diesel-Str.24</td>
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<tr>
<td></td>
<td>8015 Ottobrun (Reimerling)</td>
</tr>
<tr>
<td>Siku Fertigungsstechnik und Anlagenbau GmbH &amp; Co.KG.</td>
<td>Postfach 1136,</td>
</tr>
<tr>
<td></td>
<td>4714 Selm</td>
</tr>
<tr>
<td>T.M.G Technologie-Verwertung und Marketingges.mbH.</td>
<td>Postfach 1328,</td>
</tr>
<tr>
<td></td>
<td>5905 Freudenberg</td>
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**ITALY**

<table>
<thead>
<tr>
<th>Company Name</th>
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<tbody>
<tr>
<td>Pressindustria Engineering &amp; Plants SpA</td>
<td>&quot;Via Porto Darmolfo 35</td>
</tr>
<tr>
<td></td>
<td>1-20046 Biassono (MI)</td>
</tr>
<tr>
<td>Plastimac SpA</td>
<td>P.le G. Cesare n 9</td>
</tr>
<tr>
<td></td>
<td>1-20145 Milano</td>
</tr>
<tr>
<td></td>
<td>ph. 4985851</td>
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</table>

**SWITZERLAND**

<table>
<thead>
<tr>
<th>Company Name</th>
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<tbody>
<tr>
<td>Broendle AG E.</td>
<td>Industriestr.31,</td>
</tr>
<tr>
<td></td>
<td>8305 Dietlikon</td>
</tr>
<tr>
<td>Dopaq</td>
<td>Hinterbergstr.32</td>
</tr>
<tr>
<td>Dosiertechnik-Pneumatik AG</td>
<td>6330 Cham</td>
</tr>
<tr>
<td>Mapaq Maschinen &amp; Plastic AG</td>
<td>Schwarztorstr.26</td>
</tr>
<tr>
<td></td>
<td>3007 Bern</td>
</tr>
<tr>
<td>Meyer &amp; Cie AG A.H.</td>
<td>Badenerstr.329</td>
</tr>
<tr>
<td></td>
<td>8040 Zürich</td>
</tr>
<tr>
<td>Sprittechnik AG</td>
<td>Wiesenstr.468</td>
</tr>
<tr>
<td></td>
<td>9327 Tubach</td>
</tr>
<tr>
<td>Company Name</td>
<td>Address</td>
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<td>--------------</td>
<td>----------------------------------------------</td>
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<tr>
<td>CIC Ralphs Ltd.</td>
<td>Unit 38/39, Second Ave. Westfield, Mitsomer Norton, Bath Aron BA3 4BD</td>
</tr>
<tr>
<td>Compounding Ingredients Ltd</td>
<td>Unit 217 Walton Summit Center, Bamber Bridge, Preston, Lancashire, PR5 8AL</td>
</tr>
<tr>
<td>Bridgetown Industries Ltd</td>
<td>Green Lane, Bridgetown Cannock, Staffordshire WS11 3JW</td>
</tr>
<tr>
<td>Ryva Engineering (MIC) Ltd</td>
<td>Unit 2/3 Westpoint Industrial Estate, Hargreaves St. Oldham Lancashire, OL9 4ND</td>
</tr>
<tr>
<td>Hytek Mouldings Ltd</td>
<td>Wallcroft Industrial Estate, Retford, Notts DN22 7SS</td>
</tr>
<tr>
<td>USA</td>
<td>1425 E Michigan St. Adrian, MI 49221, ph. 517-263-2121</td>
</tr>
<tr>
<td>Anderson Development Co.</td>
<td>33 Center Dr. Gilberts IL 60136 ph. 312-426-2200</td>
</tr>
<tr>
<td>Abatron Incorporated</td>
<td>1235 Freedom Rd. Mars. PA 16046</td>
</tr>
<tr>
<td>Cannon USA Inc.</td>
<td>1725 Biddle Ave. Wyandotte MI 48192</td>
</tr>
<tr>
<td>ElastoMachinery (EMB)</td>
<td>5845 w.82nd St.102 Indianapolis, IN 46278 ph.317-875-5592</td>
</tr>
<tr>
<td>Glas-Craft, Inc.</td>
<td>32 Stevens St.,Haverhill MA 01830 508-374-0303</td>
</tr>
<tr>
<td>Hudson Moulding Systems</td>
<td>826 E Fourth St., P.O.Box 6, Pittsburgh, KS 66762 ph. 316-231-1400</td>
</tr>
<tr>
<td>Michan Clay Products</td>
<td>Moby Rd, Pittsburgh PA 15205 ph. 412-746-3000</td>
</tr>
<tr>
<td>Olin Corp. Chemicals Group</td>
<td>University of Detroit 4001 West Mc Nichols Rd Detroit, MI 48221-1011 Ph. 313-927-1270</td>
</tr>
</tbody>
</table>
Twin Rivers Engineering, Inc. Cte. 27, Boothbay, ME 04537
ph. 207-633-2975

5. - R & D Institutes:

5.1 AUSTRIA

Austrian Plastics Institute
Arsenal, Objekt 213, Franz Grill Str. 5, A-1030 Wien

5.2 FRANCE

INRS
75680 Paris 14

5.3 GERMANY

German Plastic Institute
Schlossgartenstr. 6 R
D-6000 Darmstadt

Institut für Kunststoff-
verarbeitung
D-3100 Aachen

5.4 U.K.

British Urethane form
Contractors Assoc.

Univ. Manchester
Manchester, UK M60 1QD

Polytech. North, London
London UK W7 1DB

Rappra Technology Ltd
Shawbury, Shrewsbury,
Shropshire SY 4 4NR

5.5 USA

Int. Isocyanate Inst. Inc.
Parsippany, NJ

Rubicon Chem., Inc.
Woodbury, NJ 08096

Univ. of Detroit
Polymer Inst. Detroit
Michigan

Virginia Polytech. Inst.
and State Univ.
Blacksburg, Va 24061
ECN NEW PROJECT SUMMARY
New projects summarised below appeared in ECN on 18 and 25 February 1991

<table>
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<tr>
<th>Company</th>
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<th>Product</th>
<th>Capacity, tonne/year</th>
<th>Process</th>
<th>Contractor</th>
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<td>Manali Petrochemicals</td>
<td>Madras, India</td>
<td>isocyanates</td>
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ECN NEW PROJECT SUMMARY
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<th>Location</th>
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<th>Capacity, tonne/year</th>
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Note: We multiply tonne/day by 330 to get tonne/year. T - total, x1 - expansion, S - study, P - planned, A approved, U - underway
Dates given are for start-up unless otherwise stated

ECN NEW PROJECT SUMMARY
New projects summarised below appeared in ECN on 2 and 9 July 1990

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ECN EUROPEAN REVIEW
supplement dec.1990

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MDI flexibility leads ICI’s polyurethane thrust

Increasing sophistication in the polyurethanes market is causing ICI to focus its efforts on differentiating MDI formulations. Toby Shelley talked to Alan Pedder, principal executive officer of ICI’s polyurethanes business, about this and the increasingly global nature of the market.

A LITTLE over one year ago, Alan Pedder was appointed principal executive officer of ICI Polyurethanes, taking charge of the worldwide development of the business. ICI claims a 20% share in the global polyurethanes (PUR) market, which grew from under 3m tonnes/year in 1989 to nearer 5m tonnes/year in 1999, valued at around $9bn.

Development of the product will be driven by two motors: the need for increased sophistication... and the reality of internationalisation of both demand and competition, Pedder told ECN.

The increase in sophistication is already being fuelled by environmental demands. The industry has had to step up to the need to find replacements for CFC blowing agents and, along with the whole plastics sector, is now embarking on further research into product reusability and reclaimability. As political attention is focused more and more on global warming, insulation will be required to be increasingly efficient and increasingly applied. ICI is forecasting a relative slowdown in market growth (ECN 17/24 December 1990) in Europe and North America, but continued growth of 8%/year in the underdeveloped Asian market: the internationalisation of the business is clear.

Meeting the challenge of increasing sophistication will be based on the relatively recent realisation of the potential for engineering isocyanates and polyols, with consequent development of the latter: 'For the next decade or two there is an almost infinite ability to invent materials.'

ICI is pleased with the progress that has been made in finding replacements for CFCs: although environmentalists note that HCFCs have a global warming potential and HFCs may contribute to both global warming and ozone depletion. Various areas are identified as having environmentally related growth potential, one of the most obvious being the further development of weight-reducing vehicle body panels.

Isocyanates are already in commercial use as bonding for sliced up rubber tyres reused as sports stadia surfacing. Such bonding can also be used to convert vegetable matter such as grain husks into cheap and durable building blocks. Ultimately, decisions about whether to reuse or recycle will be based on 'the best economics based on routes which are available', but within a new context in which functional excellence will remain a crucial factor, although balanced by cradle-to-grave product management.

Alan Pedder believes that the structural and insulation properties of PUR have overcome the pressure exerted on the product by the CFC replacement problem. Indeed, he sees energy conservation in developing countries as a major possible area of expansion. ICI was recently involved in a UN-sponsored seminar in Beijing, discussing low CFC refrigeration. This said, and while the elastomers, automotive applications and binder sectors may show relatively higher growth, the breakdown of PUR usage is not expected to change dramatically in the present decade.

ICI Polyurethanes has restructured its marketing organisation, replacing the traditional European, North American and international departments with an all-America department, a greater Europe, Comecon, Africa department, and an Asia department. This reflects the increasing importance of developing markets and their interaction with the industrialised nations. In particular, it demonstrates that Asia is becoming an 'increasing focus of our investment' with a move into India forthcoming and a technical centre in South Korea recently sanctioned.

When he took over, Pedder said he was interested in 'increasing specialisation'. He continues to stress this, saying: 'We will tend to focus business around our ability to differentiate MDI formulations. I think we are particularly good at developing the flexible market for MDI.'

Although he declines to elaborate further about ICI's plans, he foresees increased specialisation by the leading players in the international PUR business as it adapts to the 1990s.
Polyurethanes: the learning curve†

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(Received: 12 September 1982)

Abstract: Polyurethanes have had a remarkable growth record as reactive processing chemicals. The adaptability of polyurethanes is due to the wide range of specialised chemicals available, the particular features of their processing and the wide variety of end use applications for which polyurethanes are suitable. Many problems have been met and solved during the development of polyurethanes for their many outlets. Developments in the basic chemicals, in catalysis and with the processing machinery have all been vital to success.

The users of the chemicals (the makers of the polyurethane products) have also had many major achievements in their abilities to use polyurethane chemicals effectively in many diverse applications.

1 Introduction

Polyurethanes have had a remarkable growth record since 1950 (Fig. 1); about three million tonnes of polyurethane chemicals are sold annually worldwide for use in reactive processing and there is a great diversity of applications for which these speciality polymers are used (Fig. 2). Polyurethanes do not usually compete directly with the bulk commodity thermoplastic polymers; in part, since they are significantly more expensive (Fig. 3). They do, however, compete with a large number of other materials, both natural and synthetic in a wide variety of applications. Polyurethanes are normally sold as reactive chemicals to the final processors who convert them by a multitude of reactive processing techniques into the end products, where full use can be made of the particular processing and property advantages of polyurethanes.

Polyurethanes are a family of materials which can be formulated from hard to soft, from solids to low density foams. The resulting property matrix (see Fig. 4) includes a wide variety of commercial materials, the vast majority of which are produced by reactive processing techniques. The main application sectors for polyurethanes are flexible foams in furniture and mattresses; semi-rigid foams, seating foams and elastomers in automobiles (Fig. 5); rigid

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† Based on a plenary presentation at the Plastics and Rubber Institute's Polycon '83: Reactive Processing - Opportunities and Constraints, Noordwijk, The Netherlands, May 1982.
<table>
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<td>CUSHIONS</td>
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Fig. 4 Property matrix of polyurethanes.

Insulation foams in building (Fig. 7) and refrigeration applications, flexible coatings and adhesives used in fabric constructions, paints and coating materials, and elastomers in shoe soles (Figs. 8-10). About 80% of all polyurethane chemicals are used in flexible and rigid foams.

This great diversity of products and applications has been the result of a tremendous amount of development work by the chemical suppliers, by their customers, the processors who actually make the polyurethanes, and by machinery manufacturers. This paper reviews the key features which have enabled polyurethanes to grow as major reactive materials.
polyurethane materials is formulated from relatively few basic isocyanates and a range of polyols of varying molecular weight and functionality.

- The polymer forming reactions can be catalysed, with extremely fast reaction cycles being possible. The reactions are chemically efficient and do not produce by-products.

- The polymerisation reactions can be accompanied by gas generation to produce foams. Two alternative foaming mechanisms are available. The reaction of isocyanates with water produces carbon dioxide and gives new chemical groupings (polyureas) built into the polyurethane networks. Alternatively, the exotherm from the isocyanate-hydroxyl reaction can be used to vaporise a low boiling liquid, usually a chlorofluorocarbon. Both foaming techniques give additional formulation flexibility and can produce valuable additional technical effects.

- The polymer forming reactions can be carried out continuously, to produce laminates or slab-stock foam for example, or discontinuously to give moulded articles or free rise foam blocks.

- Polyurethane reactive processing demands special machinery. At least two chemical streams must be accurately measured, without even any instantaneous excess of one stream over the other in the case of some moulding shots, and the streams must be intimately mixed and dispensed. The mixing head must be capable of operating without build-up of polymer which would eventually make it inoperable, or some operational method must be available for cleaning it. This problem can be solved by mechanical means, by intermittent solvent flushing and in other ways.

- The polymer forming reactions can be carried out continuously, to produce laminates or slab-stock foam for example, or discontinuously to give moulded articles or free rise foam blocks.

The excellent growth in the volume of polyurethanes used has been brought about by the suitability of the chemistry, the products and the application processes for important product substitution areas. Some of the growth has, of course, occurred by the increasing sales of the end products in which the polyurethanes are used. The more refrigerators which are sold for example, the more polyurethane rigid foam is used, since polyurethane rigid foams have a very high market penetration into this application sector. But to enable such growth to occur has necessitated a number of absolutely vital inventions and developments. Some of the most important advances from a long list of significant steps forward are given below:

1937–40 Chemistry developed by O. Bayer and others
1940–45 Specialised elastomers developed in Germany, UK and USA
Flexible foams from TDI and polyesters, high pressure mixing
Agitatorless low pressure mixing of foam chemicals
TDI prepolymer polyether flexible foams
Polymeric MDI introduced for rigid foams
Thermoplastic polyurethane elastomers invented
Tin/amine catalysts allow one-shot polyether flexible foams to be made
Hot cure moulding of flexible foam cushions
Rigid foam blowing by chlorofluorocarbons
MDI rigid foam refrigerator line demonstrated
Lamination processes developed
Inverse lamination process for rigid foams
Isocyanurate rigid foams developed
Polyurethane shoe soling systems introduced
Isocyanurate rigid foams introduced
Microcellular car bumpers
RIM developed
Flat block flexible foam process
Development of RIM process and applications
Moulded flexible foams from MDI

It is interesting to note that many of the key inventions were made quite a number of years ago. Although some quite significant developments are still occurring, the rate of new application penetration has certainly slowed down. This is a reflection in part of the success in the past (the most obvious new applications have been explored), and, in part, of the increasingly high cost of developing new application sectors, at a time of poor industry profitability.

The penetration of polyurethanes into all their application areas has depended on demonstrating how effective substitution of a material by polyurethanes can be achieved with benefit to the user in terms of end product quality and cost. In most instances this has meant devising new fabrication processes, since the handling of reactive chemicals makes special demands as well as giving rise to new opportunities.

The potential user has had to be convinced in each case that some significant benefit can be obtained from using polyurethanes in place of the materials traditionally used. At first sight, the raw materials costs often seem high compared with competitive materials. It has, therefore, been necessary to consider the total fabrication process (and often to demonstrate it on prototypes) to show that the overall production cost is advantageous. Once this crucial step has been made, and the new process adopted, the manufacturer has frequently been able to introduce additional benefits, by exploiting more fully the design potential of the reactive processing process and the particular attributes of polyurethanes.

4 The adaptability of polyurethanes

It is the diversity of polyurethane products and applications which perhaps is their most characteristic feature. In order to examine the adaptability of polyurethanes as reactive processing chemicals in more detail, the following aspects need to be considered:

- the chemicals
- the polymer properties
- the processing
- the equipment required.

4.1 The chemicals

The chemical suppliers have made available a wide range of isocyanates, polyols and additives. This allows a very wide variety of polyurethane end products to be made, and special effects can frequently be formulated by variations in the blends of reactive components and additives which are used. The majority of isocyanates used are based on TDI, toluene diisocyanate, or MDI, pure and polymeric versions of diphenylmethane diisocyanate, and the family of specialised MDI variants. Each of these classes of products is supplied in a number of grades suitable for particular applications. Chemical functionalities ranging from 2-0 to about 3-0 are available.

Polyols are available in even greater diversity. Polyethers are derived from propylene and ethylene oxides with starter molecules, and are available with functionalities from 2 to 6 or even 8. Low molecular weight (below 1000 say), high functionality polyethers give highly crosslinked polyurethanes with polymeric MDI and are extensively used in rigid foams. Polyol blends of functionality in the range 3-5 are often selected. The polymer networks are strong, even at low densities. Higher molecular weight polyethers (up to molecular weights of 7000) having functionalities of 2-3 give strong rubbery molecules with disocyanates, particularly when block copolymer structures are produced by the incorporation of low molecular weight diols or diamines into the formulations. The polymer chemist is able to make an immense range of useful polymer types from these intermediates, and new effects and improved starting materials are still being discovered and introduced.

Of great importance both to the polymer properties and the processing characteristics is the availability of sophisticated catalysts, mainly based on tertiary amines and tin compounds. Reactions can be made to go incredibly fast when required. Some
highly catalysed RIM formulations, for example, are sufficiently well reacted to begin demould after only 15 s following injection of the chemicals. Shot sizes of 8 kg are not now too exceptional. Important control of some competing chemical reactions can be obtained by the choice of appropriate catalysts. Tin compounds favour the urethane foaming reaction; tertiary amines may favour the water and some crosslinking reactions.

Surfactants are necessary, particularly in flexible foam technology, and very complex silicone surfactants are now available. With these, cell size, cell size distribution, the amount of closed/open cells and some processing characteristics can be influenced significantly.

Foams can be generated by the volatilisation of fluorocarbons and by CO₂ derived from the isocyanate/water reaction. These alternatives each provide different opportunities and benefits. Fluorocarbons, for example, can be induced to recondense in a reacting polyurethane when in contact with a cool surface in an overpack situation. By this means thick skins having superb surface detail can be made.

### 4.2 Polymer properties

As noted already, the types of polymer produced from available isocyanates and polyols can be varied widely from hard to rubbery, and most types can be foamed. Low density, open celled flexible foams range from 12 to 40 kg m⁻³ with typical closed cell rigid foams for insulation purposes being found in the range 30–60 kg m⁻³.

Polyurethanes are polar polymers containing many hydrogen bonded groups. In elastomers this contributes to high tensile and tear strengths, particularly where blocks of groups are arranged together, but can also introduce hysteresis losses on repeated cycling. Polyurethanes are resistant to non-polar solvents, but can be affected by some very polar liquids. The foamed rigid polyurethanes are surprisingly strong, especially when in composites formed during the reaction phase. A rigid foam of density 32 kg m⁻³ is 97% gas by volume, yet it is strong and is dimensionally stable, has a compressive strength of up to 200 kPa and a tensile strength of up to 350 kPa. When faced, even with paper, much higher strengths are available.

A low density rigid polyurethane foam having closed cells filled with a chlorofluorocarbon, has thermal insulation values which are outstanding (Fig. 11). Lambda values of 0.015 W m⁻¹ K⁻¹ or even lower can be found in freshly made samples. Long term measurements on actual unfaced samples show only slow increases in λ value, reaching about 0.023 W m⁻¹ K⁻¹ after 25 years. When impermeable facings cover the foam, very little change in λ value is detected over long periods of time. In energy conservation matters, rigid polyurethane foams have major contributions to offer in the maintenance of temperature above or below ambient.

Reinforcement—by glass for example—will stiffen elastomer mouldings and elevate heat distortion temperatures, and in rigid foam laminates will significantly improve the fire resistance performance. Since some at least of the beneficial properties of several polyurethanes, particularly the strong elastomeric products, depend on hydrogen bonded structures, we find that at temperatures of 80–100°C and above, the normal gradual equilibrium dissociation of the H-bonds begins, with consequent reductions in stiffness and strength properties. This can lead to problems of sag when conventional paint stoving techniques are the preferred methods of painting, e.g. in some car exterior parts. In these cases alternative painting techniques may be required.

### 4.3 Processing properties

Starting with two (or more) liquid streams, polyurethane processing machines essentially measure, mix and dispense them continuously or discontinuously as required. The dispensing of the mixed and reacting liquids can be done in many ways:

- as spray to give spray coatings
- into moulds to give many useful articles such as seat cushions, panels, shoe soles, etc.
- continuously to give slabstock foams, laminated materials, coated carpets, etc.
- as adhesives by a variety of application techniques to give laminates, sports surfaces, chipboard, etc.

Even quite large and complex mould shapes can be filled satisfactorily, the reacting chemicals flowing well and filling all sections, most of the flow occurring before gelation.

A very complex shape such as the space between a refrigerator shell and the inner lining may be filled
with foam in about 60 s; during this period the reacting chemicals have been injected, have foamed and have filled even quite thin sections a long way away from the injection point.

The self adhesive nature of reacting polyurethanes is a significant benefit in allowing strong composite materials to be made in a one-step process. Polyurethanes stick well to metal, to many plastics and can not be separated away from the injection point. The total fabrication process – the chemicals, the machine and the application – are thus interrelated and can not be considered in isolation.

4.4 Equipment

Many of the important features of polyurethane processing equipment have already been mentioned. Polyurethane dispensers are not particularly expensive and must be capable of:

- metering accurately at a pre-set ratio and rate, and at a controlled temperature and pressure. Liquids having viscosities from 3 to 1500 centipoise may be handled.
- mixing to blend and to nucleate the components.
- controlling accurately and varying the weight of mixed material dispensed. Shot sizes of 0.1-10 kg are possible.

Much ancillary equipment is available, including moulds, clamps, jigs, carousels and conveyors. Polyurethane reaction moulding does not generate very high pressures and moulding equipment withstanding 350 kPa (50 psi) is normally adequate.

5 Benefits and constraints

Whilst the growth of polyurethanes has depended upon many different factors, a relatively small number of key attributes has been responsible for much of the past impetus, and enabling technology has made it possible to exploit these.

1. Flexible foams are easy to produce in a variety of shapes. The products are extremely comfortable seating materials, they are durable and clean, enabling furniture and mattress materials to be produced cheaply.

2. Rigid foams which are very strong can be made at low densities, and when blown with fluorocarbons produce closed cell structures having very low levels of thermal conductivity. This has led to the widespread use of polyurethane foams in building, in refrigerated transport, in refrigerators and in freezers. Polyurethane rigid foams are superb thermal insulants.

3. Polyurethane reaction mixtures are usually exceptionally good adhesives and many surfaces in contact with reacting polyurethanes stick very strongly, enabling strong composite structures to be made in very wide variety, including panels and laminates for building, refrigerators and freezers, crash padding, and reinforced materials.

4. Reaction rates can be controlled within wide limits by catalysts and, after reaction, the polyurethanes are essentially fully reacted. Frequently no after cure is required.

5. Many polyurethane elastomers are exceptionally tough and strong, making these materials useful for example in mining equipment and specialised tyres.

6. Skinned foams with excellent surface detail can be made, for example for computer housings and simulated wood articles.

7. Machine developments have occurred at a sufficient rate to allow application, product and chemical developments to be exploited.

Since most polyurethanes are produced by reactive processing, the processor has to exercise appropriate care and control. The processor makes the final polyurethane polymer and so he has to control the many physical processing parameters which can affect their properties. Particular attention to metering ratio, temperature of the chemicals and the avoidance of water and other contamination is vital. Whilst the adhesive nature of reacting polyurethanes is a great benefit in making composites, the moulder is forced to coat his moulds, usually by using release agent sprays at intervals. Isocyanates are respiratory irritants and some exposed individuals can become sensitised, causing industrial asthma. The avoidance of this problem demands careful ongoing attention to plant and area ventilation, depending on the type of isocyanate being handled, and to operating practices. Monitoring of worker pulmonary function is also advisable at intervals.

The fire issue is one frequently associated with some polyurethanes, particularly with low density flexible foams. Much is now known about this topic, and the profound importance of composite design – the fabric, interlining, chair design and foam type for example in the case of a chair – are well established. Inappropriate use of polyurethane foams may certainly lead to increased fire risk: in common with all organic materials polyurethanes will burn, the combustion products depending crucially upon the combustion regime. Smoke formation can be a significant hazard in a polyurethane fire – again most organic materials also produce smoke in fires. Much can be done to minimise these potential hazards by careful design criteria, by the choice of suitable formulations and suitable composite
materials, and by avoidance of inappropriate use situations.

6 What can we learn from polyurethanes?

The immense amount of chemical, product, process and market development which has been associated with the growth of the use of polyurethanes since 1950, has provided some important learning for all interested in reactive processing.

6.1 The cost of the finished product is what matters

Chemical costs are very important, but so are mould costs, prototype costs, cycle times, finishing operations, reject rates, energy consumption costs and recycling opportunities. Reactive processing may give radically new possibilities for the redesign of the end product, which may allow the product manufacturer to reduce his manufacturing costs considerably and offer a better product.

In 1961, for example, a 240 litre capacity refrigerator from a major manufacturer not then using polyurethane as insulation, had an external volume of 0.665 m³ and weighed 110 kg. When redesigned using rigid polyurethane foam as insulation the same 240 litres of useful space occupied under 60% of the original external volume, and the new refrigerator weighed only 44% of the old version. Polyurethane foam therefore allowed greater useful volume, a saving in materials and, at the same time, substantially lower costs.

6.2 The chemical customer does the polymerisation

The polymerisation process must be sufficiently robust to allow reproducible products to be made routinely. The processor may need to be educated or trained to maximise the potential of the process. He may well need to consider higher standards of quality and manufacturing control than he is used to. The chemical supplier may need to provide higher levels of technical support than is necessary for the fabrication of thermoplastics for example.

6.3 New opportunities arise from process adaptability

If the reactive chemicals can be processed in several alternative ways, then many new application possibilities will be opened up. Experience has shown that the processor will experiment and will suggest new outlets.

6.4 Chemicals, process and machine are interdependent

The processor wants to make saleable end products, and so the total fabrication process needs careful attention to minimise problems. The chemical supplier will certainly need to work closely with the machine manufacturer if success is to be assured. The processor needs to understand that new technological applications require his help and commitment as well. New application developments rarely come as turnkey operations, and may be expensive and time consuming.

6.5 Polyurethanes have many unique and varied properties

The special features of polyurethanes have already been noted. Their adaptability has allowed them to become successful in many applications, and the list is still growing. They are not, of course, always the best materials in all applications, and may be quite unsuitable for some. They are, however, capable of being ‘tailored’ by formulation development to a surprising degree, thus increasing the fit of product for application. The foam outlets of polyurethanes have certainly been a major success story.

7 Where have we reached with polyurethanes?

Polyurethanes are certainly the most developed reactive processing chemical systems available today...
and chemical suppliers are able to define suitable products for many major industrial sectors. (See Figs. 12-15.) Some applications – seating cushions and refrigeration insulation for example – have become very closely associated with polyurethane foams. New uses are still being established, and the physical, mechanical and processing properties of the polyurethane family of materials are still being developed in several application sectors.

Although it has certainly come of age, the polyurethane industry is still far from being mature.
Flexible Foams

Chemical Principles

In order to produce a flexible foam, roughly the same amount of carbon dioxide must be generated in material which would otherwise become a solid rubber.

In general terms the molecular architecture required in an elastomer is known. One requires long chains with considerable freedom of rotation, tied together at frequent intervals by primary valency forces. Therefore the alkyds which are suitable for making flexible foams will be those based on the aliphatic series both as regards the diol and the acid. Thus adipic acid and sebacic acid are used, as well as the ‘dimer’ acids obtained by the dimerisation of linoleic acid. Diethylene glycol and propylene glycol are used extensively, while the trihydric alcohol which provides a crosslinking site is used in very small proportion. Trimethylolpropane and glycerol are the most commonly used triols. The molecular size is of some importance. It is found experimentally that if the molecular weight is of the order of 800-1,000 the products have a very slow recovery from elastic deformation. In order to produce rapid recovery a molecular weight of 1,500-2,000 is required. This is brought about in two ways, first by using almost equimolar ratios of carboxyl and hydroxyl groups, and second by a prolonged esterification so that virtually all the carboxyl groups originally present are consumed. A further consequence of the low acid number is that it is no longer possible to use the reaction between isocyanate groups and residual carboxyl groups to produce a useful quantity of gas, and the latter must come from added water.

Alkyds are sensitive to the isomer content of the commonly used tolylene di-isocyanate. The pure 2,4 isomer usually gives considerable after-shrinkage in flexible foams, and a mixed product containing both 2,4 and 2,6 isomer is used commercially.

In the production of flexible foams from polyethers, diols and triols are used either alone or in admixture. The molecular weight is usually around 2,000-3,000. As with the alkyds, no carboxyl groups are available for producing gas, and water must be added. When very low density foams are required a volatile fluorocarbon is dissolved in the polyether.

A major difficulty in the use of polyethers now appears. During formation of the polyol, for example by the ring opening and polymerisation of propylene oxide, the hydroxyl group formed near the end of each chain is secondary (>CH₂OH), rather than primary (−CH₂OH). The reaction with di-isocyanate is rather sluggish, while the reaction with water takes place rapidly; and thus most of the gas is lost.

Evidently one way of getting over this difficulty would be to react the di-isocyanate with the polyol before the addition of water. It was found some years ago that if the adduct so formed was carefully made with a molar excess of di-isocyanate, it had a useful shelf-life of several months. These products are generally called ‘prepolymers’, and when suitably activated with water, catalysts, and bubble modifiers they give soft and flexible foams of good quality. Low density foams are obtained by dissolving free di-isocyanate in the prepolymer (or adding it initially) to give a high NCO content, and increasing the amount of water.

The most suitable grade of tolylene di-isocyanate for polyether foams is an 80 : 20 blend of the 2,4 and 2,6 isomers. Even when this grade is used many prepolymer formulations show marked shrinkage during the early stage of cure. This defect can be overcome by crushing the foam so as to open the cells and allow the inward diffusion of air.

The necessity for crushing is obviously a grave disadvantage when it is desired to use a foamed-in-place technique. Much attention has therefore been devoted to the search for new catalysts which would speed up the rate of reaction between isocyanate groups and secondary hydroxyl groups relative to that between isocyanate and water. Tin salts such as dibutyl tin diaurate and stannous octoate, and diethylenetriamine (Dabco), have been found effective for this purpose. By using these catalysts, often in conjunction with others previously known, the direct production of foams from cheap readily available polyols is possible. This direct ‘one shot’ process, which avoids the need for making prepolymer and for crushing the foam, is of increasing importance. Table 1 gives typical formulations for polyester foams, prepolymer foams, and the ‘one shot’ method. In the so-called ‘two stage’ process, a liquid prepolymer, made initially by reacting polyether polyol, di-isocyanate, and tertiary amine catalyst, is used to make a foam by further reaction with more di-isocyanate and activator solution. In effect, therefore, the prepolymer replaces alkyd resin previously used.
Table 1: Typical Formulations for Producing Flexible Polyurethanes foams

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Prepolymer</th>
<th>One-shot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyd made from:</td>
<td>Prepolymer made from:</td>
<td>Niex Triol LG46</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>Polypropylene diol</td>
<td>Polypropylene oxide/glycerol</td>
</tr>
<tr>
<td>1.5 mole</td>
<td>mol wt. 2.025–100 g</td>
<td>polyol mol wt. 3.000</td>
</tr>
<tr>
<td>Sebacic acid</td>
<td>Tolyene di-isocyanate</td>
<td>Dial of mol wt. 3.000</td>
</tr>
<tr>
<td>1.5 mole</td>
<td>80/20 blend–33 g</td>
<td>30</td>
</tr>
<tr>
<td>Distearylene glycol</td>
<td></td>
<td>Trichlorofluoromethane</td>
</tr>
<tr>
<td>3.25 mole</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Glycol</td>
<td></td>
<td>Stannous acetate</td>
</tr>
<tr>
<td>0.5 mole</td>
<td></td>
<td>0.73</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>1.0 g</td>
<td>N-allylmorpholine</td>
</tr>
<tr>
<td>N-Co2-morpholine</td>
<td>2.0 g</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>N, N-dimethylacrylamine</td>
<td>2.0 g</td>
<td>Water</td>
</tr>
<tr>
<td>Water</td>
<td>4.0 g</td>
<td>Silicone oil</td>
</tr>
<tr>
<td>Tolyene di-isocyanate</td>
<td>(65:35 blend)</td>
<td>Tolyene di-isocyanate</td>
</tr>
<tr>
<td></td>
<td>33g</td>
<td></td>
</tr>
</tbody>
</table>

* This trade term indicates an N-allylmorpholine, made by Armour Hess Chemical Co., in which the N-substituent is a mixture of alkyl radicals derived from coconut oil.

Technology of Production

Mass-production machines such as the Henecke type were originally designed for the manufacture of flexible slab stock from polyester resins.

However, they are equally suitable for producing polyether foams and it is probable that in 1962 almost 80% of the flexible foam produced in this country is of the polyether type. During the manufacture of flexible slab a controlled amount of air is necessary to increase the initial gel stability and to obtain a uniform fine-celled structure. Details of an air-injection equipment suitable for machines producing slab stock at 180 lb/min have been described. Slab stock after cure is sliced into thin sheets by means of a slab splitter. This consists of a movable base with a roughened surface on which the thick block of foam is placed. The base is drawn forward mechanically between two uprights carrying two horizontal guides.

The top guide is fully guarded, but the bottom one has exposed along the length an endless belt or blade of flexible steel, ground to a fine cutting edge. As each successive layer is removed the base returns to its original position, while the cutter is lowered by a preset amount. Thickness of materials as little as 1/16 in. can be removed in this manner.

The foamed-in-place technique gives one great flexibility in the design of objects such as car seats and upholstery cushions which were formerly made from slab. In order to be efficient one must have a brief moulding cycle so that individual moulds can be used repeatedly. The principle is shown in Fig. 1. Shell moulds of high thermal conductivity are treated with parting agent and then conveyed beneath the mixing head to receive the charge. Foaming commences at once and the moulds are closed before entering a heating tunnel equipped with infra-red lamps. A more recent development is the use of high frequency dielectric heating.

It should be pointed out that, in the normal way, the outside skin of a moulding is very little above room temperature and is the last part to cure. Therefore the key to a short moulding cycle lies in the arrangements made to raise the skin temperature to 100°C as rapidly as possible. At this stage there is a slight contraction in volume which would otherwise lead to shrinkage, and a slight positive pressure must be exerted on the foam in order to keep the lid of the mould in contact with it. After leaving the curing tunnel the moulds are cooled, stripped, cleaned if necessary, and treated with a parting agent. They are preheated to 40°C before passing once more beneath the mixing head. Evidently the production of individual shaped items by an automatic foamed-in-place procedure is more difficult than the straightforward manufacture of slab stock. The cost of moulds and their output must be balanced against costs and output from fabrication machinery. Thus the decision as to whether an item is to be moulded or made from slab is a complex one involving technical and economic factors.

**Fig. 1: Foaming-in-place: assembly-line production.**

**BATCH-MIXING METHODS.** Because of the low viscosity and the good solubility in di-isocyanate, batch-

(Contd. on p. 495)
dyes for same combination of thickeners was higher for hot brand dye than cold brand dyes which was in turn higher than Remazol type of dyes. Hence, in reactive printing the specific structure of the dyes along with reactive system plays an important role in final softening effect.

Reference

(Contd. from p. 480)

Tensile properties such as initial modulus, extension at break and plastic deformation percentage were determined. However because of some of the unforeseen parameters ambiguous results were obtained. The parameters were identified after calculations of results and are as listed below
i) Varying number of passages given to web.
ii) Varying fineness of the needles used for Polypropylene and jute, Polypropylene.needle punched blended fabrics.

Tensile properties were determined after soil burial tests, significant difference in tensile properties was not obtained.

From above studies it could be concluded that jute, Polypropylene needlepunched sandwich blended fabrics might be useful for road construction as because covering jute with Polypropylene have had reduced extent of microbiological degradation. Long term soil burial test and large scale field trials with the help of geotechnical engineer will surely help increase the market potential of this type of fabric for geotextiles.

(Contd. from p. 490)

mixing of flexible foam formulations differs considerably from that described for rigid polyester foams.

Mixing is carried out in a matter of seconds, either by hand or with a high-speed stirrer, and the batch is poured immediately. During the gassing stage, and for some minutes afterwards, the foam is extremely soft and weak. The pressure exerted by the foam is negligible and moulds of very light construction are adequate. A knowledge of the flow pattern is important. Although the mix tends to flow sideways at first, this tops at the gel stage and thereafter the rise is mostly in an upward direction. In intricate mouldings the mix must be distributed early into the positions where it is required to foam. Failure to do this results in mouldings which are incomplete at the edge. As in the case of rigid foams, the toxic hazards associated with the use of tolylene di-isocyanate must be known and guarded against. Operators should be equipped with protective clothing and positive-feed air-masks for breathing. Adequate ventilation must be provided in areas where mixing and foaming are performed, as well as in stacking-bays and ovens where curing is completed.

FABRICATION METHODS: Flexible polyurethane foams can be cut, shaped, glued, and welded. Starting from slab stock and using a combination of these methods, specialist fabricators make a wide variety of articles. The splitting machine has already been described. In addition, band saws are used for cutting through slab in the vertical direction and portable hand cutters are popular for cutting intricate shapes. A well-known type is the Scintilla, which uses a pair of fine-toothed blades which oscillate rapidly past each other within a grooved pillar. Hot-wire shaping is employed mainly when a length of constant cross-section is required. A 'blank' rectangular rod is fed slowly forward against a stout nichrome wire formed into the required shape and maintained at a black heat.

High-frequency weldings is readily performed on standard equipment. Since the foam is slightly under the electrodes is compressed to a small fraction of its original thickness, many delightful quilted effects are possible, especially with embossed facing sheets of flexible poly (vinyl chloride) Glueing is best done with special alkyd-isocyanate adhesives. These contain a non-swelling volatile solvent so that after a short assembly time (10-15 min) the parts to be joined are simply pressed together to give a permanent flexible bond.

(To be continued)
Recent Developments in Polyurethanes – XV

S.B. Iyer

Rigid Foams

Chemical Principles

If an alkyd resin contains water or residual carboxyl groups, then on reaction with a di-isocyanate carbon dioxide is evolved. In favourable circumstances this gas becomes trapped within the mass of polyurethane and a foam is produced. Evidently a trifunctional molecule with a large number of hydroxyl groups will tend to bring about these ‘favourable circumstances’, that is to say an increase in viscosity (chain-lengthening) and finally gelation (cross-linking). This initial observation by the Bayer chemists has been exploited and developed so that a wide variety of rigid or flexible foams are produced. In this Chapter we consider rigid foams.

Two main classes have been developed, first those based on the expansion of an alkyd resin, which are known as polyester polyurethanes; next those based on the expansion of certain liquid triols with molecular weights ranging from a few hundred to a few thousand, which are themselves polymers of propylene oxide or ethylene:propylene oxides with glycerol, sorbitol, etc. Foams of the second class are known as polyether polyurethanes.

If we define an alkyd as the reaction product of a polyhydric alcohol and a polycarboxylic acid, it will be seen that a very large number of alkyds is theoretically possible. In order to be of value for making rigid foams an alkyd resin should be liquid rather than solid, capable of straightforward manufacture to a close specification and readily miscible with the chosen di-isocyanate. Additionally, the final polyurethane foam should possess adequate strength and heat-resistance.

The influence of chemical composition on the performance of the alkyd may be seen from the following facts.

Poly(ethylene adipate) and poly(ethylene terephthalate) are hard solids. The alkyds from glycerol and adipic acid, although liquid, are not very readily miscible with tolylene di-isocyanate, and a proportion of phthalic anhydride may be added to improve compatibility. A high proportion of phthalic anhydride leads to a brittle friable foam. The fluidity of an alkyd and the toughness of the foam may be increased by the substitution of propylene or diethylene glycol for glycerol, but the heat distortion temperature is lowered. Trimethylol propane yields adipates with better compatibility than glycerol, and similarly glycerol/Sebacic acid alkyds are more readily mixed than glycerol adipates.

All such alkyds are made with an excess of glycerol or other triol, a typical ratio being 3.0 moles of dicarboxylic acid to 4.0 moles of triol. Thus a considerable number of excess hydroxyl groups is available for subsequent reaction with di-isocyanate.

By stopping the esterification before it is complete, a certain number of carboxyl groups may be retained. Control of the reaction is maintained by measuring the water evolved and by periodic checks of acidity. The following analytical definitions should be known, as they are often required:

1. Acid number -- The acid number is defined as the number of milligrams of potassium hydroxide required to neutralise the acidity in one gram of resin.

2. Hydroxyl number -- The hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent of the acetic anhydride consumed in acetylation of one gram resin.

Convenient analytical procedures are given in the Appendix. The moisture content is found by the Karl Fischer or by the Dean-Stark method.

Table shows formulations for three alkyd resins which differ quite widely in their compatibility with tolylene di-isocyanate. For machine mixing a fairly low viscosity is required, which is brought about as explained above, by glycol addition at the expense of the heat-distortion temperature of the final foam.

Triols suitable for the production of rigid polyether foams may be made by the controlled polymerisation of propylene oxide and glycerol or 1,2,6-hexanetriol. This may be regarded as ether formation between terminal hydroxyl groups of glycerol and a polypropylene glycol:

\[
\begin{align*}
\text{HO(C_2H_4O)_n} & \text{OH} \\
\text{CH}_2\text{OH} & \text{HO(C_2H_4O)_n} \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]
A range of molecular weights is evidently possible, depending on the value of $n$: that is, on the molar ratios of oxide to glycerol. It will be seen that polyols of this type differ from alkyd resins in as much as no carboxyl groups are present. Any carbon dioxide will be produced by water addition. The specification will call for hydroxyl number, water content, pH value, colour, and presence of amine.

Technology of Production

When ’suitable’ alkyds or polyether triols as described above are mixed with a di-isocyanate, the foam produced is usually of poor quality. The product consists of coarse cells of irregular size and shape, while the expansion process may be inconveniently slow or excessively violent. There may be internal splitting or overall shrinkage. In an expanding foam, two different reactions are proceeding, evolution of gas and gelation of the resin. If the mass hardens too rapidly with respect to the generation of carbon dioxide, the latter develops considerable pressure and may rupture the cell walls. Conversely the gas may be produced early, while the cell walls are still soft and permeable. Under such conditions diffusion occurs and the cells may shrink. Control of the relative speeds of gassing and gelation is brought about by the use of catalysis. It has been found empirically that some of these have a greater effect on the reaction between isocyanate and hydroxyl groups than on that between isocyanate and water or carboxyl groups.

Many chemicals act as catalysts, for example caustic soda, sodium acetate, ferric acetylacetonate; but the most widely used substances are tertiary amines such as triethylamine, N,N-dimethylamine, N-substituted morpholines, and triethylenediamine (Dabco). They are chosen for reasons of solubility, volatility, lack of odour, and influence on reaction rate.

A dramatic improvement in the size and regularity of the cells can be brought about by the use of so-called ‘bubble-modifiers’. Silicone oils, polymeric substances such as thyl cellulose and cellulose acetate butyrate, and a variety of metallic soaps and organic wetting agents are effective. Their only common feature is an ability to lower the surface tension of the alkyd/isocyanate blend, though the polymers may also increase its viscosity. In accordance with the Gibbs theorem the concentration of solute (bubble-modifier) in the surface increases, the amount of energy required to create new free surfaces is decreased, and their stability once formed is improved.

If a low-density foam is required, but the amount of carbon dioxide available from residual carboxyl groups is low, water is deliberately added to the mix. Efficient dispersion of this water is necessary and an emulsifier is sometimes added. In commercial practice plasticisers, dyestuffs, or pigments are often required so that the actual composition which is caused to foam may contain six or seven components. Depending on the chemicals employed such mixtures may be unstable even in the absence of di-isocyanates. Formerly it was common to subdivide into simpler two- or three-components mixtures for storage purposes. There is nowadays a preference for choosing components which are mutually soluble and stable in the alkyd resin or polyether triol. Such systems are known as refabricated’ alkyds or polyols, and they have the great virtue that no complicated weighing or measuring operations are required.

Mass Production of Slab Foam

The original machine for production of Moltopen foam is the Henecke type (Fig. 1): The principles involved in the operation of this machine are described in detail, since later machines are simplifications or modifications to suit particular purposes.

Alkyd resin and tolylene di-isocyanate are pumped from separate thermostat-controlled storage tanks equipped with drying tubes, and blended together. In the absence of accelerators the mixture does not react appreciably during its short journey through the mixing head. Here it meets a finely divided spray of ‘activator’ in a carefully measured proportion. The activator is a solution of tertiary amines, emulsifier, and water. This solution is not very stable, and it is good practice to make it freshly each

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Early German resin</th>
<th>Sebalkyd resin</th>
<th>Experimental rigid-foam alkyd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Desmopen type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>—</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>2.5</td>
<td>—</td>
<td>3.0</td>
</tr>
<tr>
<td>Sebacic acid</td>
<td>—</td>
<td>2.0</td>
<td>—</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>0.5</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>Glycerol</td>
<td>4.0</td>
<td>4.1</td>
<td>—</td>
</tr>
<tr>
<td>Trimethylolpropane</td>
<td>—</td>
<td>—</td>
<td>3.0</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>—</td>
<td>—</td>
<td>2.0</td>
</tr>
<tr>
<td>Time of reaction with di-isocyanate</td>
<td>27 min</td>
<td>7 min</td>
<td>1 1/2 min</td>
</tr>
</tbody>
</table>

Table 1. Mixing time and molar ratios of three different alkyds producing rigid foams

(Contd. on P. 468)
The alkyd/isocyanate mixture, having been activated, now begins to react with great vigour, and it emerges from the mixing head as a thin cream. The mixing head runs back and forth on a fixed track across the width of a deep trough which is itself moving slowly backward—and at a slight inclination to the horizontal—past the mixing head. In consequence, ribbons of the creamy mixture are deposited across the bottom of the trough about 6-8 in. apart. They rapidly rise and swell, fusing together along their length, the slight tilt of the trough causing the expanding ribbons of foam to sag sideways against each other while still soft and sticky. The temperature inside the block of foam rises considerably and rapid hardening of the mass occurs. Within a minute or so the block behind the mixing head can be sawn off and stacked with others to finish its cure. Meanwhile fresh mixture is being laid down at a steady rate in the trough. The latter consists of two closely fitting sides butting against the stainless steel conveyor itself, the whole being lined with release paper.

(To be continued)
Recent Developments in Polyurathane—XIV

S.B. Iyer*

The Application of Isocyanates To Polymer Technology

General Considerations

As a result of the pioneering work of Staudinger, Mark, and others the following qualitative picture is believed to be true.

1. Small, typical organic molecules will not give materials which possess great hardness, high tensile strength, elasticity, or flexibility, giving these words their every day meaning.
2. Only where the molecular weight rises above, say, 5,000 do these properties begin to be significant.
3. All organic textile fibres, surface coatings, resinous plastics, and elastomers consist of such high molecular weight compounds.
4. These large molecules consist of smaller easily recognised units (mers) which are linked together by primary valency forces of conventional type. The length of these molecules is considerably greater than their diameter.
5. The wide difference in physical properties which are apparent in the different types of material given in (3) above are due to relatively minor differences in spatial configuration or architecture of the molecules, and also on the temperature, rather than on gross and fundamental differences in their chemistry.

There will be ample opportunity to test the truth of these generalisations, for in the following Chapters detailed information will be given on the synthesis and properties of fibres, films, rubbers, and plastics—all made from polyurethanes.

The basic rules for polymer building in organic systems were elucidated and formalised by Carothers, Kienle, and others the pioneering work of Staudinger, Mark, and others the following qualitative picture is believed to be true.

Rule 1—If a molecule has two functional groups (i.e., chemical linkages, atoms, or radicals which undergo reaction in the particular circumstances under discussion) then it can react with another bifunctional molecule to give a polymer. Such molecules are called linear, and typically they are thermoplastics. If these long molecules are capable of neat sideways packing and crystallisation, a fibre may be obtained exceptionally.

Rule 2—If a molecule having two functional groups reacts with a molecule having at least three functional groups, then a threedimensional network will eventually result. Such polymer networks are called ‘cross-linked’ structures, and they can be rigid thermoplastic or flexible vulcanised rubbers, depending on the mobility of the chains and their degree of cross-linking.

Each of these rules, in our experience, can be misunderstood by students and a word of explanation is desirable. Rule 1 states that a bi-bifunctional reaction may lead to a polymer. It does not state that a high polymer will be formed—on the contrary, unless a 1:1 ratio is taken, the molecular weight must be limited. More than once, in later Chapters, we deliberately make low molecular weight polymers by choosing ratios other than equimolar.

Rule 2 tells one nothing as to the practical utility of a particular bi-trifunctional system; but a reaction which proceeds rapidly and uncontrollably from reactant to cross-linked structure is technically useless. It is important to be able to produce, first of all, a linear or branched polymer which is capable of manipulation, and to bring about the cross-linking to the final shape at a later stage.

The Isocyanate Addition Reaction

The reader will probably be familiar with the idea of using an unsaturated molecule as an example of a bi-functional system in which polymerisation occurs by addition at double bonds. For example,

\[
\text{Catalyst} \quad \begin{array}{c}
(n + 1) \text{CH}_2=\text{CH}_2 \\
\rightarrow \\
\text{CH}_2(\text{CH}_2.\text{CH}_2)_n\text{CH}_2-\text{ethylene}
\end{array} \rightarrow \text{Polyethylene}
\]

He may also be aware of the elimination of a small unwanted molecule by a condensation between two reactive functional groups, for example the elimination of water when dicarboxylic acids and glycols react to form polymers. For example:

\[
nR(\text{CO}_2\text{H})_2 + (n + 1)R'(\text{OH})_2 \rightarrow 2n\text{H}_2\text{O} + \text{HO}.R'(\text{O}_2\text{C}R.\text{CO}_2R')_n\text{OH}
\]

He must now familiarise himself with the principle of the isocyanate addition reaction, in which a hydrogen atom present in a vulnerable group attaches itself to the nitrogen atom of an NCO group which is attacking it. Thus

\[
\text{R.NCO} + (\text{HX})\text{R'} \rightarrow \text{R.NCO} + (\text{HX})\text{R'}
\]

The most important examples in technical practice are the following:

1. The reaction between an isocyanate group and a hydroxy group is

\[ R \cdot \text{NCO} + \text{HO} \cdot R' \rightarrow R \cdot \text{NH} \cdot \text{CO} \cdot R' \]

The resulting assembly of atoms in the linkage (\(\text{NH} \cdot \text{CO} \cdot \text{O}_2\)) between \(R'\) and \(R\) is the same as that found in ethyl carbamate (urethane). It is this name which is now applied generally to the group, so that a polyurethane signifies a polymer in which a plurality of such linkages are present. In accordance with Rule 1 above, a linear polyurethane will be formed when a diol and a di-isocyanate react together, and in accordance with Rule 2 a cross-linked structure can be formed when a triol and a di-isocyanate react together.

2. The reaction between an isocyanate group and a carboxyl group is

\[ R \cdot \text{NCO} + \text{HO}_2 \cdot \text{C} \cdot \text{R} \rightarrow R \cdot \text{NH} \cdot \text{CO} \cdot R' + \text{CO}_2 \]

The reaction leads to the formation of an acid amide linkage, which is very similar to the urethane linkage in general chemical properties. Carbon dioxide is eliminated.

3. The reaction between an isocyanate group and an amine is

\[ R \cdot \text{NCO} + \text{H}_2 \cdot \text{N} \cdot \text{R'} \rightarrow R \cdot \text{NH} \cdot \text{CO} \cdot \text{NHR'} \]

This reaction gives rise to a substituted urea, evidently very similar in structure to urea itself (\(\text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2\)).

4. The reaction between an isocyanate group and water is

\[ R \cdot \text{NCO} + \text{H}_2 \rightarrow R \cdot \text{NH}_2 + \text{CO}_2 \]

It is this reaction which is used widely in the production of cellular polyurethanes, since the carbon dioxide is an excellent blowing agent. Reaction (2) is often found to provide insufficient gas, or is otherwise not available. Note also that the amine formed will normally react at once with a further quantity of di-isocyanate, as in (3).

5. The hydrogen atom which was originally attacked in a hydroxyl, carboxyl, or amine group is not eliminated; but is present in the new linkage, albeit with a very much lower chemical activity. The possibility exists for further sluggish reactions, as follows:

- \(R' \cdot \text{NCO} + R \cdot \text{NH} \cdot \text{CO} \cdot R' \rightarrow R' \cdot \text{O}_2 \cdot \text{C} \cdot \text{NR} \cdot \text{CO} \cdot \text{NR'}\)
- \(R' \cdot \text{NCO} + R \cdot \text{NH} \cdot \text{CO} \cdot R' \rightarrow R \cdot \text{CO} \cdot \text{NR} \cdot \text{CO} \cdot \text{NR'}\)
- \(R' \cdot \text{NCO} + R \cdot \text{NH} \cdot \text{CO} \cdot \text{NHR'} \rightarrow R \cdot \text{NH} \cdot \text{CO} \cdot \text{NR'} \cdot \text{CO} \cdot \text{NHR'}\)

A urethane can react to give an allophanic ester, an acid amide can react to give an acyl urea, and a substituted urea can give rise to a substituted biuret.

Another important reaction of the isocyanate group does not involve a hydrogen atom. This is the ability of the isocyanate group to react with itself under certain conditions to form dimers and trimers:

Sometimes these dimers are relatively unstable and regenerate the isocyanate on heating; sometimes, as with the dimer of tolylene di-isocyanate, the new compound is a new stable di-isocyanate of considerable importance.

It is a useful exercise to reflect upon the implications of the first reaction above. The hydroxyl groups may be phenolic or aliphatic. In the latter, they can be primary, secondary, or tertiary. The molecules containing them can be saturated or unsaturated. The isocyanates themselves can be either aromatic or aliphatic, long- or short-chain, rigid or flexible in their molecular structure. Evidently a vast number of technical combinations are possible. Similar considerations also apply to the second and third reactions, which are also capable of generating a large number of polymers.

**Manufacturing of Isocyanates:**

There are several possible synthetic routes to the production of isocyanates.

1. The phosgenation of amines or amine hydrochlorides.
2. The phosgenation of carbamic acids.

Generally speaking the direct reaction of amines is used for large scale production of aromatic di- and polyisocyanates, and the phosgenation of carbamic acids for production of aliphatic diisocyanates, while the more expensive process with amine hydrochlorides is a universal procedure for the laboratory preparation equally of aromatic or aliphatic isocyanates in good yield.

Three examples of these techniques are:

1. A solution of tolylenediamine in an inert solvent is fed slowly into an ice-cold solution of phosgene. A fine suspension forms which is the hydrochloride of the carbamic acid chloride:

   ![Diagram](https://via.placeholder.com/150)

   - \(\text{Me} \cdot \text{NH}_2 \rightarrow \text{COCl}_2 \rightarrow \text{Me} \cdot \text{NH}_2 \cdot \text{HCl}\)
   - \(\text{NH}_2 \cdot \text{CO} \cdot \text{Cl}\)
In the second stage the suspension is slowly heated with a further addition of excess phosgene. The carboxylic acid chloride group evolves HCl and changes to an NCO group, while the remaining amine hydrochloride group reacts in the usual way and supplies the second isocyanate group:

2. One mole (190g) of powdered hexamethylenediamine hydrochloride was suspended in 1 l. of dichlorobenzene and phosgenated at 190°-195°C. The solution after 18 hours was clear. The solvent was removed over a Widmer column and 160g (15%) of hexamethylene di-isocyanate were obtained with a boiling point of 132°C/15mm.

3. 345g of 1,4-diaminocylohexane were dissolved in 3 l. of o-dichlorobenzene and saturated with carbon dioxide at 90-95°C. 700g of phosgene were introduced below 0°C into the cold suspension of carbamic acid. Carbon dioxide was evolved. The solution was heated to 160°C and a further quantity of phosgene was added until a clear solution was obtained. The solvent was removed by fractional distillation to give a mixture of liquid cis-1,4-cyclohexylene di-isocyanate and solid trans-1,4-cyclohexylene di-isocyanate, m.p. 63-64°C.

Properties:
The aliphatic mono- and di-isocyanates are usually colourless lachrymatory liquids. The aromatic di-isocyanates are not such active lachrymators but the more volatile ones such as tolylene di-isocyanate produce asthmatic symptoms in sensitive subjects. In non-volatile aromatic polyisocyanates this effect is not generally noticeable and protective masks are not required.

Pure isocyanates, in the absence of catalysts, are relatively stable in storage and can be distilled under vacuum. The presence of activating nitro and chlorine groups reduces the storage life and increases general reactivity. The presence of alkyl and alkoxy groups leads to a less active molecule, particularly when in the opposition to the isocyanate group. Generally speaking the aromatic di-isocyanates are much more reactive than the aliphatic series; while with respect to the active hydrogen reactants, primary amines are more reactive than carboxylic acids and primary alcohols. Secondary alcohols are much slower than primary alcohols. Tertiary amines do not themselves react, but they are powerful catalysts for other groups. The usual method of comparing the reactivity of different functional groups is to take, for example, one particular isocyanate and find the rates of reaction between it and a series of alcohols, or amines. The procedure is then reversed and a particular alcohol, or amine, is reacted with a series of isocyanates.

The kinetic measurements are made with great care, using dilute anhydrous solutions in an inert solvent. Thus, solutions of n-butanol and P-tolyl isocyanate were allowed by Carver and Hollingsworth to react in dilute toluene solution. Samples were withdrawn at intervals and the reaction quenched in di-n-butylamine, the excess of the latter being determined by titration with 0.05N Sulphuric acid.

Stoechiometry: Having built up a picture of the speed at which reaction occurs between different reactants, with or without the presence of solvents and catalysts, it is now necessary to use the right amounts of reactant in each case.

The di-isocyanates employed technically are pure chemicals-usually of 99.5% purity or better-so their equivalent weight is not in doubt. Important exceptions are the technical grade of diphenylmethanediyl (diphenylmethane) di-isocyanate (I.C.I. Ltd.) and the polyarylene polyisocyanate of the Carwen Chemical Co.). On the other hand, technical polyols are usually mixtures of polymeric molecules, and an experimental value must be found. This is often expressed as an 'isocyanate equivalent'-in other words, the weight in grams of the polyol which reacts with one equivalent of an isocyanate. An alternative method is to give a 'reactivity number,' the number of milligrams of KOH equivalent to the CO₂H and OH groups present in one gram of the polyol or polyester resin. These two measurements can readily be interconverted: for example, a 'reactivity number' of 56.1 mg KOH per gram of resin signifies that 1,000 g of resin would be equivalent to 56.1g of KOH and therefore to one gram equivalent of any isocyanate.

Conversely, an isocyanate-terminated resin may be referred to as containing '2.1% NCO groups'. This merely means that one gram equivalent (i.e. 42g of NCO) is present in 2,000 g of resin.

More dilute solutions of isocyanate-terminated resins are often described as containing 'x mg NCO/ml of solution'. Since the solids content of the solution may not be known with certainty, this method of describing the 'isocyanate content' or reactivity is more convenient than 'per cent NCO groups', since the equivalent weight of amine or polyol can be calculated directly from the isocyanate content.

Finally, it must be remembered that water must be carefully excluded from all isocyanates and isocyanate-terminated resins during storage.

(To be continued)
Rationelle und flexible PUR-Verarbeitung

Werner Russ

Wie vielen anderen Industriezweigen blieb auch den PUR-Verarbeitern die Erkenntnis nicht erspart, daß eine kostengünstige, flexibel auf die jeweiligen Marktanforderungen reagierende Produktion ohne Rationalisierung und Automatisierung nicht möglich ist. Die Frage ist nur: Wo soll man damit anfangen, und wann kann man damit aufhören? Verständlicherweise gibt es darauf keine Antwort, die für alle PUR-Verarbeiter in gleicher Weise schlüssig und verbindlich wäre. Hier kann es lediglich darum gehen, die nahezu unübersehbare Palette der Automatisierungs- und Rationalisierungsmöglichkeiten wenigstens andeutungsweise aufzuzeigen.

„Zerlegte“ Produktionseinheit

Die Frage hängt sich auf: Wo bieten sich die Möglichkeiten? Beide man allerdings vergebend; zutreffender wäre daran zu denken, daß Produktionseinheit gegebenenfalls auch in den vorstehenden Teilen zu zerlegen ist in:

- Dosieranlage
- Transportmittel
- Werkzeuge und Werkzeugträger
- Hilfsmittel für Zufuhr und Abtransport
- Handhabungsgeräte für bestimmte Tätigkeiten

Die Dosieranlage

Bei den Dosierseinheiten stehen neue vielfältige Möglichkeiten zur Verfügung:
- selbsttätige Mischköpfe zum Einbringen in geschlossene und offene Werkzeuge
- automatisch wechselbare Mischkopfdusen
- automatische Pumpenverstellung
- automatisches Wechseln der Komponentenfarbe (4-K-D-Mischkopf)
- automatische Rezeptverstellung von Schuß zu Schuß
- automatisch geregelte Gasbeladungskontrolle

In Verbindung mit Dosiermaschinen, die in bestimmten Bereichen über eine Hochstmaß an Flexibilität verfügen, lassen diese Maßnahmen heute durchaus einen vollautomatischen Ablauf zu.

Transportmittel

Früher waren Transporteinrichtungen gewissermaßen Einzweckanlagen, die waren für ein genau definiertes Teil gebaut, und wenn die Produktion dieses Teils ausfiel, waren auch die Transportanlagen mehr oder weniger am Ende. Sie konnten überhaupt nicht oder allenfalls mit kostspieligen Umrüstungsaktionen neuen Erfordernissen angepaßt werden. Das Flurrundtischsystem einer Firma aus Lemförde hat dagegen nahezu unbegrenzte Möglichkeiten, sich Produktionsänderungen problemlos realisieren lassen. Damit hat dieses System schon von vornherein entscheidende Möglichkeiten zur rationellen Fertigung eröffnet (Bild 2). Dennoch läßt sich auch auf diesem Gebiet noch eine Menge tun. Transporteinrichtungen können zur Automatisierung der Produktion beispielsweise folgendermaßen beitragen:

- automatischer Bewegungsablauf mit einer Positionierungsgenauigkeit von ± 1 mm
- automatisches Temperieren der...
Rationelle und flexible PUR-Verarbeitung

weilen unterschiedlichen Werkzeuge durch mitlaufende Tempenergeräte - automatisches Trennen in allen Bereichen
- effektive Befüllung der Werkzeuge, z. B. durch Auslassen der Werkzeuge die wegen der Kapazitätsauslastung vorübergehend nicht benötigt werden.

Werkzeuge und Werkzeugträger

Ein besonders hoher Stellenwert bei den Bemühungen, die Produktion zu automatisieren, kommt auch der Konstruktion und der Ausstattung der Werkzeuge zu. Im einzelnen heißt das:
- automatische Werkzeugidentifizierung
- automatisches Öffnen und Schließen des Werkzeugs
- automatischer Verschluß des Angusses (Bild 3)
- Einbau automatischer Entformungshilfen


Hilfsmittel für Zu- und Abtransport

Die für die Fertigteilherstellung notwendigen Halbzeuge und Rohstoffe können heute schon automatisch zu- und abgeführt werden. Neben dem automatischen Befüllen der Arbeitsbehälter gibt es indes weitere Automatisierungs möglichkeiten:
- automatische Zuführung von Einlege- teilen
- automatischer Abtransport der Fertig- teile zur Weiterbearbeitung oder zur Lä- gerung

Handhabungsgeräte für bestimmte Tätigkeiten

Der Begriff Handhabungsgeräte läßt sich bspw. durch den zeigenden Terminus Roboter ersetzen. Bei der PUR-Verarbeitung sind damit hauptsächlich Hilfsmittel gemeint, die dann eingesetzt werden können, wenn solche Tätigkeiten automatisiert werden sollen, die sich ständig wiederholen oder die sich auf die Mitarbeiter belastend auswirken können. Dazu gehören vor allem:

Einführen von Werkzeugen
Platzierung von Einlege- teilen
Fertigstellung von Fertigteilen und ihre Weiterleitung (Bild 4).
Rationelle und flexible PUR-Verarbeitung

Bild 5: Die von EMB patentierte automatische Pumpenentlüftung verhindert Kri­
stallisation und Kavitation und somit Pro­
duktionsausfall

- Applikation von En­setten oder sonsti­
gen Identifizierungsmerkmalen
- Lackierarbeiten

Last not least: die Wartung

Es ist eine Tatsache, daß jedes Produktions­mittel eines bestimmten Maßes an Wartung bedarf. Dennoch müssen auch PUR-Verarbeiter nicht vor der Wartung fliehen. Dazu gehört die regelmäßige Überprüfung der Pumpenentlüftung, um Kri­
stallisation und Kavitation zu verhindern. Die von EMB patentierte automatische Pumpenentlüftung verhindert Kri­
stallisation und Kavitation und somit Pro­
duktionsausfall.

Bild 6: Automatische Vorrichtung zur Nachstellung von Dichtungen an Kolben­
dosiermaschinen (Werkbilder: Elasto­
gran)

Kosten-Nutzen-Analyse gibt Auskunft

Es sollten eingangs angegeben werden, daß die PUR-Verarbeiter den auf spezi­
sischen Verarbeitungsprodukten basie­enden Automatisierungsgrad selbst ermit­
teln. Ein Patentrecht gibt es hier ge­
dankbar wenig wie auf anderen Gebieten. Deshalb ist die Effizienz der aufgezeigten Maßnahmen in einer Kosten­
Nutzen-Analyse jederzeit nach­zu­
derbar.

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teil

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Design

Optimizing a PU Formulation by the Taguchi Method

By the careful choice of a small set of initial trials according to the Taguchi Method, a polyurethane (PU) formulation for a commercial appliance was quickly and efficiently developed.

The Taguchi Method

The Taguchi Method is a strategy for off-line quality control, conducted at the product and process design stages of the manufacturing cycle to improve product manufacturability and reliability, and to reduce product development and lifetime costs. Dr. Taguchi developed his ideas approximately forty years ago as a communications engineer in Japan. Today, he and his systems are becoming well known in the United States, particularly by organizations supplying the automotive industry.

In the United States, Dr. Taguchi is often exclusively associated with statistical experimental design. But actually, Dr. Taguchi's method is a comprehensive, three-stage process for direct product development in which statistical experimentation is simply a tool. Taguchi's three stages are system design, parameter design, and tolerance design. System design is the process of applying scientific and engineering principles to develop a working prototype. Tolerance design is a method for determining final product specifications. Whereas these stages are essentially equivalent to the traditional activities of scientists and engineers, parameter design is the distinguishing characteristic of the Taguchi Method.

Parameter Design

Parameter Design is a process in which design parameters under the direct control of the product designer are varied in a scientific fashion to determine the best or optimum settings for these variables. For practically any product, there is a working range of possible settings of the variables. For example, in a polyurethane formulation, the product designer can select particular settings of water contents, chlorofluorocarbon-11 (CFC-11) concentrations, and catalyst types to produce a usable foam. Different combinations of these design settings or levels, however, will also vary the quality of the product under development. Although an acceptable product may be produced, it is likely that a particular combination of levels will produce a superior product.

According to Taguchi, the product designer must not only produce a working prototype, but must also explore the parameter settings fully to develop the one that works best. Unfortunately, in the West, parameter design is often passed over or performed poorly simply because efficient methods to study the parameter design space are unknown. The tool Dr. Taguchi recommends for parameter design experiments is statistical experimental design, which greatly improves both the efficiency and reliability of experimental work. In particular, Dr. Taguchi recommends orthogonal array experiments as the basic tool for optimization.

Orthogonal Array Experiments

The function of an orthogonal array is to select a subset of the entire parameter design space, i.e., all combinations of

<table>
<thead>
<tr>
<th>Table I</th>
<th>Factors and Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Number of levels</td>
</tr>
<tr>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>Poly. type</td>
<td>4</td>
</tr>
<tr>
<td>Catalyst</td>
<td>5</td>
</tr>
<tr>
<td>package</td>
<td>4</td>
</tr>
<tr>
<td>Surfactant</td>
<td>3</td>
</tr>
<tr>
<td>Water wt% 2</td>
<td>10</td>
</tr>
<tr>
<td>CFC-11 wt% 2</td>
<td>25, 35</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>2</td>
</tr>
<tr>
<td>type</td>
<td>3</td>
</tr>
<tr>
<td>Constraints</td>
<td>105, hydroxyl number = 410 ± 20, all surfactant conc @ 1%</td>
</tr>
</tbody>
</table>

*Sohelia R. Lunney and Joseph M. Sutej, Mobay Corporation, Pittsburgh, Pennsylvania*
Design

Table 2. Taguchi L25 Screening Experiment.

<table>
<thead>
<tr>
<th>Polyol/ Trial water</th>
<th>Surfactant</th>
<th>CFC-11 Isocyanate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>D</td>
<td>4</td>
</tr>
<tr>
<td>E</td>
<td>E</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3. Laboratory Screening Experiment Results.

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>Cream time, sec</th>
<th>Gel time, sec</th>
<th>Core density, pcf</th>
<th>k-Factor Btu in/h F ft²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>10</td>
<td>1</td>
<td>613.7</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>26</td>
<td>1</td>
<td>133</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>13</td>
<td>1</td>
<td>127</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>11</td>
<td>1</td>
<td>122</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10</td>
<td>1</td>
<td>122</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>14</td>
<td>1</td>
<td>122</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>122</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>122</td>
</tr>
</tbody>
</table>

The Basic Approach

Dr. Taguchi's approach to industrial experimentation is outlined below:

- Define the problem and the experimental objectives.
- Assemble a group knowledgeable with the problem area, and brainstorm factors and levels to be included in the design.
- Design the experiment by selecting and modifying an appropriate orthogonal array.
- Conduct the experiment, analyze the data, and interpret the results.
- Run confirmatory trials to determine whether the optimal settings derived from the parameter design experiment actually result in visible improvements.

The team approach and brainstorming are employed to prevent preconceived notions from unduly biasing the scope of the experiment. Further, the stress on confirmatory trials follows from the fact that all fractional-factorial designs achieve their economies through confounding main effects with interactions among factors. If Dr. Taguchi's recommendations are followed, the resulting parameter design experiments will often confound the main effects of interest with two-factor and higher-order interactions.

Usually, two-factor interactions are assumed to be not present in an orthogonal array screening experiment or they will at least be dominated by the main effects of interest. In chemical systems, this is often a highly questionable assumption. Its lack of validity, if present, will be shown by the confirmatory trials. Additional trials will then be required to understand exactly what effects and interactions are important.

Experts in the field of study often can assess from first principles or experience whether interactions should be accounted for in the initial screening experiments. According to Dr. Taguchi, this further demonstrates the need for engineers and scientists to design their own statistically guided experiments.

Formulation Development Application

This study was conducted shortly after one of the authors attended a two-week training session in the Taguchi Method. Its objective was to find a commercially feasible application for an experimental polyol product. A brainstorming session was conducted to select factors and levels for investigation. The initial objective of this project was to screen a number of...
**TABLE 4: Optimum Factor Combinations in Order of Significance for the Responses.**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>
| A. | Cream time, sec | Target 5-6
   | Catalyst: 3, 4 or 5
   | Polyol: B or C
   | Water: 1 or 5 |
| B. | Set time, sec | Target 26-30
   | Polyol: B, C, or D
   | Water: 1 or 5
   | Catalyst: 3, 4, or 5
   | CFC-11 25 |
| C. | Core density,pcf | Target 1.50-1.60
   | CFC-11: 35
   | Water: 1 or 5
   | Polyol: B or C |
| D. | Flow, cm | Target 125-140
   | CFC-11: 35
   | Water: 1 or 5
   | Polyol: B |
| E. | Free rise density,pcf | Target 1 or 20
   | CFC-11: 35
   | Water: 1 or 5
   | Polyol: B |
| F. | k-Factor, Btu in/hr °F ft² | Target smallest best
   | Polyol: A
   | Catalyst: 3
   | Water: 0 or 5
   | CFC-11 25 |

possible formulation combinations to determine exactly what parameter settings, if any, produced a reasonable foam product.

The factors and levels listed in Table 1 for investigation in this initial screening study were assigned to Taguchi's L̄₀ orthogonal array using some advanced techniques of design construction that are beyond the scope of this article. Taguchi's method for assigning orthogonal array experiments may be found in his System of Experimental Design (AS1 Press, 1987). The resulting experiment is presented in Table 2.

The construction of this design required repetition of certain factor levels of the catalyst variable more than others as a consequence of the balancing property of the orthogonal array. While a four-level column for the polyol/water factor could be included using Taguchi's recommendations without losing the balancing property of the array, a five-level column cannot be constructed directly. Instead, a seven-level column was created for the catalyst variable and two extra levels were replaced with an existing level considered to be of great importance. Taguchi calls this procedure "dummy treatment" and has a detailed discussion of it in his book.

In order to use the L̄₀ orthogonal array, it was necessary to combine the water and polyol levels using a technique called combination design. Thus, the main effects of both polyol and water were estimated under the assumption that no interaction existed between the two factors.

**Experimental Procedure**

Reactivity profile and friability (subjective rating) were determined from hand-mix foams prepared in 1-gal paper cans. Free rise densities were measured on core samples of open blow foams. Height of rise at gel, final rise height, and flow ratio were determined in a flow tube.

Minimum-fill-density and packed panels were prepared in a 2- x 3- x 25-in mold press at 120°F. Core densities and k-factors were determined from core samples of packed panels. The "freeze stable density" of a foam is defined as the lowest density above the minimum-fill-density that exhibits no significant changes in dimensions after being held at 20°C for at least 2 hrs. The bottom sections of the packed panels were tested for compressive strength.

Isocyanate and masterbatch temperatures were maintained at 20°C. Masterbatches were cooled down to 12°C before panels were prepared in the mold press.

The 16 trials were performed in a completely random fashion to avoid experimental bias from unknown sources of variation. The randomized sequence is shown in Table 3 along with values of some of the nine response variables studied. Other variables included flow and demold properties.

Most of the foams produced were of poor quality, as expected, since the purpose of the study was to deliberately induce variation into the results to determine important factor effects. The notable exception was trial #14, a low-density foam system with good freeze stability and thermal conductivity.

**Data Analysis**

The analysis was done in two parts. First, the statistical significance for each response was assessed using the Analysis of Variance or ANOVA. This procedure essentially determines whether the total variation observed in a set of trials is due to chance and simultaneously determines the contribution of each factor to the total variation.

**TABLE 5: Factor Settings in Order of Decreasing Performance for Optimal Foam Performance.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>Level</td>
</tr>
<tr>
<td>Polyol</td>
<td>C or E</td>
</tr>
<tr>
<td>CFC-11</td>
<td>35</td>
</tr>
<tr>
<td>Water</td>
<td>1.5</td>
</tr>
<tr>
<td>Catalyst</td>
<td>3.4 or 5</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>11</td>
</tr>
</tbody>
</table>

**TABLE 6: Confirmatory Trials Suggested by Table 5.**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Polyol</th>
<th>Catalyst</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>3</td>
<td>Pass</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>3</td>
<td>Fail</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>4</td>
<td>Pass</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>4</td>
<td>Fail</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>5</td>
<td>Pass</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>5</td>
<td>Fail</td>
</tr>
</tbody>
</table>


The analysis was done in two parts. First, the statistical significance for each response was assessed using the Analysis of Variance or ANOVA. This procedure essentially determines whether the total variation observed in a set of trials is due to chance and simultaneously determines the contribution of each factor to the total variation.

Second, for those factors that were determined to be statistically significant, the levels responsible for the best performance were identified. The underlying model of this screening experiment was too complex to be analyzed by the simple analysis tools of the Taguchi Method. Instead, the results were analyzed using the General Linear Models procedure contained in the SAS statistical analysis program. These analyses revealed a significant "lack of fit" for many of the responses, i.e., the assumptions concerning the absence of interactions among the factors was unjustified. Nevertheless, several main effects of importance were identified for each response.

The results are summarized in Table 4, in which the relative importance of factors and their optimal setting is presented in descending order of significance. The various responses differ with respect to their optimal factor and treatment combinations. For example, density and flow are most strongly influenced by the CFC-11 and polyol factors, while the catalyst is the single most significant factor affecting cure time.

A desirability scale was assigned to each response to establish those factors that produced the best overall performance. These factors and their levels are shown in Table 5. The analyses indicated no significant difference among any of the surfactants and only a slight preference for one of the isocyanates, so these two factors were set at their most economical levels.
Design

At this stage, foam performance was judged more critically, and the foams were graded on a “pass fail” basis to simplify interpretation. The results listed in Table 6 clearly indicate that polyols B and C are not equivalent, as suggested by the initial design. Instead, all foams produced with polyol C were too fast for existing commercial processing.

The properties of the acceptable foams given in Table 7 demonstrate remarkable similarities, especially their kinetic properties. Obvious differences exist, however, in their thermodynamic properties, especially thermal conductivity. Presumably, these differences are due to the catalyst. The data in Table 7, however, are not sufficient to reliably estimate the effect of catalyst. These data do suggest that the experimental polyol will indeed produce a commercial product.

Final Product Optimization

Polyol B (Multanol E-9250) was further studied by means of Response Surface Methodology. The objectives of this final study were to remove remaining ambiguities about the effects of catalyst, water content, and CFC-11 content; to develop an advanced computational model for all important parameters of the urethane product; and to determine the optimum settings for all parameters. The result of these final studies was a commercial product (Tables 8 and 9), now under patent protection, with good thermal conductivity (k-factor) and, as illustrated in Figs. 1 and 2, exceptional demold characteristics. The demold properties of this product result in increased productivity for the customer without capital investment, in accordance with the Taguchi philosophy.

Conclusions

1. Taguchi’s group approach to problem solving resulted in highly efficient use of both personnel and material resources. Although more time was required to plan experiments, the overall time required to complete this project was far less than

![FIGURE 1. Demold properties. By butt opening method](image1)

![FIGURE 2. Demold properties. % thickness change method](image2)
required for conventional experiments. Further, the wealth of information obtained during the brainstorming sessions did serve to prevent experimental bias and ensure a broad search for applications.

2. The 16-trial screening experiment, although somewhat complicated, made very efficient use of technical resources and identified critical factors and levels for further study.

3. The six additional confirmatory trials removed some ambiguities concerning blend composition and verified that commercially feasible foams could be produced from the experimental polyol.

4. The authors found Taguchi's orthogonal arrays to be too restrictive and inefficient for final product optimization, so nonlinear methods were used for this purpose. Thus, in the authors' laboratory, the Taguchi Method has become a screening tool in formulations development.

5. A commercial product, Multanol E-9280, with exceptional demold properties was perfected as an end result of this study.

Although some of Dr. Taguchi's techniques are controversial and are a matter of dispute among statisticians, the Taguchi concept of direct product design has been accepted and promoted by Mobay management and is currently being directed toward the CFC issue in rigid foam formulations.

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Je nach Aufarbeitung stehen unterschiedliche Stationär- und Mobilanlagenkonzepte im gewünschten Automationsgrad zur Verfügung, die aus folgenden Bausteinen zusammengesetzt werden:

### Anlagenbausteine

**Dosiermaschinen:** Zur Verfügung stehen zwei unterschiedliche Verfahren zur Dosierung der Rohstoffkomponenten: Die Pumpendosierung RIM-Star und die Kolbendosiermaschinen aus der KK-Serie. Beide Dosiermaschinen basieren auf Baukastensystemen und können genau nach Produktionsbedürfnissen zusammengestellt werden.


Polyurethan-Verarbeitung

- Absaugsysteme, gegebenenfalls mit Frischluftzu- 
  fuhr, entsprechend den gesetzlichen Vorschriften,
- Wärmerückgewinnungsanlagen,
- Sprühanlagen für manuellen oder vollautomatischen Trennmittel- bzw. Farbeintrag,
- Handlinggeräte für die Zu- 
  fuhr von Einlegezeilen, die Teilentnahme, den Abtransport der Produkte, Abfälle usw.,
- Komponenten-Tanklager und Vormischstationen sowie Bild 2 Neunachsiger Mischkopf-Roboter für den vollautomatischen Komponentenaus- 
  trag. Die Überlagerung der programmierten Bahnrutschen mit der eingestellten Geschwindigkeit des kontinuierlich umlaufenden Formenträger-Förderers erfolgt vollautomatisch.

- Sicherheitseinrichtungen. 
  Steuerung, Prozeßdatenerfassung: Abhängig vom Automatisierungsgrad und sonstigen Anforderungen kommen Relais-, SPS- und NC-Steuerungen zum Einsatz. Durch die modulare Bauweise wird eine hohe Flexibilität erreicht.

Einfache Dateningabe: An der Prozeßüberwachung PUC werden Produktionsdaten wie Teilegewicht, Mischungsverhältnis, Material- 
  alternaturen, Drucke, Schützzeiten und deren Toleranzen am Industriemonitor: über eine Folientastatur eingegeben. Alle Daten lassen sich speichern und stehen nach einer Produktionsumstellung wieder zur Ver- 
 fügung. Die Prozeßparameter werden erfaßt, über- 
  wacht und können als Schaumprotokoll mit Teile- 
  nummer und Uhrzeit ausgedruckt oder auch einem Leitrechner übermittelt werden.

Der Benutzer wird über ein Menü durch das Programm geführt und bekommt angezeigt, welche Tasten zu betätigen sind. Ein weiterer Bedienkomfort ist die automatische Bahn- 
  geschwindigkeitskorrektur des Mischkopf-Roboters bei Schutzzeitwechsel. Ebenso synchronisiert sich die Roboterbewegung automatisch mit den kontinuierlich umlaufenden Schäum- 
  formen und überlagert ihre im stationären Zustand programmierten Bahnrutschen automatisch mit der Ge-

schwindigkeit des Förde- 
  rers.

Produkt, Produktivität, Fertigungstechnik, Her- 
  stellungsschritte und Herstel- 
  zeltzeiten führen zu den grundsätzlichen Entschei- 
  dungen zwischen zwei Anlag- 
  kenkonzepten.

Stationärenanlagen

Beispiel: Anlage zum Hinterschaumvorn der unter- 
  schiedlichen PKW-Teppich- 
  chen. Die Anlage besteht aus einer RIM-Start Pum- 
  pendosierrmaschine mit 19 Mischköpfen zum Schäu- 
  men in geschlossenen Formen. Pro Schaumvorgang sind je nach Teppich zwi- 
  schen einem und vier Mischköpfen angeschlossen. Die Produktionsdatenerfas- 
  sung PUC überwacht die Produktion und protokolliert jeden einzelnen Schuß. Neun Formenträger stehen zu Dreifachgruppen zusammenzusammengaß taus und 150° nach hinten geschwenkt. Die Schaumprogramme werden freigegeben. Der geschlossene For- 
  träger kann noch während des Schaumvorganges seine vorgewählten oder opt. 
  malen Molkenlagen schwenken. Die Positionen verteilen sich zwischen 30° und 150° nach hinten. Auf Stationäranlagen 
  werden z.B. PKW-Teppiche und Motorradsitze hinten- 

Mobilanlagen

Beispiel: Rundtisch anlage zur Herstellung von textil- 
  hinterschaumten PKW-Sitz- 
  zeilen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhärten. Das Produk- 
  tionskonzept für die runde 
  fettung von Auto- 
  mobil-Sitzelementen ist nach den spezifischen An- 
  forderungen des Auf- 
  abers entwickelt und im 
  maßgeschneiderte Polyure- 
  than-Anlage umgesetzt. Der Taktbetrieb wird in Taktbetrieb, die Zonen mit unterschiedlichen Stauhären...


Beispiel: Ovalanlage - kontinuierlich umlaufend zur Herstellung von PKW-Sitzteilen mit unterschiedlichen Stauhärten (Bild 3).

Bis zu 60 unterschiedliche Schaumkammern (Rücksitz, Vordersitz und entsprechende Lehnenden) werden gleichzeitig produziert. Die wesentlichen Bausteine dieser Anlage:

- E-Gitteranlage mit einem Duplex- und einem UL-Mischkopf,
- Mischkopf-Roboter, neunachsig und NC-gesteuert.
- Umlaufanlage mit Energieversorgungseinheiten,
- Formenträger und Absaug- und Sicherheitsanordnung.

8.9 Standards for Polyurethanes:

American Chemical Society for Testing Materials (ASTM)

Index:

- Polythanes
  - free toluene diisocyanates in urethane prepolymer/coating solutions, by gas chromatography, test, (D 3432) 06.02
  - furniture and automotive cushioning, bedding, and similar applications, spec., (D 3453) 09.02
  - isocyanate groups in urethane materials/prepolymers, test, (D 2572) 06.02
  - suspended matter, test, (D 4670) 08.03
  - vinyl-coated/urethane-coated indoor upholstery fabrics, spec., (D 3690) 07.01

- Polythanes—coatings
  - n-butyl acetate (99.5 % grade) in, spec., (D 3726) 06.03
  - ethyl acetate (99.5 % grade) in, spec., (D 3727) 06.03
  - free toluene diisocyanates in urethane prepolymer/coating solutions, by gas chromatography, test, (D 3432) 06.02
  - isocyanate group content, test, (D 2572) 06.02
  - methyl ethyl ketone in, spec., (D 3729) 06.03
  - 2-ethoxyethyl acetate (99 % grade) in, spec., (D 3728) 06.03

- Polythanes—foam
  - bonded, spec., (D 3490) 09.02
  - isocyanate raw materials, testing, (D 1638) 06.03, 08.02, 09.02, 09.02
  - polyol raw materials, testing, (D 2849) 08.02
  - polyurethane (high resilience), spec., (D 3770) 09.02
  - rate-of-rise (volume increase) properties, test, (D 2237) 08.02
  - rigid, spec., (D 2341) 08.02
  - slab, bonded, and molded, testing, (D 3574) 09.02
  - toluene diisocyanate, for, spec., (D 1786) 08.02

- Polythanes—microcellular
  - flexural recovery, test, (D 3768) 09.02
  - high temperature sag, test, (D 3769) 09.03
  - shoe sole materials, spec., (D 3851) 09.02
  - testing, (D 3489) 09.02

- Polythanes—polyurethane insulation
  - composite perlite board/rigid cellular polyurethane composite roof insulation, spec., (C 984) 04.06
  - design considerations/spray application, practice, (C 945) 04.06
  - hydroxyl numbers of polyols, test, (D 4274) 08.03
  - membrane-faced rigid cellular polyurethane roof insulation, spec., (C 1013) 04.06
  - primary hydroxyl content of polyether polyols, by nuclear magnetic resonance spectroscopy, test, (D 4273) 08.03
  - repairing, practice, (C 950) 04.06
  - spray-applied rigid cellular polyurethane thermal insulation, spec., (C 1029) 04.06

- Polythanes—polyurethane raw materials
  - hydroxyl numbers, test, (D 4274) 08.03
  - primary hydroxyl content, by nuclear magnetic resonance spectroscopy, test, (D 4273) 08.03
  - urethane foam raw materials, testing, (D 2349) 08.02

- Polythanes—polyurethane raw materials (isocyanates)
  - acidity of toluene diisocyanate, test, (D 4667) 08.03
  - amine equivalent of crude/modified isocyanates, test, (D 4666) 08.03
  - assay, test, (D 4665) 08.03
  - freezing point of toluene diisocyanates, mixtures, test, (D 4664) 08.03
  - hydrolyzable chlorine content of toluene diisocyanate, test, (D 4663) 08.03
  - isomer content of toluene diisocyanate, test, (D 4660) 08.03
  - specific gravity, test, (D 4659) 08.03
  - total chloride, test, (D 4661) 08.03

- Polythanes—polyurethane raw materials (polyls)
  - acid/alkalinity numbers, test, (D 4662) 08.03
  - sodium/potassium content, test, (D 4668) 08.03
  - specific gravity of polyls, test, (D 4669) 08.03
  - unsaturation of polyls, test, (D 4671) 08.03
  - water content of polyls, test, (D 4672) 08.03

British Standard Institute (BSI)

Index:

- Polyurethane
  - coated fabrics, for upholstered furniture, DD07
  - coated fabrics, for water resistant clothing, 3545(1)
  - coated nylon fabric, for mattress covers, 5223
  - enamelled copper round winding wires, 6811(3.1)
  - flexible foam for loadbearing applications, 3379
  - flexible foam sheeting for laminates, 4021
  - polyurethane-based cold poured sealants, for concrete pavements, 521
  - preformed rigid foam, for thermal insulation of pipework, 5608
  - rigid foam produced by press injection method, 6586
  - rigid foam, for construction sites, 5241
  - rigid foam, for on-site production, 5241
  - rigid foam, slab form, 4840
  - rigid foam board, 4841
  - sprayed rigid foam, for thermal insulation of roofs, 7021
  - threads, methods of test, 5421(2)
- Polyurethane foam mattresses, 4571
- Polyurethane foam pillows, 5340
- Polyurethane foams
  - hospital mattresses, 5223(2)
  - hospital pillows, 5223(3)
Standard Specification for
Rigid Urethane Foam

1. Scope

1.1 This specification covers a class of rigid cellular materials known as urethane foam or rigid cellular materials made from urethane raw materials where other types of repeated structural units are present such as polycarboximide or polyisocyanurate. Urethane foam may be generally defined as an expanded cellular product produced by a catalyzed reaction of polyisocyanates with polyhydroxy compounds. The detail requirements of this specification apply to the core material of the sprayed, laminated, molded, or foamed part. In the event that the product does not lend itself to testing of the core, specific test samples shall be agreed upon by the seller and the purchaser.

1.2 The values stated in SI units are to be regarded as the standard.

Note 1—For specific applications refer to ASTM Committee D-10 on Packaging, C-16 on Thermal and Cryogenic Insulating Materials, (in particular ASTM Specification C 591 for Rigid Perfumed Cellular Urethane Insulation), and F-7 on Aerospace Industry Methods.

2. Referenced Documents

2.1 ASTM Standards:
C 203 Test Methods for Breaking Load and Flexural Properties of Block-Type Thermal Insulation
C 273 Method for Shear Test in Flatwise Plane of Flat Sandwich Constructions or Sandwich Cores
C 355 Test Method for Water Vapor Transmission of Thick Materials
D 149 Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies
D 257 Test Methods for D-C Resistance or Conductance of Insulating Materials
D 790 Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Material

D 1621 Test Method for Compressive Properties of Cellular Plastics
D 1622 Test Method for Apparent Density of Cellular Plastics
D 1623 Test Method for Tensile and Tensile Adhesive Properties of Rigid Cellular Plastics
D 1673 Test Methods for Relative Permittivity and Dielectric Factor of Expanded Cellular Plastics Used for Electrical Insulation
D 1898 Practice for Sampling of Plastics
D 2126 Test Method for Response of Rigid Cellular Plastics to Thermal and Humid Aging
D 2842 Test Method for Water Absorption of Cellular Plastics
D 2856 Test Method for Open Cell Content of Cellular Plastics by the Air Pycnometer
D 2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
D 3892 Practice for Packaging/Packing of Plastics

2.2 Military Standard:
MIL-STD-105 Sampling Procedures and Tables for Inspection by Attributes

3. Classification

3.1 The rigid urethane foam covered in this specification shall be designated by a type number, composed of the desired cell limit for each property (Note 2) in the shown in Table 1.

Note 2—For properties that are affected by the anisotropy of foam, the direction of measurement shall be specified in the test report or as agreed upon by the seller and the purchaser.

Note 3—A product is specified by a ten-digit number, the first three representing level 0 to 9 of property 1, density; the second, level 0 to 9 of property 2, compressive strength; and so on. Thus a material specification of 3306056490 would have the following requirements:

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.033 g/cm³, max</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>103 kPa (15 psi), min</td>
</tr>
<tr>
<td>Burning rate</td>
<td>unspecified</td>
</tr>
<tr>
<td>Closed cells (porosity)</td>
<td>90 % min</td>
</tr>
<tr>
<td>Water absorption</td>
<td>unspecified</td>
</tr>
<tr>
<td>Water vapor permeability</td>
<td>3.0 perm-in. max</td>
</tr>
</tbody>
</table>

Dimensional stability:
- After 7 days at -29 ± 3°C: 5 % max linear change
- After 7 days at 38 ± 1°C and 90 to 100 % RH: 10 % max linear change
- After 7 days at 70 ± 1°C: 1 % max linear change

Flexural strength: unspecified
TABLE 1  Detail Requirements

<table>
<thead>
<tr>
<th>Property Order No</th>
<th>Property and Units</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Core density max. g/cm³ (lb/ft³)</td>
<td>0.016</td>
<td>0.026</td>
<td>0.033</td>
<td>0.040</td>
<td>0.048</td>
<td>0.080</td>
<td>0.128</td>
<td>0.400</td>
<td>0.960</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compressive strength, min. kPa (psi)</td>
<td>41</td>
<td>69</td>
<td>103</td>
<td>172</td>
<td>241</td>
<td>310</td>
<td>552</td>
<td>1,379</td>
<td>2,758</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Flammability*</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type A, less than 50%</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type B, greater than 50%</td>
<td>unspec.</td>
<td>unspec.</td>
<td>unspec.</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Closed cells (porosity), min. %</td>
<td>unspec.</td>
<td>10</td>
<td>50</td>
<td>70</td>
<td>80</td>
<td>85</td>
<td>90</td>
<td>95</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Water absorption max. g/1000 cm³ (g/cc) of surface</td>
<td>unspec.</td>
<td>976</td>
<td>488</td>
<td>244</td>
<td>976</td>
<td>488</td>
<td>391</td>
<td>244</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Water vapor permeability, max. perme-v at 23 ± 1°C</td>
<td>unspec.</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dimensional stability after 7 days at -29 ± 3°C (102 ± 5°F), max. % linear change</td>
<td>unspec.</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Dimensional stability after 7 days at 70 ± 1°C (158 ± 1°F) max. % linear change</td>
<td>unspec.</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Dimensional stability after 7 days at 38 ± 1°C (99 ± 1°F) and 90 to 100% RH, max. % linear change</td>
<td>unspec.</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Plural strength, min. kPa (psi)</td>
<td>unspec.</td>
<td>131</td>
<td>103</td>
<td>138</td>
<td>172</td>
<td>207</td>
<td>276</td>
<td>414</td>
<td>1379</td>
<td>2758</td>
</tr>
<tr>
<td></td>
<td>Intal k-factor as produced, max.</td>
<td>unspec.</td>
<td>1.36</td>
<td>1.49</td>
<td>1.61</td>
<td>1.74</td>
<td>1.86</td>
<td>1.98</td>
<td>2.11</td>
<td>2.48</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>(Btu-in/h ft²-F)</td>
<td>(0.11)</td>
<td>(0.12)</td>
<td>(0.13)</td>
<td>(0.14)</td>
<td>(0.15)</td>
<td>(0.16)</td>
<td>(0.17)</td>
<td>(0.20)</td>
<td>(0.25)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>k-factor as received by purchaser, max.</td>
<td>unspec.</td>
<td>1.49</td>
<td>1.61</td>
<td>1.74</td>
<td>1.86</td>
<td>1.98</td>
<td>2.11</td>
<td>2.23</td>
<td>2.48</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>(Btu-in/h ft²-F)</td>
<td>(0.12)</td>
<td>(0.13)</td>
<td>(0.14)</td>
<td>(0.15)</td>
<td>(0.16)</td>
<td>(0.17)</td>
<td>(0.18)</td>
<td>(0.20)</td>
<td>(0.25)</td>
<td></td>
</tr>
</tbody>
</table>

* Flammability—Various governmental boards have assorted regulations based on ASTM Method E 84. Test for Surface Burning Characteristics of Building Materials. E 119, Test for Surface Flammability of Materials Using a Radiant Heat Energy Source. and other test methods. The regulations are not the same for all bodies using them. Hence, the regulation of the government having jurisdiction should be consulted.

Note 4—Although the table theoretically indicates the possibility of many different combinations and products, these cannot all exist due to interactions between properties. For example, as density increases, compressive strength increases, and it is therefore not simultaneously possible to have maximum strength and minimum density. Similarly, many of the other properties listed "improve" with increasing density.

Note 5—Other properties, such as shear strength, tensile strength, electrical properties, etc., may be added to the specification, as agreed upon by the seller and purchaser.

Note 6—The physical properties of a foam are not represented by the values in any given vertical column. Refer to Notes 2 and 3 for interpretation and designation of foam requirements.

6. General Requirements

6.1 These plastic compositions shall be uniform and shall conform to the requirements prescribed in this specification. The color and form of material shall be as agreed upon by the seller and the purchaser. Odor shall not be objectionable.

6.2 All materials and workmanship shall be in accordance with good commercial practice and the resulting cellular urethane foam shall be free of defects affecting serviceability.

6.3 When the finished product does not lend itself to testing or to the taking of specimens because of complicated shape, small size, metal or fabric inserts, adhesion to metal, or other reasons, test slabs as agreed upon between the seller and the purchaser shall be prepared.

6.4 When differences due to the difficulty in obtaining suitable specimens from the finished parts arise, the seller and the purchaser may agree on acceptable deviations. This can be done by comparing the results of standard specimens and those obtained on actual parts.

6.5 The frequency of sampling shall be in accordance with accepted statistical practices and as agreed upon between the seller and the purchaser.
7. Test Methods

7.1 The properties enumerated in this specification shall be determined in accordance with the following methods. Modifications in the procedures may be agreed upon by the seller and the purchaser.

7.1.1 Conditioning—Unless otherwise specified, the test specimens shall be conditioned without external stress at 23 ± 1°C (73.4 ± 1.8°F) and 50 ± 2% relative humidity for a minimum of 24 h before testing.

7.1.2 Test Conditions—Tests shall be conducted under known conditions of temperature and humidity or as specified in the individual test procedure. In cases of dispute, the tests shall be made at a temperature of 23 ± 1°C (73.4 ± 1.8°F) and in an atmosphere of 50 ± 2% relative humidity.

7.1.3 Core Density—Method D 1622.

7.1.4 Compressive Strength—Procedure A of Method D 1621.

7.1.5 Thermal Conductivity—Method C 177 at a mean temperature of 22.8 to 25.0°C (75 ± 2°F).

7.1.5.1 For this specification, thermal conductivity can also be determined by Method C 518 at a mean temperature of 22.8 to 25.6°C (75 ± 2°F).

7.1.6 Water Vapor Permeability—Methods C 355 using the wet or the desiccant method. Specimens 25.4 mm (1 in.) thick shall be tested and the mean value reported.

7.1.7 Flammability—Method D 2863.

7.1.8 Flexural Strength—Procedure A of Method D 790 or Method C 203. Size of test specimen shall be 25.4 by 25.4 by 152.4 mm.

7.1.9 Shear Strength—Method C 273.

7.1.10 Tensile Strength—Method D 1623.

7.1.11 Water Absorption—Method D 2842.

7.1.12 Resistance to Simulated Service Conditions—Method D 2126.

7.1.13 Porosity—Method D 2856.

7.1.14 Electrical Properties—Methods D 1673 or Method D 257.

Note 8—Specific conditions (for example, sample size, humidity, temperature, etc.) shall be agreed upon by the seller and the purchaser.

7.1.15 Dielectric Strength—Methods D 149.

8. Number of Tests

8.1 One set be considered sufficient for testing each batch or lot. The minimum average for specimens tested shall be above the requirements prescribed in this specification. The number and designation of tests listed in Section 7 required to establish conformity of a material to this specification, shall be agreed upon by the seller and the purchaser.

8.2 Routine inspection may be limited to those required to identify the material to the satisfaction of the purchaser. The purchaser shall state in the contract or order the tests that the seller will be required to make on shipment for identification of the materials.

9. Retest and Rejection

9.1 If any failure occurs, the materials may be retested to establish conformity in accordance with agreement between the purchaser and the seller.

10. Packaging and Marking

10.1 Packaging—The material shall be packaged in standard commercial containers so constructed as to ensure acceptance by common or other carriers for safe transportation: the lowest rate to the point of delivery, unless otherwise specified in the contract or order.

10.2 Marking—Shipping containers shall be marked with the name of the material, form and quantity contained therein, as defined by the contract or purchase order under which shipment is made, and the manufacturer's batch, lot or control number, or both. The shipping containers shall be marked also with the name of the manufacturer and the number of the contract or order.

10.3 All packing, packaging, and marking provisions of Practice D 3892 shall apply to this specification.

SUPPLEMENTARY REQUIREMENTS

S1. Quality Assurance Provisions for Government and Military Procurement

S1.1 Sampling for inspection and testing shall be carried in accordance with the recommendations of Practice D 1898.

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252
Standard Specification for Flexible Cellular Materials—Urethane for Furniture and Automotive Cushioning, Bedding, and Similar Applications

This specification covers flexible cellular urethane foams intended for such uses as inserts for furniture, mattresses, and similar applications. This specification provides material and dimensional requirements and methods of tests for specific properties of density, compression set, humid age resistance, and dynamic fatigue resistance. This specification includes references to government regulations for burning characteristics of flexible cellular materials used in specified applications.

1. Classification

1.1 This classification covers six grades of flexible cellular urethane foam that may be selected for use according to load grade and general physical properties. Table 1; four grades have dynamic fatigue properties, Table 2; three grades for static fatigue properties, Table 2A.

2. Uses of Purchase

Any product represented as complying with this specification shall meet all the requirements listed herein for its particular classification.

5. Physical Requirements

5.1 The material shall conform to the requirements for physical properties prescribed in Tables 1, 2, and 2A.

6. Test Methods

6.1 The physical tests shall be in accordance with Methods D 3574.

7. Burning Characteristics

7.1 Table 3 lists applicable government regulations on burning characteristics of material used in specified applications.

8. Dimensions

8.1 For Use as Mattress Inserts:

8.1.1 Sizes—The standard thickness and tolerance specified in Table 4. These sizes have been adopted for mattress inserts to coordinate the insert with mattress ticking and other bed constructions. The other dimensions are specified in Table 7A of Simplified Practice Recommendations R2-62.

8.1.2 For Use as Furniture Cushion Inserts—The allowable tolerances on dimensions of furniture cushion inserts shall be as shown in Table 5.

9. Inspection

9.1 Inspection of the material shall be agreed upon in writing by the purchaser and the seller as part of the purchase contract.

9.2 Testing for conformance to requirements shall be done in accordance with the appropriate sections of Methods D 3574. The specific test methods in this reference to be used for each test shall be as listed in Tables 1 and 2, except as specified in 9.3. Burning tests in the reference are listed in Table 3.

9.3 If a specimen 380 by 380 by 100 mm (15 by 15 by 4 in.) cannot be obtained, an appropriate size, as well as its corresponding indentation force deflection (IFD) value shall be agreed upon by the purchaser and seller. In those cases where foams having thicknesses of (100 mm) 4 in. are not available, the following reduced IFD values are suggested:

- 75 mm (3 in.) — 90 % of 100 mm (4 in.) ILD value
- 50 mm (2 in.) — 80 % of 100 mm (4 in.) ILD value
- 25 mm (1 in.) — 70 % of 100 mm (4 in.) ILD value

In all cases, the IFD tolerances specified in Table 1 shall apply. For example, a 50-mm (2-in.) thick Grade 120 N (12
kg/27 lb) foam will have a 25% ILD value of 96 ± 14 N (21.6 ± 3.0 lb) = 82 to 110 N (18.6 to 24.6 lb).

10. Re-test and Rejection

10.1 If any failure occurs, the materials may be retested to establish conformity in accordance with agreement between the purchaser and the seller.

11. Packaging, Marking, and Labeling

11.1 Packaging—The material shall be packed in standard commercial containers, so constructed as to ensure acceptance by common or other carriers for safe transportation at the lowest rate to the point of delivery, unless otherwise specified in the contract or order.

11.2 Marking—The shipping container shall be marked with the name, type, and quality of material in accordance with the contract or order under which the shipment is made. The shipping container shall also be marked with the name of the manufacturer and the contract or order number.

11.3 Label—In order that purchasers may identify products complying with all requirements of this specification, producers choosing to produce such products in accordance with this voluntary specification may include a statement in conjunction with their name and address on invoices, sales literature, and the like. The following statement is suggested:

"This product conforms to all the requirements of Grade _____, performance grade _____ established in ASTM Standard Specification D 3453. Full responsibility for the conformance of this product with a standard is assumed by (name and address of producer/distributor)."

TABLE 1 Specific Physical Properties of Flexible Cellular Material

<table>
<thead>
<tr>
<th>Grade Number</th>
<th>English</th>
<th>Metric</th>
<th>25% Indentation Force Deflection (FMD) Values*</th>
<th>Indentation Force Ratio</th>
<th>Compression Test Method*</th>
<th>Compression Set After Deflection, % max</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>44</td>
<td>196 ± 18 (44 ± 4)</td>
<td>19</td>
<td>15</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>151</td>
<td>34</td>
<td>151 ± 14 (34 ± 3)</td>
<td>19</td>
<td>15</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>120</td>
<td>27</td>
<td>120 ± 14 (27 ± 3)</td>
<td>19</td>
<td>15</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>93</td>
<td>21</td>
<td>93 ± 14 (21 ± 3)</td>
<td>19</td>
<td>15</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>67</td>
<td>15</td>
<td>67 ± 14 (15 ± 3)</td>
<td>18</td>
<td>20</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>40</td>
<td>9</td>
<td>40 ± 14 (9 ± 3)</td>
<td>18</td>
<td>20</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Test method</td>
<td></td>
<td>12 to 18</td>
<td>12 to 18</td>
<td>31 to 37</td>
<td>83 to 87</td>
<td>83 to 87</td>
</tr>
</tbody>
</table>

* Tolerances have been established to provide for grade designations. Closer tolerances, when desirable for specific applications, may be agreed upon between the purchaser and the seller.

** See Methods D 3574, Sections 76 to 82

TABLE 2 Dynamic Fatigue Performance Grades

<table>
<thead>
<tr>
<th>Grade</th>
<th>Description</th>
<th>TML</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Heavy duty</td>
<td>30, max</td>
</tr>
<tr>
<td>BD</td>
<td>Normal duty</td>
<td>31 to 50</td>
</tr>
<tr>
<td>CD</td>
<td>Light duty</td>
<td>51 to 70</td>
</tr>
<tr>
<td>DD</td>
<td>Unclassified</td>
<td>71 to 100</td>
</tr>
</tbody>
</table>

TABLE 2A Static Fatigue Performance Grades of Uncored Urethane Foam

<table>
<thead>
<tr>
<th>Grade</th>
<th>Description</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Heavy duty</td>
<td>cushions, mattresses</td>
</tr>
<tr>
<td>BS</td>
<td>Normal duty</td>
<td>arm rests, seat backs</td>
</tr>
<tr>
<td>CS</td>
<td>Light duty</td>
<td>arm rests, seat backs</td>
</tr>
</tbody>
</table>

* See Methods D 3574, Sections 76 to 82

290
These governmental bodies have issued regulations based on Test Method ASTM D 3453. The regulations are not the same for all bodies issuing them. Here, the FAA is the government having jurisdiction should be consulted. The standard should be used to measure and describe the properties of products, or assemblies in response to heat and flame under controlled test conditions and should not be used to describe or appraise the fire or fire test of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire test which takes into account all of the factors which are pertinent to an analysis of the fire hazard of a particular use.

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>Applicable Government Regulation for Specified Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Application</td>
</tr>
<tr>
<td>Automotive</td>
<td>dot MVSS 362</td>
</tr>
<tr>
<td>Mattress and cushion</td>
<td>FAR Part 25 853, Paragraph (6), and Appendix F</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>E 1624-00</td>
</tr>
</tbody>
</table>

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Designation: D 2849 – 69 (Reapproved 1980)\(^1\)

An American National Standard

Standard Methods of Testing Urethane Foam Polyol Raw Materials\(^1\)

This standard is issued under the fixed designation D 2849; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (\(\epsilon\)) indicates an editorial change since the last revision or reapproval.

The committee responsible for this standard has voted its withdrawal. In the absence of substantial reasons that it should be continued, the Society will approve withdrawal from publication in May 1989.

\(^{1}\) NOTE—Section 2 was added editorially and subsequent sections renumbered in August 1985.

1. Scope

1.1 These methods cover the testing of polyol raw materials used in preparing urethane foams, including both polyesters and polyethers containing carboxyl, primary or secondary hydroxyl groups, or both.

Note 1—Urethane foams are cellular products that vary from soft elastic types to those which are hard and rigid. These foams are made by the interaction of polyhydroxy compounds, water, and an organic isocyanate. The reactions involved in the manufacture of these foams can be modified in many ways. Basic materials, especially tertiary amines, act as catalysts and accelerate the reaction, whereas acidic materials retard it. The uniformity and size of the cells are affected by the addition of surface-active agents. Usually nonionic or cationic surfactants are employed. Fillers, plasticizers, and colors are also added in many cases to give specific properties to the foam.

1.2 The procedures appear in the following order:

<table>
<thead>
<tr>
<th>Sections</th>
</tr>
</thead>
</table>
| Sampling | 4  
| Saponification and Potassium | 6 to 20  
| Vol and Alkalinity Numbers | 21 to 30  
| Hydroxyl Number | 31 to 52  
| Uranation | 53 to 60  
| Water | 61 to 70  
| Saturated Matter | 71 to 73  
| Specific Gravity | 74 to 79  
| Vacancy | 80 to 91  
| Color | 92 to 103  

1.3 The values stated in SI units are to be regarded as the standard.

2. Referenced Documents

2.1 ASTM Standards:

D618 Methods of Conditioning Plastics and Electrical Insulating Materials for Testing\(^2\)

D1193 Specification for Reagent Water\(^3\)

D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)\(^4\)

E 1 Specification for ASTM Thermometers\(^5\)

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis\(^6\)

E 203 Test Method for Water Using the Karl Fischer Reagent\(^6\)

E 308 Method for Computing the Colors of Objects by Using the CIE System\(^7\)

3. Purity of Reagents

3.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.\(^8\) Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean water conforming to Specification D 1193.

4. Sampling

4.1 Polyesters and polyethers usually contain molecules covering an appreciable range of molecular weights. These have a tendency to fractionate during solidification. Unless the material is a finely-ground solid it is necessary to melt (using no higher temperature than necessary) and mix the resin well before removing a sample for analysis. Many polyols are hygroscopic and care should be taken to provide minimum exposure to atmospheric moisture during the sampling.

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\(^{1}\) These methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Plastics.  
\(^{2}\) Annual Book of ASTM Standards, Vol 08.01.  
\(^{3}\) Annual Book of ASTM Standards, Vol 08.01.  
\(^{4}\) Annual Book of ASTM Standards, Vol 06.01 and 06.03.

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