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PREFACE

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 1971-1981 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 accesible to developing countries.

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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, PU 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 (8.1.11), 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 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 alicyclic 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 classed as polyether polyols, polyester polyols and natural products. Initially, polyester polyols were the preferred raw material for PUs. At present polyether polyols are used in the greatest volume because of low cost and a wide choice of types. Most commercial polyether polyols are based on the less expensive propylene or ethylene oxides or are a combination of the two.

The chemical suppliers have made available a wide range of isocyanates, polyols and additives.

PU's 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 volatil 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 volatil material. Flexible foams are based on polyoxypropilenediols of 2000 molecular weight and triols up to 4000. Rigid foams are based on polyether made from sorbitol, methyl glucosyde 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 laminating 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). 5% 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, calendaring, extrusion, etc.

RIM 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. RIM 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 RIM or reinforced RIM (RRIM).

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

Millable 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 bases 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.

PLOYURETHANES MANUFACTURE

1.-Retrospective Search of Information Sources for the period
1980-1991 (*)

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*Information sources: Chemical abstracts
Engineering index

1.2 ABSTRACTS*:

- 1.- 111:10513p Application of the Taguchi method to development of appliance systems. Dunney, G. G. (Seej. Eng. Technol. 1989, Pittsburg, PA 15205 (USA). *J. Appl. Polym. Sci.* 1989, 37(1), 1-12 (1989). (En;Pol;urethane;ab). 089-64 (En). The Taguchi method for cost sheet design of appls and its application to polyurethane appls are discussed. Efficiency of the method in industrial experimentation is demonstrated. A discussion of the application to a challenging formulation problem. The example illustrates how a small set of initial trials, carefully chosen in accordance with the Taguchi method, eventually leads to a successful formulation. A discussion of the phys. properties, interpretation and anal. of the data is also included.

- 2.- 111:10512p Optimizing a polyurethane foam formulation by the Taguchi method. Dunney, G. G. (Seej. Eng. Technol. Joseph M. Minbay Corp. Pittsburg, PA USA). *West Eng. J.* 1989, 1(1), 19-24 (1989). (En). The Taguchi Method for optimizing formulation criteria is applied to the com. development of Multanrol E 9280 polyurethane. see p.59

- 3.- 111:10513p Process and apparatus for mixing flocculates with foams in polyurethane production. Hebers, Gunter (Kloetner Ferromatik Desma (G.m.b.H.) Ger. Offen. DE 3614993 (Cl. E29B7 14). 23 Nov 1989. Appl. 03 May 1988. 12 pp. The foam mixing process uses a cylinder in which a screw, rotating towards the outlet, is driven in the vertical axis and can be displaced axially when mixing is complete.

- 4.- 111:10512p Machines for polyurethane processing. Redkar, S. M. (Chemicolour Ind. Ltd., Bombay, India). *Pop. Plast.* 1989, 34(1), 21-2, 24-6, 28-30 (Eng). A review with no refs. on machines for polyurethane processing is presented giving a general classification of polyurethane processing plants and machinery based on 3 types of final product, i.e. (1) machines for cellular products, (2) machines for noncellular products such as thermoplastic processing and casting, and (3) machines for coating on textiles. A classification chart is also given.

- 5.- 064009 Anlagenkonzepte im Baukastensystem fuer jede Anwendung. [Polyurethane processing - modular design plant for all applications]. The paper talks about availability of Polyurethanes processing machinery on modular basis. This modular-designed plant can be obtained with different levels of automation depending on the need. In German. see p.64
Anon. *Plasterarbeiten* v 40 n 6 Jun 1989 p 26, 28-29

- 6.- 111:10513p Recent developments in polyurethanes. XVI. Gov. S. B. (Salemra, India). *Man-Arise Text. India* 1988, 11(11), 45-51 (1988). (En). A review with no refs. on polyurethane flexible foams and control of prods. see p.47

*Complete documents can be obtained from: British Library Lending Div.
 Boston Spa, Wetherby, W. Yorkshire
 United Kingdom, LS23 7BQ

- 7.- 111: 98525j Recent developments in polyurethanes XV. Iyer, S. B. (Sasmira, Bombay, India). *Man-Made Text India* 1988, 31(10), 447-46, 468 (Eng). The prepn. of rigid polyurethane foams from polyesters or polyethers and diisocyanates is discussed. The effects of compn., catalysts, and bubble modifiers on the product foams are discussed. Mass prodn. of slab foam is also discussed. see p.50
- 8.- 110: 252100 Recent developments in polyurethanes XIV. Iyer, S. B. (Sasmira, India). *Man-Made Text India* 1988, 31(10), 447-6 (Eng). A survey of isocyanates, the properties of isocyanates, and the chem. of isocyanate acids, reactions with hydroxy, carboxylic acid, and amino groups in the application of isocyanates to polymer technol. are briefly discussed. see p.53
- 9.- 110: 214278k Expansion of applications of polymer foams. Seymour, Raymond B. (Dep. Polym. Sci., Univ. South. Mississippi, Hattiesburg, MS 39406-0076 USA). *Rev. Plast. Mod.* 1989, 57(393), 407-11, 414 (Span). A review with 29 refs. on fabrication and uses of cellular plastics (or polymer foams). Environmental issues fluorocarbon propellants in foam fabrication; manif. of com. foams (polyurethanes, polystyrene, PVC, polyolefins); and uses (synthetic foams, structural materials, moldings) are discussed.
- 10.- 110: 115718z Polyurethane and its base materials. Preparation and properties of isocyanates. A. Naszai, Sándor. (Eot. Saba (Borsodi Vegyi Komb., Kazincbarcika, Hung.). *Magy. Kém. Lapja* 1988, 43(10), 378-83 (Hung). A review with 78 refs. covers the prepn., anal., and toxicol. of isocyanates. The prepn. and properties of diaminodiphenylmethane and MDI are discussed in detail.
- 11.- 109: 56112z Plastics in high tech industries by LJOI A.D. Krishnamurthy, H. (Hindustan Org. Chem. Ltd., India). *Chem. Age India* 1988, 39(3), 149-58 (Eng). Developments in engineering plastics, e.g. polyamides, polycarbonates, polyoxymethylenes, PTFE, and polyurethanes, their processing technol., and current and future applications in India are discussed.
- 12.- 109: 27012m Chemistry of wastes. 59. Murata, Tokun. (Junkan Shiger, Kenkyusho K. K., Japan). *Gekkan Haisyutsu* 1988, 14(1), 239-43 (Japan). A review with no refs. on chem. and toxicol. characteristics of waste plastics (e.g. melamine resins or urethane resins) dumped in landfill sites, including current status, controlling principal org. hazardous constituents, and the utilization of the waste plastics.
- 13.- 108: 205105k Synthesis of polyurethanes. Kobayashi, Shiro; Maeda, Shimichiro. (Coll. Eng., Tohoku Univ., Sendai, Japan). *Kobunshi Kagaku* 1987, 36(11), 522-7 (Japan). A review with 23 refs. on the prepn. of urethane polymers for various uses (including coatings, foams, rubber, etc.) as well as the prepn. of isocyanates and also, esp. long chain polyols for manif. of the urethanes.

- 14.- 083733 POLYURETHANES (PUR). 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 polyurethanes by major segment, assess developments and implications in terms of polyurethane raw materials is reviewed and the structural changes which are taking place in the industry is described.
Mills, R. *Kunstst Ger Plast* v 77 n 10 Oct 1987 p 62-63.
- 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 ageing 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 pipework and narrow cavities). The article highlights some of the important trends in in-situ foaming, covering both spray-applied and liquid-dispersed molecules.
Colvin, B.G. (British Urethane Form Contractors Assoc). *Insul J (Rickmansworth Engl)* v 31 n 9 Dec 1987 p 26-28.
- 16.- 106: 214492t Fundamental studies in reactive processing of polyurethane-based polymerizations. Lee, Yeh Ming Leo (Ohio State Univ., Columbus, OH USA). 1986. 313 pp. (Eng). Avail. Univ. Microfilms int.. Order No. DA8703580. From *Diss. Abstr. Int*
- 17.- 092567 GUIDE TO FORMULATING AND COMPOUNDING POLYURETHANES. Versatile polymers obtained from reacting isocyanate and polyol polyurethanes can be formulated to make a variety of products, from furniture to decorative ceiling beams. (Author abstract)
Abbate, F.W. (Dow Chemical USA, Midland, MI USA). *Plast Compd* v 9 n 4 Jul-Aug 1986 5p between p 20 and 27.
- 18.- 104: 31696n The polyurethane industry in Argentina. D'Agostino, C.; Bostedt, H.; Hubohm, E.; Gonzalez Pous, S.; Restano, M.; Binder, C. (Petroquim, Rio III S A, Spain). *Indi Quim* 1985, 277, 10-21 (Span). A review with no refs. on industrial aspects of the chemical processing, and uses of polyurethanes in Argentina, including the history, present state, and future prospects of the industry.
- 19.- 092629 RAW MATERIAL SYSTEMS FOR RIGID POLYURETHANE FOAM. Various end-use dependent methods of producing rigid polyurethane foam require the raw material systems with controlled reaction profile 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 foam 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 autor abstract).
Kapps, Manfred (Bayer AG, Leverkusen, West Ger). *Kunstst Ger Plast* v 75 n 6 Jun 1983 p 11-14.

20.- 102: 18553p Step growth polymerization. Part II. Developments in polyurethanes. Sparrow, D. J., Naiton, A. G. (Org. Div., ICI PLC, Blackley, UK). *Macromol Chem (London)* 1984, 8, 93-7 (Eng). Isocyanate products and processes, polyurethane polyols, catalysis, mechanism of isocyanate reactions, rigid and flexible foams, and reaction-injection moulding are reviewed with 85 refs.

21.- 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-application. New developments in raw materials and additives as well as optimization of products for new usages are described. Advances in processing technology, mostly concerned with the PUR-sector, have contributed quite considerably to the above average success in the market. Such pressing subjects as health and safety at work and protection of the environment are also briefly discussed. 44 refs.
Schwenke, W. *Kunstst Ger Plast* v 74 n 10 Oct 1984 p 38-41.

22.- 089242 PROGRESSI NELLA TECNOLOGIA DEGLI ESPANSI POLIURETANICI (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.
Ann. Mater Plast Elastomeri 1 Jan 1984 p 28-30.

23.- 103: 88698j Opportunities and constraints. Polyurethanes: the learning curve. Allport, D. C. (Org. Div., ICI Polyurethanes, Blackley Manchester, UK M9 3DA). *Pap. Proc. - POLYCON React Process* 1983, 15-35 (Eng). *Plast. Rubber Inst.*: London, UK. The processing and properties of polyurethanes are reviewed with no refs.

24.- 103: 88122z Apparatus for mixing at least two chemically reactive plastic components. Andreas, Johann; Kiezing, Helmut; Schuster, Klaus; Taubenmann, Peter; Thiele, Helm (Elasto-ran Maschinenbau G.m.b.H. und Co.) *Ger. Offen. DE 3,334,375* (Cl. B29B1/06), 11 Apr 1985. *Appl.* 23 Sep 1983; 10 pp. The title app., esp. useful for polyurethane manuf., comprises a mixing chamber, inlets for introducing reactive resin components to the mixing chamber, an outlet for the mixture, a means for returning the components to a storage chamber when the inlets are closed, and a means for maintaining a const. pressure on the components during return to the storage chamber and during addition to the mixing chamber. The app. gives mixts. of high quality.

25.- 102: 86777m Continuous production of plastic foam. Griffiths, Anthony Charles Murray (Hyman International Ltd.) *Brit. UK Pat. Appl. GB 2,138,723* (Cl. 329D27/04), 31 Oct 1984, *GB Appl.* 83/1,733, 21 Jan 1983; 10 pp. Polyurethane foam having uniform properties is prepd. by feeding reactants to the bottom of a vertical app. through a nip into a diverging area while the foam is removed at the top by pinned conveyors. Thus, a mixt. of polyether polyol 100, water 4.3, silicone surfactant 0.9, amine catalyst 0.2, Sn catalyst 0.28, fluorocarbon blowing agent 1.5, and TDI 85.6 parts each fed through the nip in the reactor. The compn. foamed in the vertical section, had rise time 110 s, d. 22 kg/m³, net throughput 20.4 kg/min, and vertical velocity 0.32 m/min.

26.-

101.111791g Polyurethane formulation calculations. Liu, Houjun (Shanxi Prov. Inst. Chem. Ind., Peop. Rep. China). *Hecheng Xiangjiao Gongye* 1984, 7(3), 185-6 (Ch). Equations are given for calcg. the amt. of polyisocyanate and polyisocyanate prepolymer. The isocyanate compn.-OH compn. equiv. ratio was maintained at 0.97-1.03 to obtain theor. mol. wt. >25,000.

27.-

100.192595a Mixing method and apparatus for polyurethane manufacture. Airo S.p.A. (Japan). Kokai Tokkyo Koho JP 9 15,423 [84 15,423] (Cl. C08G19/08), 25 Jun 1982, 12 pp. Appl. 82/20,594, 06 Apr 1982; 7 pp. A simple and efficient mixing of ingredients in the title process involves feeding of high-pressure jets of the usual 2 monomers through horizontal inlets on opposite walls of a mixing chamber, while a non-reacting 3rd component (e.g., colors, release, etc.) is fed in the direction vertical to the monomer feeds, and the direction of the 3rd component is the direction intended for the material.

28.-

099792 RATIONELLE UND FLEXIBLE PUR-VERARBEITUNG. [Rational and Flexible PUR-Processing]. This paper is concerned with equipment and its automatization used in the processing of polyurethanes, particularly of polyurethane foams. Details are given of the dosing equipment, means of transportation of material and products, molds and mold carriers, auxiliary transport equipment, hand tools for specific purposes; cost analysis. In German.

see p.56

Russ. Werner (Elastogran Maschinenbau GmbH, Strasslach, West Ger). *Plastverarbeiter* v 34 n 8 Aug 1983 p 682-684.

29.-

099753 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.

Bauman, Bernard D. (Air Products & Chemicals Inc., Allentown, Pa. USA); Burdick, Trisha E.; Bye, Mark L.; Galla, Edward A. *J Cell Plast* v 19 n 6 Nov-Dec 1983 p 381-384

30.-

099807 POLYURETHANE, STAND DER TECHNIK UND KUENFTIGE 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. **Polyure-POLYURETHANES—Research—**Contd. thanes 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. Forecast for the future developments is included. In German

Oertel, Guenter (Bayer AG, PU-Anwendungstechnik, Leverkusen, West Ger). *Plastverarbeiter* v 34 n 7 Jul 1983 p 623-628.

- 31.- 074892 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.
Origgi, Pietro; Amann, Massimo. *Mater Plast Elastomeri* n 9 Sep 1982 p 522-528.
- 32.- 96: 4884x A kinetic study of reactions between polymers. Racois, A.; Walsh, D. J. (Lab. Synth. Org., Univ. Mans, 72017 Le Mans, 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.
- 33.- 95: 48306t Fact sheet: production and use of polyurethane foams. Mahieu, J. C. (INRS, 75680 Paris, 14 Fr.). *Cah. Notes Doc.* 1981, 102, 69-72 (Fr). The main operations used in prodn. of cellular polyurethane products and health risks assocd. with them are discussed. Procedures for avoiding harmful effects from handling polyurethanes are recommended.
- 34.- 94: 176734x Urethane coatings. June, 1970-June, 1980 (citations from the Engineering Index data base). Van Put, Walter (New England Res. Appl. Cent., Storrs, CT USA). *Report 1980, NERACEINT0347; Order No. PB80-856944*, 83 pp. (Eng). Avail. NTIS. From *Gov. Rep. Announce. Index (U. S.) 1980, 80(26)*, 5695. A bibliog. with 69 refs. covers formulations and applications of urethane coatings, such as fabrics, automobile parts, plastics, concrete, transportation industry, rubber, and PVC substrates. Solventless formulations, shrinkage prevention, and energy savings of urethane coatings are also included.
- 35.- 92: 199077h The synthesis and properties of polyurethane resins. Volume 2. 1973-October, 1979 (a bibliography with abstracts). Cavagnaro, Diane M. (Natl. Tech. Inf. Serv., Springfield, VA USA). *Report 1979, Order No. PB80-800477*, 270 pp. (Eng). Avail. NTIS. From *Gov. Rep. Announce. Index (U. S.) 1980, 80(2)*, 236. A bibliog. review with 293 refs.
- 36.- 92: 164804r Foamed plastics. Part 1. Polyurethane foams (a bibliography with abstracts). Cavagnaro, Diane (Natl. Tech. Inf. Serv., Springfield, VA USA). *Report 1979, Order No. PB80-802143*, 296 pp. (Eng). Avail. NTIS. From *Gov. Rep. Announce. Index (U. S.) 1980, 80(3)*, 369. This updated bibliog. contains 289 abstrs., 24 of which are new entries to the previous edition, on fabrication, phys. properties, chem. properties, and applications of polyurethane foams. The application include structural panels, floats, buoyant materials, thermal insulation, and packaging materials.

1.3 REFERENCES ** :

- 1.- 114: 102857z Crosslinking and network formation in polyurethane systems with excess isocyanate. Dusek, Karel; Spruceva, Jilena (Inst. Macromol. Chem., Czechoslovak Acad. Sci., 162 05 Prague, Czech.) *Coll. Polym.* 1990, 9(2), 65-68 (Eng).
- 2.- 114: 44024n Production of flexible polyurethane slabstock foams without halogenated blowing agents. McKenna, E. H.; Grace, O. M.; Smiecinaki, T. M. (BASF Corp., Wyandotte, MI 48192 USA). *Proc. SPI Annu. Tech./Mark. Conf.* 1989, 32nd Polyurethanes 89), 510-14 (Eng).
- 3.- 114: 7441r Perspective of polyurethane manufacture. Fedotova, N.; Anarova, S. M.; Kirichenko, N. G.; Bogdanova, E. D. (USSR). *Plast. Massy* 1990, (9), 3-4 (Russ). A review with 2 refs. on developments of polyurethane manuf.
- 4.- 114: 170001w Processes in production and use of polyurethanes in national economy. Petrov, E. A.; Anarova, S. M.; Fedotova, S. N.; Kirichenko, N. G.; Bogdanova, E. D. (USSR). *Plast. Massy* 1990, (8), 10-13 (Russ).
- 5.- 114: 60797f Recent activity in technologies of thermosetting-plastics. Polyurethane. Tanaka, Michio (Kure Chem. Ind. Ltd., Osaka, Japan 532). *Kogyo to Kogyo* 1990, 3(2), 1990, 64(5), 48-60 (Japan).
- 6.- 112: 180607r Manufacture of polyurethane products by mixing isocyanates and polyols before addition of catalysts. Kumasaka, Sadao; Tada, Satomi; Fujii, Osamu; Kuza, Shigeo; Katsuki, Koretoshi (Human Industry Corp.) *Jpn. Kokai Tokkyo Koho JP 01,294,743 [89,294,743]* (Cl. C08J9/02), 28 Nov 1989. *JP. Appl.* 88/22,570, 02 Feb 1988; 5 pp.
- 7.- 112: 146941p Manufacture of rigid polyurethane foams. Ono, Tamiro; Nozawa, Toshio (Mitsui Toatsu Chemicals, Inc.) *Jpn. Kokai Tokkyo Koho JP 01,278,540 [89,278,540]* (Cl. C08J9/14), 08 Nov 1989. *Appl.* 88/105,464, 30 Apr 1988; 6 pp.
- 8.- 112: 100145y Some new uses of castor oil in chemical industries. Mukherjee, R. N. (Chem. Eng. Dep., Jadavpur Univ., India). *J. Inst. Eng. (India), Part CH* 1989, 69(2), 64-7 (Eng).
- 9.- 112: 57415z Apparatus for manufacture of urethane polymer foams and elastomers. Kumasaka, Sadao; Tada, Satomi; Katsuki, Koretoshi; Fujii, Osamu; Kuza, Shigeo (Human Industry Corp.) *Jpn. Kokai Tokkyo Koho JP 01,213,323 [89,213,323]* (Cl. C08G18/08), 26 Aug 1989. *Appl.* 88/36,754, 19 Feb 1988; 4 pp.
- 10.- 111: 115761b Formation, structure and properties of crosslinked polyurethanes. Dorozhkin, V. P.; Kirpichnikov, P. A. (Kazan. Khim.-Tekhnol. Inst., Kazan, USSR). *Usp. Khim.* 1989, 58(3), 521-59 (Russ).

- 11.- 110: 16658s Low-viscosity isocyanate-terminated polyurethanes and improved compatibilizer for castor oil-based polyurethanes. Kawanishi, Takao; Kawanishi, Toshiaki; Kawanishi, Toshiaki. *J Polym Sci Part A: Polym Chem* 1987, 25(11), 2515-25. (Eng.)
- 12.- 110: 16659s Apparatus for manufacturing polyurethane polymer materials. Cobos, Walter R.; Witt, Rudolph; Kopp, G.; Chanz, John H.; Suidman, Laurence B.; Norison, Gern. *US Pat* 4,773,031 (Cl. 261-128; C06J9/00), 10 Oct 1988, US Appl. 783,102, 02 Oct 1985; 16 pp. Cont.-in-part of U.S. Pat. No. 783,101, abandoned.
- 13.- 110: 19467s High-pressure mixing - towards modern polyurethane processing. *Prosa. F. Fed. Rep. (Ger.) Kunststoffe* 1989, 34(1-2), 22-7 (Ger.).
- 14.- 110: 19550q Polyurethanes from renewable resources. Stanford, John L.; Smith, Richard H.; Fawc, John L.; Donnelly, Michael; Inst. Sci. Technol., Univ. Manchester, Manchester, UK. *ACS Symp. Ser.* 1989, 383, 1-10. (Eng.)
- 15.- 110: 59029j Apparatus for manufacture of polyurethane foam slabs. Kumasaka, Sadao; Otsu, Goken; Fujii, Osamu; Kameyama, Goro; Imai, Masao (Human Industry Corp.); Faming Zhuangli Shengqing Gonghai Shuomingshu CN 84,104,431 (Cl. C08J9/04), 13 Jan 1988; Appl. 02 Jul 1986; 12 pp.
- 16.- 110: 2426z Polyurethanes. Pearson, R. G. (London Sch. Polym. Technol., Polytech. North Lodge, London, UK N7 2DB). *Spec. Polym.* 1987, 150-50 (Eng.). Edited by Brown, Robert William. Blackie, Glasgow, UK. A review with 4 refs. on the chem. of formation, properties, and applications of urethane polymers.
- 17.- 110: 16659s Hydrophilic carboxylated polyurethanes. Johnston, Christian W.; Giffenart, John H. (T.M. Adams Counter Ltd.). *US Pat* 4,769,773 (Cl. 261-128; C06J9/00), 10 Oct 1988, US Appl. 783,102, 02 Oct 1985; 16 pp.
- 18.- 109: 5573r Advances in polyurethane science and technology. Frisch, Kurt C. (Polymer Inst., Univ. Detroit, Detroit, MI 48221 USA). *Proc. Water-Borne Higher-Solids Coat. Symp.* 1987, 14th, 402-27 (Eng.). A review with 66 refs. on the advances and important trends in polyurethane coatings, rubber, foam, and plastics.
- 19.- 108: 10840u Progress in polyurethanes. Wiroza, Dymunt (Wyzsza Szk. Inz., Slodmu, Pol.). *Polimery (Warsaw)* 1987, 32(11-12), 423-34 (Pol.).
- 20.- 108: 16686a Trends in the development of polyurethane foams in Poland. Cierniak, Grazyna; Szczepkowski, Leonard; Ciesta, Tadeusz (Zakl. Chem. "Organika-Zachem", Bydgoszcz, Pol.). *Polimery (Warsaw)* 1987, 32(11-12), 480-4 (Pol.).

- 21.- 107: 14481 *Use of polyurethane foams in processing - safety aspects of PUR products.* Michalski, J. (KNO, Brugge, Belg.). *Plast. Rubber* 1987, 40(3), 29-31 (Neth).
- 22.- 107: 21335v *Use of polyurethane wastes. I. Methods for recovery of polyurethane wastes.* Kornetka, Zygmunt W.; Muszynska, Urszula (OBR Przem. Opon. "Stomil", Poznan, Pol.). *Polimery (Warsaw)* 1987, 32(3), 111-14 (Pol).
- 23.- 106: 137451j *Foaming and molding of polyurethanes.* Fujimoto, Kazuo (Sumitomo Bayer Urethane Co. Ltd., Japan). *Pettech (Tokyo)* 1987, 10(3), 69-74 (Japan). A review with 3 refs. on polyurethane foam prodn. and reaction injection molding.
- 24.- 105: 135113w *Polyurethane foams.* Kumasaka, Sadao (Human Industry Corp.) Jpn. Kokai Tokkyo Koho JP 61 78,845 (86 78,845) (Cl. C03J9/04). 22 Apr 1986, Appl. 84/24,857. 27 Sep 1984: 3 pp.
- 25.- 104: 225530u *Trends in polyurethane science and technology.* Fruch, Kurt C. (Polym. Inst., Univ. Detroit, Detroit, MI 48221 USA). *Prog. Plast.* 1986, 31(3), 17-21 (Eng). A review with no refs. on important trends in polyurethane science and technol. including flexible foams, rigid foams, elastomers, coatings, reaction injection molding (RIM), reinforced RIM, prosthetics, and polyblends.
- 26.- 091788 **POLIURETANI FLESSIBILI A BASE DI MDI (MDI Base Flexible Polyurethanes).** New and unusual uses are foreseen in the United States for these polyurethanes, already well-known in Europe: from absorbent products to contraceptives, from tampons for medical use to small pots used for plant germination. The annual growth rate until 1990 could be about 10 percent. (Author abstract) is Italian.
Assoc. Mater. Plast. Elastomeri n 4 Apr 1986 p 206-210.
- 27.- 106: 103380k *Apparatus for continuous molding of polyurethanes.* Gebarowski, Stanislaw; Landy, Franciszek (Centralny Ośrodek Badań i Rozwoju Przemysłu Betonów "Cebet") Pol. PL 126,551 (Cl. C08G85/00). 31 Oct 1985, Appl. 223,002. 25 Mar 1986: 4 pp.
- 28.- 104: 163085y *Polymer Journal.* Vol. 16, No. 1, 1984. *Polimery (Warsaw)* 1984, 31(1), 1-16 (Pol.). *Polimery (Warsaw)* 1984, 31(1), 1-16 (Pol.). *Polimery (Warsaw)* 1984, 31(1), 1-16 (Pol.). Appl. 84/55,653. 15 May 1984: 4 pp.
- 29.- 103: 165976f *Synthesis and use of polyurethanes in medicine.* Lipatova, T. E.; Lipatov, Yu. S. (USSR). *Zh. Vses. Khim. (Ura in D. I. Mendeleeva)* 1985, 30(4), 438-46 (Russ). A review with 65 refs. on compn., prepn., and properties of polyurethanes for medicinal use. Biocompatibility and mechanism of polyurethanes biodegradn. with some examples were discussed.
- 30.- 103: 143178q *Segmented copolymers with emphasis on segmented polyurethanes.* Abouzahr, Saadeddine; Wilkes, Garth L. (Dep. Chem. Eng., Virginia Polytech. Inst. and State Univ., Blacksburg, VA 24061 USA). *Process., Struct. Prop. Block Copolym.* 1985, 166-207 (Eng). Edited by Folkes, M. J. Elsevier Appl. Sci.: London, UK.

- 31.- 103: 134530x Polyurethane: the protein polymer. Seymour, Raymond B. (Dep. Polym. Sci., Univ. South. Mississippi, Hattiesburg, MS 39406-10076 USA). *Pop. Plast.* 1984, 30(5), 14-16 (Eng). A review with 36 refs. on the history and uses of polyurethanes, esp. elastomers; their outstanding versatility.
- 32.- 091858 AUMENTA LA PRODUTTIVITA' DELLE MACCHINE PER POLIURETANI. [Machines for Polyurethanes Increase their Productivity]. Improvements in the system of loading and in the mixing heads and an ever increasing use of electronics and robotics are opening the way to automation of productions with more and more rapid cycles also for large components. (Author abstract) In Italian.
Ann. Mater. Plast. Elastomeri n 12 Dic 1983 p 671-673
- 33.- 102: 7507d Research in the field of polyurethanes in Romania. Stoianescu, Felicia A. (Cent. Cercet. Mater. Plast., ICECHIM, Bucharest, Rom.). *Rev. Chim. (Bucharest)* 1984, 35(8), 716-717 (Rom). A review with 26 refs.
- 34.- 101: 193174v Polyurethane foam: production technologies and applications. Gref, Hubert (Wetteren, Neth.). *Kunstst. Rubber* 1984, 37(8), 14-18 (Neth). A review with no refs.
- 35.- 101: 172513z Is it really necessary to use an auxiliary blowing agent in the production of flexible slabstock polyurethane foams? First approach to foams expanded with water only. Consoli, S.; Rosso, G.; Pizzolo, P. (Polyurethane RI Cent., Montepolimeri, S.p.A., Porto Marghera, Italy). *J. Cell. Plast.* 1984, 20(3), 200-8 (Eng). The prodn. of polyurethane foams of different hardness values having d. >21 kg/m³ using water as the only blowing agent was demonstrated.
- 36.- 101: 172163a Linear diisocyanate polyaddition products. Dienerich, D. (Bayer A.-G., Leverkusen, Fed. Rep. Ger.). *FH-Texte* 1984, 39(Chem. Technol. Makromol. Stoffe), 7-40 (Ger). The history of polyurethanes and urethane rubber is reviewed without refs.
- 37.- 100: 175740b Synthesis and properties of model polyurethane systems. Hwang, Kirk Kweng Shung (Univ. Wisconsin, Madison, WI 53706 USA). 1983. 324 pp. (Eng). Avail. Univ. Microfilms Int., Order No. DA6323379. From *Diss. Abstr. Int. B* 1984, 44(9), 1271.
- 38.- 100: 175312p Formation and properties of polymer networks. Experimental and theoretical studies. Stanford, J. L.; Stepto, R. F. T.; Still, R. H. (Inst. Sci. Technol., Univ. Manchester, Manchester, UK M60 1QD). *ACS Symp. Ser.* 1984, 243(Charact. Highly Cross-Linked Polym.), 1-20 (Eng). A review with 25 refs. on reactions forming tri- and tetrafunctional polyurethane and trifunctional polyester networks.
- 39.- 092615 NEUES ZUR FORMTEILFERTIGUNG AUS POLYURETHAN - WERKZEUGAUFLEGUNG; ERHOEHUNG DER FORMTEILQUALITAET. [Advances in the Manufacturing Technology of Polyurethane Articles - Mold Design; Enhancement of Article Quality].
Mudler, Henry (Inst fuer Kunststoffverarbeitung, Aachen, West Ger). *Plastverarbeiter* v 35 n 8 Aug 1984 p 65-73.

- 40.- 099691 POLYURETHANE - A VERSATILE MATERIAL IN A CHANGING WORLD. Topics discussed are the following: urethane raw materials; changing manufacturing techniques; low combustion foams; reaction injection molding; urethane binders and adhesives; medical uses; and polyurethane blends.
Froeh, K.C. (Univ of Detroit, Polymer Inst, Detroit, Mich, USA). *Plas Rubber Int* v 8 n 1 Feb 1983 p 17-19.
- 41.- 099701 POLYURETHANES: THE LEARNING CURVE.
Allport, D.C. (ICI Polyurethanes, Organics Div, Manchester, Engl). *Plast Rubber Process Appl* v 4 n 2 1984 p 173-190.
- 42.- 100: 193972f Polymerization and characterization of segmented polyurethanes. Saleem, M.; Ghaffar, A. (Dep. Chem., Quaid-i-Azam Univ., Islamabad, Pak.). *Pak. J. Sci. Ind. Res.* v. 83, 5(3), 156-61 (Eng).
- 43.- 100: 1570n Foaming technology. Urethane foam. Kusuta, Osamu; Inada, Tetsuo; Kato, N.; Takano, Masaru. *ANNUAL REPORT OF THE SOCIETY OF POLYMER SCIENCE AND TECHNOLOGY* 1983, v. 24, p. 1-14. A review with 20 refs.
- 44.- 99: 141626a Device for the production of a reaction mixture from flowable foam-forming or solid-forming components. Coblenz, Rolf; Schulte, Klaus; Ebeling, Wilfried; Evertz, Dieter (Bayer A.-G.) U.S. US 4,399,104 (Cl. 422-111; B01J14/00). 16 Aug 1983. DE Appl. 2,936,223. 07 Sep 1979; 8 pp.
- 45.- 099705 POLYURETHANE - NEW PATHS TO PROGRESS - MARKETING - TECHNOLOGY, PROCEEDINGS OF THE SPI INTERNATIONAL TECHNICAL/MARKETING CONFERENCE, 6TH, 1983.
Assoc SPI, Polyurethane Div, New York, NY, USA). *Polyurethane - New Paths to Prog - Mark - Technol. Proc of the SPI Int Tech/Mark Conf, 6th, San Diego, Calif, USA, Nov 2-4 1983* Publ by SPI, New York, NY, USA, 1983. Distributed by Technomic Publ Co, Lancaster, Pa, USA 520 p.
- 46.- 99: 127567q Toxicity of isocyanates in the manufacture of polyurethane materials. Walczyk, Wladyslaw; Ciesla, Tadeusz (Pol.). *Polimery (Warsaw)* 1982, 27(12), 468-71 (Pol). A review with 67 refs.
- 47.- 99: 106376m State of the technology and future development of polyurethanes. Oertel, Guenter (Fed. Rep. Ger.). *Plastverarbeiter* 1983, 34(7), 623-8 (Ger). A review with no refs.
- 48.- 99: 54620q Urethane polymers. Ulrich, H. (Uppjohn Co., Kalamazoo, MI USA). *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.* 1983, 23, 576-608 (Eng). Edited by Grayson, Martin; Eckroth, David. Wiley: New York, N. Y. A review with 38 refs.
- 49.- 99: 54403w Urethane oligomers - safe, solventless, and energy efficient. Bluestein, Claire (CAPTAN Assoc., Inc., Lyndhurst, NJ 07071 USA). *Proc SPI Annu Tech/Mark Conf* 1982, 27th Meet. Minds: Mark. Polyurethane Technol., 49-53 (Eng). A review with 2 refs.

- 50.- 98:144396g Polyether polyols for rigid polyurethane foams. Toho Chemical Industry Co., Ltd. Jpn. Kokai Tokkyo Koho JP 57,168,919 [82,168,919] (Cl. C08G65/26). 18 Oct 1982. Appl. 81/53,047. 10 Apr 1981: 3 pp.
- 51.- 98:96588y Results of 15 years of rigid polyurethane foam quality supervision. Zehendner, Horst (Forschungsinst. Waermschutz e.V., D-8032 Graefelfing, Fed. Rep. Ger.). *Cell. Polym.* 1982, 1(3), 211-20 (Eng). A review with 9 refs.
- 52.- 98:98587x The search for low-smoke polyurethane foams. Murch, Robert M.; Kehr, Clifton L. (W. R. Grace and Co., Columbia, MD 21228 USA). *Proc. Int. Conf. Fire Saf.* 1982, 7, 23-33 (Eng). A review with 24 refs. esp. concerning variations in polymer structure and additive formulations for fire-resistant polyurethane foams.
- 53.- 98:5138j Step growth polymerization. Part II. Developments in polyurethanes. Sparrow, D. J.; Walton, I. G. (Org. Div., ICI Ltd., Blackley, UK). *Macromol. Chem. (London)* 1982, 2 69-76 (Eng). A review. with 94 refs.
- 54.- 97:183263h New polyurethane-based cellular plastics. Petrov, E. A.; Gommen, R. A.; Esipov, Yu. L.; Kryuchkov, F. A. (USSR). *Plast. Massy* 1982, (9), 31-4 (Russ). A review with no refs. of prepn., properties, and uses of elastic, semirigid, and rigid polyurethane foams.
- 55.- 97:183256h Studies of the formation and properties of polyurethanes suitable for reaction injection molding. Stanford, J. L.; Stepto, R. F. T.; Still, R. H. (Dep. Polym. Fibre Sci., Univ. Manchester Inst. Sci. Technol., Manchester, UK M60 1QD). *Polym. Sci. Technol.* 1982, 18(React. Injection Molding Fast Polym. React.), 31-54 (Eng). A review with 30 refs.
- 56.- 97:72869r Preparation and study of isocyanate polymers. III. Infrared spectroscopic study of the reaction kinetics of polyurethane formation. Farkas, Ferenc (Graboplast, Gyor, Hung.). *Magy. Kem. Lapja* 1982, 37(4), 177-82 (Hung).
- 57.- 97:7570x Current status and trends in the production and use of polyurethanes outside the USSR. Murashov, Yu. S.; Petrov, E. A. (USSR). *Khim. Prom-st. Rubezhom* 1982, (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.
- 58.- 96:218723s Mixing process and apparatus for multicomponent synthetic resins, especially polyurethanes. Owada, Takeshi Jpn. Kokai Tokkyo Koho JP 82 21,415 (Cl. C08G18/05), 04 Feb 1982, Appl. 80/95,925, 14 Jul 1980: 4 pp. Chem reactive components (e.g. polyisocyanates and polyols) are injected into a mixing chamber so that the 2 streams impinge at an angle and at the same time hit a wall, to efficiently mix the components.
- 59.- 96:200187k The synthesis of polyurethanes. Khomenkova, K. K. (USSR). *Polimery--80 (Vosem'desyat)* 1980, 3-16 (Russ). Edited by Lipatov, Yu. S. Izd. Naukova Dumka: Kiev, USSR. A review with 49 refs.

- 60.- 96:145060m A mixer for synthetic resins. Polyurethane Engineering K. I. Jpn. Kokai Tokkyo Koho JP 81,148,512 (Cl. B29B1/06). 18 Nov 1981. Appl. 80/51,840. 19 Apr 1980; 4
- 61.- 95:151533h Optimization of selected ingredients of formulations for polyurethanes. Kopal, Pavel; Babula, Frantisek; Turcany, Josef; Sulo, Stefan (Partizanske, Czech.). *Kozarstvo* 1981, 31(5), 122-6 (Slo).
- 62.- 95:116423f Semirigid polyurethane foams. Daiichi Kogyo Seiyaku Co., Ltd. Jpn. Kokai Tokkyo Koho 81 53,126 (Cl. C08G18/48). 12 May 1981. Appl. 79/130,638. 08 Oct 1979; 4 pp.
- 63.- 95:99861s Method and apparatus for recovering polyurethane from wastes. Schuetz, Wilhelm; Prajnar, Bronislav. *Ger. Offen.* 2,951,617 (Cl. C08J11/04). 02 Jul 1981. Appl. 21 Dec 1979; 30 pp.
- 64.- 95:98806b Dimensionally stable one-component polyurethane foams using a two-compartment pressure pack containing an isocyanate-terminated prepolymer in the inner container and pressure medium in the outer container. Pauls, Mathias (BASF A.-G.) U.S. 4,263,412 (Cl. 521-114; C08G18/14). 21 Apr 1981. Ger. Appl. 2,842,242. 28 Sep 1978; 8 pp.
- 65.- 95:98791t Rigid urethane polymer foams. Hitachi, Ltd. Jpn. Kokai Tokkyo Koho 81 45,917 (Cl. C08G18/66). 25 Apr 1981. Appl. 79/120,671. 21 Sep 1979; 8 pp.
- 66.- 94:210746q Apparatus and method for a foamable mixture from at least two fluid, foam-forming reactants and aggregates. Kreuzer, Karl D.; Schulte, Klaus (Bayer A.-G.) U.S. 4,242,306 (Cl. 422-133; B01J19/18). 30 Dec 1980. Ger. Appl. 2,828,506. 29 Jun 1978; 7 pp.
- 67.- 94:176295e Process and apparatus for continuous production of polyurethane foam. Boon, Derk Jan (Reeves Brothers, Inc.) S. African 79 06,048 (Cl. C08G/). 29 Oct 1980. US Appl. 962,166. 20 Nov 1978; 31 pp.
- 68.- 94:176296f Method and apparatus for the manufacture of flexible polyurethane foam articles. Woods, George (Imperial Chemical Industries Ltd.) Eur. Pat. Appl. 23,749 (Cl. C08G18/08). 11 Feb 1981. Brit. Appl. 79/22,988. 02 Jul 1979; 15 pp.
- 69.- 94:122647c Rigid polyurethanes. Abell, Jesper (Jydsk Teknol. Inst., Den.). *Plast Panorama Scand.* 1980, 30(5), 29, 31, 32-4 (Dan). A review with no refs. on rigid polyurethanes, their manuf., properties, applications, and demand.
- 70.- 94:104543m Polyurethane foam moldings with a skin. Sanyo Chemical Industries, Ltd. Jpn. Kokai Tokkyo Koho 80,133,417 (Cl. C08G18/14). 17 Oct 1980. Appl. 80/2,887. 14 Jan 1980; 7 pp.

- 71.- 94: 85197b Biodegradable polymer materials. Ligatova, T. E.; Pkhakadze, G. A. (USSR). *Vopr. Akad. Nauk Ukr. RSN* 1980, (12), 22-30 (Ukrain). A review with 43 refs. of the work conducted at the Ukrainian Academy of Sciences on biodegradable polyurethanes for medical application (prosthetic devices, adhesives, etc.).
- 72.- 93: 163077m Mixing apparatus for urethane polymer-forming components. Elastogran Maschinenbau G.m.b.H. und Co. Jpn. Kokai Tokkyo Koho 80 77,514 (Cl. B29B1/06), 11 Jun 1980. Ger. Appl. 2,838,798, 06 Sep 1978; 4 pp. Two urethane
- 73.- 93: 151128u Light-resistant polyurethane foams. Toyota Gosei Co., Ltd. Jpn. Kokai Tokkyo Koho 80 73,723 (Cl. C08G18/14), 03 Jun 1980, Appl. 78/145,958, 28 Nov 1978; 5 pp.
- 74.- 93: 133152t Development of lower cost polyurethane modified polyisocyanurate and polyurethane rigid foams. Hughes, Joseph M.; Clinton, John L. (Tech. Serv. Appl. Res. Lab., Rubicon Chem., Inc., Woodbury, NJ 08096 USA). *J. Cell. Plast.* 1980, 16(3), 152-8 (Eng). *Urol* 11 [64641-71-8].
- 75.- 93: 133131k A review of polyurethane. II. Raw materials. Iwata, Keiji (Nippon Polyurethane Serv. Co., Ltd., Japan). *Porima Daijesuto* 1980, 32(4), 44-53, 132 (Japan). A review with 14 refs. I. Akahoshi
- 76.- 93: 133132m A review of polyurethane. III. Raw materials and flexible foam. Iwata, Keiji (Nippon Polyurethane Serv. Co., Ltd., Japan). *Porima Daijesuto* 1980, 32(5), 70-81 (Japan). A review with 11 refs. I. Akahoshi
- 77.- 93: 133144a Family of MDI-based isocyanates. Present situation and development. Allport D. C. (ICI Ltd., Engl.). *Rev. Gen. Caoutch. Plast.* 1980, 602, 75-81 (Fr). The prepn. of MDI [$\text{CH}_2(\text{C}_6\text{H}_4\text{NCO})_2$] [101-24-8] and its applications in polyurethanes, foams, urethane rubber, adhesives, etc. are discussed.
- 78.- 93: 96189u Polyurethane foams. Nakai, Masahiro (Sanwo Chemical Industries, Ltd.) Jpn. Kokai Tokkyo Koho 80 48,214 (Cl. C08G18/14), 05 Apr 1980, Appl. 79/91,396, 17 Jul 1979; 6 pp.
- 79.- 93: 95672c Isocyanate-based polymers. Iwakura, Yoshio; Kurita, Keisuke; Nguyen Chau (Fac. Eng., Seikei Univ., Musashino, Japan). *Int. Prog. Urethanes* 1980, 2, 99-124 (Eng). A review, with 31 refs., of the prepn. and properties of polymers from diisocyanates and bis(*N*-hydroxyimides) or saccharides and of high-temp. polymers of *O*-phenylurethane derivs.
- 80.- 92: 42659b Dosage in the production of polyurethane plastics. Osinski, Ulrich (Maschinenfabr. Hennecke G.m.b.H., Birlinghoven, Fed. Rep. Ger.). *Dossieren Kunststoffech.* 1978, 265-77 (Ger). VDI-Verlag: Duesseldorf, Fed. Rep. Ger. A review without refs. of methods and app. for combining polyols, isocyanates, catalysts, blowing agents, fillers, etc., in the manuf. of polyurethanes.

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

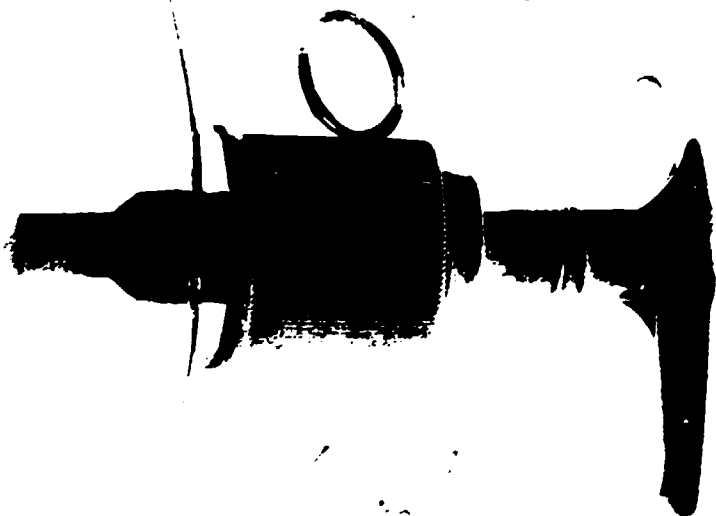
- 2.1 RIM-Fundamentals of Reaction Injection Moulding
C.W.Macosko, 1989, 257pp.
- 2.2 The ICI Polyurethanes Book
Woods, G. J. Wiley & Sons, 1987, 330pp
- 2.3 Polyurethanes in Medicine
Lelah, M.D., CRC Press, 1986, 240pp., \$39.00
- 2.4 Equipment for Processing Plastics and Rubber, Series KHM-2
Equipment for the Production of Moulding Polyurethanes.
Review Information.
Befedov, A.S., Apanasenko, E.E., Kondurov, A.P., 1986.
46pp., (Russ) rub 0.73.
- 2.5 Polyurethane Handbook
Oertel, G., Ed: Macmillan Publishing Co., 1985, 626 pp.
\$128.00.
- 2.6 Organosilicon Polyurethanes
Kuznetsova, V.P. et.al., 1984, 221pp, (Russ) rub 2.90.
- 2.7 Plastic Handbook, Vol.7: Polyurethanes. 2nd Ed.
Ed. Hanser, Munich, 1983, 664pp. (Ger), DM 346.
- 2.8 Modified Polyurethanes
Omelchenko, S.I., Kadurina, T.I., Ed. Naukova Dumka, Kiev,
1983, 226pp. (Russ) rub 2.80.
- 2.9 Polyurethane: Kunststoff Handbook
Becker/Braun
- 2.10 Polyurethane-Based Composite Materials
Buist, J.M. et.al., Ed. Khimiya: Moscow, 1982, 238pp.
(Russ) rub 1.40.
- 2.11 Physical Chemistry of Polyurethanes
Omelchenko, S.I., Ed. Naukova Dumka, Kiev, 1981, 104 pp.
(Russ) rub 0.70.
- 2.12 Synthesis of Polyurethanes
Omelchenko, S.I., Ed. Naukova Dumka, Kiev, 1981, 140pp.
(Russ) rub 0.11.
- 2.13 Advances in Urethane Science and Technology
Vol.8, Ed. Technomic Publishing Co., 1981, 274pp.
- 2.14 International Progress In Urethanes
Vol.3, Ashida, K., Frisch, K.C., Ed. Technomic, 1981,
259pp.

- 2.15 ACS Symposium Series, Vol. 172: Urethane Chemistry and Applications (Based on a symposium Sponsored By the Macromolecular Secretariat, at the 2nd Chemical Congress of the North American Continent(180th ACS National Meeting), Las Vegas, Nevada.
Edwards, K.H., Ed. American Chemical Society, 1981, 590pp.
- 2.16 International Progress in Urethanes
Vol.2, Ashida, K., Frisch, K.C., Ed. Technomic publishing Co., 1980, 173pp.
- 2.17 Developments in Polyurethane
Vol.1, Buist, J.H., Ed. Applied Science Publishers, Ltd, London, 1978, 280pp.
- 2.18 Urethane abstracts
1971., n. \$115. Technomic Publishing Co., Inc.
- 2.18 Urethane Plastics and Products
1971., n. \$95. Technomic Publishing Co.
- 2.19 Urethanes Technology
1984. q. £13.50. Crain Communications Ltd.

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Becker/Braun
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Polyurethane

Herausgegeben von Günter Oertel

7



3. Some worldwide Polyurethanes Producers

3.1 U.S. Producers

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Flexible Products Division, 3558 2nd St North
Minneapolis, MN 55412

Alpha Foam Systems, Inc.
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Foamcraft Inc.
P O Box 15246 Sarasota FL 33579

Gallagher Corp.
3966 Morrison Dr. Gurnee IL 60031

Molded Dimensions, Inc.
701 Sunset Rd. Port Washington, WI 53074

Newage Industries Inc.
Plastics Div., 2300-21 Maryland Rd., Willow Grove PA
19090

Plast-O-Menc, Inc.
21300 Doral Rd., Waukesha, WI 53187

Rubber Millers Inc.
709 S. Caton Ave. Baltimore MD 21229

Urethane Products Industries, Inc.
4950 Hudson-Stow Dr., Stow OH 44224

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Cran Midwest
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Elliott Company of Indianapolis, Inc.
9200 Zionsville Rd., Indianapolis, IN 46268

Foam Enterprises
136308 Watertower Circle, Minneapolis, MN 55441

Nott Co.
Rubber Fabrication Div., 1724 New Brighton Blvd., PO Box
1422, Minneapolis, MN 55440

Ohio Rubber Co.
Orthane Div., Interstate 35W, Dept U, Centon, TX 76201

Presto Manufacturing Co.
4A Franklin Ave., Brooklyn, NY 11211

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Dennis Chemical Co.
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Furane Plastics, Inc. Sub
M & T Chemicals, Inc., 5121 San Fernando Rd. W. Los
Angeles, CA 90039

Goodrich Company, BF
Specialty Polymers & Chemicals Division, 6100 Oak Tree
Bld., Cleveland, OH 44131

Kenics Corp.
Kenics Pl., North Andover, MA 01845

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624 Schuyler Ave., Lyndhurst, NJ 07071

Sannacor Industries, Inc.
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P O Box 241, Scotch Plains, NJ 07076

Company

Address

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(c)

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Anderson Development Co.

(pp)

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ph. 517-263-2121

Atochem North America, Inc.

266 Harristow Rd.,
Glen Rock, NJ 07452
ph. 201-447-3300

Dow Chemical

2020 Dow Center Midland
MI 48640

Ferro Corp,
Bedford Chemical Div.

(c)

7050 Krick Rd. Bedford,
OH 44146 ph. 216-641-8580

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W.R. Grace & Co,
Organic Chemical Div.
Specialty Chemicals Unit
(pp)

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

ICI Polyurethanes Group,

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15205-9741 ph. 412-777-2000

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

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(pp)

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tics Co, Inc. Specialty Chemicals
Div.
(c,i)

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

E.F. Whitmore & Co.
(p)

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Mazzanini, S.r.l., Giuseppe, Via A.
Grandi, 12, Zona Industriale
Terrafino, I-50053 Empoli (FI)
T. (0571) 82250

Switzerland

ROMAY AG, Gontenschwilerstrasse,
CH-5121 Oberkulm (AG) T. (064)
461106, Tx: 961578

Turkey

IMEKS Sinaî Mamulîer Dis ve İc
Ticaret A.Ş., Dogus Han Büyükdere
Cad. 42/8, Mecidiyeköy, TR- İstanbul
T. (1) 1722872, Tx: 23176



You find the instructions
how to use the book in
front of the pink section

Please note the comprehensive ABC
brochure behind the title pages

3.4 European Producers: Supplementary and tentative list

GERMANY

Ashland Südchemie Kernfest GmbH	Postfach 440-D-4010 Hilden
BF Goodrich Chemical (Deutschland) GmbH	Cörlitzer-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 Erkenschwick
EW Betriebe Emmerling & Weyl GmbH Siemenstr. 9 and Co. Werner	D-6252
Geier + Voss GmbH	8208 Kolbermoor/Rosenheim Postfach 1260
Häger & Kässner GmbH	Postfach 449-D-4730 Ahlen Westf.
Hefela GmbH	Postfach 1180, D-5227 Windeck/Rosbach
Iromer Chemie GmbH	Hafenringstr. 1-3 D-4500 Osabrück
Vosschemie GmbH Chemische	Postfach 1355 D-2082 Vetersen
<u>U.K.</u>	
Akzo Chemie UK Ltd	1-5 Queens Rd., Hirsham 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
CRP Marine Ltd.	15-20 Greenhey Place, East Gillibrands, Skelmersdale, Lancashire, WN8 9SA
Lankro	P.O.Box 1, Eccles Manchester M30 0BH ph. 61-789-7300
Durham Chemicals Ltd	Wedgwood Way, Stevenage Berts. SG1 4QM

Unitex Ltd. ph. 438-734000
Halfpenny Lane,
Knaresborough,
North Yorkshire, HG5 0PP

ITALY:

Ausind S.p.A. 13 Corso Sempione
21053 Castellanza
ph. 331-501100

Lati S.p.A. 21040 Vedano Olona

AUSTRIA:

Vianova Kunstharz A.G. 104 Altmannsdoeferstr.
1120 Vienna
ph. 1-85050

FRANCE:

Electra-Unic-Industri 21, rue Gambetta 95300
Pontoise ph. 1-30383285

Plastibel 21 89350 Champignelles
ph. 86451023

Souplethane 32-34 Route des Fusilles
92000, Nanterre
ph. 1-42046352

SWITZERLAND:

Crisco AG Sevelen
ph. 085-5643132

Maag 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-Nashi,
Higashi-Ku Osaka
ph. 6-201-2461

Hodogaya Chemical Co Ltd. 4-2 Toranomon,
1-Chome, Minato-Ku
Tokyo 105
ph. 03-504-8631

Kamatsuya Kagaku KK

890 Ogiwara,
Hidaka-Machi, Hidaka Gun
Wakayama Pref.649-12
ph. 73-863-2007

Mitsui Toatsu Chemicals

3-2- 5,Kasumigaseki,
Chiyoda-Ku, Tokyo
ph. 2223622

Sumitomo Bayer Urethane Co,Ltd

3 Souke, 1 Chome,
Kukuchi, Amagasaki
City, Hyogo Pref.661
ph. 06499-2401

Takeda Chemical Industries

2-3-6,Dosho-Mashi,Chuo-Ku
Osaka 541

Toyo Tire & Rubber Co. Ltd

1-17-18 Edobori, Nishi-Ku
Osaka
ph. 6-441-8801

INDIA

Hindustan

81 Maharshi Karve Marg.
Bombay 400.002
ph. 22-314271

Sasmira

Bombay

ISRAEL

Thio-Atim International

6 Hazorfim Street,
(1986) Ltd
Ramon Yam, Bat Yam 59605
Israel

SINGAPORE

Geneplast Private Limited

18, Neythal Rd.
SG 2262
ph. 2652177

Industrial Engineering Suppliers

98, Owen Rd
SG 082-Sing.

Insutech Thermal & Engineering(S)
Pte Ltd

50 Pal Crescent
SG-1232 Sing.

TAIWAN

Nan Pao Resins Chemical Co.,Ltd

12 Nan Hai Village
Shee Kang Shiang
Tainan, Taiwan
ph. 6-795-2801

3.6 Australian, Canadian and African Producers:

AUSTRALIA

Barham-Quinn PTY.Ltd

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

Frankston Manufacturing Co.
PTY.Ltd

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

AC Matrick Chemicals PTY.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

Industrials Orethanes (PTY) Ltd

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

3.7 Latin American Producers:

BRASIL

JM Do Brasil Ltd

Caixa Postal 123
13100 Campinas Brazil
ph. 192-641700

CHILE

Industrias Quimicas Soler
Chilena Ltda

Manchester 2838, Santiago
ph. 513452- 516679

COLOMBIA

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

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

Basf Quimica Colombiana

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

Compania Quimica Borden

SM 20M-75 Cali
ph.615257

ECUADOR

Esflo S.A

Km 8.5 Via A. Mantas
ph. 651-657

Plastex S.A.

Panamericana Sur Km 5.5
Apdo. 2485
ph.263854

PERU

TecnoquimicaS.A.

Pista a la Atarjea 1152
El Agustino
ph.276000

VENEZUELA

Sintesis C.A.

Av. Codazzi, Sta. Monica
ph. 6613638

Venetan C.A.

Av. Venezuela,
Torre Clemente, Piso 6
El Rosal
Ph. 9869311

4. Some Equipment Suppliers and Consultancy Services:

GERMANY

Battenfeld Maschinen Fabriken GmbH

Postfach 1164-65
D5882 Weinerzhagen

Cannon Deutschland GmbH

Postfach 1162
D-6052 Muhlheim/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 Munchen

Glas Mate Kunststoffver-
arbeitungsanlagen GmbH

Otto-Scheugenpflug-Str.16
D-6050 Offenbach-Bieber

Grenzbach Maschinenbau GmbH

Postfach 11 55,
8854 Asbach-Bäumenheim
(Eamlar)

Gusmer-Guscrafft GmbH

Liebigstr.8,
D-6054 Rodgau 6

Hennecke GmbH Maschinenfabrik

Postfach 1180
5205 Sankt Augustin 1
(OT Birlinghoven)

Hermann Jennert KG Maschinen
und Anlagenbau

Lindenplatz 62
5900 Siegen (Geisweid)

D.J. Keil KG Ing.Büro

Freiherr vom Stein Str.2
D-6107 Reinheim

Kern-Liebers

D-723 Schramberg

Klöckner Ferromatic Desma GmbH

Postfach 1140
D-2807 Achim
ph. 04202-50-0

Krauss-Maffei Aktiengesellschaft

Postfach 50 03 40
8000 München 50

Lackfa Isolierstoffe GmbH & Co.

Industriestr.2
D-2084 Rellingen 2

Lotsch und Partner Modelbau GmbH
& Co.

Flügelstr.7
D-4600 Dortmund 41
ph. 0231-402410

Puroll K-M-E GmbH & Co. KG.

Rudolf-Diesel-Str.24
8019 Otobrun
(Reimerling)

Siku Fertigungstechnik und
Anlagenbau GmbH & Co.KG.

Postfach 1136,
4714 Selm

T.M.G Technologie-Verwertung und
Marketingges.mdB.

Postfach 1328,
5905 Freudenberg

ITALY

Pressindustria Engineering &
Plants SpA

Via Porto Darnolfo 35
I-20046 Biassono (MI)

Plastimac SpA

P.le G. Cesare n 9
I-20145 Milano
ph. 4985851

SWITZERLAND

Broendle AG E.

Industriestr.31,
8305 Dietlikon

Dopag
Dosiertechnik+Pneumatik AG

Hinterbergstr.32
6330 Cham

Napag Maschinen & Plastic AG

Schwarztorstr.26
3007 Bern

Meyer & Cie AG A.H.

Badenerstr.329
8040 Zurich

Spritztechnik AG

Wiesenstr.468
9327 Tubach

CIC Ralphs Ltd.	Unit 38/39, Second Ave. Westfield, Midsomer Morton, Bath Avon BA3 4BN
Compounding Ingredients Ltd	Unit 217 Walton Summit Center, Bamber Bridge, Preston, Lancashire, PR5 8AL
Bridgetown Industries Ltd	Green Lane, Bridgetown Cannock, Staffordshire WS11 3JW
Ryma Engineering (NIC) Ltd	Unit 2/3 Westpoint Industrial Estate, Bargreaves St. Oldham Lancashire, OL9 1ND
Rytek Mouldings Ltd	Mallcroft Industrial Estate, Retford, Notts DN22 7SS
<u>USA</u>	
Anderson Development Co.	1425E Michigan St. Adrian, MI 49221, ph. 517-263-2121
Abatron Incorporated	33 Center Dr. Gilberts IL 60136 ph. 312-426-2200
Cannon USA Inc.	1235 Freedom Rd. Mars. PA 16046
Elastogran Machinery (EMB)	1725 Biddle Ave. Wyandotte MI 48192
Glas-Craft, Inc.	5845 w. 82nd St. 102 Indianapolis, IN 46278 ph. 317-875-5592
Hudson Moulding Systems	32 Stevens St., Haverhill MA 01830 508-374-0303
Nichan Clay Products	826 E Fourth St., P.O. Box 6, Pittsburgh, KS 66762 ph. 316-231-1400
Nobay Corp., Machinery Group	Nobay Rd, Pittsburgh PA 15205 ph. 412-746-3000
Olin Corp. Chemicals Group	120 Long Ridge Rd, Stamford CT 06904-1355 ph. 203-356-2000
Polymers Technologies, Inc.	University of Detroit 4001 West Mc Nichols Rd Detroit, MI 48221-1011 Ph. 313-927-1270

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.

Inst. Sci. Technol.
Univ. Manchester
Manchester, UK M60 1QD

London Sch. Polym. Technol.
Polytech. North, London
London UK N7 8DB

Rappra Technology Ltd
Shawbury, Shrewsbury,
Shropshire SY4 4NR

5.5 USA

Int. Isocyanate Inst. Inc.
Parsippany, NJ

Rubicon Chem., Inc.
Tech. Serv. Appl. Res. Lab.
Woodbury, NJ 08096

Univ. of Detroit
Polymer Inst. Detroit
Michigan

Virginia Polytech. Inst.
and State Univ.
Blacksburg, Va 24061

6. INTERNATIONAL PROJECT REVIEW

ECN NEW PROJECT SUMMARY

New projects summarised below appeared in ECN on 18 and 25 February 1991

Company	Location	Product	Capacity, tonne/year	Process	Contractor	Total erected cost	Start-up date/status
Manali Petrochemicals	Madras, India	isocyanates					S

ECN NEW PROJECT SUMMARY

New projects summarised below appeared in ECN on 3 and 10 December 1990

Company	Location	Product	Capacity, tonne/year	Process	Contractor	Total erected cost	Start-up date/status
Dow Quimica	Aratu, Bahia state, Brazil	polyols	40 000			\$17m	1992
Shell International Chemical	Far East	styrene PO polyols	320 000 140 000 140 000				--- S 1994

ECN NEW PROJECT SUMMARY

New projects summarised below appeared in ECN on 13 and 20/27 August 1990

Company	Location	Product	Capacity, tonne/year	Process	Contractor	Total erected cost	Start-up date/status
Shell International Chemical/Mitsui Toatsu	Western Europe	MDI	50 000	Mitsui Toatsu		\$200m	S end 1993

Note: We multiply tonne/day by 330 to get tonne-year. T - total, (x) - 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

Company	Location	Product	Capacity, tonne/year	Process	Contractor	Total erected cost	Start-up date/status
Montedipe	Porto Marghera, Italy	MDI TDI	(x) (x) 20 000 110 000T				1992 1991

ECN EUROPEAN REVIEW

supplement dec.1990

Companies buying or investing/
companies acquired or set up

Mitsui & Co/Borsod-Aabony Kombinat

Location

Lipany/Hungary

Products/Business

Polymethylene

Stake

40%

Cost

100m

8. BIBLIOGRAPHY

8.1 Books, reports, and journal articles:

- 8.1.1 Modern Plastics Mid-October Encyclopedia Issue 91
- 8.1.2 Encyclopedia of Polymer Science and Engineering
J. Wiley and Sons., 2nd. Ed., 1988
- 8.1.3 Chemical Processes Industries
Shreve, R.W., 4th. Ed., 1977
- 8.1.4 Encyclopedia of Chemical Technology
Kirk Othmer, 3rd.Ed., 1983
- 8.1.5 Polyurethanes, The all Purpose Polymers?
World Plastic & Rubber Technology 1989
- 8.1.6 Polyurethanes: The Learning Curve
Plastic and Rubber Processing and Applications
Vol.4, n 2, 1984
- 8.1.7 Recent Developments in Polyurethanes- IV
Man-Made Textiles in India, Nov.1987
- 8.1.8 Progress in Polyurethane Elastomers
Progress in Rubber and Plastic Technology, Vol.3, n 3
1987
- 8.1.9 Which Polyurethane and where to use it
Water Eng.(Cleveland), V.99, n 1, Jan. 1984
- 8.1.10 What Polyurethane?, Where?
Rubber World, Sept., 1984
- 8.1.11 Cambia il mercato dei Poliuretani
Water Plast Elastomeri 1 Jan. 1985

8.2 Directories:

- 8.2.1 Directory of the World Producers 1989/1990
- 8.2.2 CEC 88
- 8.2.3 Industrial Exports Directory 1991
- 8.2.4 OPD Chemical Buyer
- 8.2.5 Directory of Research and Technology 1990 (Organiza-
tions active in Product Development For Business)
R.R Bowker, 24 Ed.
- 8.2.6 Seisst Industrie Katalog 88
- 8.2.7 International and Plastics Handbook
Saechtling, 1983
- 8.2.8 Chemical Plant Contractor Profiles 4th.Ed., 1983
- 8.2.9 Wer baut Maschinen und Anlagen 89

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 tonne/year in 1980 to nearer 5m tonne/year in 1989, 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 face 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 recyclability 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

'For the next decade or two there is an almost infinite ability to invent materials.'

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 HFCs have a global warming potential and HCFCs 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 gram 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.

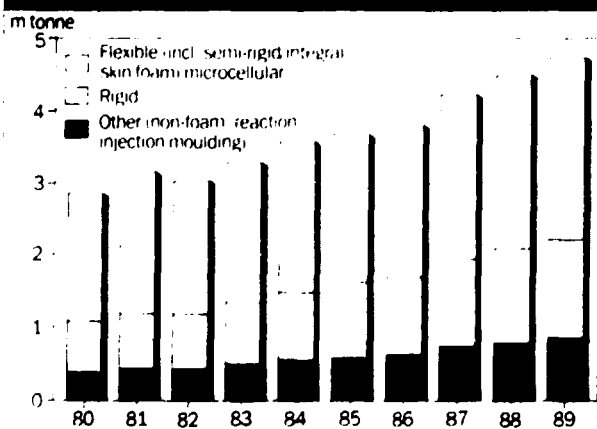
Alan Pedder believes that the structural and insulation properties of PUR have overcome the pressure exerted on the product by the CFC replacement problem. Indeed, he sees energy conservation in developing countries as a major possible area of expansion. ICI was recently involved in a UN-sponsored seminar 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.'

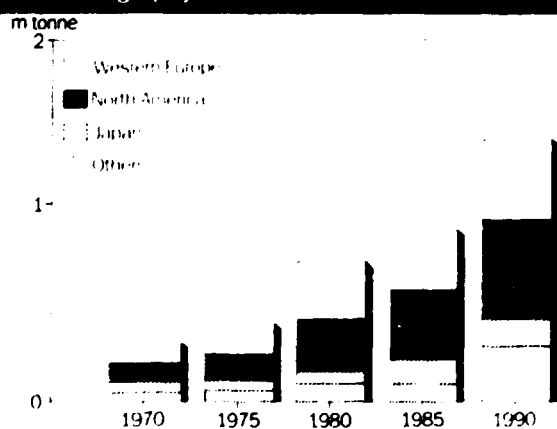
Although he declines to elaborate further about ICI's plans, he foresees increased specialisation by the leading players in the international PUR business as it adapts to the 1990s. ■

Growth in total polyurethanes use 1980-1989



Source: ICI

Rigid polyurethane foam markets 1970-1990



Source: ICI

Polyurethanes: the learning curve†

D. C. Allport

ICI Polyurethanes, Organics Division, Hexagon House, Blackley, Manchester M9 3DA, Great Britain

(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

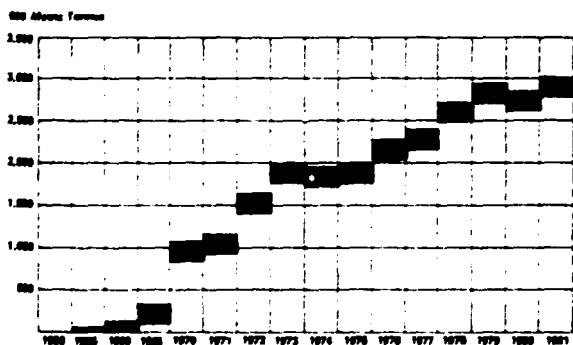


Fig. 1 Growth of polyurethanes.

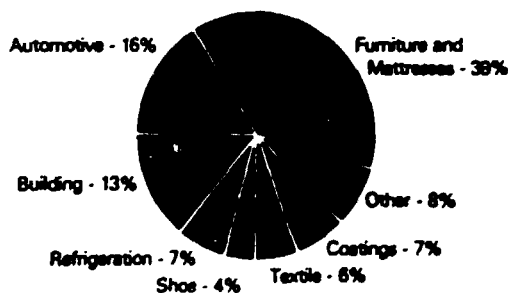


Fig. 2 World consumption of polyurethanes - 1981.

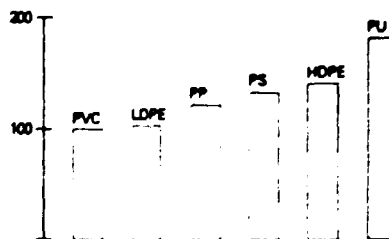


Fig. 3 Cost indices of polyurethanes - January 1983, average German prices.

† Based on a plenary presentation at the Plastics and Rubber Institute's Polycon '83: Reactive Processing - Opportunities and Constraints, Noordwijkerhout, The Netherlands, May 1982.

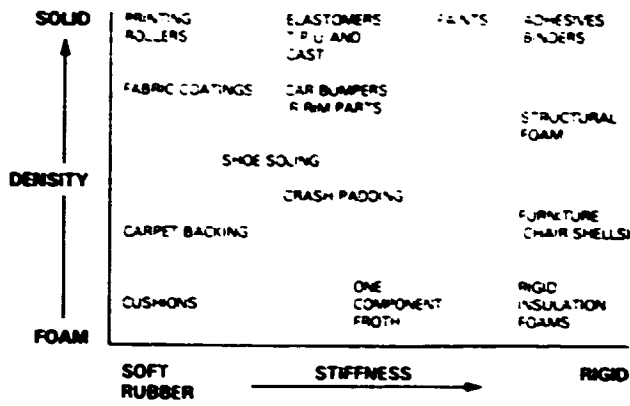


Fig. 4 Property matrix of polyurethanes.

insulation foams in building (Fig. 6) and refrigeration (Fig. 7) 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



Fig. 5 Polyurethane seating, head restraints, arm rests and crash padding in a modern car.

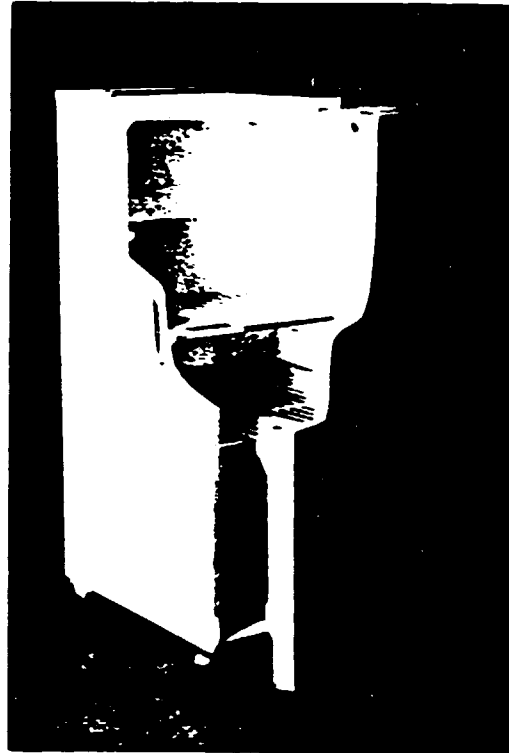


Fig. 7 Polyurethane rigid foam refrigerator insulation.

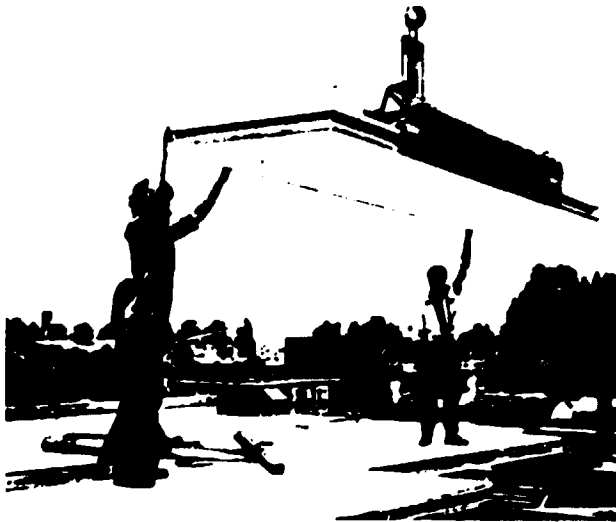


Fig. 6 Polyurethane rigid foam roof panels.



Fig. 8 Pouring mixed polyurethane chemicals into a shoe sole mould.

P
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2
A
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pi

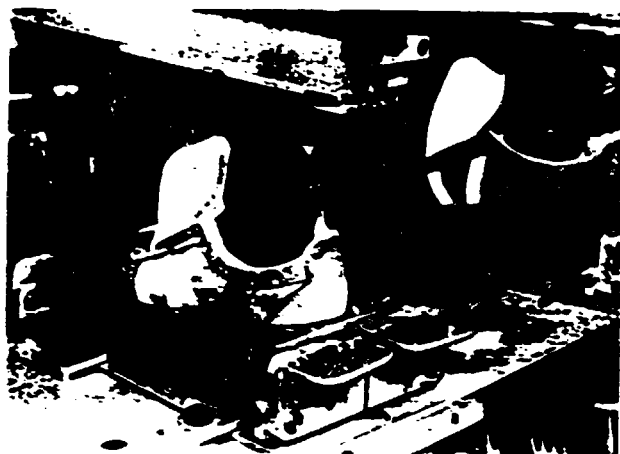


Fig. 9 Shoe uppers in place over the reacting polyurethane shoe sole mixture.



Fig. 10 Sports shoes with polyurethane soles.

processing polymers and points to some important lessons for other reactive processing systems in the future.

2 Polyurethanes – what do they have in common?

Although polyurethanes show great diversity, they have many common attributes and characteristics:

- As materials they are used as substitution products. For example, they have successfully substituted springs and webbing in furniture, and they have substituted glass and mineral fibres in some insulation applications. They have been able to replace materials in particular applications only because of favourable overall property and cost benefits.
- Polyurethanes are all based on the exothermic reaction of polyisocyanates with molecules containing alcoholic groups. Several other chemical reactions are also available to polyurethane formulators and are indeed crucial to several applications. The whole spectrum of

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.

3 The growth of polyurethanes

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

- 1953 Flexible foams from TDI and polyesters. high pressure mixing
- 1955 Agitatorless low pressure mixing of foam chemicals
- 1956 TDI prepolymer polyether flexible foams
- 1957 Polymeric MDI introduced for rigid foams
- 1958 Thermoplastic polyurethane elastomers invented
- 1959 Tin/amine catalysts allow one-shot polyether flexible foams to be made
- 1960 Hot cure moulding of flexible foam cushions
- 1960-65 Rigid foam blowing by chlorofluorocarbons
- 1963 MDI rigid foam refrigerator line demonstrated
- 1964-65 Lamination processes developed
- 1964 Inverse lamination process for rigid foams
- 1968 Isocyanurate rigid foams developed
- 1967-69 Polyurethane shoe soling systems introduced
- 1968 Isocyanurate rigid foams introduced
- 1968 Microcellular car bumpers
- 1967-70 RIM developed
- 1970 Flat block flexible foam process
- 1974-79 Development of RIM process and applications
- 1979 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 diisocyanates, 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 CO_2 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 $30\text{--}60 \text{ kg m}^{-3}$.

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 $0.015 \text{ W m}^{-1} \text{ K}^{-1}$ 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 $0.023 \text{ W m}^{-1} \text{ K}^{-1}$ after 25 years. When impermeable facings cover the foam, very little change in value is detected over long periods of time. In energy conservation matters, rigid polyurethane foams have

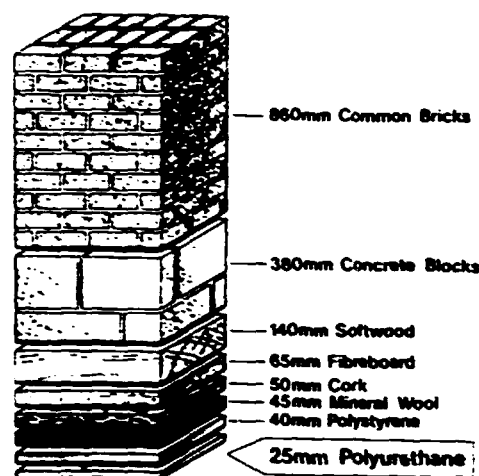


Fig. 11 Equivalent thickness of common building and insulation materials required to achieve the same degree of insulation (dry conditions).

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 $80\text{--}100^\circ\text{C}$ 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, chip-board, 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 to most natural materials. Many opportunities for composite manufacture are thus available.

The processing characteristics are very dependent upon the formulation chosen and on the machine parameters used, and thus choices between interacting variables may have to be made. The end product properties may also be related to the machine type, to heat flows and to the exotherms produced. 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 are 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 sup-

plier 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



Fig. 12 RIM polyurethane elastomer tractor front.



Fig. 13 Metal faced polyurethane rigid foam building element.

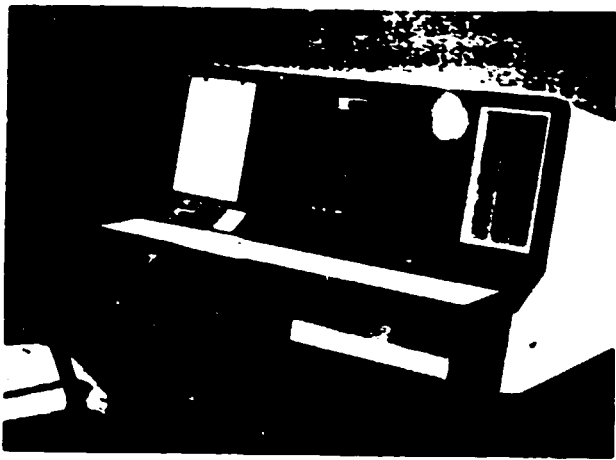


Fig. 14 RIM polyurethane structural rigid foam body scanner housing.



Fig. 15 RIM polyurethane elastomer automobile soft front end.

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.

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Recent Developments in Polyurethanes – XVI

S.B. Iyer*

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 infrequent 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 ($> \text{CH.OH}$), rather than primary ($-\text{CH}_2.\text{OH}$). 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 dilaurate 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.

*Sasmira

Table I: Typical Formulations for Producing Flexible Polyurethane foams

Polyester		Prepolymer	Oneshot	
Alkyd made from:		Prepolymer made from:	Niax Triol LG ₃ 6	100
Adipic acid	1.5 mole	Polypropylene diol mol. wt. 2,025-100 g	Polypropylene oxide/glycerol polyol mol. wt. 3,000	30
Sebacic acid	1.5 mole			
Diethylene glycol	3.25 mole	Toluene di-isocyanate	80/20 blend-33 g	100 g
Glycerol	0.5 mole	N-ethylmorpholine	1.0 g	
Cellulose acetate butyrate	1.0 g	Triethylamine	0.3 g	
N-Coco-morpholine*	2.0 g	Water	2.3 g	
N, N-dimethylethylamine	2.0 g	Silicone oil	0.3 g	
Water	4.0 g			
Toluene di-isocyanate (65:35 blend)	33g		Toluene di-isocyanate (80:20 blend)	36.7 g

* 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 Hencke 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 $\frac{1}{16}$ 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 flash 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.

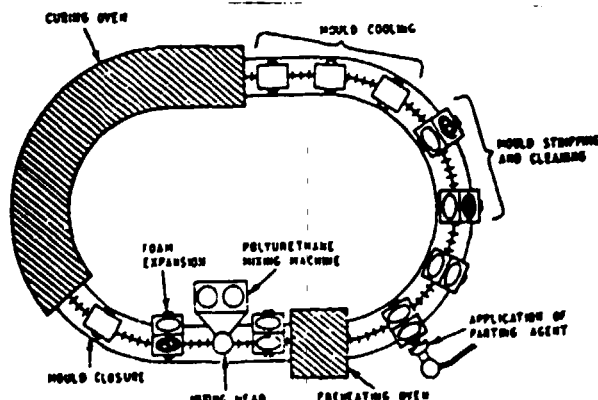


Fig. 1: Foaming-in-place: assembly-line production.

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

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(Contd. from p. 475)

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

1. M.D. Teli and Ruby Dugar: Man Made Textiles in India, XXXI (1), 24 (1968).

(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 immediately 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 lo-

wered. Trimethylol propane yields adipates with better compatibility than glycerol, and similarly glycerol/sebacic acid alkyds are more readily mixed than glyceryl 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:

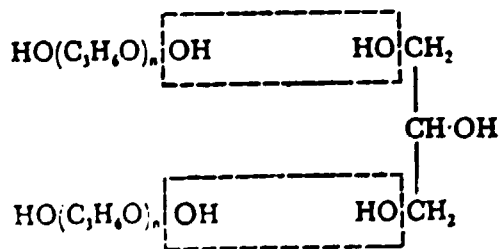
1. *Acid number* -- The acid number is defined as the number of milligrams of potassium hydroxide required to neutralise the acidity in one gram of resin.

2. *Hydroxyl number* -- The hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to 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:



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

Reactant	Early German resin Desmophen type	Sebalkyd resin	Experimental rigid-foam alkyd
Succinic acid	--	0.5	--
Adipic acid	2.5	--	3.0
Sebacic acid	--	2.0	--
Phthalic anhydride	0.5	0.5	--
Glycerol	4.0	4.1	--
Trimethylolpropane	--	--	3.0
Diethylene glycol	--	--	2.0
Time of reaction with di-isocyanate	27 min	7 min	1 1/2 min

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 gasing 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-dimethylcetamine, 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 merit that no complicated weighing or measuring operations are required.

Mass Production of Slab Foam

The original machine for production of Moltopren 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

(Contd. on P. 468)

(Contd. from P. 448)

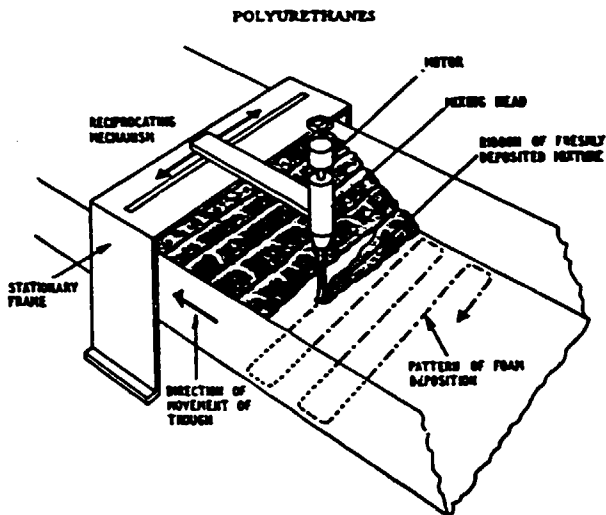


Fig. 1. Principle of the Hencks machine.

day. In order to obtain good dispersion of the activator it is delivered under pressure from a Bosch pump of the diesel-injection type.

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)

(Contd. from P. 449)

stretching the fabric is guided with complete lack of lengthwise tension on a conveyor belt to the plaiter.

Depending on operational requirements, the machine is offered in different versions and combinations. For example, the low-cost "Santastretch-Mini" and the "Santastretch-Standard" can be combined with the tube slitting and spreading machine, model "Santa-Cut". The "Santastretch-Weko" has a spray applicator from Weko Biel AG integrated for the exact application of impregnating liquors on both sides of the fabric, and the "Santastretch-Plus" permits wet-on-wet impregnation, for example, with synthetic resin. Moreover, the "Sandoflex®" process, which approaches mercerisation of knitted fabric in tubular form, can be applied.

The advantages of this machine can thus be summed up as follows:-

--- All controls and measuring instruments are fitted in full view of the operator at the front of the

machine.

--- Economical processing technique is afforded by continuous operation.

--- Disentangling, hydroextracting and stretching in one single operation.

--- Elimination of 1....2 processes and correspondingly low production costs.

--- Tensionless, automatic fabric transport through the entire machine.

--- Increased productivity, since it is no longer necessary to stop the machine in order to change the expander to accommodate different width.

--- No edge marking by stretching after the squeezing process.

--- High expression by using special squeeze-extraction rollers.

--- The controlled stretching and compacting process is the ideal prerequisite for the following dry finishing process resulting in reduced residual shrinkage of the finished goods.

Technical data:

Fabric speed	0.... 80 m/min.
Adjustable overfeed during stretching	0.... 25%
Connected load	4... 8kW
Compressed air	6 bar
Working widths	1000.... 1800 mm
(on versions with slitting device)	1000.... 2400 mm)

Monofilament Monitor

Sensor Metric, Inc. announced its MF-9000 series, on-line, real-time measurement systems for extrusion line monitoring of average diameter or (mass) and short length defect detection. The system consists of a manifold containing from 8 to 140 SMI sensor elements, a signal processing cabinet, an IBM PC-AT host computer and a printer.

The system automatically documents the quality of each package at doff time for quick segregation and grading according to the company. Automated trend analysis, data storage and/or closed loop extrusion line control are also available depending on user needs.

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 other workers about 25-30 years ago.

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

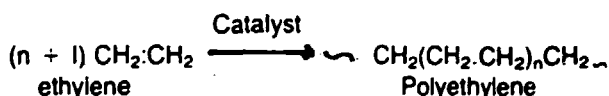
groups, then a threedimensional network will eventually result. Such polymer networks are called 'cross-linked' structures, and they can be rigid thermoset plastics or flexible vulcanised rubbers, depending on the mobility of the chains and their degree of cross-linking.

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.

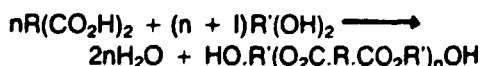
Rule 2 tells one nothing as to the practical utility of a particular bi-trifunctional system; but a reaction which proceeds rapidly and uncontrollably from reactant to cross-linked structure is technically useless. It is important to be able to produce, first of all, a linear or branched polymer which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

The Isocyanate Addition Reaction

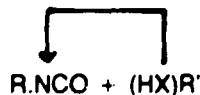
The reader will probably be familiar with the idea of using an unsaturated molecule as an example of a bi-bifunctional system in which polymerisation occurs by addition at double bonds. For example,



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 polyesters. For example:



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



*Sasmira, Bombay-25.

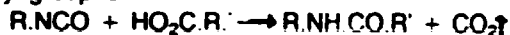
The most important examples in technical practice are the following

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



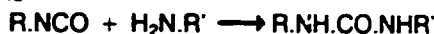
The resulting assembly of atoms in the linkage (NH.CO₂) between R' and R is the same as that found in ethyl carbamate (urethane). It is this name which is now applied generally to the group, so that a polyurethane signifies a polymer in which a plurality of such linkages are present. In accordance with 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



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



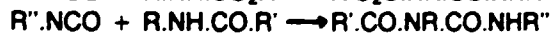
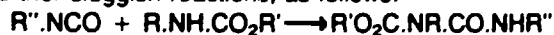
This reaction gives rise to a substituted urea, evidently very similar in structure to urea itself (NH₂.CO.NH₂).

4. The reaction between an isocyanate group and water is



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).

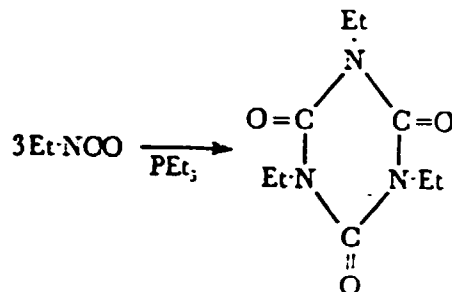
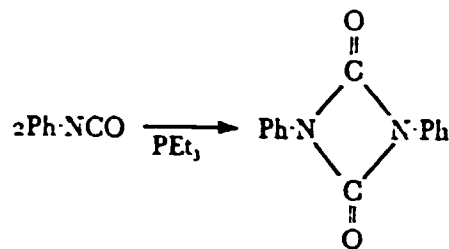
5. The hydrogen atom which was originally attacked in a hydroxyl, carboxyl, or amine group is *not eliminated*, but is present in the new linkage, albeit with a very much lower chemical activity. The possibility exists for further sluggish reactions, as follows:



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:

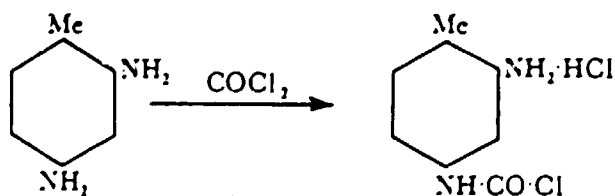
There are several possible synthetic routes to the production of isocyanates.

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

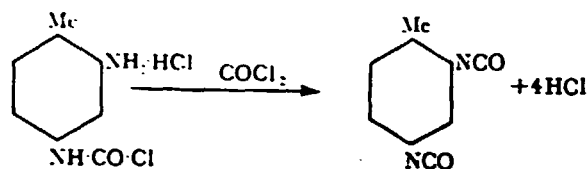
Generally speaking the direct reaction of amines is used for large scale production of aromatic di- and polyisocyanates, and the phosgenation of carbamic acids for production of aliphatic diisocyanates, while the more expensive process with amine hydrochlorides is a universal procedure for the laboratory 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:



In the second stage the suspension is slowly heated with a further addition of excess phosgene. The carbamic 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-diaminocyclohexane 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 *o*-position 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.

Stoichiometry: 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 drängt sich auf: Wo liegen sich welche Möglichkeiten? Bevor man allerdings versucht, darauf näher einzugehen, empfiehlt es sich, eine Produktionseinheit gleichsam in ihre wichtigsten Teile zu zerlegen, nämlich in:

- Dosiereinheit
- Transportmittel
- Werkzeuge und Werkzeugträger
- Hilfsmittel für Zu- und Abtransport
- Handhabungsgeräte für bestimmte Tätigkeiten

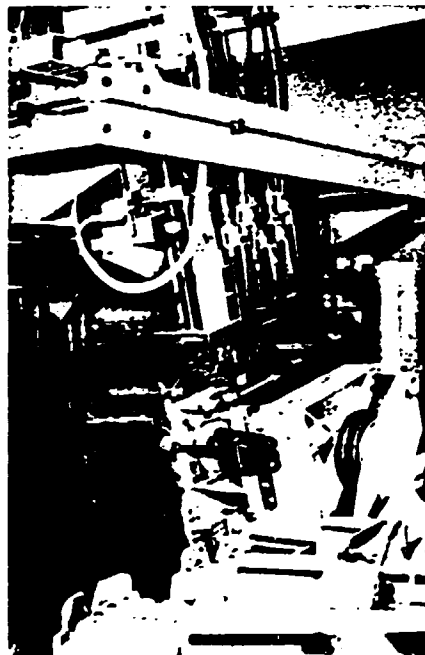


Bild 1 Mischkopfportal zum automatischen Befüllen von Werkzeugen

Außerdem muß man darauf hinweisen, daß die Automatisierung einer gesamten Produktionseinheit, freiprogrammierbare Steuerungen und austauschende Programm-Speicherkapazitäten voraussetzt. Ansonsten ist die Möglichkeit einer Anpassung an neue Erfordernisse nicht gegeben. Es sei denn, man nimmt einige Produktionsverfahren entgegen.

Die Dosiereinheit

Bei den Dosiereinheiten stehen heute vielfältige Möglichkeiten zur Verfügung:

- selbstreinigende Mischköpfe zum Eintragen in geschlossene und offene Werkzeuge,
- automatische Mischkopfportale zur Beschickung der Werkzeuge (Bild 1);
- automatisch verstellbare Mischkopfdüsen,
- automatische Pumpenverstellungen
- automatisches Wechseln der Komponentenfarbe (4-D-Mischkopf),
- automatische Rezeptverstellung von Schuß zu Schuß,
- automatisch gereigte Gasbeladungskontrolle.

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

Transportmittel

Früher waren Transporteinrichtungen gewissermaßen Einzweckanlagen, sie waren für ein genau definiertes Teil gebaut, und wenn die Produktion dieses Teils auslief, 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, weil 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 folgendes beitragen:

- automatischer Bewegungsablauf mit einer Positionierungsgenauigkeit von ± 1 mm
- automatisches Temperieren der Mi-

Bild 1
Bild 2
Tran

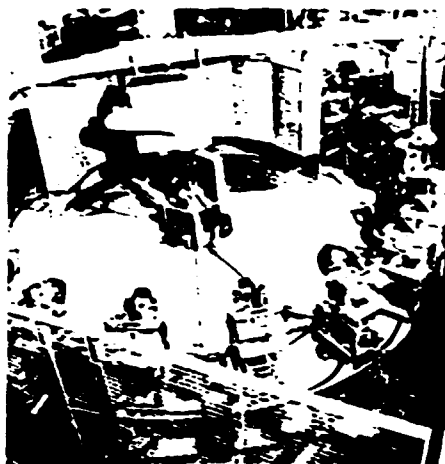


Bild 2 Das Konzept dieser Rundtischanlage erlaubt eine problemlose Anpassung an alle Fertigerfordernisse durch flexible Aufstellungsmöglichkeiten von Formträgern unterschiedlicher Beschaffenheit

weilen unterschiedlichen Werkzeuge durch mitlaufende Temperiergeräte

- automatisches Takteln in allen Ebenen
- selektive Befüllung der Werkzeuge (zum Beispiel 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

Um diese Möglichkeiten ausschöpfen zu können, muß man allerdings schon bei der Konstruktion der Werkzeuge berücksichtigen, welche Handhabungsgeräte und welche Werkzeug-Schnellwechselsysteme in der Produktion angewendet werden sollen. Nur dadurch können die einzelnen Maßnahmen den gewünschten Erfolg bringen

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 Automatisierungsmöglichkeiten

- automatische Zuführung von Einlege-teilen
- automatischer Abtransport der Fertig-teile zur Weiterbearbeitung oder zur Lagerung

Handhabungsgeräte für bestimmte Tätigkeiten

Der Begriff Handhabungsgeräte läßt sich bequem durch den zeitgemäßen Terminus Roboter ersetzen. Bei der PUR-Verarbeitung sind damit jene Einrichtungen gemeint, die dann eingesetzt werden können, wenn solche Tätigkeiten automatisiert werden sollen, die sich ständig wiederholen oder die sich auf die Mitarbeiter belastigend auswirken können. Damit sind vor allem gemeint

- Eintrennen von Werkzeugen
- Platzierung von Einlegern in die Werkzeuge
- Entnahme von Fertigteilen und ihre Weiterleitung (Bild 4)

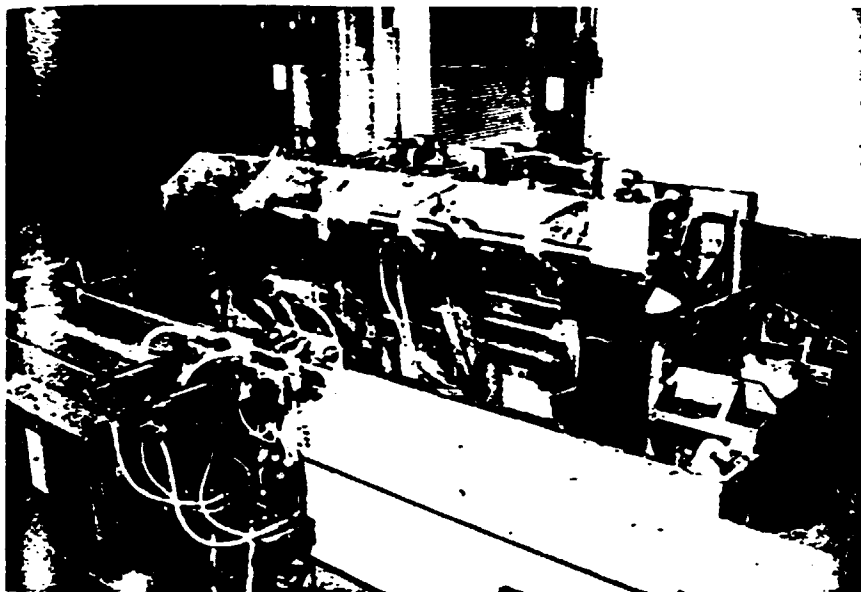
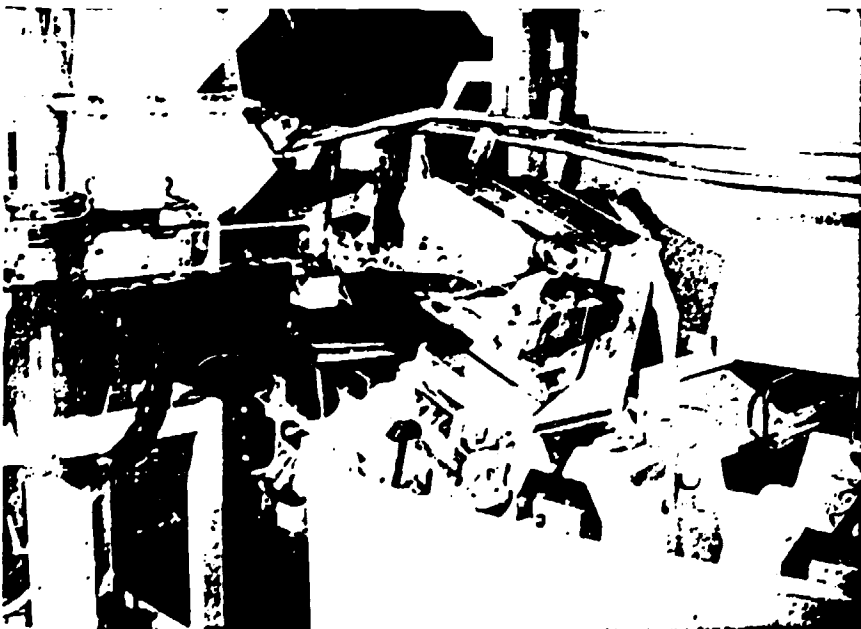


Bild 3 Schaumwerkzeug mit automatischem Angußverschluss

Bild 4 Automatische Entnahme eines Fertigteils mittels Roboter an einer EMB-Transporteinrichtung in der Automobilindustrie



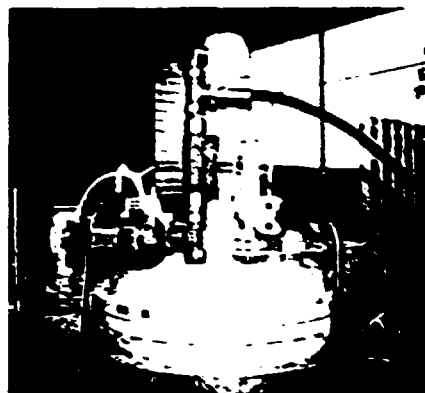


Bild 5 Die von EMB patentierte automatische Pumpenluftung verhindert Kristallisation und Kavitation und somit Produktionsausfall

- Applikation von Etiketten oder sonstigen Identifizierungsmerkmalen
- Lackierarbeiten

Last not least: die Wartung

Es ist eine Binsenweisheit, daß jedes Produktionsmittel eines bestimmten Maßes an Wartung bedarf. Dennoch müssen sich auch PUR-Verarbeiter

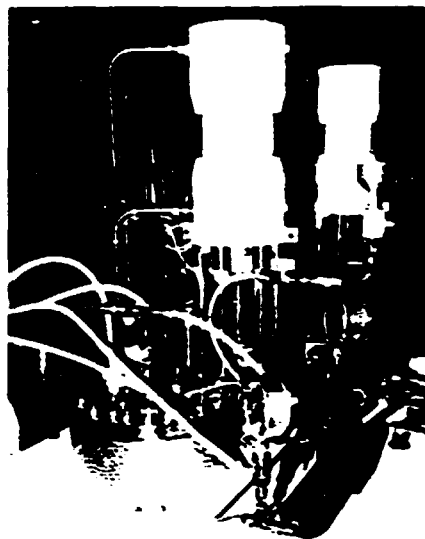


Bild 6 Automatische Vorrichtung zur Nachstellung von Dichtungen an Kolbendosiermaschinen (Werkbilder: Elastogran)

diese Tatsache ständig vor Augen halten. Der höchste Automatisierungsgrad wird nämlich zunichte gemacht, wenn durch Versäumnisse in der Wartung

Produktionsstopps auftreten. Die automatische Filteranleihe dient der Vermeidung von Verschleiß und damit auch dem Energieverbrauch. Automatische Abschaltung der Düse nur während Blockade.

- automatische Schmelzbeheizung mit Hinweis auf die Förderleistung
- automatische Entlüftung der Pumpe (Bild 5);
- automatische Nachstellen von Dichtungen (Bild 6);
- automatische Filteranleihe mit selbstreinigenden Filtern
- automatische umschaltbare Feinreinigung der Komponentenleitung nach dem Mischkopf

Kosten-Nutzen-Analyse gibt Auskunft

Wie schon eingangs angedeutet, muß jeder PUR-Verarbeiter den auf seine spezifischen Verhältnisse zugeschnittenen Automatisierungsgrad selbst ermitteln. Ein Patentrezept gibt es hier genauso wenig wie auf anderen Gebieten. Dessen ungeachtet ist die Effizienz der aufgezeigten Maßnahmen in einer Kosten-Nutzen-Analyse jederzeit nachweisbar.

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▲ Automatische CHARVO Vertikal-Spritzanlage zum Lackieren von senkrecht hängend geförderten Teilen mit dünnen Schichten aus Lack



Automatische Lackier-Spritzanlage CHARVO Vertikal für das automatische Spritzen von senkrecht hängend geförderten Teilen. Der Charakteristikum schließt die Lücke zwischen dem Handcontroller und dem Spritzroboter.

CHARVO MASCHINENBAU GmbH

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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.

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Pittsburgh, Pennsylvania

The powerful tools of statistical experimental design can greatly enhance the efficiency and reliability of chemical systems development. Its application to product design can reduce manufacturing variations and improve the field performance of chemical systems developed from components having the lowest possible cost. Moreover, statistical experimental design promotes a team approach to experimentation in which unfruitful paths are discovered and dropped quickly, and attention is directed exclusively to promising alternatives. This approach often results in rapid, efficient product development.

In Japan, the use of experimental design for product development is considered to be part of an upstream quality control effort. The Japanese refer to these techniques that improve quality upstream from the manufacturing line as "off-line

quality control." This article describes the application of the Taguchi Method, a methodology for direct product development developed by Dr. Genichi Taguchi, to the problem of finding commercial applications for an experimental polyol.

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 con-

TABLE I Factors and Levels.

Factor	Number of levels	Description
Polyol type	4	A, B, C, D
Catalyst package	5	1, 2, 3, 4, 5
Surfactant type	3	S1, S2, S3
Water, wt-%	2	0.5, 1.5
CFC-11, wt-%	2	25, 35
Isocyanate type	2	11, 12

Constraints: Isocyanate index = 105; hydroxyl number = 410 ± 20 ; all surfactant conc. @ 1%.

tents, 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

Design

possible parameter settings that will provide the essential information to determine optimal factor settings. Orthogonal arrays are standard plans for multifactor experiments that have a pairwise balancing property such that every parameter test setting occurs with every test setting of all other design parameters the same number of times. This pairwise balancing property, or orthogonality, gives excellent downstream reproducibility of laboratory results with greater precision than can be obtained from "one-factor-at-a-time" experiments because the conclusions about factor effects are all based over the entire range of test settings for the other design parameters.

Usually it is not efficient to conduct a thorough study of the parameter space unless there are only a few factors and levels of interest. Consider an experiment involving seven factors. Assuming that two or three levels are spaced "boldly," an excellent strategy of reducing the size of the investigation would be to limit the study to those levels. Yet, all possible combinations of two or three levels would still require 128 and 2187 trials, respectively. In these cases, the experimenter may drop some factors to further reduce the size of the study.

According to Dr. Taguchi, it is far better to include as many factors as possible in the initial screening and reduce the number of trials by using an orthogonal array because that experiment can often extract the essential information about the main effects, and sometimes two-factor interactions, with far fewer trials. In the example, a seven-factor main-effect study at two levels can be accomplished

with an 8-trial orthogonal plan (L_8) and at three levels with a 27-trial orthogonal plan (L_{27}). This simply amounts to studying a fraction of all possible combinations described by the complete factorial experiment. Thus, orthogonal array experiments are often fractional-factorial experiments, which have been commonly used in the chemical industry for over forty years. Innovations provided by Dr. Taguchi that make the designs more applicable to polyurethane screening problems include:

- linear graphs to aid in the design of complicated screening experiments involving both main effects and interactions;
- provisions for including multilevel factors into two- and three-level orthogonal arrays;
- techniques that permit factors with various numbers of levels to coexist in a standard orthogonal array; and
- a complete system for statistical experimental design that can be learned quickly by technical people having a minimum of prior training in statistics.

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/or 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 actu-

ally result in visible improvements.

The team approach and brainstorming are encouraged 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

Continued on page 29

TABLE 2 Taguchi L_{16} Screening Experiment.

Trial	Polyol/ water	Catalyst	Surfac- tant	CFC-11	Isocyanate
1	A	3	S2	25	11
2	B	1	S2	35	12
3	C	3	S1	35	12
4	D	1	S1	25	11
5	B	3	S1	25	12
6	A	2	S1	35	11
7	D	3	S2	35	11
8	C	2	S2	25	12
9	B	3	S3	25	11
10	A	4	S3	35	12
11	D	3	S2	35	12
12	C	4	S2	25	11
13	A	3	S2	15	12
14	B	4	S2	15	11
15	C	1	S2	15	12
16	D	1	S2	15	11

TABLE 3 Laboratory Screening Experiment Results.

Trial no.	Cream time, sec	Gel time, sec	Core den- sity, pcf	k-Factor Btu in/h F ft ²
4	11	40	1.94	0.127
16	5-6	26	1.96	0.133
12	4	13	1.77	0.137
11	7	30	1.56	0.122
5	5	30	1.59	0.122
14	3-4	30	1.35	0.120
8	9	36	1.31	0.122
1	7	39	2.17	0.119
15	3	29	1.44	0.127
10	6-7	43	1.16	0.120
9	4-5	29	1.15	0.122
2	10-11	55	1.61	0.137
3	4	27	1.41	0.114
13	7	31	2.13	0.117
7	14	42	1.11	0.111
6	14	42	1.11	0.111

TABLE 4 Optimum Factor Combinations in Order of Significance for the Responses.

A. Cream time, sec Target: 5-6 Catalyst: 3, 4, or 5 Polyol: B or C Water: 1, 5
B. Gel time, sec Target: 26-30 Polyol: B, C, or D Water: 1, 5 Catalyst: 3, 4, or 5 CFC-11: 25
C. Core density, pcf Target: 1.50-1.60 CFC-11: 35 Water: 1, 5 Polyol: B or C
D. Flow, cm Target: 125-140 CFC-11: 35 Water: 1, 5 Polyol: B or C Isocyanate: 11
E. Free rise density, pcf Target: 1.20 CFC-11: 35 Water: 1, 5 Polyol: B
F. k-Factor, Btu/in/h °F ft ² Target: smallest best Polyol: A Catalyst: 3 Water: 0, 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 L_{16} 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* (ASI 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 the 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 L_{16} 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 panel density above the minimum-fill-panel 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.

Factor	Level
Polyol	B or C
CFC-11	35
Water	1, 5
Catalyst	3, 4, or 5
Isocyanate	11

TABLE 6 Confirmatory Trials Suggested by Table 5.*

Trial	Polyol	Catalyst	Result
1	B	3	Pass
2	C	3	Fail
3	B	4	Pass
4	C	4	Fail
5	B	5	Pass
6	C	5	Fail

*Levels: CFC-11 = 35, Water = 1, 5, Isocyanate = 11. Surfactant level S1 used for all trials.

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 far 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 assumption 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 cream 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

TABLE 7. Properties of Foams That Passed Confirmatory Trials.

Property	Trial/catalyst		
	1/3	3/4	5/5
Cream time, sec	4	5	4
Gel time, sec	27	28	30
Tack free, sec	42	45	40
Height of rise, cm	147	144	144
Free rise density, pcf	1.12	1.10	1.10
Core density, pcf	1.34	1.35	1.35
Molded overall density, pcf	1.45	1.55	1.52
k-Factor, initial	0.125	0.124	0.120
Stu in/h FF ft ²			

Confirmatory Trials

Using the information in Table 5, the six additional experiments described in Table 6 were performed to determine the best combination of polyol and catalyst. Note that only one of the confirmatory trials, #5, was observed as part of the original experiment (trial #14). A characteristic of statistical experimental design is that a sequential approach to experimentation is promoted, in which information from an initial experiment is used as a guide for further experimentation.

The confirmatory trials represent a full-factorial experiment for two levels of polyol and three levels of catalyst. According to the results of the initial experiments, most of the properties of these foams should all be essentially equivalent. However, the additional trials are absolutely required for verification purposes because the analysis of the first 16

trials indicated that the assumption of no interaction among the factors was not strictly valid.

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 in 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 (Multranol E-9280) 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

TABLE 8. Commercial Formulation.

Component	Weight %
Polyol B (E-9280)	69.45
Surfactant, catalyst	2.35
Water	1.20
CFC-11	27.00
Total	100.00
Polymeric MDI	97.2

TABLE 9. Properties of Commercial Formulation.*

Processing data: isocyanate resin	
Temperature, °F	110-120
Pour pressure, psi	1500/1500
Reactivity data: sec	
Cream time	2-3
Gel time	35
Tack free	50
Density, pcf	
Free rise	1.12
Minimum fill	1.35
Freeze stable	1.35
Molded core	1.52
k-Factor, initial	0.120
Stu in/h FF ft ²	
Compressive strength, psi	
Parallel at yield	19.1
Perpendicular at yield	16.3
Dimensional stability:	
Δ vol. change @	
-30°C, 1 day	0.6
+70°C, 1 day	0.8

*HK-100 machine, MQ 12-2 mixing head.

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

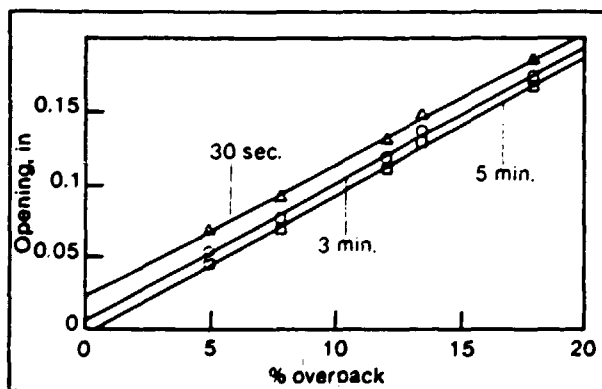


FIGURE 1. Demold properties by Bell opening method.

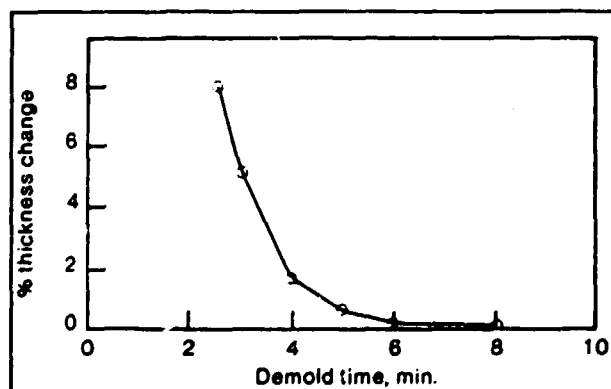


FIGURE 2. Demold properties, % thickness change method.

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, Multranol 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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Der Polyurethan-Verarbeitung mißt ein Münchner Maschinenbau-Unternehmen große Bedeutung bei. Während Spritzgießmaschinen ein jährliches Wachstum von 10 bis 15% – entsprechend dem allgemeinen Marktzuwachs – aufweisen, zeigte sich bei PUR-Maschinen eine Steigerung von 20 bis 25%, die sich zunächst auch noch fortsetzen wird. Gründe hierfür liegen in dem breiter gewordenen Anwendungsspektrum und der damit verbundenen Erneuerung der Anlagen. Rund ein Viertel der PUR-Verarbeiter sind in puncto Maschinen auf dem neuesten Stand. Bei kleineren Maschinen rechnet man mit einer Einsatzdauer von etwa sieben Jahren, danach werden sie überholt bzw. verkauft; größere Maschinen sind 20 bis 25 Jahre im Einsatz. Insbesondere in Sachen Systemtechnik ist der Bedarf noch hoch.

Auf den PUR-Anlagen wird ein großes Teilespektrum in den unterschiedlichsten Branchen nach verschiedenen Fertigungsverfahren produziert. Dazu gehört das Hinterschäumen von PKW-Teppichen, Armaturenbrettern und Sitztextilien ebenso wie das Umschäumen von Warmwasserboilern und Automobil-Fenstern.

Anlagen für den gesamten Hochdruck-Reaktionsbereich stehen zur Verfügung:

- Weichschaum,
- Hartschaum,
- Integralschaum (auch lichtechte Systeme),
- Hart- und Weichschaumhinterfüllungen,
- EA-Schaum,
- RRIM,
- High-Speed-Systems (Polyharnstoffe),
- Hochtemperaturverarbeitung,
- artverwandte Systeme.

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 Produk-



tionsbedürfnissen zusammengestellt werden.

Mischköpfe: In Größenabstufungen stehen fünf Mischkopffamilien zur Verfügung: Linear-Mischköpfe, Umlenk-Mischköpfe (auch in Duplex-Ausführung), Füllstoff-Mischköpfe, Kurzhub-Mischköpfe (Bild 1) und Nyrin-Mischköpfe. Es werden Mischköpfe in Zwei-, Drei- und Vierkomponentenausführungen angeboten. Eine neukonzipierte, hochpräzise Schußzeiterfassung am Mischkopf ermöglicht Schußzeiten mit höchster Wiederholgenauigkeit, zum Teil unter 0,5 s.

Mischkopfmanipulatoren: Je nach Anforderung und Automationsgrad stehen einfache Manipulatoren, automatische Handlinggeräte oder NC-gesteuerte Roboter zur Verfügung. Alle Ausführungen wurden speziell für den Einsatz in der PUR-RIM-Fertigung ausgelegt.

Für den präzisen Komponentenaustausch in reproduzierbaren Bahnkurven, bei

Bild 1 Kurzhubmischkopf. Der kurz gestaltete Mischkopf wirkt kürzeste Schaltzeiten an

unterschiedlichen Anordnungen vor allem Mobilanlagen, für gleichzeitige Produktion verschiedener Teile bei kontinuierlich fortgeführten Anlagen werden gesteuerte Roboter eingesetzt (Bild 2). Sie arbeiten mit hohen Beschleunigungen und Geschwindigkeiten und ermöglichen ein präzises Anfahren aller Anlaufpunkte. Sämtliche Linienantriebe gleiten in exakten und kraftig dimensionierten Präzisionskugelführungen und werden von büstentypischen Gleichstromservomotoren mit Getriebe- und Kegelumlaufspindeln angetrieben. Für die genaue Positionierung sorgen inkrementale Weg-Meß-Systeme. Faltenbalgabdeckungen verhindern ein Verschmutzen der aufwendigen Technik.

Formenträger: Der Formenträger muß auf die Anlage, das Produkt, den Werkstoff und das Fertigungsverfahren abgestimmt sein. Das Formenträger-Programm besteht aus mehreren Typenreihen unterschiedlicher Größen und Kinematiken. Nach den Anforderungen des Produkts können die erforderlichen Aufspannflächen, Öffnungsweiten, Parallelhübe, Schließ- und Aufreißkräfte sowie zusätzlich benötigte Schwenkachsen für die Schäum- und Reaktionsanlagen gewählt werden.

Peripheriebausteine: Zu den kompletten Anlagen gehören auch:

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- Handlinggeräte für die Zufuhr von Einlegeteilen, 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 Bahnkurven 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 Dateneingabe: An der Prozeßüberwachung PUC werden Produktionsdaten wie Teilgewicht, Mischungsverhältnis, Materialtemperaturen, Drücke, Schußzeiten und deren Toleranzen am Industriemonitor über eine Folientastatur eingegeben. Alle Daten lassen sich speichern und stehen nach einer Produktionsumstellung wieder zur Verfügung. Die Prozeßparameter werden erfaßt, überwacht und können als Schäumprotokoll mit Teilenummer und Uhrzeit ausgedruckt oder auch einem Leitreechner 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 Bahngeschwindigkeitskorrektur des Mischkopf-Roboters bei Schußzeitwechsel. Ebenso synchronisiert sich die Roboterbewegung automatisch mit den kontinuierlich umlaufenden Schäumformen und überlagert ihre im stationären Zustand programmierten Bahnkurven automatisch mit der Ge-

schwindigkeit des Förderers.

Produkt, Produktvielfalt, Produktionsleistung, Herstellungsschritte und Herstellzeiten führen zu der grundsätzlichen Entscheidung zwischen zwei Anlagenkonzepten.

Stationäranlagen

Beispiel: Anlage zum Hinterschäumen von unterschiedlichen PKW-Teppichen. Die Anlage besteht aus einer RIM-Star Pumpendosiermaschine mit 19 Mischköpfen zum Schäumen in geschlossenen Formen. Pro Schäumvorgang sind je nach Teppich zwischen einem und vier Mischköpfe angeschlossen. Die Produktionsdatenerfassung PUC überwacht die Produktion und protokolliert jeden einzelnen Schuß. Neun Formenträger stehen zu Dreifachgruppen zusammengefaßt in Absaugkabinen. Zu der kompletten Anlage gehören auch Tanklager, Vormischstation, Trennmittel-Sprühanlagen, Werkzeugtemperierungen und ein Vakuumaggregat. **Produktionsablauf:** Das Gestell ist bis zu 30° nach vorne geschwenkt (Bedienposition), der obere Formaufspannrahmen geöffnet (maximal 90° schwenkbar), der Teppich wird eingelegt, der Aufspannrahmen geschlossen und verriegelt.

Die Schäumform wird mit einem hydraulischen Linearhub geschlossen, der Schließdruck gleichmäßig über ein pneumatisches Druckkissen aufgebracht, die Schließeinheit in die optimale Schäumlage zwischen 30° nach vorne und 150°

nach hinten geschwenkt, die Schäumprogramme werden freigegeben.

Der geschlossene Formträger kann noch während des Schäumeintrages seine vorgewählte und optimale Reaktionslage geschwenkt werden. Auch diese Position befindet sich zwischen 30° nach vorne und 150° nach hinten.

Auf Stationäranlagen werden z. B. FKW-Teppiche und Motorradsitze hinterschäumt, ebenso finden sie Einsatz beim Umschäumen von Fensterscheiben und kleineren Elektroboilen.

Weitere Einsatzgebiete sind die Herstellung von Skiern und technischen Teilen in Integral-Hartschaum.

Mobilanlagen

Beispiel: Rundtischanlage zur Herstellung von textilhinterschäumten PKW-Sitzen mit unterschiedlicher Stauchhärten. Das Produktionskonzept für die rationale Fertigung von Automobil-Sitzelementen ist nach den spezifischen Anforderungen des Auftraggebers entwickelt und in eine maßgeschneiderte Polyurethan-Anlage umgesetzt worden. Im Taktbetrieb werden sämtliche Elemente der Sitzausstattung für Kraftfahrzeuge vollständig und direkt textilverkleidet hergestellt. Die einzelnen Sitzelemente erhalten unterschiedliche Stauchhärten der Schäume in genau definierten Zonen. Der Kombination der Zonen und der Härtenuancen sind kaum Grenzen gesetzt, alle Bausteine der Anlage sind so ausgelegt, daß auch ausgefallene Problemstellungen in kürzester Zeit verwirklicht werden können.

Dosieranlage: Erstmals wurden zehn Dosierkolben bei voller Regelung zu einem Naßteil zusammengefaßt. Auf einer Floppy-Disc stehen 64 Schäumprogramme zur Verfügung. Jedes Programm kann aus 16

unterschiedlichen Teilschüssen bestehen, wobei jedem einzelnen Teilschuß eine eigene Dosierleistung, ein besonderes Mischungsverhältnis und eine individuelle Treibmittelzudosierung zugeordnet werden kann.

Mischkopfprinzip: Die speziellen und variationsreichen Anforderungen an den Komponentenaustrag werden von zwei Duplexmischköpfen realisiert, die synchron eingesetzt werden können. Das Konzept ermöglicht eine breite Differenzierung in der Dosierleistung und den Wechsel auf verschiedene Grundkomponenten von einem Schuß zum anderen.

Steuerung mit Qualitätsprotokoll: Dosieranlage, Roboter, Rundtisch sowie jeder einzelne Formträger verfügen über eine eigene Steuerung. Unser Multimikroprozessorsystem PUC 04 steuert und regelt die einzelnen Dosiereinheiten unabhängig voneinander und realisiert die geforderten Genauigkeitsanforderungen des Mischungsverhältnisses und Teilgewichts. Ein übergeordneter Master ko-

ordiniert die einzelnen Regelkreise kontrolliert Grenzwerte überprüft Temperaturen, Drucke, Fullstände etc. Die qualitätsbestimmenden Prozessparameter und eventuelle Störungen werden erfaßt, angezeigt und bei Bedarf ausgedruckt.

Die hohen Anforderungen an Präzision und Reproduzierbarkeit machen den Einsatz von Robotern erforderlich. Auf Kundenwunsch kamen zwei Gelenkknickarm-Roboter zum Einsatz.

Rundtisch für 30-Sekundentakt: Der Rundtisch mit den 16 Formteilen läuft auf Rollen, die am Boden verankert sind und sich in der Höhe einnivellieren lassen. Diese Lösung benötigt keinen sauberen und gepflegten Boden und keine Laufschienen. Der Antrieb erfolgt über einen Gleichstromgetriebemotor und eine Umschlingungskette. Ein vom Antrieb unabhängiges Weg-Meßsystem sorgt für die exakte Positionierung. Die Fahrzeit pro Takt beträgt ca. 8 Sekunden.

Formträger mit ausgefeilter Kinematik: Für den optimalen Ablauf der Produktion läßt sich der Formträger in fünf verschiedene Positionen fahren. Zum Auftragen des Trenn-

mittels kann die obere Formspannplatte um bis zu 90° nach vorne geschwenkt und auf die gewünschte Bedienhöhe abgesenkt werden. Darüber hinaus verhindert diese Position die Verschmutzung der unteren Formteilhälfte mit Trennmittel. Für die ideale Reaktionslage und zum Reinigen der Entlüftungsbohrungen schwenkt die geschlossene Schließeinheit um bis zu 90° nach vorne. Zu der kompletten Produktionseinheit gehört auch eine in das Formträger-Grundgestell integrierte Hubeinrichtung mit einem präzisen 2,5 m Vertikalhub. Die Hubeinrichtung dient zum Verfahren einer Vorrichtung, die das faltenfreie, konturgerechte Verformen des Textils im Formenunterteil ermöglicht.

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

Bis zu 60 unterschiedliche Schaumkissen (Rücksitze, Vordersitze und entsprechende Lehnen) werden gleichzeitig produziert. Die wesentlichen Bausteine dieser Anlage:

- Dosieranlage mit einem Duplex- und einem UL-Mischkopf,
- Mischkopf-Roboter, neunachsig und NC-gesteuert,
- Umlaufanlage mit Energieversorgungseinheiten,
- Formträger und
- Absaug- und Sicherheitseinrichtung.

Dosiermaschine: Drei RIM-Star-Pumpendosiermaschinen mit jeweils unabhängiger Acht-Punkte-Servovertstellung auf den Isocyanatseiten und eine Zwei-Punkte-Verstellung auf den Polyolseiten realisieren eine optimale Härtevarianz. Drei Pumpendosierstränge benötigen in der Regel auch drei Mischköpfe. Wir setzen unseren Duplex-Umlenkmischkopf mit zwei Dosierkammern und einer Umlenkammer ein und kommen mit nur zwei Misch-

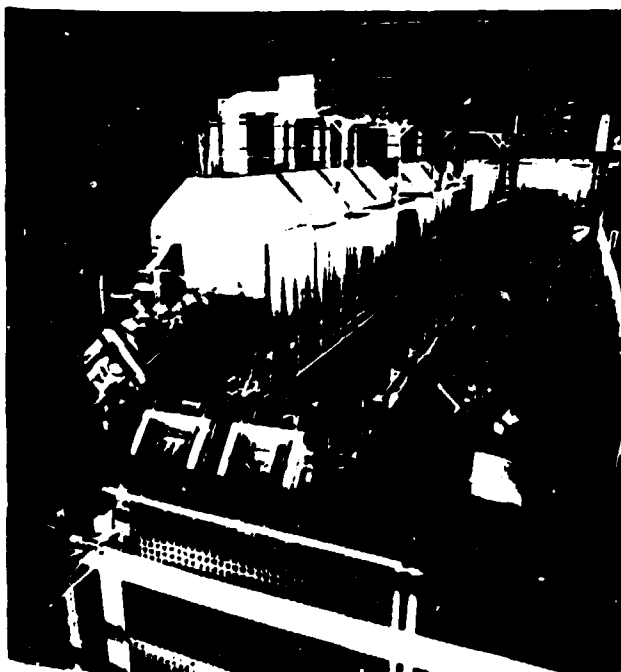
köpfen aus. Neben dem großen Austragsleistungsunterschied bietet diese Lösung auch den schnellen Wechsel auf verschiedene Grundkomponenten von einem Schuß zum anderen.

Mischkopf-Roboter: Der hier eingesetzte neunachsige Mischkopfroboter ist eine Variante des Baukastensystems. Der mechanische Aufbau zum Verfahren der beiden Mischköpfe besteht im wesentlichen aus je zwei in horizontaler Ebene rechtwinklig zueinander stehenden, linear unabhängigen voneinander programmier- und verfahrbaren Achsen. Unmittelbar vor jedem Mischkopf sind zwei Schwenkachsen angeordnet, mit horizontal, rechtwinklig zueinander stehenden Achslagen. Die siebente Achse verläuft vertikal und dient dem Anheben und Absenken der Mischköpfe. Alle Bewegungen sind programmierbar.

Die Vorteile der kontinuierlich umlaufenden Ovalanlagen:

- Die Schaumaustragskurven lassen sich bei stehendem Conveyor einfach programmieren.
 - Die Überlagerung der stationär programmierten Bahnkurven mit jeder beliebig eingestellten Geschwindigkeit des umlaufenden Förderers erfolgt vollautomatisch.
 - Die programmierte Schäumkurvengeschwindigkeit ändert sich automatisch bei Schäumzeitenänderung.
- Das Transportsystem besteht aus einem oval, kontinuierlich umlaufenden Schleppkettenförderer mit 30 Laufwagen zur Aufnahme von 30 Doppel-Formträgern mit Pneumatik-Druckkissen und hydraulischer Schwenkung von oberer Aufspannplatte und Gestell. Zusätzliche Wagen nehmen die Aggregate zur Energieversorgung der Formträger auf. Auf der Rückseite einzelner Laufwagen sind Temperiergeräte für die Formen installiert.

Bild 3 Ovalanlage zur Herstellung von Pkw-Kissen mit unterschiedlichen Stauchhärten (Werkbilder: Krauss-Maffei)



8.9 Standards for Polyurethanes :

American Chemical Society for
Testing Materials (ASTM)
Index :

Urethanes

- free toluene diisocyanates in urethane prepolymers/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

Urethanes—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 prepolymers/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

Urethanes—foam

- bonded, spec., (D 3490) 09.02
- isocyanate raw materials, testing, (D 1638) 06.03, 08.02, 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, Δ (D 3574) 09.02
- toluene diisocyanate for, spec., (D 1786) 08.02

Urethanes—microcellular

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

Urethanes—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

Urethanes—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

Urethanes—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 diisocyanate 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 chlorine, test, (D 4661) 08.03

Urethanes—polyurethane raw materials (polyols)

- acid/alkalinity numbers, test, (D 4662) 08.03
- sodium/potassium content, test, (D 4668) 08.03
- specific gravity of polyols, test, (D 4669) 08.03
- unsaturation of polyols, test, (D 4671) 08.03
- water content of polyols, test, (D 4672) 08.03

British Standard Institute (BSI)
Index :

Polyurethane

- coated fabrics, for upholstered furniture, DD?7
- coated fabrics, for water resistant clothing, 3546(1)
- coated nylon fabric, for mattress covers, 5455
- coated nylon hospital 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, 5211
- 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, 4751
- Polyurethane foam pillows, 5340
- Polyurethane foams
 - hospital mattresses, 5223(2)
 - hospital pillows, 5223(3)



Standard Specification for Rigid Urethane Foam¹

This standard is issued under the fixed designation D 2341; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

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 polycarbodiimide 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 Preformed Cellular Urethane Insulation), and F-7 on Aerospace Industry Methods.

2. Referenced Documents

2.1 ASTM Standards:

- C 177 Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded Hot Plate^{2,3}
- C 203 Test Methods for Breaking Load and Flexural Properties of Block-Type Thermal Insulation²
- C 273 Method for Shear Test in Flatwise Plane of Flat Sandwich Constructions or Sandwich Cores⁴
- C 355 Test Method for Water Vapor Transmission of Thick Materials⁵
- C 518 Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Heat Flow Meter²
- D 149 Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies⁴
- D 257 Test Methods for D-C Resistance or Conductance of Insulating Materials⁴
- D 790 Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Material⁴

¹ This specification is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D 20.22 on Cellular Plastics.

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² Annual Book of ASTM Standards, Vol 04.06.

³ Annual Book of ASTM Standards, Vol 08.01.

⁴ Annual Book of ASTM Standards, Vol 15.03.

⁵ Discontinued, see 1981 Annual Book of ASTM Standards, Part 18

D 1621 Test Method for Compressive Properties of Cellular Plastics⁶

D 1622 Test Method for Apparent Density of Cellular Plastics⁶

D 1623 Test Method for Tensile and Tensile Adhesion Properties of Rigid Cellular Plastics⁶

D 1673 Test Methods for Relative Permittivity and Dielectric Loss Factor of Expanded Cellular Plastics Used for Electrical Insulation⁶

D 1898 Practice for Sampling of Plastics⁶

D 2126 Test Method for Response of Rigid Cellular Plastics to Thermal and Humid Aging⁶

D 2842 Test Method for Water Absorption of Cellular Plastics⁶

D 2856 Test Method for Open Cell Content of Cellular Plastics by the Air Pycnometer⁶

D 2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Cellular Plastics (Oxygen Index)⁶

D 3892 Practice for Packaging/Packing of Plastics⁷

2.2 Military Standard:

MIL-STD-105 Sampling Procedures and Tables for Inspection by Attributes⁸

3. Classification

3.1 The rigid urethane foam covered in this specification shall be designated by a type number, composed by 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 method or as agreed upon by the seller and the purchaser.

NOTE 3—A product is specified by a ten-digit number, the first digit 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 Type 3306056490 would have the following requirements:

Density	0.033 g/cm ³ , max
Compressive strength	103 kPa (15 psi), min
Burning rate	unspecified
Closed cells (porosity)	90 % min
Water absorption	unspecified
Water vapor permeability	3.0 perm-in., max

Dimensional stability:

After 7 days at $-29 \pm 3^\circ\text{C}$	5 % max linear change
After 7 days at $38 \pm 1^\circ\text{C}$ and 90 to 100 % RH	10 % max linear change
After 7 days at $70 \pm 1^\circ\text{C}$	1 % max linear change
Flexural strength	unspecified

⁶ Annual Book of ASTM Standards, Vol 08.02

⁷ Annual Book of ASTM Standards, Vol 08.03

⁸ Available from Naval Publications and Forms Center, 5801 Tabor Road, Philadelphia, PA 19120.


 D 2341

TABLE 1 Detail Requirements

Property Order No	Property and Units	Cell Limits									
		0	1	2	3	4	5	6	7	8	9
1	Core density max, g/cm ³ (lb/ft ³)	unspecified	0.016 (1.00)	0.026 (1.60)	0.033 (2.10)	0.040 (2.50)	0.048 (3.00)	0.080 (5.00)	0.128 (8.00)	0.400 (25.0)	0.960 (60.0)
2	Compressive strength, min, kPa (psi)	unspecified	41 (6.0)	69 (10.0)	103 (15.0)	172 (25.0)	241 (35.0)	310 (45.0)	552 (80.0)	1379 (200.0)	2758 (400.0)
3	Flammability ^a	unspecified									
	Type A, less than	unspecified	23								
	Type B, greater than	unspecified	23								
4	Closed cells (porosity), min, %	unspecified	10	50	70	80	85	90	95		
5	Water absorption, max, g/1000 cm ² (lb/ft ²) of surface	unspecified	976 (2.0)	488 (1.0)	244 (0.5)	97.6 (0.2)	48.8 (0.1)	39.1 (0.08)	24.4 (0.05)	9.8 (0.02)	
6	Water vapor permeability, max, perm-in at 23 ± 1°C	unspecified	50.0	20.0	10.0	5.0	3.0	2.0	1.0	0.5	
7	Dimensional stability after 7 days at -29 ± 3°C (-20.2 ± 5.4°F), max, % linear change	unspecified	25	20	15	10	8	5	3	2	1
8	Dimensional stability after 7 days at 38 ± 1°C (99.4 ± 1.8°F) and 90 to 100% RH, max, % linear change	unspecified	25	20	15	10	8	5	3	2	1
9	Dimensional stability after 7 days at 70 ± 1°C (158 ± 1.8°F), max, % linear change	unspecified	25	20	15	10	8	5	3	2	1
10	Flexural strength, min, kPa (psi)	unspecified	131 (19.0)	103 (15.0)	138 (20.0)	172 (25.0)	207 (30.0)	276 (40.0)	414 (60.0)	1379 (200.0)	2758 (400.0)
11	Initial k-factor as produced, max, kg-cal-cm/h-m ² -°C (Btu-in/h-ft ² -°F)	unspecified	1.36 (0.11)	1.49 (0.12)	1.61 (0.13)	1.74 (0.14)	1.86 (0.15)	1.98 (0.16)	2.11 (0.17)	2.48 (0.20)	3.10 (0.25)
12	k-factor as received by purchaser, max, kg-cal-cm/h-m ² -°C (Btu-in/h-ft ² -°F)	unspecified	1.49 (0.12)	1.61 (0.13)	1.74 (0.14)	1.86 (0.15)	1.98 (0.16)	2.11 (0.17)	2.23 (0.18)	2.48 (0.20)	3.10 (0.25)

^a Flammability—Various governmental bodies have issued regulations based on ASTM Method E 84, Test for Surface Burning Characteristics of Building Materials, E 162, 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, most 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.

4. General Requirements

4.1 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.

4.2 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.

5. Detail Requirements

5.1 The structure of rigid urethane foam consists of a network of cells. It is manufactured in sheet, block, molded, or specific shapes and is prepared by batch, machine, or spray techniques.

5.2 Test properties shall conform to individual requirements as agreed upon between the seller and the purchaser as described in Table 1 and indicated by the type designation.

Tests other than those shown in Table 1 shall be as agreed upon by the seller and the purchaser.

6. Sampling

6.1 When possible, a core sample (Note 7) shall be used for the test specified. Representative samples of the lot being examined shall be selected at random as required.

NOTE 7—A core specimen equal to 12.7 mm (0.5 in.) minimum trim from a skin surface is recommended.

6.2 When it is necessary or advisable to obtain specimens from the article, as in those cases where the entire sample is not required or adaptable for testing, the method of cutting and the exact position from which specimens are to be taken shall be specified.

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 part 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 $23 \pm 1^\circ\text{C}$ ($73.4 \pm 1.8^\circ\text{F}$) and $50 \pm 2\%$ 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 $23 \pm 1^\circ\text{C}$ ($73.4 \pm 1.8^\circ\text{F}$) and in an atmosphere of $50 \pm 2\%$ 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 ($75 \pm 2^\circ\text{F}$).

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 ($75 \pm 2^\circ\text{F}$).

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 tests 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 each 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 at 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.

S1.2 Selection of acceptable quality level (AQL) and of inspection level (IL) shall be made with consideration of the specific use requirements. This is discussed in Sections 7 and 8 of Recommended Practice D 1898, with reference to Military Standard MIL-STD-105.

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Designation: D 3453 - 80 (Reapproved 1985)

Standard Specification for Flexible Cellular Materials—Urethane for Furniture and Automotive Cushioning, Bedding, and Similar Applications¹

This standard is issued under the fixed designation D 3453; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

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 are 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

This specification covers flexible cellular urethane foams intended for such uses as inserts for furniture seats, mattresses, and similar applications.

This specification provides material and dimensional requirements and methods of tests for specific properties of load bearing, compression set, humid age resistance, and dynamic fatigue resistance.

This specification includes references to government regulations for burning characteristics of flexible cellular material used in specified applications.

1. Referenced Documents

1.1 ASTM Standards:

D 3574 Method for Testing Flexible Cellular Materials—Slab, Bonded, and Molded Urethane Foams²

E 162 Test Method for Surface Flammability of Materials Using a Radiant Heat Energy Source³

1.2 Other Documents:

DoC FF4-72 Standard for the Flammability of Mattresses⁴

DoT MVSS 302 DoT Motor Vehicle Safety Standard⁴

DoT Federal Aviation Regulation (FAR), Part 25.853,

Paragraph (b), and Appendix F⁴

Simplified Practice Recommendation R2-62 Bedding

Products and Components (Mattresses, Springs, Bedsteads, and Cots)⁵

1. Classification

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

1. Basis of Purchase

1.1 Any product represented as complying with this specification shall meet all the requirements listed

¹ This specification is under the jurisdiction of ASTM Committee D-11 on Flexible Cellular Materials and is the direct responsibility of Subcommittee D11.33 on Flexible Cellular Materials.

² This specification was approved Oct. 31, 1980. Published December 1980. Originally designated D 3453 - 76. Last previous edition D 3453 - 76.

³ See Book of ASTM Standards, Vol 09.02.

⁴ See Book of ASTM Standards, Vol 04.07.

⁵ Available from the Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402.

Reprinted from the Clearing House for Federal Scientific and Technical Information, 5285 Port Royal Rd., Springfield, VA 22151.

kg/27 lb) foam will have a 25 % ILD value of 96 ± 14 N (21.6 ± 3.0 lbf) = 82 to 110 N (18.6 to 24.6 lbf).

10. Retest 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 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 conformance with this voluntary specification may include a statement in conjunction with their name and address on labels, invoices, sales literature, and the like. The following statement is suggested:

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

TABLE 1 Specific Physical Properties of Flexible Cellular Material

Grade Number		25 % Indentation Force Deflection (IFD) Values ^a , N (lbf)	Indentation Force Ratio 65 %/25 % min	Compression (comp) Set ^b After 90 % Deflection, % max	Moisture Resistance	
Metric, N	English, lbf				Compression Force Deflection Loss % max	Compression Set After Deflection, % max
196	44	196 ± 18(44 ± 4)	19	15	20	20
151	34	151 ± 14(34 ± 3)	19	15	20	20
120	27	120 ± 14(27 ± 3)	19	15	20	20
93	21	93 ± 14(21 ± 3)	19	15	20	20
67	15	67 ± 14(15 ± 3)	18	20	20	25
40	9	40 ± 14 (9 ± 3)	18	25	—	30
Test method ^c		12 to 18	12 to 18	31 to 37	83 to 87 (Procedure J ₁)	83 to 87 (Procedure J ₂)
Specimen size ^d mm (in.)		380 × 380 × 100 (15 × 15 × 4)	380 × 380 × 100 (15 × 15 × 4)	50 × 50 × 25 (2 × 2 × 1)	50 × 50 × 25 (2 × 2 × 1)	50 × 50 × 1 (2 × 2 × 1)

^a 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.

^b To be expressed as a percent of the original thickness.

^c See Section 6 for an explanation of the test methods referenced.

^d See Section 9.3 when indicated specimen sizes are not available.

TABLE 2 Dynamic Fatigue Performance Grades

Grade	Description	TLN ^a
AD	Heavy duty use	30, max
BD	Normal duty use	31 to 50
CD	Light duty use	51 to 70
DD	Unclassified	71 to 100

^a See Methods D 3574, Sections 76 to 82.

TABLE 2A Static Fatigue Performance Grades of Uncured Ethylene Urethane Foam

Grade	Description	Applications	TLN ^a
AS	Heavy duty	cushions, mattresses	25
BS	Normal duty	arm rests, seat backs	30
CS	Light duty	misc padding	40

^a See Methods D 3574, Sections 67 to 74.

TABLE 3 Applicable Government Regulation for Specified Applications

Type	Application	Regulation
Automotive		Dot MVSS 302
Mattress and cushion		Doc FF 4-72
Aircraft		FAR Part 25 853, Paragraph (6), and Appendix F
Miscellaneous		E 162 ^{a, b}

TABLE 4 Thickness and Tolerance for Mattress Inserts

Nominal Thickness		Plus		Minus	
mm	in	mm	in	mm	in
100	4	4.6	$\frac{3}{16}$	1.6	$\frac{1}{16}$
125	5	4.8	$\frac{3}{16}$	1.6	$\frac{1}{16}$
150	6	4.8	$\frac{3}{16}$	3.2	$\frac{1}{8}$

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

TABLE 5 Dimensional Tolerances for Furniture Cushion Inserts

Thickness					
Nominal		+		-	
mm	in.	mm	in.	mm	in.
25 to 75	1 to 3	3.2	$\frac{1}{8}$	1.6	$\frac{1}{16}$
Over 75 to 125	3 to 5	4.8	$\frac{3}{16}$	1.6	$\frac{1}{16}$
Over 125	over 5	4.8	$\frac{3}{16}$	3.2	$\frac{1}{8}$

Length and Width					
Nominal		±			
mm	in.	mm	in.	mm	in.
25 to 305 incl	1 to 12 incl	3.2	$\frac{1}{8}$		
Over 305 to 610 incl	12 to 24 incl	6.4	$\frac{1}{4}$		
Over 610 to 1220 incl	24 to 48 incl	9.6	$\frac{3}{8}$		
Over 1220	over 48	12.7	$\frac{1}{2}$		

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Standard Methods of Testing Urethane Foam Polyol Raw Materials¹

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 (ϵ) 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 resilient types to those which are hard and rigid. These foams are made by the interaction of polyhydroxy compounds, water, and an organic polyisocyanate. 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:

	Sections
Sampling	4
Sodium and Potassium	6 to 20
Acid and Alkalinity Numbers	21 to 30
Hydroxyl Number	31 to 52
Unsaturation	53 to 60
Water	61 to 70
Suspended Matter	71 to 73
Specific Gravity	74 to 79
Viscosity	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:

- D 618 Methods of Conditioning Plastics and Electrical Insulating Materials for Testing²
- D 1193 Specification for Reagent Water³
- D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)⁴

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. Current edition approved Dec. 19, 1969. Published February 1970.

² Annual Book of ASTM Standards, Vol 08.01.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vols 06.01 and 06.03.

E 1 Specification for ASTM Thermometers⁵

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis⁶

E 203 Test Method for Water Using the Karl Fischer Reagent⁶

E 308 Method for Computing the Colors of Objects by Using the CIE System⁷

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.

⁵ Annual Book of ASTM Standards, Vol 14.01.

⁶ Annual Book of ASTM Standards, Vol 15.05.

⁷ Annual Book of ASTM Standards, Vol 14.02.

⁸ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopoeia."