



DOW POLYURETHANES
Flexible Foams

Flexible Polyurethane Foams



Dow Plastics

Flexible Polyurethane Foams

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Preface

Welcome to the second edition of Dow's book on Flexible Polyurethane Foams. This year, we at Dow are celebrating our 100th year as a chemical company and also our 40th year as a supplier to the polyurethane industry. It is our hope that this new, expanded edition will be of help to you our valued customer in the understanding and development of flexible polyurethane foam technology. With the extensive text, over 200 illustrations and over 1200 references to the original published literature, this book should serve as a starting point for any technical problem you are trying to solve.

In the six years since the first edition, an incredible amount of activity and development has occurred in this supposedly maturing industry. This second edition, contains all of the original work plus over 100 pages of updates on new and on-going issues affecting the flexible polyurethane foam industry. An entirely new chapter has been added to discuss the rapidly growing area of noise, vibration and harshness (NVH) control foams. A new appendix listing some of the commercially available surfactants has also been added.

A personal note of thanks is extended to each of the 37 co-authors. Without their dedication, this project could never have been completed.



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July, 1997

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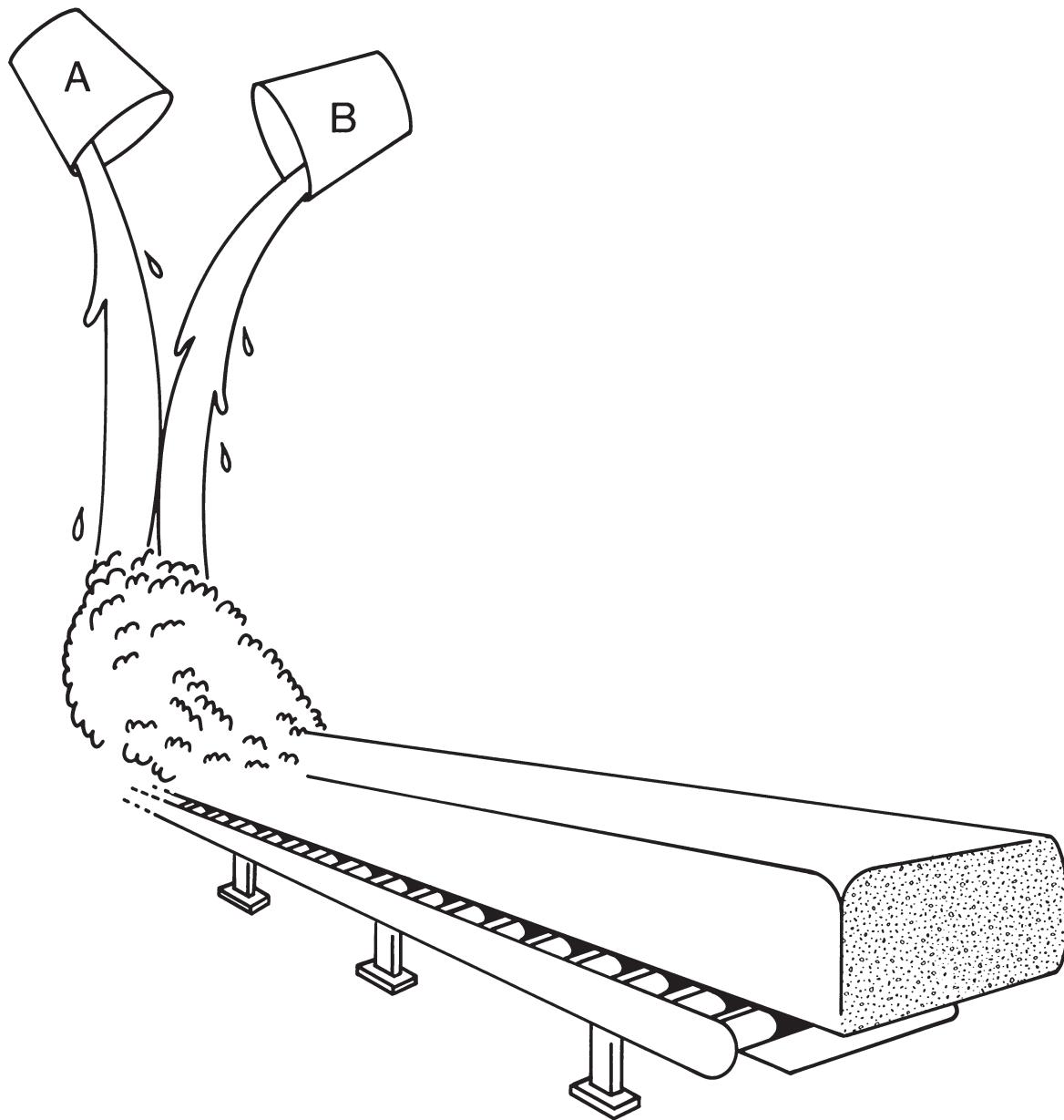
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Chapter 1

Introduction



Like many other polymer families, flexible polyurethane foams are produced according to the general scheme of mixing A with B to give an $(AB)_n$ block copolymer. The unlimited nature of components A and B, together with the many possible application and production schemes, make polyurethanes a diversified and exciting field in which to work.

Chapter 1

Introduction

R. Herrington

HISTORICAL BACKGROUND

The commercial products known as polyurethanes are chemically complex polymeric materials, usually formed by the reactions of liquid isocyanate components with liquid polyol resin components. Although these products are all termed polyurethanes, other identifiable chemical linkages may also be present such as urea, allophanate and biuret. The fundamental addition polymerization reaction of diisocyanates with alcohols to produce high polymers was discovered in 1937 by Prof. Dr. Otto Bayer and co-workers in the laboratories of the German I. G. Farben Industrie.^{1,1}

From their early work pulling “High quality fibers and bristles ... from the polymer melt” came the further research and experimentation that led to the first laboratory-produced flexible polyurethane foam in 1941.^{1,2}

The first pilot plant production of flexible polyurethane foam was announced in Germany in 1952.^{1,3} Commercial production of flexible polyurethane foam began in 1954.^{1,4-1,5} Using the German technology, numerous companies worldwide raced to introduce polyurethanes commercially to fill many industrial and consumer needs. The first foams were based primarily on the reaction of an aromatic isocyanate with a polyester polyol. However, these foams proved unable to withstand many in-use temperature and humidity conditions and often failed by crumbling away.^{1,6-1,7} Better performance was obtained with foams based on polyether polyols. These polyols, introduced by BASF Wyandotte and The Dow Chemical Company in 1957, gave a flexible foam that was less affected by hydrolysis and was more comfortable and considerably more durable. By 1958, the combination of polyether polyols, new catalysts and new silicone-based surfactants made possible the so-called “one shot” foam technology which paved the way for commercial quantities of more economic foams with significantly improved physical properties.^{1,8}

DOW CHEMICAL POLYURETHANES



NORTH AMERICA:

Sarnia, Ontario, Canada
Freeport, Texas
Laporte, Texas
Dalton, Georgia
Midland, Michigan
Tlaxcala, Mexico

LATIN AMERICA:

Guaruja, Brazil
San Lorenzo, Argentina
Bogota, Colombia
Sao Paulo, Brazil

EUROPE:

Ahlen, Germany
Correggio, Italy
Delfzijl, The Netherlands
Estarreja, Portugal
Istanbul, Turkey
Stade, West Germany
Ribaforada, Spain
Tarragona, Spain
Meyrin, Switzerland
Zwijndrecht, Belgium
Durban, RSA
Terneuzen, The Netherlands

PACIFIC:

Gotemba, Japan
Kinu Ura, Japan
Yokkaichi, Japan
Altona, Australia
Nankang, Taiwan
Yoecheon, Korea
Ningbo, PRC
Map-Ta-Phut, Thailand

Figure 1.1 Dow's Major Global Polyurethane Facilities

Figure 1.1 shows Dow's major global polyurethane facilities. Following its initial entry into the market in 1957, Dow built a polyether polyol plant in Freeport, Texas, in 1958. In 1963, Dow built a polyether polyol plant in Sarnia, Ontario, Canada. Over the next three decades, additional plants were built in The Netherlands, Australia, Spain, Brazil, Japan, Argentina, Colombia, Taiwan, Belgium, Thailand and The People's Republic of China.

In the early 1960's, Dow was first to introduce ethylene-oxide-capped polyols for flexible foam. The resulting faster reactivity, due to the presence of primary hydroxyl groups, permitted the fast cure needed for hot-molded and high-resiliency foams. Dow was also the first to produce amine-capped polyether polyols.

In the mid-1960's, Dow pioneered heteropolymer technology (mixed oxide feed) which resulted in slabstock foam grade polyols containing a random mixture of both ethylene and propylene oxide molecules in their structure. These products provided better processability and lower unsaturation than the 100 percent propylene oxide predecessors. As a result, nearly all slabstock polyols manufactured today are based on heteropolymer technology.

In the mid-1970's, Dow commercialized air-frothed flexible foam for application to the back of carpet. In the mid-1980's, Dow developed new process technology for making styrene-acrylonitrile copolymer polyols from which white-colored foam could be produced. Another significant development by Dow was the discovery of permanent static-dissipating foam technology for use in packaging sensitive electronic parts.

Concurrent with advances in the development of polyols, whole families of diisocyanates have come on the global scene. By the early 1950's, the two basic starting products were toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). In 1976, Dow expanded and strengthened its polyurethane chemicals position by constructing a major TDI plant at Freeport, Texas. It added the MDI family of products with the acquisition of the Polymer Chemicals Division of the Upjohn Company in 1985.

Upjohn's isocyanate activity over the years had resulted in a number of commercial firsts. In 1959, The Carwin Company (later acquired by Upjohn) introduced a polymeric methylene diisocyanate under the trademark PAPI. MDI's polymeric form gave it several advantages over TDI, including a lower vapor pressure. In 1960, the Carwin Company built a plant at LaPorte, Texas. Subsequent expansion of that plant and construction of additional facilities in Japan, The Netherlands, Portugal, Germany and Korea gave Dow a major global supply position.

Dow's position in the global market was strengthened in the 1980's through the acquisition of two major systems formulation houses (Corradini and Hager-Kassner) and by the purchase of British Petroleum's polyurethane business. These acquisitions together with an increased global presence has made Dow the largest supplier of polyurethane chemicals in the world.

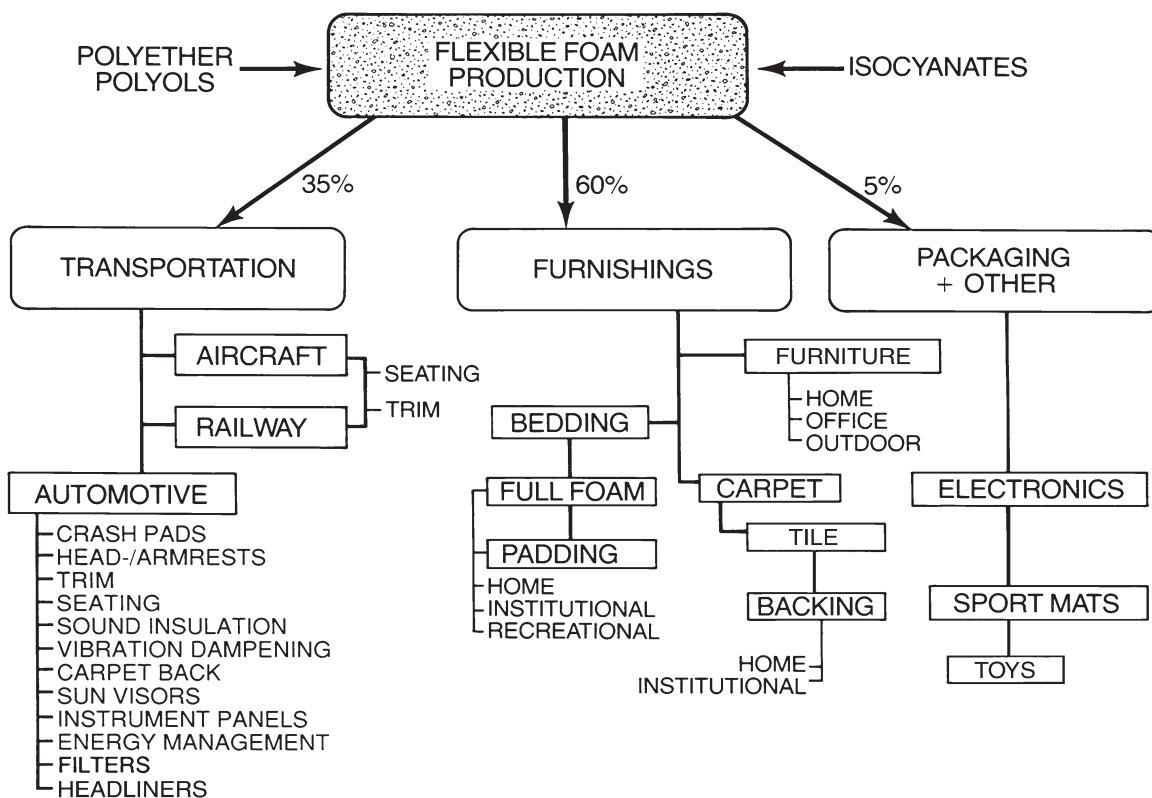


Figure 1.2 Applications for Flexible Polyurethane Foam

APPLICATIONS FOR FLEXIBLE POLYURETHANE FOAM

The greatest advantage offered by polyurethanes is their versatility, both in finished product properties and ease of production and application. Figure 1.2 is a product chart for flexible polyurethane foams. By the proper choice of isocyanate and polyol, products can be made with properties ranging from the downy softness of very low-density flexible foams to the high strength of elastomeric bubble-free castings. The phenomenal success of polyurethanes in capturing applications previously held by alternative cushioning materials is recorded in References 1.9-1.26.

Polyurethanes can be generated on the job site from liquid components by the techniques of pouring, frothing or spraying. More commonly, foams are produced in large quantity in plants specifically designed for the type of foam desired. Foams can be mixed by hand or by machinery specifically designed for that purpose.

Because of their availability in wide ranges of softness or firmness and resiliency, lightweight polyurethane flexible foams offer degrees of comfort to humans and protection to inanimate objects not approached by any other single cushioning material. Modern-day flexible foams are relatively unaffected by moisture and normal cleaning procedures. They are considerably more resistant to degradation than the older latex-based foams and are easily used in modern upholstery applications. The potential uses and multiplicity of properties from these materials are practically endless.

POLYURETHANE FOAM MARKETS

From a modest commercial start in the early 1950's, flexible polyurethane foams have grown in sales volume to occupy the sixth position among all major plastics sold today. Growth of the industry was slow in the beginning, but gradually gained momentum as the advantages offered by the new plastic foams became more evident. Total global sales volume, of flexible foams, was only about 400 million pounds in 1960. By 1970, the industry exceeded the 1.5 billion pound mark and continued growing to over 9 billion pounds by 1995 as shown in Figure 1.3.^{1.27-1.31}

BILLIONS OF POUNDS

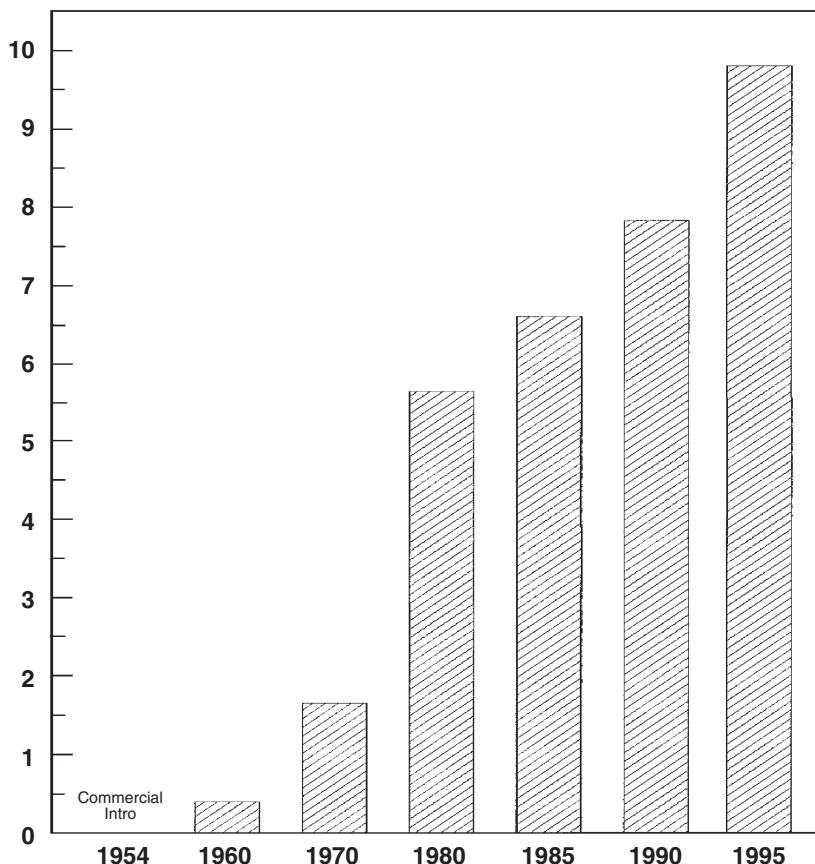


Figure 1.3 Global Market for Flexible Polyurethane Foam

Most flexible foams reach the consumer through their use in the industrial manufacture of end products such as upholstered furniture, mattresses, automobiles and clothing. Additionally, consumers benefit from the use of these materials in all forms of public transportation and commercial seating.

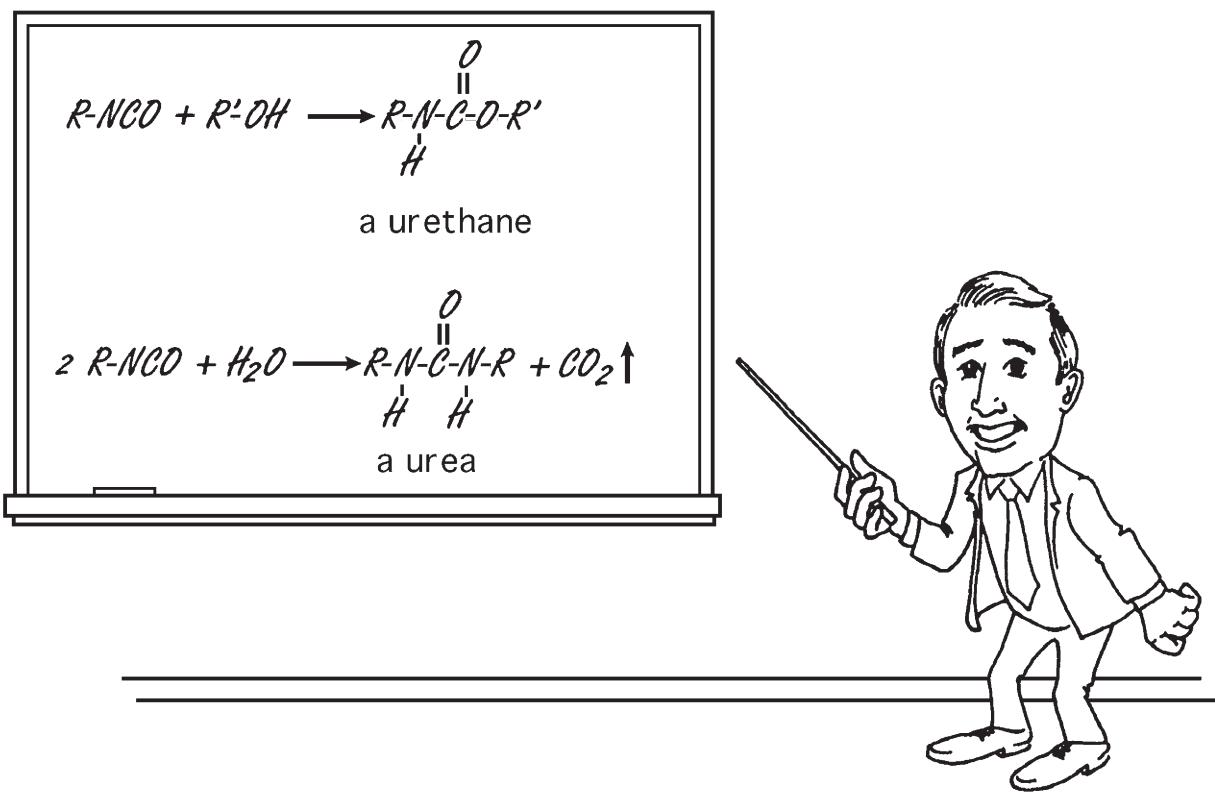
References

- 1.1 Bayer, O. "Polyurethanes"; *Mod. Plast.* **1947**, 24, 149-152, 250-262.
- 1.2 Bayer, O. "The Diisocyanate Polyaddition Method-Polyurethane"; *Ang. Chem.* **1947**, 59, 257-272.
- 1.3 Hochtlen, A. "Fortschritte in der Chemie und Verarbeitung der Polyurethane"; *Kunststoffe* **1952**, 42/10, 303-310.
- 1.4 Brochhagen, F. K. "Neuere Erfahrungen bei der Herstellung von Schaumstoffen auf Polyurethane-Basis"; *Kunststoffe* **1954**, 44/12, 555-558.
- 1.5 Tenhoor, R. E. "The World Market for Urethane Chemicals"; *Chem. Eng. News* **1963**, 41, 94-104.
- 1.6 Winkler, J. "Effects of Foaming Catalysts On Aging of Urethane Foams"; *SPE J.* **1956**, 12/11, 23-25.
- 1.7 Ferrari, R.J.; Sinner, J.W.; Bill, J.C.; Brucksch, W.F. "Compounding Polyurethanes"; *Ind. Eng. Chem.* **1958**, 50/70, 1041-1044.
- 1.8 Frisch, K. C. "History of Science and Technology of Polymeric Foams"; *J. Macromol. Sci. Chem.*, **1981**, A15(6), 1089-1112.
- 1.9 "Polyurethane and Polyester Foams"; *Mod. Plast.* **1954**, 32/3, 106-108, 214-216.
- 1.10 Editorial, "Polyurethane Race; Foams Away First"; *Chem. Week* **1954**, 75/10, 82-84.
- 1.11 "Polyurethanes on the way"; *Mod. Plast.* **1955**, 32/12, 102-104, 212-215.
- 1.12 Beutel, A.C., et. al. "Polyurethanes, A Versatile Synthetic for a Dynamic Era"; *Harvard Graduate School Report*; Polyurethane Associates: Cambridge, Mass., 1956.
- 1.13 Editorial, "Current Developments in Foamed Polyurethanes"; *British Plast.* **1956**, 29/1, 5-9, 39.
- 1.14 "Urethane Plastics - Polymers of Tomorrow"; *Ind. Eng. Chem.* **1956**, 48/9, 1383-1388.
- 1.15 "The Battle Is On In Flexible Foams"; *Mod. Plast.* **1957**, 35/1, 115-121, 238-247.
- 1.16 Buist, J.M.; Lowe, A. "The Properties of Polyurethanes and their applications"; *Plastics Int. Trans.* **1959**, 27, 13-27.
- 1.17 Editorial, "Foam comes into fashion"; *British Plast.* **1961**, 34/8, 408-417.
- 1.18 Erlich, V.L. "Fabric-Foam Laminates, their status today"; *Mod. Text. Mag.* **1963**, 44/2, 37-40.
- 1.19 Saunders, J.H.; Frisch, K.C. *Polyurethanes Chemistry and Technology, Part II, Technology*; Interscience: New York, 1964.
- 1.20 Bender, R.J. *Handbook of Foamed Plastics*; Lake Publishing Corporation: Libertyville, Illinois, 1965.
- 1.21 Frisch, K.C.; Saunders, J. H. *Plastic Foams, Part I*; Marcel Dekker: New York, 1972.

- 1.22 Oertel, G. "Polyurethanes in their fifth decade"; *Kunststoffe* **1981**, 71, 2-7.
- 1.23 Allport, D.C. "Polyurethanes: the learning curve";
Plastics and Rub. Proc. and Appl. **1984**, 4/2, 173-180.
- 1.24 Oertel, G. *Polyurethane Handbook*; Hanser: New York, 1985.
- 1.25 Woods, G. *The ICI Polyurethanes Book*; Wiley and Sons: Chichester, England, 1987.
- 1.26 Ulrich, H. "Urethane Polymers"; In *Encyclopedia of Chemical Technology, Third Edition*; John Wiley and Sons: New York, 1982; Vol.23, 576-608.
- 1.27 Nortman, P.B. "Markets for flexible foams"; *Plast. Tech.* **1960**, December, 42-49.
- 1.28 Wouters, R.P. "Flexible Foams"; *Conference Papers, UTECH 88*: Crain Communications: London, 1988; 6-11.
- 1.29 Manno, P. J. "A Focus on Polyurethanes: The Decade Ahead"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 5-8.
- 1.30 *Facts and Figures of the U.S. Plastics Industry*; Society of the Plastics Industry: Washington, D.C., 1990, 51-54.
- 1.31 Manno, P. J. "1990 Polyurethanes Demand - The Americas"; In *1991 U.S. Foamed Plastics Markets and Directory*; Technomic: Lancaster, Pa., 1991, 5-9.

Chapter 2

Basic Chemistry



The chemistry of the isocyanate group can be traced back to the pioneering work of Wurtz (1849) and Hofmann (1850). Dozens of reactions are known, but the ones of most commercial significance are those leading to the formation of polyurethane polymers. Polyurethanes are formed by the reaction of a polyisocyanate with a polyhydroxy, or polyol compound. The reaction of polyisocyanates with water is a convenient way to produce a gas useful for blowing the polymer to produce a foam structure.

Chapter 2

Basic Chemistry

R. Herrington, L. Nafziger, K. Hock, R. Moore, F. Casati, W. Lidy

Polyurethane chemistry is based on the reactions of isocyanates with active hydrogen-containing compounds. Isocyanates are compounds having one or more of the highly reactive isocyanate group (-N=C=O). This group will readily react with hydrogen atoms that are attached to atoms more electronegative than carbon. Of the many compounds fitting this description, those of primary interest for polyurethane forming reactions are listed in Table 2.1.

Table 2.1 Active Hydrogen Compounds in Order of Decreasing Reactivity with Isocyanates

| Active Hydrogen Compound | Typical Structure | Relative Reaction Rate Uncatalyzed at 25C |
|--------------------------|---|---|
| Primary Aliph. Amine | $\text{R}-\text{NH}_2$ | 100,000 |
| Secondary Aliph. Amine | R_2-NH | 20,000-50,000 |
| Primary Aromatic Amine | $\text{Ar}-\text{NH}_2$ | 200-300 |
| Primary Hydroxyl | $\text{R}-\text{CH}_2-\text{OH}$ | 100 |
| Water | $\text{H}-\text{O}-\text{H}$ | 100 |
| Carboxylic Acid | $\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{OH}$ | 40 |
| Secondary Hydroxyl | $\text{R}-\overset{\text{R}}{\underset{\text{CH}-\text{OH}}{\text{C}}}-\text{OH}$ | 30 |
| Ureas | $\text{R}-\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{NH}-\text{R}$ | 15 |
| Tertiary Hydroxyl | $\text{R}-\overset{\text{R}}{\underset{\text{C}-\text{OH}}{\underset{\text{R}}{\text{C}}}}-\text{OH}$ | 0.5 |
| Urethane | $\text{R}-\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{O}-\text{R}$ | 0.3 |
| Amide | $\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{NH}_2$ | 0.1 |

The reactivity of the isocyanate group can be explained by considering the resonance possibilities presented in Figure 2.1.

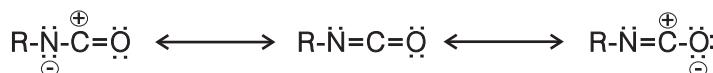


Figure 2.1 Major Resonance Structures Of The Isocyanate Group

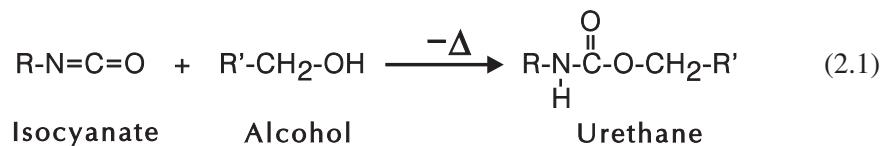
Electron density is expected to be greatest on the oxygen atom and least on the carbon atom. This results in the oxygen atom having the largest net negative charge, the carbon a net positive charge, and the nitrogen, an intermediate net negative charge.

The normal reactions essentially involve addition to the carbon-nitrogen double bond. A nucleophilic center from an active hydrogen-containing compound attacks the electrophilic carbon. The active hydrogen atom then adds to the nitrogen atom. Electron-withdrawing groups attached to the isocyanate molecule increase the reactivity of the NCO group toward nucleophilic groups. Electron-donating groups reduce reactivity. Thus, in most reactions, aromatic isocyanates are more reactive than aliphatic isocyanates. Steric hindrance effects on either the isocyanate or the active hydrogen compound will affect the reaction. Extensive reviews of isocyanate reactions can be found in References 2.1 -2.6.

Formation of a flexible polyurethane foam is a complex process involving many ingredients and at least two competing reactions.

THE POLYMERIZATION REACTION

The polyurethane polymer-forming reaction occurs between an isocyanate and an alcohol as follows:



This is an addition process for which the heat (Δ) of reaction has been reported to be approximately 24 kcal/mole of urethane.^{2,7} Depending on the choice of starting materials, the R and R' groups may also contain isocyanate or isocyanate-reactive groups respectively. When extended to polyfunctional reactants, this reaction provides a direct route to cross-linked polymers as illustrated conceptually in Figure 2.2.

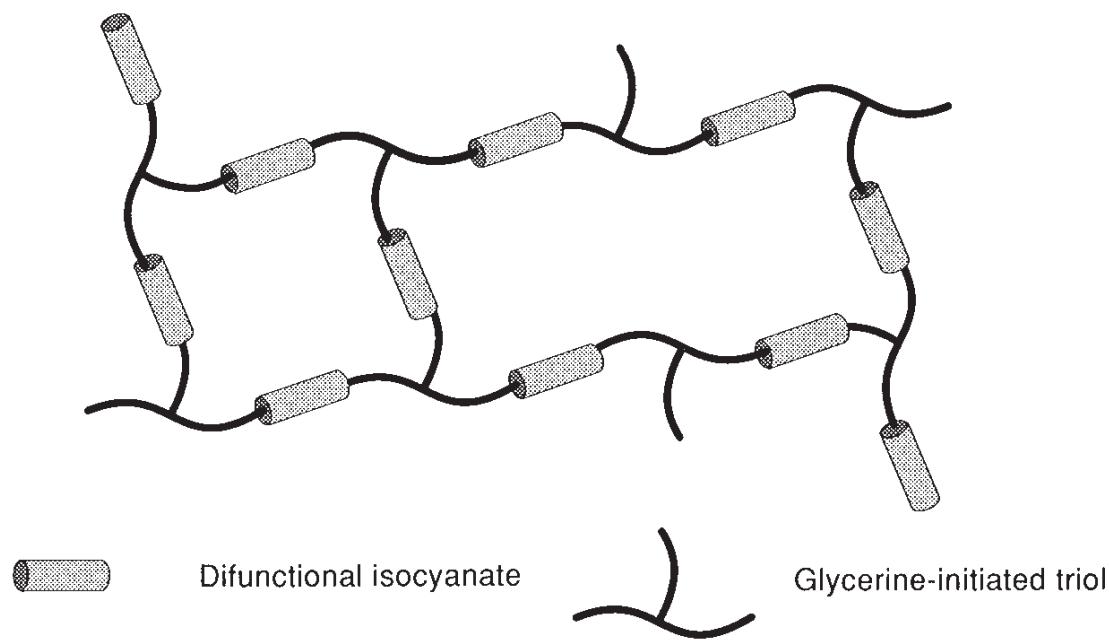
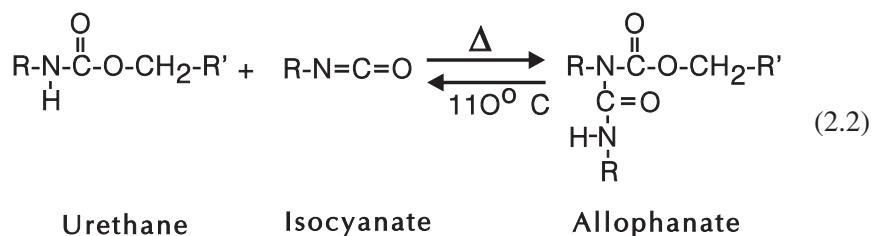


Figure 2.2 Cross-linking in Polyurethane Polymers

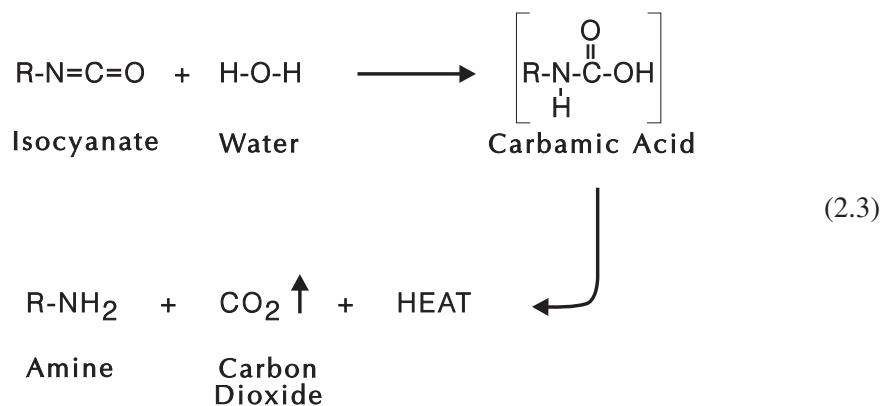
The hydrogen on the nitrogen atom of the urethane group is capable of reacting with additional isocyanate to form an allophanate group.



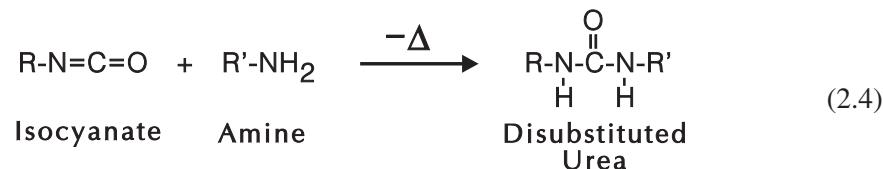
Note that the formation of allophanate is a high temperature, reversible reaction. If actually formed in normal flexible foams, the allophanate linkage would serve to cross-link the polymer further. The catalysts generally used in foam formulations do not promote this reaction, and temperatures greater than 110°C are necessary for significant allophanate formation. Other comments on the likelihood of allophanate formation can be found in References 2.8-2.13.

THE GAS-PRODUCING REACTION

To make a foam, the polyurethane polymer must be expanded or blown by the introduction of bubbles and a gas. A convenient source of gas is the carbon dioxide produced from the reaction of an isocyanate group with water.

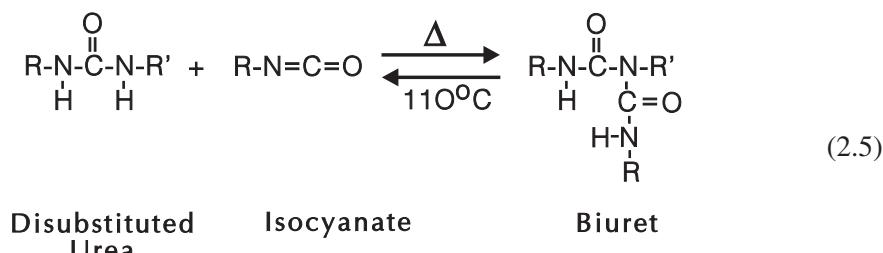


The intermediate product of this reaction is a thermally unstable carbamic acid, which spontaneously decomposes to an amine and carbon dioxide. Diffusion of the carbon dioxide into bubbles previously nucleated in the reacting medium causes expansion of the medium to make a foam. Further reaction of the amine with additional isocyanate gives a disubstituted urea.



The approximate total heat release per mole of water is 47 kcal.

Again, if the isocyanate and amine molecules are polyfunctional, a cross-linked polymer will result. Another conceptual method of cross-linking the polymer is by reaction of a hydrogen from the disubstituted urea with a free isocyanate group to form a biuret linkage.^{2.14}



Since this reaction is also reversible, there is debate about whether allophanates and biurets actually exist in the final polyurethane foam.^{2.15}

Blowing can also be achieved by the physical addition of a low-boiling nonreactive liquid to a foam formulation. Historically, the most commonly used physical blowing agents were the chlorofluorocarbons, urethane grade methylene chloride and trichloroethane. Vaporization of these liquids by heat from the exothermic reactions produces gas molecules which diffuse into nucleated bubbles and contribute to foam expansion.

BASIC FOAM COMPONENTS

Flexible polyurethane foam recipes normally contain a host of ingredients selected to aid in achieving the desired grade of foam.^{2,16} Table 2.2 lists the most common ingredients and typical concentration ranges used in the production of flexible polyurethane foam.

Table 2.2 Formulation Basics for Flexible Polyurethane Foams

| Component | Parts by Weight |
|-------------------------|-----------------|
| Polyol | 100 |
| Inorganic Fillers | 0-150 |
| Water | 1.5-7.5 |
| Silicone Surfactant | 0.5-2.5 |
| Amine Catalyst | 0.1-1.0 |
| Tin Catalyst | 0.0-0.5 |
| Chain-Extender | 0-10 |
| Cross-Linker | 0-5 |
| Additive | Variable |
| Auxiliary Blowing Agent | 0-35 |
| Isocyanate | 25-85 |

The general role/effect of each of these classes of polyurethane components will be discussed below.

POLYOLS

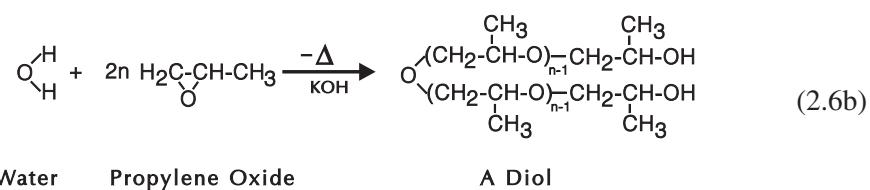
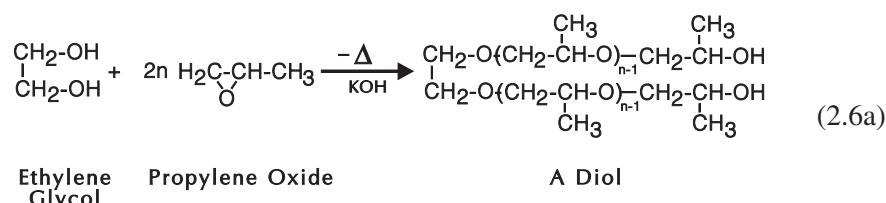
The polyol is a source of hydroxyl or other isocyanate reactive groups. Processing and properties of the resultant foam can be markedly influenced by the choice of starting polyol structure. Ninety percent of all flexible foams produced today are made from polyether type polyols. These polyols may be broadly grouped into the following categories.

- Polyoxypolypropylene diols.
- Polyoxypolypropylene triols.
- Polyoxypolypropylene tetrols and higher analogs.
- Ethylene-oxide-capped diols, triols, tetrols and higher analogs.
- Random and block polymers of the above in which the polyol is made with both ethylene and propylene oxides. When the oxides are fed as a mixed feed, the products are termed hetero polyols.
- Graft or copolymer polyols which contain stable dispersions of a solid particulate polymeric phase in the liquid polyol phase.
- Cross-linkers which are typically short-chain polyfunctional molecules added to increase load bearing or initial foam stability.

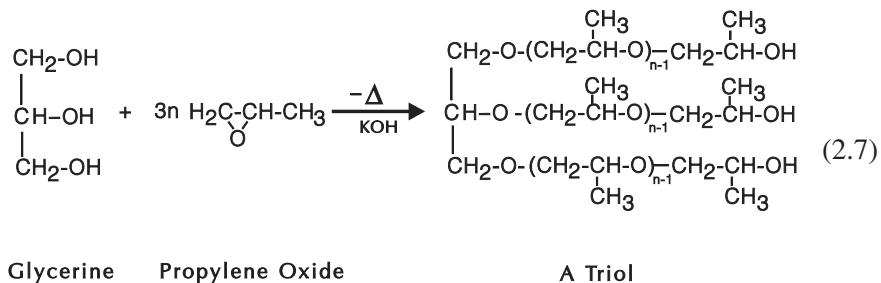
The exact composition will be selected to tailor the foam for a given application and to allow its processing in commercial plants that differ widely in capabilities. Today there are a large number of polyol variations, made necessary in part by the fact that what works well in one customer's plant or geographic location may not work well in another location with seemingly identical conditions.

Polyol Preparation

A polyether polyol is the polymeric reaction product of an organic oxide and an initiator compound containing two or more active hydrogen atoms. The active hydrogen compound in the presence of a base catalyst initiates ring opening and oxide addition, which is continued until the desired molecular weight is obtained. If the initiator has two active hydrogens, a diol results.



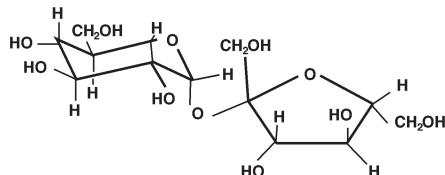
If a trifunctional initiator such as glycerine is used, oxide addition produces chain growth in three directions, and a triol results.



These reactions are exothermic. Propylene oxide for example, releases approximately 22 kcal/mole.

Other commonly used initiators for the manufacture of flexible foam polyols are listed in Table 2.3.^{2,17} Blends of these initiator compounds are also used.^{2,18-2,19}

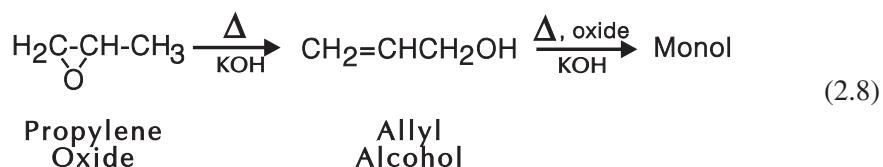
Table 2.3 Common Initiators for Flexible Foam Polyols

| Desired Functionality | Example Initiator | Initiator Structure |
|-----------------------|---|--|
| 2 | Water | $\text{H}-\text{O}-\text{H}$ |
| 2 | Ethylene glycol | $\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 2 | 1,2-Propylene glycol | $\begin{array}{c} \text{CH}_3-\text{CH}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ |
| 3 | Glycerine | $\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{CH}-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 3 | Trimethylolpropane | $\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 4 | Ethylene diamine (1,2-diaminoethane) | $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ |
| 4 | Pentaerythritol | $\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 5 | Diethylene triamine | $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{NH}_2 \\ \diagdown \\ \text{HN} \\ \diagup \\ \text{CH}_2-\text{CH}_2-\text{NH}_2 \end{array}$ |
| 6 | Sorbitol | $\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$ |
| 8 | Sucrose |  |

In actual practice, two side reactions preclude the production of a pure polyol from any chosen initiator compound. The first side reaction involves

the formation of a diol when oxide adds to water. Water is usually present in small amounts in the initiator compound, in the catalyst and in the incoming oxide feed. In other cases, water is purposely added to a triol initiator for example, in order to improve the elongation of the foam produced from that polyol. With care it is possible to produce polyols containing as little as two mole percent diol. For some applications, polyols containing up to about twenty-five mole percent diol have been used.

A further reduction in polyol functionality occurs when propylene oxide isomerizes at reactor conditions to form allyl alcohol.^{2.20-2.22}



That alcohol then serves as an initiator site for the production of a monohydroxy molecule. A general equation that allows for the estimation of polyol net functionality from a knowledge of monol and diol contents is presented below. Other calculational scenarios are available.^{2.23-2.28}

$$\text{Functionality} = \frac{\% \text{OH} / 1.7}{\text{UNSAT} + \frac{(\% \text{OH} / 1.7) - \text{UNSAT}}{\text{NOMINAL FUNCT.- MOLE \% DIOL}}} \quad (2.9)$$

Unsat in the above equation refers to the analyzed concentration of monol in a one gram sample of the final polyol.^{2.29} Values are entered in the form 0.XXX (i.e., 0.055 meg/gram). The nominal functionality is that expected for the initiator or blend of initiators used. Diol content comes from either analysis or process modelling. An example of the impact monol concentration has on calculated functionality of a polyol is given in Table 24.

Table 2.4 Monol Impact On Calculated Functionality Of 5000 mw Triol

| VORANOL 4703 Polyol at 2% diol, 1% OH | | | |
|---------------------------------------|------|-----------------|-----------------------------|
| UNSAT (meg/g) | wt.% | MONOL* mole% | Calculated Functionality |
| 0.00 | 0 | 0 | 2.98 |
| 0.01 | 0.5 | 5.1 | 2.88 |
| 0.02 | 1.0 | 10.1 | 2.79 |
| 0.03 | 1.5 | 15.2 | 2.71 |
| 0.04 | 2.0 | 20.3 | 2.65 |
| 0.05 | 2.5 | 25.5 | 2.57 |
| 0.06 | 3.0 | 30.4 | 2.50 |
| 0.07 | 3.5 | 35.4 | 2.41 |
| 0.08 | 4.0 | 40.5 | 2.34 |
| 0.09 | 4.5 | 45.6 | 2.28 |
| 0.10 | 5.0 | 50.7 | 2.22 |

* Assuming monol is 500 mw

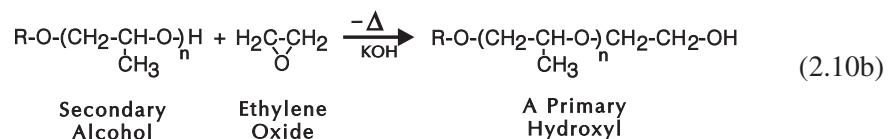
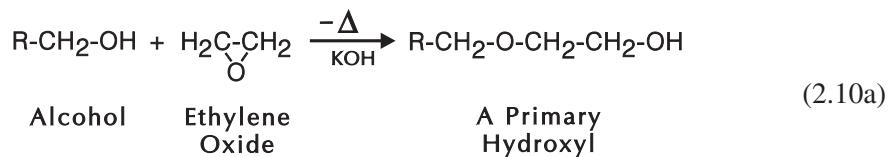
A number of synthetic routes to lower monol containing polyols have been reported.^{2.30-2.38}

The properties of the finished polyol depend largely on the oxide or mixture of oxides used. Table 2.5 lists Dow's four oxides which can be used to impart a wide range of physical and chemical characteristics to a polyol.

Table 2.5 Alkylene Oxides Useful for Polyol Production

| Oxide | Structure |
|-------------------------|--|
| Ethylene Oxide (EO) | $\text{H}_2\text{C}-\overset{\text{O}}{\text{CH}_2}$ |
| Propylene Oxide (PO) | $\text{H}_2\text{C}-\overset{\text{O}}{\text{CH}}-\text{CH}_3$ |
| 1,2-Butylene Oxide (BO) | $\text{H}_2\text{C}-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_3$ |
| Epichlorohydrin | $\text{H}_2\text{C}-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{Cl}$ |

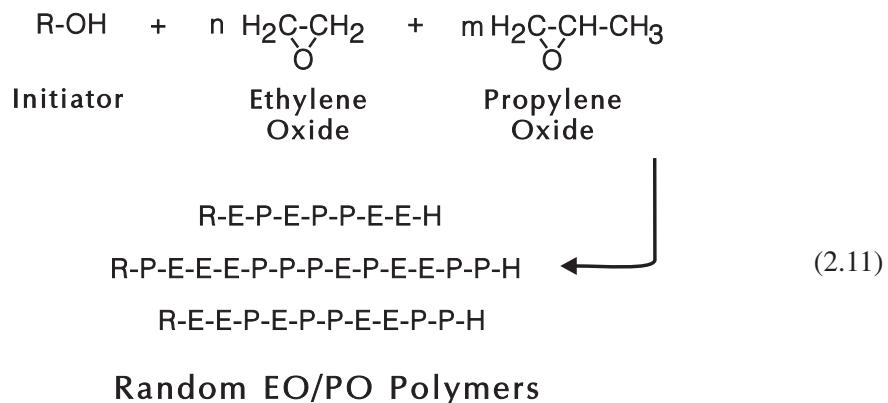
Commercially, propylene oxide and ethylene oxide are the most widely used. When the polymerization is conducted using propylene oxide, as illustrated above, secondary terminal hydroxyls result. If the polymerization is carried out entirely with ethylene oxide or if a propylene oxide based polyol is capped with additional ethylene oxide, a primary hydroxyl group results:



The heat of reaction for ethylene oxide is approximately 27 kcal/mole. Under certain conditions, ethylene oxide will undergo side reactions which result in hazy polyol.^{2.39-2.41} Primary hydroxyl groups are generally stated to be three times more reactive with isocyanate than secondary hydroxyls. This increased reactivity is useful in the short production cycles needed for the various types of molded foam.

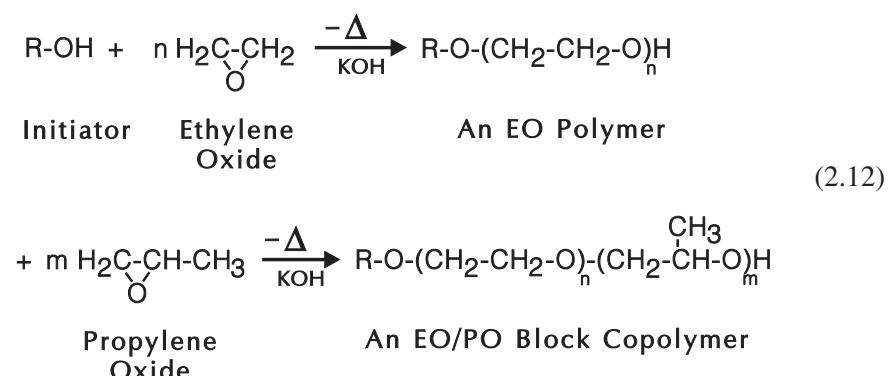
If a mixture of oxides is used, a hetero polyol with improved water and isocyanate compatibility is obtained, which is useful in the production of certain slabstock foams. Although ethylene oxide has a higher

polymerization rate than propylene oxide, and primary hydroxyls are more reactive than secondary, the polymerization is basically random, and a wide variation in hetero polyol composition is available:



$$\text{E} = -(\text{CH}_2-\text{CH}_2-\text{O})- \quad \text{P} = -(\text{CH}_2-\underset{\text{CH}_3}{\text{CH-O}})-$$

A final production scheme for polyols involves the sequential addition of different oxides to produce what is called a block polyol:



For additional introductory reading on polyether polyols, the reader is encouraged to see References 2.42-2.45. Various manufacturing processes for polyether polyols are described in References 2.46-2.53.

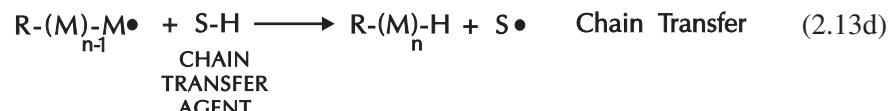
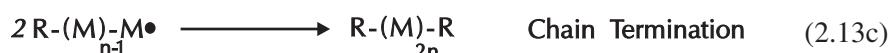
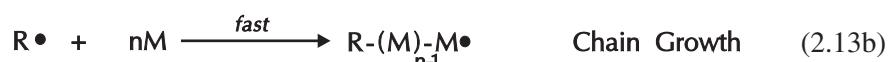
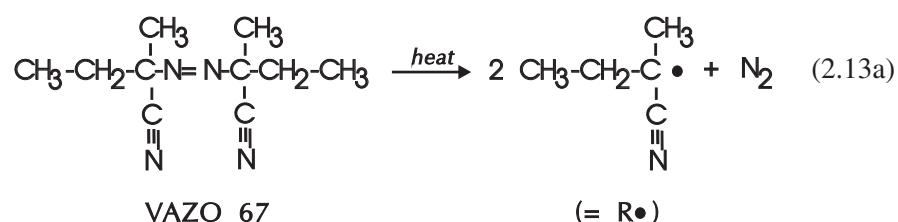
Graft Copolymer Polyols

Polyether polyols can be “filled” with other organic polymers to produce viscous, white to off-white, fluids that are useful in making foams of higher hardness than can be obtained using the unmodified polyols alone. Filled polyols also aid foam processing by improving cell-openness. The filler polymer is normally formed by *in situ* polymerization of monomers in a polyol base, through either free radical or step addition processes.^{2.54} The successful preparation of stable, colloidal dispersions requires that the particles have some type of steric stabilization to prevent flocculation of the suspension.^{2.55} This stabilization is typically provided by a “grafting” process in which either the base polyol or a special added stabilizer molecule

copolymerizes with the monomers to form a copolymer. Within the classification of graft copolymer polyols, there are two important composition classes to discuss.

Chain-Growth Copolymer Polyols

The use of steric stabilization to prepare dispersions in nonaqueous media using free-radical polymerization was first developed by ICI in the 1950's.^{2,54} The first use of nonaqueous dispersion polymerization techniques to prepare polymer dispersions in the polyether polyols was reported in 1966.^{2,56} The basic chemical reactions which occur during a free-radical polymerization are shown in Equations 2.13a-2.13d.



Where M = blend of Styrene/Acrylonitrile monomers

First, free-radicals are generated from the breakdown of an initiator molecule, typically an azobis aliphatic nitrile compound (Equation 2.13a). These radicals react with monomer molecules in a very fast reaction process known as chain-growth polymerization (Equation 2.13b). In this reaction, high-molecular-weight polymer is formed quickly as the monomers are consumed. This is considerably different from the slower step-growth polymerization of isocyanates and polyols. The chain-growth process is terminated by the coupling of two different radical chain ends (Equation 2.13c). The rate at which these chain ends find each other and terminate slows as the viscosity of the polymerization medium increases. This can lead to the formation of ultra-high-molecular-weight or even cross-linked polymer structures. To minimize this event, chain transfer agents are often added to the polymerization mixture. The chain transfer agents are low-molecular-weight compounds which are capable of rapid diffusion through the polymerization medium. These agents react with growing chain ends and terminate the growth of chains (Equation 2.13d). The new radical end formed can initiate new polymer chain growth. Chain terminating agents will act to stop chain growth and do not reinitiate polymerization. These types of agents will eventually slow down and stop the polymerization. An excellent monograph describing chain-growth polymerization has been written.^{2,57}

The first commercial copolymer polyols were based on the use of acrylonitrile as the sole monomer.^{2,56} These dispersions contained 20% poly(acrylonitrile) by weight and had viscosities of 3000-5000 mPa•s. These products were used for the production of cold-molded high resiliency (HR) foam where improvements in hardness, strength, foam processing, and cell-opening led to commercial success. The grafting of the polyol chains to the poly(acrylonitrile) was proven by separating the solid particles from the polyol serum-phase and demonstrating that the particles contained polyol which could not be solvent-extracted. The grafting process was reported to have occurred by the abstraction of hydrogen from the polyol backbone to form radicals which then initiated polymerization of the acrylonitrile. This so-called “natural” grafting to polyether polyols has been reported to occur when using reactive monomers such as acrylonitrile and vinyl acetate.^{2,56,2,58} As copolymer polyol products continued to evolve and to be used in other areas such as slabstock foam, deficiencies in the 100% acrylonitrile products were found. Among these were notable discoloration in slabstock foams. This led to the development of styrene-acrylonitrile (SAN) mixtures as the preferred monomers for making copolymer polyols.^{2,59} These copolymer polyols require the use of a more efficient stabilizer molecule to form the grafted portion of the polymer. This is because the copolymerization of styrene and acrylonitrile is quite favorable, and the tendency for free radicals to be generated on the polyol molecule is reduced. The stabilizers used are called “macromers” or “macromolecular monomers.” These are polyols which have been functionalized in some fashion with a vinyl moiety which will readily undergo copolymerization with SAN monomers.^{2,59-2,61} The use of macromers in the synthesis of copolymer polyols is shown in Figure 2.3.

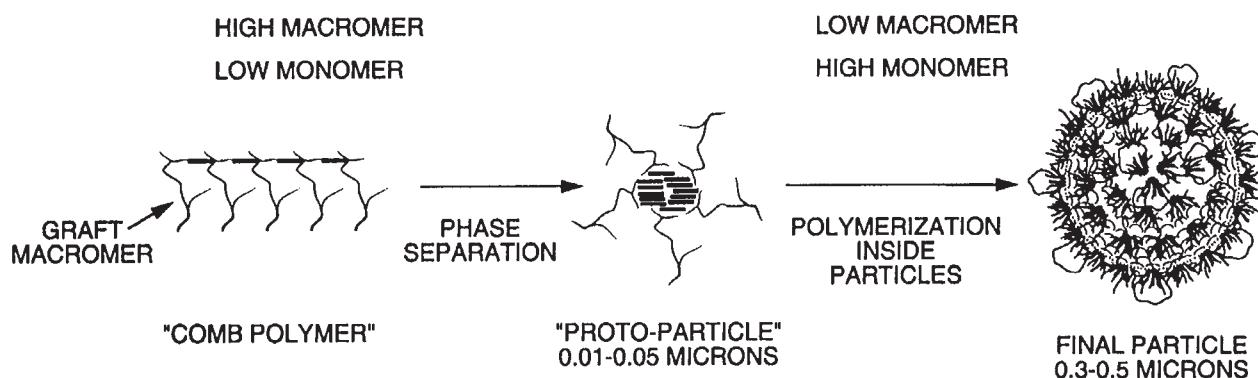


Figure 2.3 Use of Macromer In Copolymer Polyol Synthesis

The polymerization starts with a charge of macromer and base polyol in a reactor. Initiator and monomers are fed to this mixture and polymerization starts. During the early stage, in which the reaction mixture is homogeneous, the polymer produced is rich in graft polyol. These types of polymers are called “comb” polymers. The backbone is copolymer chains and the “teeth” of the comb are the macromer.^{2,54} At some point early in the process (approximately 1-3% of the total monomer added) these comb polymers associate together into a spherical structure in which the insoluble copolymer

portions are located in the center of the sphere, and the macromer chains are located on the outside where they can interact with the continuous polyol phase. These spherical structures are called “proto particles” or “seed particles,” and are similar to the micelle structures formed when surfactants are added to water. This step is called the “nucleation” step, and the reaction mixture turns from clear to white. Once these initial particles are nucleated, the polymerization mechanism changes and the polymerization occurs mainly inside the particles. Here the process resembles a bulk polymerization because the high viscosity slows down the termination process. The polymerization rate increases, and generally no new particles are formed. During this stage the particles grow from their initial size of 0.01-0.05 microns to a final size of approximately 0.3-0.5 microns. The final size is governed by the amount of monomer, and the number of particles which are formed. Typical particle size distributions for these dispersions are narrow and monodisperse. Compositions based on 100% styrene have also been reported.^{2,62}

Using a macromer process, it is possible to produce high-solids copolymer polyols with comparatively low viscosities. For HR molded and slabstock foam applications, copolymer polyols which are 25-40% solids with viscosities of 2500-7000 mPa•s are commonly used. For conventional slabstock foam applications, 40-43% solids products with viscosities of 4000-6000 mPa•s are used. These latter products are used mainly for making prime carpet underlay.

A review of copolymer polyol processes and economics is given in Reference 2.63.

Step-Growth Copolymer Polyols

PHD Polyols (Polyharnstoff Dispersion)

In addition to the copolymer polyols made using free-radical polymerization processes, copolymer polyols are also made using step-growth methods. The first of these products to be introduced was PHD (polyharnstoff dispersion) polyol. PHD polyols are dispersions of polyurea particles in conventional polyols. These polyols are prepared by the reaction of diamine (hydrazine) with a diisocyanate (toluene diisocyanate) in the presence of a polyether polyol. The polymerization and grafting mechanisms are substantially different from those in SAN copolymer polyols. In the step-growth polymerization of diamines and diisocyanates, the polyureas formed are initially low-molecular-weight oligomers. These oligomers quickly phase separate from the continuous phase. Because the reaction of the base polyol with the diisocyanate is slower than the diamine-diisocyanate reaction, their tendency to form small “seed” particles is substantially less than that of SAN polyols. This leads to lower incorporation of polyol grafts and poorer control of the nucleation process. Larger particle sizes and broader distributions versus SAN polymer polyols are the result. These polymerizations produce more polyol-grafted polymers later in the reaction that lead to the formation of new smaller particles, further broadening the particle size distribution. The step-growth mechanism does not build high molecular-weight polymer in the rapid fashion that the chain-growth mechanism does. Final molecular

weight of the polymer produced in this process is considerably lower than that found in SAN copolymer polyols. The viscosity of PHD polyols is higher than SAN copolymer polyols. The first generation of PHD polyols was 20% solids with viscosities of 3000-3500 centipoise.^{2.64-2.65} More recent products containing 28% solids have been reported.^{2.66}

The manufacturing process for PHD polyols is reviewed in References 2.53 and 2.63.

PIPA Polyols (Poly Isocyanate Poly Addition)

PIPA polyols are similar to the PHD polyols, but contain instead, dispersed particles of polyurethane formed by the *in situ* reaction of an isocyanate and an alkanolamine; e.g., triethanol amine.^{2.67-2.74} In general, the amine is blended into a conventional polyol and the mixture is quickly contacted with, for example, toluene diisocyanate, under rapid stirring. If accelerated by an organotin catalyst, the reaction may reach completion in as little as five minutes. Dispersion stability again requires that a minor grafting reaction also occur with the base polyol. A process for preparing a PIPA polyol in a conventional SAN copolymer polyol has been reported.^{2.75}

PIPA polyols are typically made and used by foam producing companies that have acquired patent licenses. Processes for preparing dispersions up to 80% solids have been described.^{2.53}

Other Copolymer Polyols

Epoxy Dispersion Polyols

A filled polyol based on dispersions of cured epoxy resins in conventional base polyols has been reported.^{2.76-2.77} Particle stabilization is accomplished with the use of a special polyol that reacts in a preferential manner with the epoxy resin. The epoxy particles are reported to be higher modulus fillers with improved hydrogen bonding characteristics.

Polyisocyanurate Dispersion Polyols

Dispersions of polyisocyanurate particles in conventional polyols have been reported.^{2.78} The particles are prepared in a solvent, dispersed into the polyol and the solvent removed to give the final product. Stabilization of the particles is aided by reacting the polyisocyanurate particles with a monofunctional, halogenated alcohol.

Melamine Dispersion Polyols

Improved flammability performance has been reported using melamine based copolymer polyols.^{2.79} The effects of melamine particle size on resultant foam physical properties has been discussed.^{2.80}

Polyol Characterization

With so many potential compositions, it is important to have adequate criteria for characterizing a polyol. Some of the more commonly used criteria will be discussed below.

Functionality - arises from the choice of initiator or blend of initiators. Defined simply as the average number of isocyanate reactive sites per molecule. For example, a four-functional initiator, such as pentaerythritol would give a nominal four-functional or tetrol polyol. In calculating functionality, two important variables must be considered: level of monol and level of diol. A net functionality is calculated by inserting those values into Equation 2.9 above.

Hydroxyl Number - a measure of the amount of reactive hydroxyl groups available for reaction. This value is determined in a wet analytical method and is reported as the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of the sample. A review of wet chemical methods for this analysis is available.^{2.81} An infrared method has also been described.^{2.82} The most commonly used methods are available in ASTM D 4274-88.^{2.83}

Equivalent Weight - classically defined as the molecular weight of a polyol divided by its functionality. Functionality of a polyol is complex because of the presence of monols from propylene oxide isomerization and diols (derived from water). In practice, the equivalent weight is calculated from the analyzed hydroxyl (OH) number. The equivalent weight is necessary for isocyanate requirement calculations and is derived from the following expression:

$$\text{Equivalent Weight} = \frac{56.1 \times 1000}{\text{OH Number}} \quad (2.14)$$

Primary Hydroxyl Content - The distribution of primary and secondary hydroxyl groups directly affects the reactivity of a polyol with isocyanates. In general, polyol reactivity increases as primary hydroxyl content increases (see example data in Figure 2.4). The earliest measurements of primary and secondary hydroxyl contents were based on differences in solution based reaction rates.^{2.84-2.86} Nuclear magnetic resonance (NMR) is now the preferred analytical method. With NMR, the primary and secondary hydroxyl end groups can be distinguished from one another and from the ethylene oxide and propylene oxide units in the polyol chain.^{2.87-2.93} Details of the recommended test procedures can be found in ASTM D 4273-88^{2.94}. A polarographic method has also been reported.^{2.95}

Cloud Point - The cloud point of a polyol is defined as the temperature in degrees centigrade, at which a solution of the polyol in a water or water-alcohol mixture becomes turbid upon heating.^{2.96-2.98} Cloud point decreases with increasing polyol molecular weight and increases with the addition of ethylene oxide to the polyol. This analysis is taken to be a measure of the water solubility, surfactant properties and reactivity of a polyol. Since polyols have inverse solubility in water, higher cloud points indicate increases in these important performance attributes.

CPR - the CPR(controlled polymerization rate) value defines quantitatively the weakly basic materials present in a polyol. These materials are not defined qualitatively but are determined as the total weak acid salts of the strong bases. These salts may act as catalysts for the reaction of polyols with isocyanates. The reported number is ten times the number of milliliters of 0.01 N HCl necessary to neutralize 30 grams of polyol sample. More discussion of the CPR concept can be found in Reference 2.99.

Reactivity - a measure of the rate at which a polyol undergoes reaction to make a polyurethane polymer. A test measuring viscosity build in a model reaction with isocyanate has been in use since 1960.^{2.100-2.106} In recent years a refined Brookfield Viscosity Test (BVT) has proven useful for reactivity quantification of ethylene-oxide-capped polyols.^{2.107} Example data in Figure 2.4 show how polyol reactivity varies with increasing primary hydroxyl content (at a constant unsat).

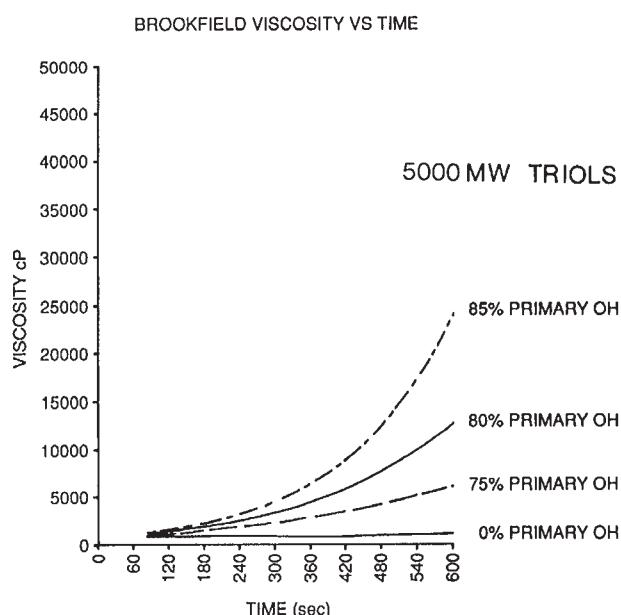


Figure 2.4 Effect of Primary Hydroxyl Content on Reactivity

The BVT has also been found useful for detecting polyol contamination. Other viscosity-based reactivity tests have been described.^{2.104, 2.108-2.110}

Apparent polyol reactivity in this type of model reaction can also be strongly influenced by the polymer-chain-terminating effects of monol (unsat). The contribution of monol to viscosity build for a wide range of primary hydroxyl levels in typical molded foam polyols is illustrated in Figure 2.5.

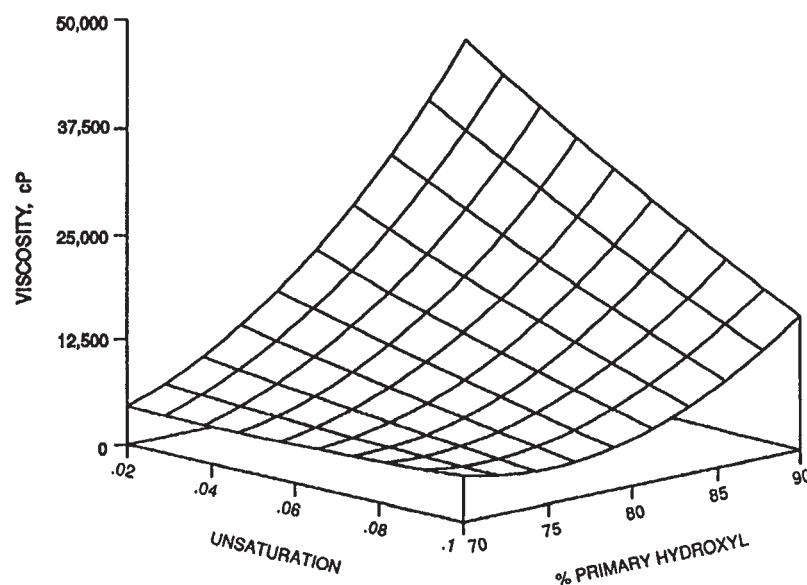
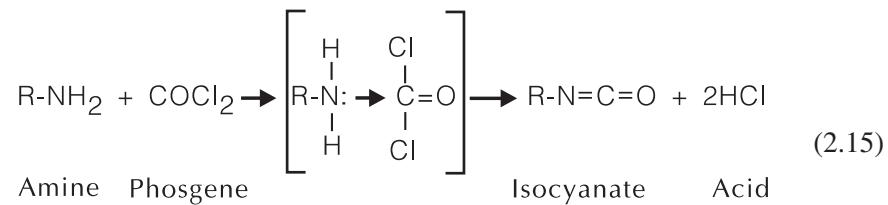


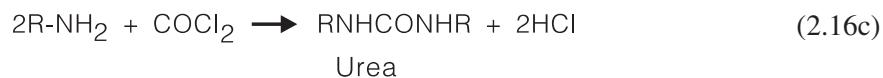
Figure 2.5 Combined Effect of Monol and Primary Hydroxyl on Viscosity Build In Model Polyol-TDI Reaction

ISOCYANATES

The isocyanate provides the source of NCO groups to react with functional groups from the polyol, water and cross-linkers in the formulation. All the isocyanates used in the industry today contain at least two isocyanate groups per molecule. The most commercially viable methods of producing isocyanates involve the phosgenation of an amine as illustrated below:



The reaction is normally carried out in a chlorinated aromatic solvent chosen for utility in removing excess phosgene in latter purification steps.^{2,4} The process is complicated by several side reactions:^{2,111}



Under phosgenation conditions, the urea by-product is converted to a carbodiimide. Further reaction of the carbodiimide with phosgene gives a chloride-containing adduct which can carry chloride through to the final product.^{2,4} General reviews of isocyanate manufacturing processes are found in References 2.112-2.115.

TOLUENE DIISOCYANATE

In flexible foams, the isocyanate most commonly used is toluene diisocyanate (TDI). The two most important isomers of TDI are shown in Figure 2.6. Toluene diisocyanate is commercially prepared by the general reaction scheme shown in Figure 2.7.

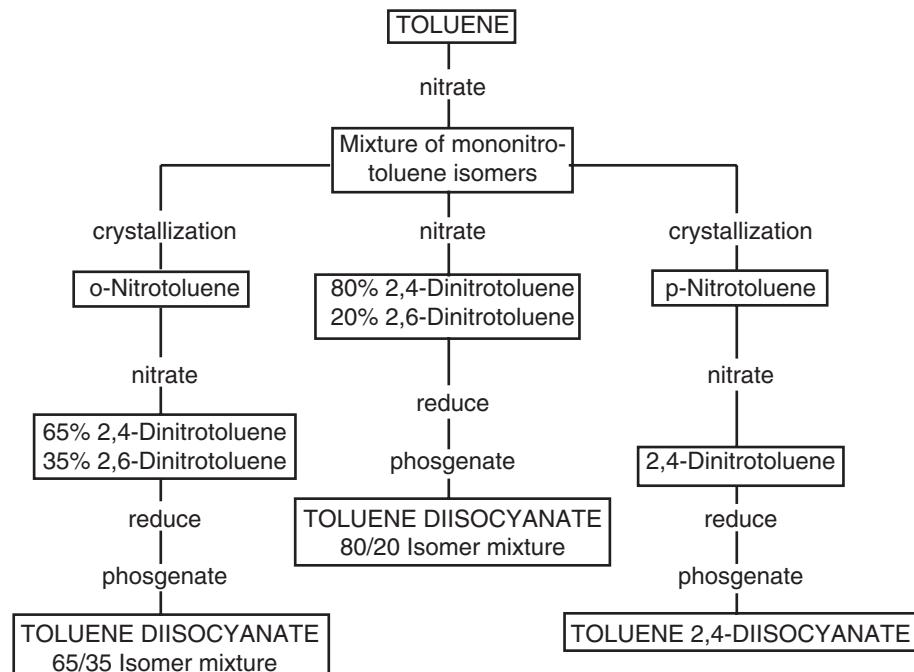
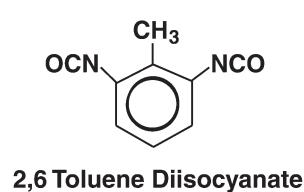
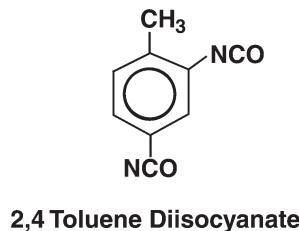
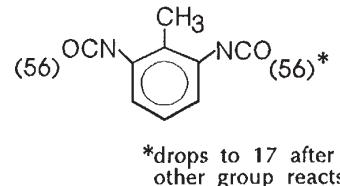
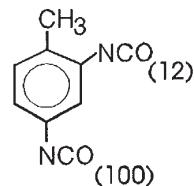


Figure 2.6 Isomers of TDI

Figure 2.7 General Scheme For TDI Production

An 80:20 blend ratio of TDI isomers is obtained by the double nitration of toluene, followed by reduction to the amine and phosgenation to the diisocyanate. If a pure 2,4 isomer or a 65:35 isomer blend ratio is desired, the reaction scheme must be stopped after a single nitration of toluene. Crystallization procedures are then used to obtain the pure ortho or pure para-nitrotoluene molecules needed to produce the desired isocyanates. The final products are purified by distillation. Organic chlorides and residual acidity are the main variables in final product composition. Detailed reviews of commercial manufacturing processes are presented in References 2.116-2.118.

The 2,4 isomer is more reactive than the 2,6 isomer.^{2.2, 2.119-2.120} Within a given molecule, steric hindrances affect the reaction of the various isomer positions. At room temperature, the relative reaction rates are:^{2.121}



As reaction temperatures approach 100 °C, steric effects are overcome and both positions have about equal reactivity.^{2,122}

Varying the isomer ratios can have dramatic effects on polymer properties.^{2,123-2,127} Higher-load-bearing foams can be prepared using the 65:35 isomer blend. Catalysts adjustments necessary to overcome the lower reactivity of this blend ratio are detailed in Reference 2.128. In some systems, the addition of a modified TDI or a polymeric MDI to the TDI reduces the hardness of the foam by interfering with the alignment of the polyurea hard-segments and the effective degree of hard and soft-segment segregation.

MDI

Various forms of diphenylmethane diisocyanate (MDI) are used in high resiliency, semiflexible and microcellular foams. MDI is prepared from aniline, formaldehyde and phosgene according to the following general reaction scheme.

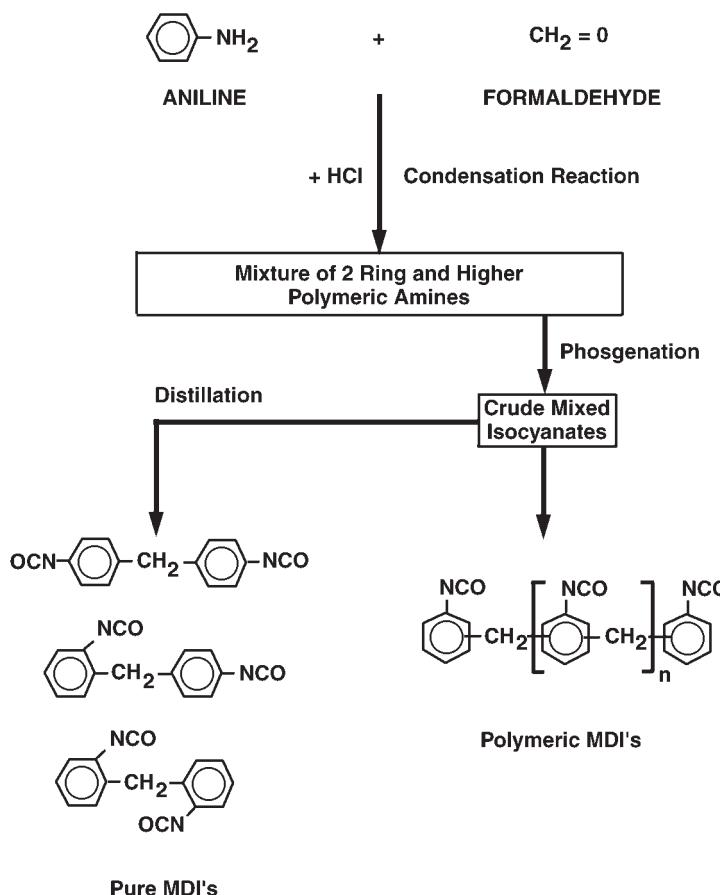


Figure 2.8 General Scheme For MDI Production

The undistilled crude reaction mixture resulting from the phosgenation of the polyamine mixture, contains varying amounts of di, tri and higher functionality isocyanates. A typical ring count distribution is shown in Figure 2.9.

Market demand for the pure MDI isomers dictates that the reactions be optimized for maximum production of two-ring material. Detailed reviews of typical manufacturing processes can be found in References 2.129-2.131.

Pure two-ring isomers are solids at ambient temperatures but can be liquified by inclusion of carbodiimide structures. The sterically free isocyanate groups of the 4,4' and 2,4' isomers are too reactive for use in standard foam formulations. This, together with cost and solids handling problems, precludes the use of pure MDI in flexible foams.

The polymeric MDI's are differentiated by viscosity, functionality and reactivity. Polymeric MDI's have lower vapor pressure than TDI. Blends of polymeric MDI with TDI are also used. Dow presently offers more than a dozen pure, modified and polymeric forms of MDI.^{2.132}

WEIGHT PERCENTAGE

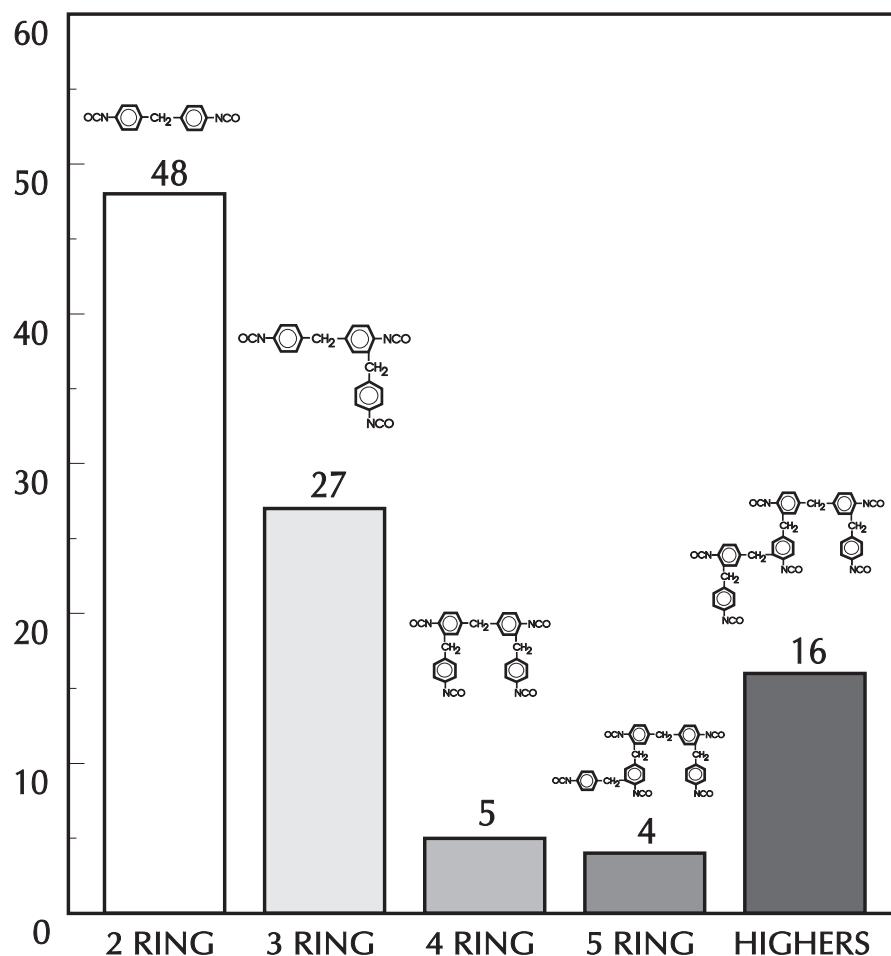


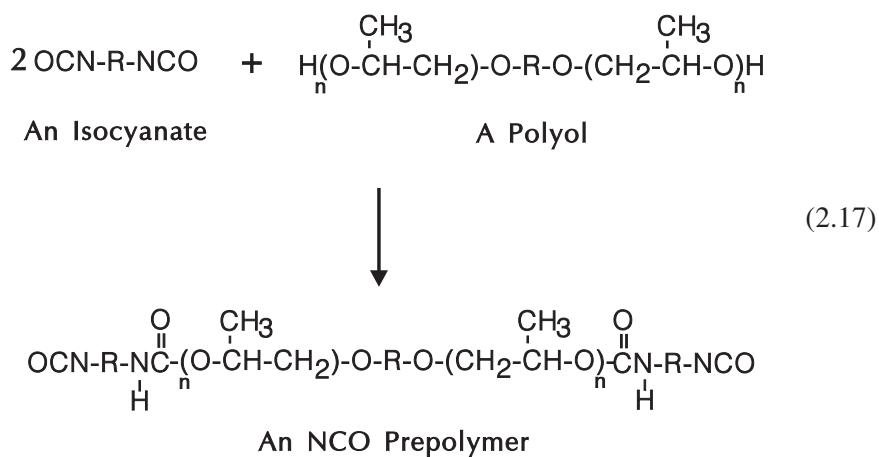
Figure 2.9 Typical Ring Count Distribution
In Crude MDI's

PREPOLYMERS

Prepolymers are liquid intermediates between monomers and a final polymer. They are formed by reacting an excess of either polyol or isocyanate so that the product is still liquid and contains the reactive functional group of the reagent in excess. Prepolymers offer the following advantages:

- A reduced vapor hazard because of increased molecular weight of the isocyanate component (vapor pressure of any free isocyanate is reduced according to mole fraction);
- Increased viscosity leading to better mixing of foam components;
- Improved hard-segment formation by prereacting of chain extenders incompatible with normal foam components;
- Control of desired or undesired side reactions by prereacting some ingredients under precisely regulated conditions.

Hydroxyl-tipped prepolymers were popular in the early days of polyurethanes. Most prepolymers in use today are isocyanate-tipped. A strict prepolymer is formed (see example Reaction 2.17) when just enough polyisocyanate is added to react with all hydroxyl sites available.



If there is excess or residual free isocyanate monomer present, the product is called a quasi-prepolymer. Like other isocyanates, the final prepolymer can react to form all the normally expected structures.

A typical procedure for prepolymer preparation is given in Reference 2.133. The important variables involved in producing low-free-isocyanate prepolymers have been discussed.^{2.134-2.139} Stable, nongelling prepolymers can only be prepared when stoichiometry, moisture, base contamination and temperature are closely controlled.

Additional reviews and foaming procedures are given in References 2.140-2.146.

Isocyanate Index

The amount of isocyanate required to react with the polyol and any other reactive additives is calculated, as described in Chapter 6, in terms of stoichiometric equivalents. This theoretically stoichiometric amount of isocyanate may then be adjusted upwards or downwards, depending on the foam system and the required final properties. The amount of isocyanate used relative to the theoretical equivalent amount is known as the Isocyanate Index:

$$\text{Isocyanate Index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} \times 100 \quad (2.18)$$

Variation of the index in a foam has a pronounced effect on the hardness of the final foam. This increase in hardness has been shown to be directly related to increased covalent cross-linking resulting from more complete consumption of isocyanate reactive sites caused by the presence of excess isocyanate groups.

In the production of flexible slabstock foams, the isocyanate index normally ranges from 105 to 115. Within this range, the hardness of the foam can be readily and safely controlled. In general, foam becomes harder with increasing index. There is, however, a point beyond which hardness does not increase and other physical properties begin to suffer.

Increasing the isocyanate index also affects the reaction profile. With increasing index, cream time is reduced and a higher bun height is obtained^{2.149}. The presence of more unreacted isocyanate also increases the tack-free time and slows the rate of foam cure.

The ability of excess isocyanate groups to react and build further load is dependent on the ambient humidity conditions during foam cure. Higher humidity promotes softer foam. This phenomenon which has been called “summer softening” is discussed in References 2.147-2.148.

The hardness of molded foams may also be adjusted by varying the isocyanate index. In commercial processes, foam hardness may require adjustment from mold to mold or to compensate for changes in the shape of various cushions. Isocyanate indexes in the range of 85 to 110 are common. By using suitable MDI-based isocyanates, it is possible to make foam that is stiffer at the edges than at the center by using automatic index changing of the dispensed foam as it is poured into various sections of the mold.

FILLERS

Finely divided inert inorganic fillers are often purposely added to foam formulations to increase density, load bearing and sound attenuation. All other foam physical properties are generally sacrificed. Typical results are described in References 2.150-2.154. Depending on the nature of the filler, the overall cost of the final foam may be reduced.

Typical fillers include the many grades of barium sulphate and calcium carbonate. Care must be taken to dry the fillers or to know the precise water content available and factor that data into the foam calculations. Normal concentrations used are from 20 to 150 parts per hundred parts polyol. These fillers are heavy and will settle out of a polyol mixture unless constant agitation is used. Due to their abrasive nature, mineral fillers can also increase wear on machinery components. Calcium carbonate fillers have a significant effect on the gelling reaction and necessitate a re-balancing of the blowing and gelling reactions. A general review of fillers for plastics applications is presented in Reference 2.155.

WATER

Water is a source of active hydrogens. Only demineralized water should be used for foam production. Isocyanate reacts with water to give carbon dioxide gas and polyurea molecules. The gas diffuses into nucleated bubbles and aids in foam expansion. The polyurea molecules enter into and contribute to the properties of the final polymer.

The compatibility of water with various polyether polyols has been studied.^{2.156}

SURFACTANTS

Almost all flexible polyurethane foams are made with the aid of nonionic, silicone-based surfactants. In broad terms, surfactants perform several functions. They:

- Lower surface tension;
- Emulsify incompatible formulation ingredients;
- Promote nucleation of bubbles during mixing;
- Stabilize the rising foam by reducing stress concentrations in thinning cell-walls; and
- Counteract the defoaming effect of any solids added to or formed; e.g., precipitated polyurea structures, during the foam reaction.

Among these functions, stabilization of the cell-walls is the most important. By doing this, the surfactant prevents the coalescence of rapidly growing cells until those cells have attained sufficient strength through polymerization to become self-supporting. Without this effect, continuing cell coalescence would lead to total foam collapse. Surfactants also help to control the precise timing and the degree of cell-opening. A more detailed discussion of surfactant effects is provided in Chapter 3. Selection of a surfactant or surfactant combination for any given foam system is a task requiring literature review, supplier consultation and small-scale foam experimentation.^{2.157}

Within each foam formulation, a minimum level of surfactant is needed to produce commercially acceptable foam. Figure 2.10 summarizes the basic effects of varying surfactant concentration.

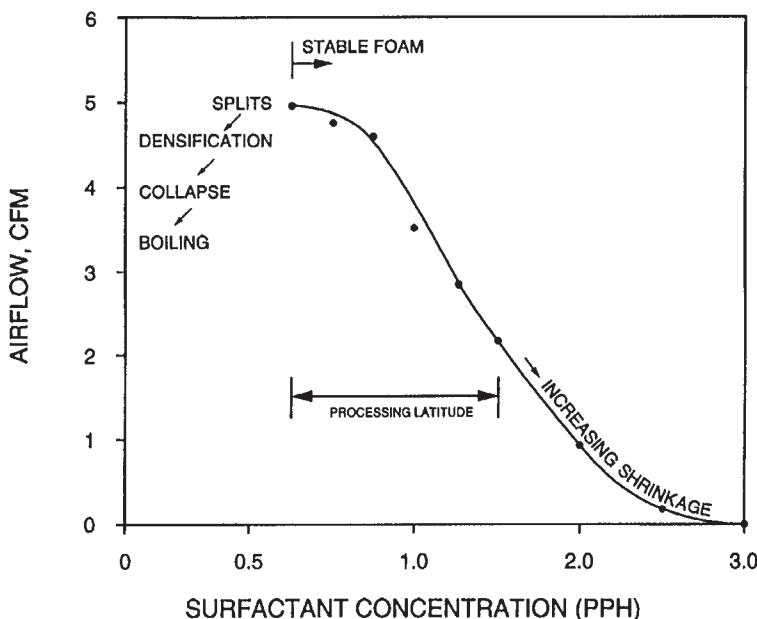


Figure 2.10 Typical Effect of Silicone Surfactant

In the absence of a surfactant, a foaming system will normally experience catastrophic coalescence and exhibit the event known as boiling. With addition of a small amount of surfactant, stable yet imperfect foams can be produced. With increasing surfactant concentration, a foam system will show improved stability and cell-size control. At optimum concentrations, stable open-cell foams may be produced. At higher surfactant levels the cell-windows become overstabilized and the resulting foams are tighter with diminished physical properties. Today the majority of flexible foams are made from a class of surfactants identified as polysiloxane-polyoxyalkylene copolymers. These materials are often represented conceptually by the various head/tail configurations shown in Figure 2.11.

The polyoxyalkylene polymer (or polyol) portion of the surfactant aids in solubilization of the surfactant into the bulk polyol and participates in the overall emulsification effect. The silicone end of the molecule lowers the bulk surface tension.

Several detailed reviews of silicone-glycol surfactant production methods are available.^{2,158-2,160} The typical synthesis route begins with the reduction of sand to silicon metal. This is accomplished at high heat in an electric furnace.



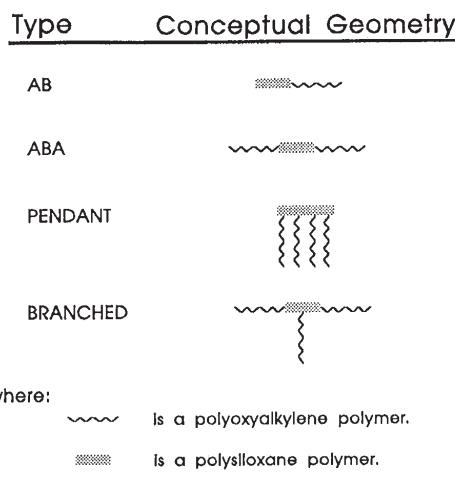


Figure 2.11 Some Conceptual Geometries for Surfactant Molecules

After cooling, the silicon metal is converted to a fine powder, then reacted with methyl chloride in the presence of a copper catalyst to produce a mixture of methyl chlorosilanes (commonly called the SiCl fluids).

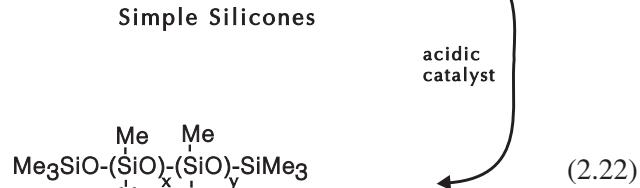


Mixture of SiCl Fluids

Where Me = methyl group

Selected mixtures of these methyl chlorosilanes are hydrolyzed and further processed to yield the simple silicones shown on the right-hand side of equation 2.21.

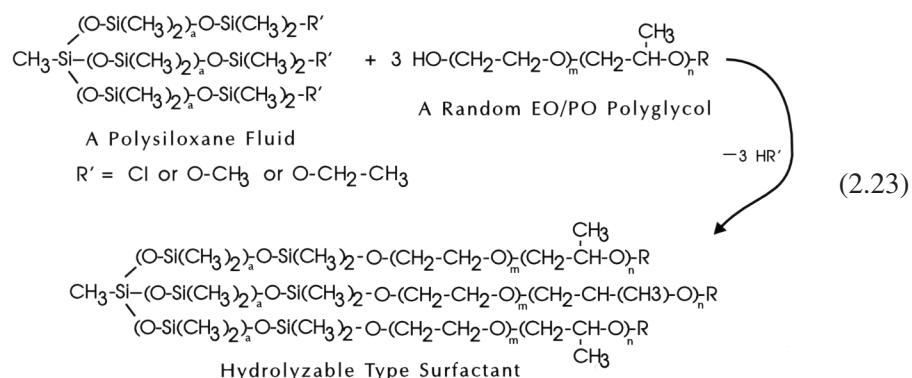
For example:



Additional processing and the introduction of an acidic catalyst yields an SiH type of polysiloxane fluid.

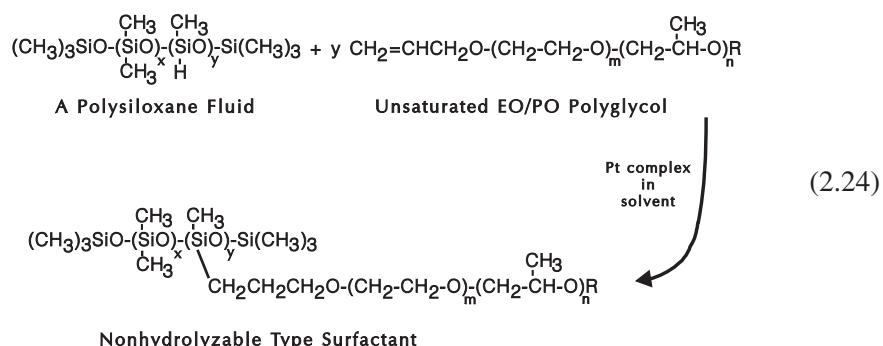
Other combinations of the methyl chlorosilanes can be used to prepare branched or cross-linked polysiloxane fluids. The chain length of the polysiloxane formed can be controlled by varying the amount of end blocker (Me_3SiCl) used in the initial hydrolysis step.

The SiH type polysiloxane fluid can be used to prepare either a hydrolyzable or nonhydrolyzable type of surfactant. If the fluid is reacted with a normal hydroxyl-terminated polyglycol monol the bond formed is a silicon-oxygen-carbon (SiOC) type. The typical synthetic route to a hydrolyzable type surfactant is illustrated in Equation 2.23.



In some extreme conditions and with exposure to water, this type of surfactant may break apart to form the siloxane and polyglycol molecules again. If this occurs, the individual molecules would no longer exhibit the surfactant effect, and may even act as defoamers.

Nonhydrolyzable type surfactants are typically prepared from the reaction of the polysiloxane fluid with an unsaturated polyglycol of the general form shown in Equation 2.24. The R group should not be a simple hydrogen or a hydroxyl group.



Platinum complexes catalyze the rapid addition of the siloxane's hydrogen atom across the double bond of the glycol to give a water-stable silicon-carbon (SiC) bond.

To meet the needs of different foam systems, the surfactant structure is modified by changing the length and composition of the polydimethylsiloxane backbone and/or the number, length and composition

of the pendant polyether chains.^{2.161} For each type of slabstock foam, there is an optimum balance between the silicone and glycol moieties of the surfactant.^{2.162} Blends of polyoxyethylene/polyoxypropylene block copolymers with traditional silicone surfactants have been used to improve foam porosity.^{2.163} The special requirements of a polyester foam surfactant have been described.^{2.164}

The high resiliency (HR) type foams are higher viscosity, faster reacting systems that also require specially designed silicone surfactants.^{2.165-2.168}

Additional in-depth reviews of surfactant technology can be found in References 2.169-2.171.

CATALYSTS

Virtually all commercially manufactured flexible polyurethane foams are made with the aid of at least one catalyst. Of the many classes of compounds investigated, the amines and the organometallics have been found most useful. Various combinations of catalysts are used in order to establish an optimum balance between the chain propagation (isocyanate with hydroxyl) reaction and the blowing reaction (isocyanate with water). The polymer formation rate and gas formation rate must be balanced so that the gas is entrapped efficiently in the gelling polymer and the cell-walls develop sufficient strength to maintain their structure without collapse or shrinkage. Catalysts are also important for assuring completeness of reaction or “cure” in the finished foam.

The selection of a catalyst system for a particular grade of foam is a complex task requiring literature review, supplier consultation and small-scale experimentation at the cup and box foam scales.^{2.172-2.173} Further refinement is usually needed at full production-scale.

Amine Catalysts

Tertiary amines are the most commonly used flexible polyurethane foam catalysts. Generally regarded as blowing catalysts, most amines also offer some contribution to the gelling reaction.^{2.174} The catalytic activity of amines is due to the presence of a free electron pair on the nitrogen atom.

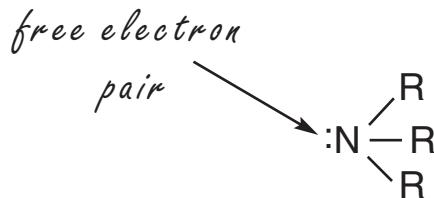


Figure 2.12 Tertiary Amines Have a Free Electron Pair

Steric hindrance about the nitrogen atom and the electronic effects of substituent groups are the main factors influencing the relative catalytic activity of various amines. In some foam systems, combinations of various

amines are used in an attempt to balance the gelling and blowing reactions so that the foaming process can be adequately controlled.

The type and concentration of amine catalyst(s) can be selected to satisfy process requirements such as cream times, rise profiles, gel times and even cure of the outer surface skin. Choice of amine may also affect the foam properties such as airflow and load bearing through influences on the primary and secondary foam reactions.^{2.175-2.177}

Some amines impart a residual odor to the foam, which may limit their use in applications such as bedding and upholstered furniture. The use of the more volatile amines may reduce odor in the final product but may also reduce cure due to rapid loss of the catalyst. High volatility often results in low flash points, high vapor pressures and attendant handling problems. Many catalyst suppliers have introduced catalysts containing an isocyanate reactive group to help tie the molecule into the polymer network. While desirable in some applications, this process generally decreases the net catalytic activity of the molecule. Reactive amines with improved catalytic activity have been reported.^{2.178} An extensive listing of commercial catalysts is provided in the Appendix.

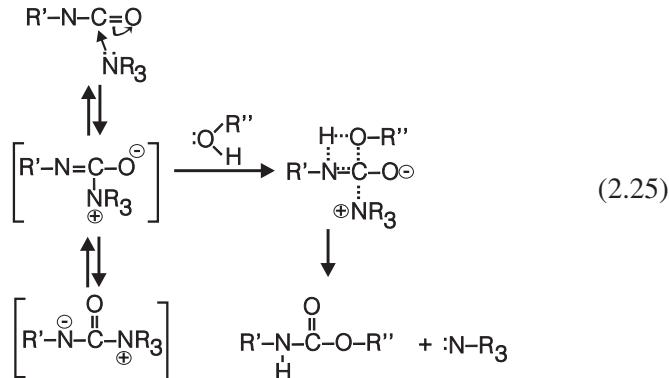
In general, requirements for good catalytic activity include:

- The catalyst is a strong nucleophile capable of attacking the carbon of the isocyanate group;
- The catalyst is capable of readily forming an active hydrogen amine complex; and
- The catalyst is soluble in water and forms stable hydrogen bonds with water.

Many proposed mechanisms of catalytic activity can be found in the open literature. Comprehensive review articles can be found in References 2.179-2.181.

Formation of Isocyanate-Amine Complex

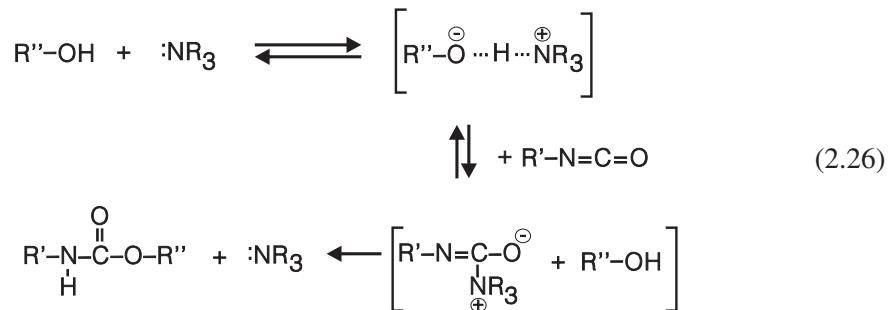
First proposed by Baker and Holdsworth in 1947 (Ref. 2.182), this mechanism proposes reversible nucleophilic attack on the carbon atom by the amine to form an activated complex. With aromatic isocyanates the carbonyl and aromatic groups both have moderate electron-withdrawing effects.



With the formation of an amine complex, the nitrogen atom of the isocyanate group is activated and readily reacts with hydrogen atoms from any water or polyol sources in the vicinity.

Formation of Active Hydrogen-Amine Complex

A more recent proposal by Farkas and Strohm (Ref. 2.183, 1965) involves the formation of an amine - active hydrogen complex.

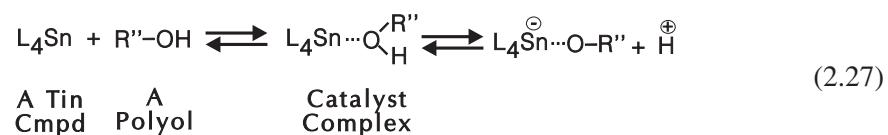


Farkas and Strohm demonstrated that this latter mechanism supports the observed increase in catalytic activity of an amine with increasing basicity.

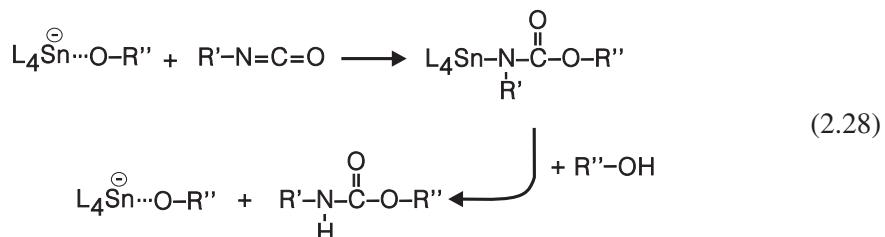
Organometallic Catalysts

The polymer forming or gellation reaction between the isocyanate and a polyol is promoted by organometallic catalysts. Of the many metals available, tin compounds are the most widely used. These compounds act as Lewis acids and are generally thought to function by interacting with basic sites in the isocyanate and polyol compounds.

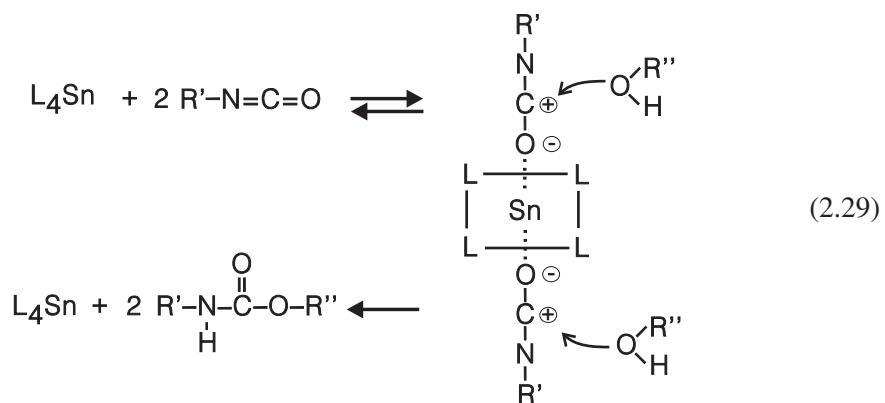
Three complementary mechanisms for activated complex formation can be envisaged. In the first, the polyol is activated by formation of a complex with the tin catalyst.



L symbolizes a ligand substituent to the tin molecule. From the tin alcohol adduct, the tin alkoxide can react with isocyanate to give a carbamate, which further reacts with additional polyol to propagate the polymer and regenerate the catalytic species.

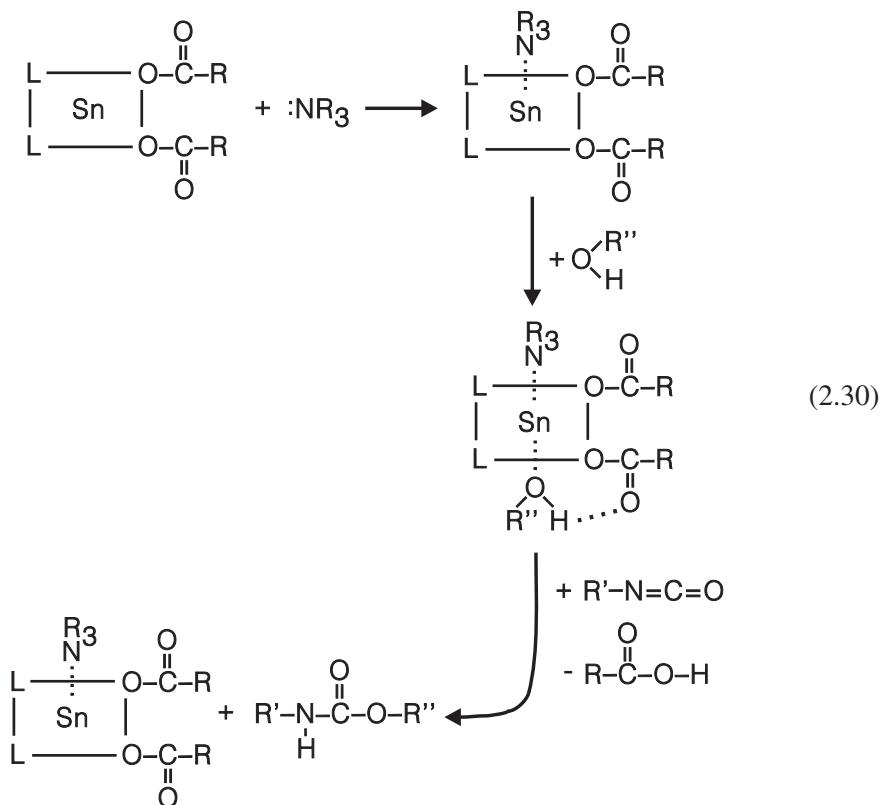


The second conceptual mechanism involves activation of isocyanate molecules.



Polyol attacks this complex at the isocyanate carbon atom to again propagate the polymer and regenerate the catalyst.

The final mechanism attempts to accommodate the experimentally observed synergism between organometallic compounds and amine catalysts. Tertiary amines are stronger Lewis bases than isocyanates and alcohols, and their complexation to metal compounds is expected. This tin-amine complex then accepts a polyol molecule to further activate the complex and promote formation of a tin alkoxide. A leaving carboxylate group accepts the proton and opens a position for insertion of an isocyanate group. Further reaction of the complex with additional polyol propagates the polymer and regenerates the catalytic species.



For flexible slabstock foam, stannous octoate (tin II 2-ethyl hexoate) is the preferred gelling catalyst. Special handling is necessary since the compound is easily hydrolyzed and oxidized in the presence of water and tertiary amines. In a given slabstock foam formulation, varying the concentration of stannous octoate will produce the typical results shown in Figure 2.13. The actual concentration levels must be determined experimentally for each foam formulation.^{2.184-2.186}

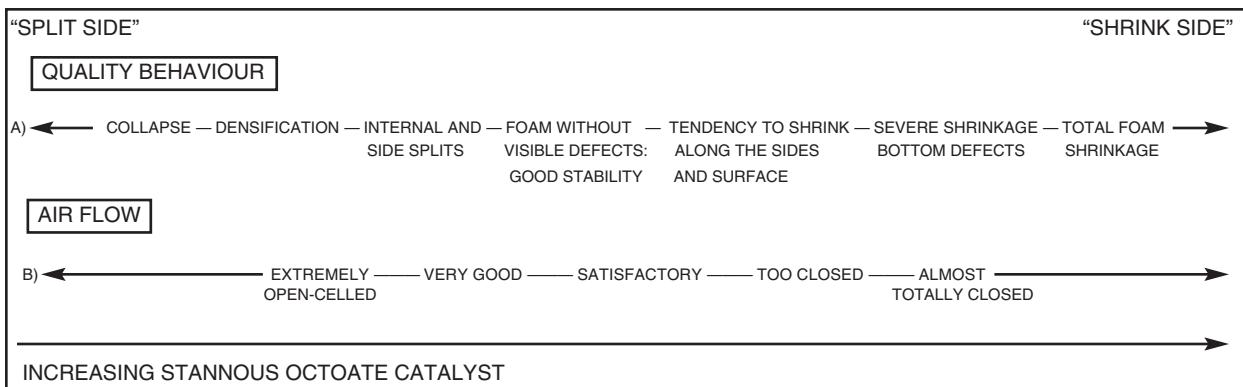


Figure 2.13 Effects of Increasing Stannous Octoate Catalyst

Foam splits occur when there is insufficient gellation to balance the blowing or gas evolution reaction. At some point, the motive force of the expanding gas bubbles exceeds the tensile strength of the polymer matrix and a physical separation (a split) occurs. From that point, a small increase in stannous octoate concentration will give a good open foam with some relaxation or ‘sigh back’. Further increase in catalyst concentration will eventually prevent the relaxation and the foam will become progressively tighter. At higher tin levels, slight to severe shrinkage results as the foam begins to gel faster, giving stronger cell windows that are more difficult to burst.

In molded foam production, higher overall levels of catalyst concentration are used to increase the rate of final polymerization and cure. These steps are necessary to reduce mold occupation times so that the part can be removed and further processed in an acceptable time frame. The upper limit of catalyst concentration is usually governed by its effect on cream time of the dispensed foam. Cream times faster than about two seconds result in flow and lid-closing problems.

Delayed Action Catalysts

In recent years, a growing desire for better in-mold flowability and faster curing along with a need to balance foam reactivities in the dual-hardness process has lead to the development of delayed action catalysts.^{2.187-2.189} These are compounds that are not very active at room temperature but become effective when the initial reaction exotherm warms up the foaming mass. The most common approach is to use a tertiary amine salt in a suitable solvent such as a low-molecular-weight glycol or water. Tertiary amine salts with organic acids such as carbonic, formic,

acetic, 2-ethylhexanoic and lactic acids have been introduced. Catalyst activity, phase separation and metal corrosion problems have been reported when acid blocked amines are formulated with normal amine catalysts in the presence of water. Another type of delayed action catalyst are the thermo-sensitive catalysts whose activity increases dramatically with increasing temperature.^{2.190-2.191}

ADDITIVES

Various additives may be incorporated into a foaming system to impart specific desired properties. A general review of additives for plastic products is presented in Reference 2.192. Some of the more common additives used in flexible foams will be discussed below.

Colorants

Many flexible foam products are color coded during manufacture to identify product grade, to conceal yellowing, or to make an appealing consumer product. The historical method of coloring foam was to blend in traditional pigments or dyes. Typical inorganic coloring agents included titanium dioxide, iron oxides and chromium oxide. Organic pigments originated from the azo/diazo dyes, phthalocyanines and dioxazines, as well as carbon black. Typical problems encountered with these colorants included high viscosity, abrasive tendencies, foam instability, foam scorch, migrating color and a limited range of available colors. Recent advances in the development of polyol-bound colorants are described in References 2.193-2.197. A detailed review of coloring technologies for polyurethanes is available.^{2.198}

UV Stabilizers

All polyurethanes based on aromatic isocyanates will turn dark shades of yellow upon aging with exposure to light. An excellent review of weathering phenomena in polyurethanes is available.^{2.199} The yellowing is a surface event that is not a problem for most foam applications.^{2.200-2.204} Light protection agents, such as hydroxybenzotriazoles, zinc dibutyl thiocarbamate, 2,6-ditertiary butylcatechol, hydroxybenzophenones, hindered amines and phosphites have been used to improve the light stability of polyurethanes.^{2.205-2.206} Color pigments have also been used successfully.^{2.207}

Flame Retardants

Low-density, open-celled flexible polyurethane foams have a large surface area and high permeability to air and thus will burn given the application of sufficient ignition source and oxygen. Flame retardants are often added to reduce this flammability, at least as it is measured by various specific, often small-scale tests, conducted under controlled laboratory conditions.^{2.208} The choice of flame retardant for any specific foam often depends upon the intended service application of that foam and the attendant flammability testing scenario governing that application. Aspects of flammability that may

be influenced by additives include the initial ignitability, burning rate and smoke evolution.

The most widely used flame retardants are the chlorinated phosphate esters,^{2.209-2.210} chlorinated paraffins^{2.211-2.218} and melamine powders^{2.219-2.221} have also been used. These and many other compositions are available from specialty chemical suppliers. Typical flexible foam formulations containing added flame retardants are given in References 2.222-2.223. An excellent review of this subject has been given by Papa and Kuryla.^{2.224}

Bacteriostats

Under certain conditions of warmth and high humidity, polyurethane foams are susceptible to attack by microorganisms.^{2.225-2.228} When that is a concern, additives against bacteria, yeast or fungi are added to the foam during manufacture.^{2.229-2.232}

Plasticizers

Nonreactive liquids have been used to soften a foam or to reduce viscosity for improved processing. The softening effect can be compensated for by using a polyol of lower equivalent weight, so that a higher cross-linked polymer structure is obtained. These materials increase foam density and often adversely affect physical properties.

Cell-Openers

In some polyurethane foams it is necessary to add cell-openers to obtain foam that does not shrink upon cooling. Known additives for inducing cell-opening include silicone-based antifoamers, waxes, finely divided solids, liquid perfluocarbons, paraffin oils, long-chain fatty acids and certain polyether polyols made using high concentrations of ethylene oxide. More discussion of cell-opener compounds is provided in Chapter 3.

Antistatic Agents

Some flexible foams are used in packaging, clothing and other applications where it is desired to minimize the electrical resistance of the foam so that buildup of static electrical charges is minimized. This has traditionally been accomplished through the addition of ionizable metal salts, carboxylic acid salts, phosphate esters and mixtures thereof. These agents function either by being inherently conductive or by absorbing moisture from the air. The desired net result is orders of magnitude reduction in foam surface resistivity. Problems with permanence of the effect and corrosion of electronic components led to the development of STATURE static control additive technology.^{2.233-2.235} Polyurethane foams containing the patented STATURE additive provide reliable, noncorrosive static protection regardless of humidity conditions.

Compatibilizers

Compatibilizers are special molecules that allow two or more nonmiscible ingredients to come together and give one clear, homogeneous liquid phase. Many such molecules are known to the polyurethane industry and typical improvements resulting from compatibilization have been discussed.^{2.236-2.238} Known classes of compatibilizer compounds include: amides,^{2.239-2.242} amines,^{2.243-2.245} hydrocarbon oils,^{2.246} phthalates,^{2.247} polybutylene glycols,^{2.248} and ureas.^{2.249-2.251}

AUXILIARY BLOWING AGENTS

Auxiliary blowing agents may be used in a foam formulation to aid in attaining densities and softness not obtainable with conventional water-isocyanate blowing chemistry. Until recently, the auxiliary blowing agent most often used in preparing extra-low-density and/or soft foam was fluorocarbon 11.^{2.252} Technology for using urethane grade methylene chloride as an auxiliary blowing agent was developed in the 1970's.^{2.253-2.255} Acetone has been used successfully^{2.256-2.258} and liquid carbon dioxide is growing in popularity.^{2.259-2.268} The use of dialkyl dicarbonates has been proposed.^{2.269-2.270} Many other agents are currently under investigation because of the suspected role of chlorofluorocarbons in the ozone depletion issue.^{2.271-2.279} A concise history of the chlorofluorocarbons issue is available.^{2.280}

Auxiliary blowing agents function by absorbing heat from the exothermic reactions, vaporizing and providing additional gas useful in expanding the foam to a lower density. Since they are nonreactive and contribute nothing to the polymer structure, such blowing agents give softer foams than those blown to the same density with only water. Because the auxiliary blowing agent acts as a heat sink, higher total catalyst package levels are generally needed to maintain adequate cure of the foam. In the case of methylene chloride, delayed action amine catalysts are needed to overcome processing problems.^{2.281}

References

- 2.1 Pinner, S. H. "Chemistry and Technology of the Organic Isocyanates"; *Plastics (London)* **1947**, 11, Apr./May, 206-211, 215.
- 2.2 Cooper, W.; Pearson, R. W.; Darke, S. "Isocyanate Reactions and the Structure of Polyurethanes"; *The Industrial Chemist* **1960**, 3, 121-126.
- 2.3 Saunders, J. H.; Frisch, K. C. *Polyurethanes, Chemistry and Technology, Part I, Chemistry*; Interscience: New York, 1962.
- 2.4 Sayigh, A. A. R.; Ulrich, H.; Farrissey, W. J. "Diisocyanates"; In *Condensation Monomers*; Wiley-Interscience: New York, 1972, 369-476.
- 2.5 Satchell, D.P.N.; Satchell, R.S. "Acylation by Ketens and Isocyanates. A Mechanistic Comparison"; *Chem. Soc. Rev.* **1975**, 4/2, 231-250.
- 2.6 Richter, R.; Ulrich, H. "Synthesis and preparative applications of isocyanates"; In *The chemistry of cyanates and their thio derivatives, Part 2*; Patai, S., Ed., John Wiley and Sons: New York, 1977.

- 2.7 Lovering, E. G.; Laidler,K.J. "Thermochemical Studies of Some Alcohol-Isocyanate Reactions"; *Can. J. Chem.* **1962**, 40, 26-30.
- 2.8 Smith, H. A. "Catalysis of the Formation of Urethanes"; *J. Appl. Polym. Sci.* **1963**, 7, 85-95.
- 2.9 Smith, H. A. "Effect of Urethane Groups on the Reaction of Alcohols with Isocyanates"; *J. Polym. Sci. :Part A-1* **1968**, 6, 1299-1306.
- 2.10 Hartley, F. D.; Cross, M. M.; Lord, F. W. "The Mechanism of Polyurethane Foam Formation"; In *Advances in Polyurethane Technology*; Buist, J.M.; Gudgeon, H. Eds., Maclarens and Sons: London, 1968, 127-140.
- 2.11 Cole, K. C.; Van Gheluwe, P.; Dueck, C. L.; Martineau, P.; LeRoux, J. "Thermal and FT-IR Analysis of the Polyurethane Foaming Reaction: The Effect of the Isocyanate Index"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988; 2-10.
- 2.12 Spirkova, M.; Kubin, M.; Dusek, K. "Side Reactions In The Formation Of Polyurethanes: Stability Of Reaction Products Of Phenyl Isocyanate"; *J. Macromol. Sci.-Chem.* **1990**, A27(4), 509-522.
- 2.13 Dusek, K.; Spirkova, M. "Crosslinking and Network Formation in Polyurethane Systems with Excess Isocyanate"; *Cell. Polym.* **1990**, 9/2, 693.
- 2.14 Kurzer F. "Biuret and Related Compounds"; *Chem. Rev.* **1955**, 56, 95-197.
- 2.15 Saunders, J. H.; Hansen, R. H. "The Mechanism of Foam Formation"; In *Plastic Foams, Part I*; Marcel Dekker: New York, 1972, 23-108.
- 2.16 Abbate, F.W. "Guide to formulating and compounding polyurethanes"; *Plast. Cmpd.* **1986**, 9/4, 20, 23-24, 26-27.
- 2.17 Hill, B.G. "Polyols for urethanes"; *Chemtech* **1973**, Oct., 613-616.
- 2.18 Sparrow, D.J.; Thorpe, D. "Polyols for Polyurethane Production"; In *Telechelic Polymers, Vol. 2, 'Synthesis and Application'*; Goethals, E.J., Ed., CRC Press: Boca Raton, Florida, 1989, 203.
- 2.19 Friedli, H.R.; "In *Reaction Polymers*"; Gum, W.F.; Riese, W.; Ulrich, H., Eds., Hanser: Munich, 1992, 68.
- 2.20 Dege, G. J.; Harris, R. L.; MacKenzie, J. S. "Terminal Unsaturation in Polypropylene Glycol"; *J. Amer. Chem. Soc* **1959**, 81, 3374-3379.
- 2.21 Simons, D. M.; Verbanc, J. J. "The Polymerization of Propylene Oxide"; *J. Polym. Sci.* **1960**, 44, 303-311.
- 2.22 Steiner, E. C.; Pelletier, R. R.; Trucks, R. O. "A Study of the Polymerization of Propylene Oxide Catalyzed by Anhydrous Potassium Hydroxide"; *J. Amer. Chem. Soc.* **1964**, 86, 4678-4686.
- 2.23 Fogiel, A.W. "Effective Functionality and Intramolecular Reactions of Polyisocyanates and Polyols"; *Macromol.* **1969**, 2/6, 581-587.
- 2.24 Livigni, R.A.; Herold, R.J.; Elmer, O.C.; Aggarwal, S.L. "Poly (Propylene Ether) Polyols Prepared With a Zinc Hexacyanocobaltate Complex Catalyst"; In *Polyethers, ACS Symposium Series No. 6*; Vandenberg, E.J., Ed., American Chemical Society: Washington, 1975, 29-31.

- 2.25 Stanford, J.L.; Stepto, R.F.T. "A Study of Intramolecular Reaction and Geletion during Non-Linear Polyurethane Formation"; *Brit. Polym. J.* **1977**, 6, 124-132.
- 2.26 Miller, D.R.; Valles, E.M.; Macosko, C.W. "Calculation of Molecular Parameters for Stepwise Polyfuncional Polymerization"; *Polym. Eng. Sci.* **1979**, 19/4, 272-283.
- 2.27 Barksby, N.; Allen, G.L. "Low Monol Polyols and Their Effects in Urethane Systems"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 445-450.
- 2.28 Carr, R.H.; Hernalsteen, J.; Devos, J. "Determination of Functionality and Functionality Distribution of Polyether Polyols by Quantitative ¹³C NMR Spectroscopy"; *J. Appl. Polym. Sci.* **1994**, 52/8, 1015-1022.
- 2.29 David, D.J.; Staley, H.B. *Analytical Chemistry Of The Polyurethanes, Vol 16, Part III*; Wiley-Interscience: New York, 1969, 291-292.
- 2.30 Patent U.S. 3,271,462, M. H. Earing to Wyandotte Chemical Company, September 6, 1966.
- 2.31 Patent U.S. 3,278,457, to General Tire Corporation, October 11, 1966.
- 2.32 Patent U.S. 3,393,243, M. Cuscurida to Jefferson Chemical Corporation, July 16, 1968.
- 2.33 Patent U.S. 3,485,861, R.L. McKellar and M.C. Musolf to Dow Corning Corporation, December 23, 1969.
- 2.34 Herold, R.J.; Linigim, R. A. *Polymerization Kinetics and Technology, Advances in Chemistry Series No. 128*; American Chemical Society: Washington, 1973.
- 2.35 Bleijenberg, K.C. "Novel polyols via new manufacturing routes"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988; 185-187.
- 2.36 Schuchardt, J.L.; Harper, S.D. "Preparation of High Molecular Weight Polyols Using Double Metal Cyanide Catalysts"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 360-364.
- 2.37 Patent U.S. 5,010,187, A.J. Heuvelsland to Dow Chemical Company, April 23, 1991.
- 2.38 Hinz, W. "A New Synthetic Approach to High Molecular Weight Polyetherpolyols"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 519-523.
- 2.39 Penati, A.; Maffezzoni, C.; Moretti, E. "Practical and Theoretical Molecular Weights in Polyaddition Reactions of Ethylene and Propylene Oxide"; *J. Appl. Polym. Sci.* **1981**, 26, 1059-1071.
- 2.40 Baize, T. H. "Polymerization of Ethylene Oxide"; *Ind. Eng. Chem.* **1961**, 53/11, 903-906.
- 2.41 Powell, D.G.; Puig, J.E.; van Leuwen, B.G. "Polyols and Requirements for Ambient Cure Foams"; *J. Cell Plast.* **1972**, 8/2, 90-99.
- 2.42 Gaylord, N. G., Ed.; Polyethers. *Vol. I. Polyalkylene Oxides and Other Polyethers*; Interscience: New York, 1963.
- 2.43 Furukawa, J.; Saegusa, T. *Polymerization of Aldehydes And Oxides*; Interscience: New York, 1963, 125-208.

- 2.44 Newton, R. A. "Propylene Oxide Polymers and Higher 1,2-Epoxyde Polymers"; In *Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition*; John Wiley & Sons: New York, 1982; Vol. 18, 633-645.
- 2.45 Schauerte, K.; Dahm, M.; Ditler, W.; Uhlig, K. "Raw Materials"; In *Polyurethane Handbook*; Oertel, G., Ed., Hanser: New York, 1985, 42-50.
- 2.46 Hampton, H.A.; Hurd, R.; Shearing, H.J. "Recent Developments in Polyurethanes"; *J. Oil Col. Chem. Ass.* **1960**, 43, 96-123.
- 2.47 Yost, C. W.; Plank, C. A.; Gerhard, E. R. "Oxypropylation Of Glycerol, A Study of Variables"; *Ind. Eng. Chem. Prod. Res. Dev.* **1967**, 6/2, 113-115.
- 2.48 Yen, Y. C. "Polyols from Ethylene Oxide and Propylene Oxide"; *Process Economics Program Report No. 45*; Stanford Research Institute: Menlo Park, California, 1968.
- 2.49 Wright, P.; Cumming, A. P. C. *Solid Polyurethane Elastomers*; Gordon and Breach: New York, 1969, 66-68.
- 2.50 Guibert, R. M.; Plank, C. A.; Gerhard, E. R. "Kinetics of the Propylene Oxide-Oxypropylated Glycerol Reaction"; *Ind. Eng. Chem. Process Des. Develop.* **1971**, 10/4, 497-500.
- 2.51 Christianson, L.R.; Dheming, M.; Ochoa, E.L. "The Economics of a Polyether Plant"; *J. Cell Plast.* **1977**, 13/2, 111-117.
- 2.52 Hampton, H.A.; Hurd, R.; Shearing, H.J. "Recent Developments in Polyurethanes"; *J. Oil Col. Chem. Ass.* **1960**, 43, 96-123.
- 2.53 Sparrow, D. J.; Thorpe, D. "Polyols for Polyurethane Production"; In *Telechelic Polymers, Vol. 2, 'Synthesis and Application'*; Goethals, E.J., Ed., CRC Press: Boca Raton, Florida, 1989, 181-228.
- 2.54 Barrett, K. E. T. *Dispersion Polymerization in Organic Media*; John Wiley and Sons: London, 1975.
- 2.55 Napper, D.H. *Polymeric Stabilization of Colloidal Particles*; Academic Press: London, 1983.
- 2.56 Kuryla, W. C.; Critchfield, F. E.; Platt, L. W.; Stamberger, P. "Polymer/ Polyols, a New Class of Polyurethane Intermediates"; *J. Cell. Plast.* **1966**, 2/2, 84-96.
- 2.57 Bamford, C.H.; Tipper, C.F.H. *Free Radical Polymerization*; Elsevier: New York, 1976.
- 2.58 Kahrs, K.H.; Zimmermann, J.W. "Die Pfropfcopolymerisation von Vinylestern auf Polyalkylenoxyde"; *Makromol. Chem.* **1962**, 58, 75-103.
- 2.59 Critchfield, F. E.; Koleske, J. V.; Priest, D. C. "Poly (Styrene co acrylonitrile) polyols. Modulus enhancing polyols for urethane polymers"; *Rubber Chem. Tech.* **1972**, 45, 1467-1484.
- 2.60 Cloetens, R.; Lidy, W. A.; Phillips, B. D.; Thomas, D. B. "Polymer Polyols Properties and Applications"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 480-489.
- 2.61 Ramlow, G.G.; Heyman, D.A.; Grace, O.M. "New Graft Polyols for High Load-Bearing Foams"; *J. Cell Plast.* **1983**, 19/4, 237-242.

- 2.62 Shears, J.H.; Dam, C.G.; Vandichel, J.C.; Verstraete, H. "POSTECH Polyols: A New Generation of Polymer Polyols for Enhanced Load Bearing and High Resilience Foams"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 150-155.
- 2.63 Yen, Y. C.; Tsao, T. S. "Polyols For Polyurethanes"; *Process Economics Program Report No. 45A*; Stanford Research Institute: Menlo Park, California, 1982, 119-152.
- 2.64 Spitler, K. G.; Lindsey, J. J. "PHD Polyols, A New Class of PUR Raw Materials"; *J. Cell Plast.* **1981**, 17/1, 43-50.
- 2.65 Vehlewald, P.; Volland, R. "PHD Polyethers-Key Products For The Manufacture Of All-Foam Cushioning"; *Kunststoffe* **1983**, 73/8, 439-443.
- 2.66 Koshute, M. A.; Freitag, H. A. "Second Generation PHD Polyol for Automotive Flexible Molding"; *Proceedings of The SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 502-507.
- 2.67 Patent U.S. 4,260,530, A. Reischl, H. Muller and K. Wagner to Bayer, April 7, 1981.
- 2.68 Patent U.S. 4,374,209, J.P. Rowlands to Interchem International S.A., February 15, 1983.
- 2.69 Pickin, K. "PIPA-Process For The Future"; *Urethanes Tech.* **1984**, June, 23-24.
- 2.70 Patent U.S., 4,452,923, W.G. Carroll and P. Farley to Imperial Chemical Industries, June 5, 1984.
- 2.71 Patent U.S. 4,554,306, W.G. Carroll to Imperial Chemical Industries, November 19, 1985.
- 2.72 Patent U.S. 5,068,280, J.M. Pal, J.P. Cosman and K. Tan to Dow Chemical Company, November 26, 1991.
- 2.73 Patent U.S. 5,179,131, S.E. Wujcik, D.L. Christman and O.M. Grace to BASF Corporation, January 12, 1993.
- 2.74 Patent U.S. 5,292,778, K.J. Van Veen and G.R. Blair to Woodbridge Foam Corporation, March 8, 1994.
- 2.75 Patent U.S. 4,785,026, E.L. Yeakey and M. Cuscurida to Arco Chemical Company, November 15, 1988.
- 2.76 Knight, J. E. "Polyols For Higher Load Bearing Foam"; *Proceedings of The SPI-27th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982; 225-227.
- 2.77 van der Wal, H. R. "Epoxy Dispersion Polyols: A Novel Polymer-Modified Polyol for Improved Loadbearing and Resiliency"; *Proceedings of The SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 493-497.
- 2.78 Patent U.S. 4,326,043, T. Narayan and J.T. Patton to BASF Wyandotte Corporation, April 20, 1982.
- 2.79 Sam, F.O.; Stefani, D.; Gallo, B. "High Performance Flexible Polyurethane Foams with Improved Fire Behavior"; *Proceedings of the Polyurethane World Conference 1993*; Technomic: Lancaster, Pa., 1995, 62-69.

- 2.80 Kageoka, M.; Tairaka, Y.; Kodama, K. "Effects of Melamine Particle Size on Flexible Polyurethane Foam Properties"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 62-69.
- 2.81 Carey, M.A.; Wellons, S.L.; Elder, D.K. "Rapid Method For Measuring The Hydroxyl Content of Polyurethane Polyols"; *J. Cell Plast.* **1984**, 20/1, 42-48.
- 2.82 Turley, P.A.; Pietrantonio, A. "Rapid Hydroxyl Number Determination by Near Infrared Reflectance Analysis"; *J. Cell Plast.* **1984**, 20/4, 274-278.
- 2.83 "Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols"; American Society for Testing and Materials, D 4274-88; ASTM Philadelphia, 1990.
- 2.84 Hanna, J.G.; Siggi, S. "Primary and Secondary Hydroxyl Group Content of Polypropylene Glycols"; *J. Polym. Sci.* **1962**, 56, 297-304.
- 2.85 Crummett, W.B. "Determination of the Primary Hydroxyl Group Content of Polypropylene Glycols"; *Anal. Chem.* **1962**, 34/9, 1147-1150.
- 2.86 Hendrickson, J.G. "The Determination of Primary Alcohol Groups in Polyglycols Using Triphenylchloromethane"; *Anal. Chem.* **1964**, 36/1, 126-128.
- 2.87 Mathias, A.; Mellor, N. "Analysis of Alkylene Oxide Polymers by Nuclear Magnetic Resonance Spectrometry and by Gas-Liquid Chromatography"; *Anal. Chem.* **1966**, 38/3, 472-477.
- 2.88 Manatt, S.L.; Lawson, D.D.; Ingham, J.D.; Rapp, N.S.; Hardy, J.P. "A Trifluoroacetylation-Fluorine-19 Nuclear Magnetic Resonance Technique for Characterization of Hydroxyl Groups in Poly (Propylene) Oxides"; *Anal. Chem.* **1966**, 38/8, 1063-1065.
- 2.89 van Leuwen, B.G.; Powell, D.G.; Puig, J.E.; Natoli, F.S. "Physical And Chemical Approaches To Ideal Cushioning Foams"; In *Advances In Urethane Science and Technology, Vol. 2*; Frisch, K.C.; Reegen, S.L., Eds.; Technomic: Westport, Conn., 1973, 173-190.
- 2.90 Groom, T.; Babiec, J.S.; van Leuwen, B.G. "End Group Analysis of Polyether Polyols by Nuclear Magnetic Resonance (NMR) Spectroscopy"; *J. Cell Plast.* **1974**, 10/1, 43-46.
- 2.91 Williams, D.A.R.; Dyke, R.; Malcomson, S.; Massey, S. "Analysis of Primary Hydroxyl Content of Polyether Polyols. A Comparative Study"; *J. Cell. Plast.* **1983**, 19/2, 121-124.
- 2.92 LeBas, C.L.; Turley, P.A. "Primary Hydroxyl Content in Polyols Evaluation of Two Nuclear Magnetic Resonance (NMR) Methods"; *J. Cell. Plast.* **1984**, 20/3, 194-199.
- 2.93 Noshiro, M.; Jitsugiri, Y.; Kozawa, S.; Shimada, T. "Analysis of EO/ PO Polyether Polyols by NMR"; In *International Progress In Urethanes, Vol.5*; Ashida, K.; Frisch, K.C., Eds.; Technomic: Lancaster, Pa., 1988, 28-44.
- 2.94 "Standard Test Methods for Polyurethane Raw Materials: Determination of Primary Hydroxyl Content of Polyether Polyols"; American Society for Testing and Materials, D 4273-83; ASTM: Philadelphia, 1990.
- 2.95 Deily, J.R. "The Polarographic Determination of Secondary Hydroxyl Groups in Urethane Polyols"; *J. Cell. Plast.* **1983**, 19/2, 76-82.

- 2.96 Lowe, A.J.; Chandley, E.F.; Leigh, H.W.; Molinario, L. "Some Effects of Molecular Structure on the Production of Flexible Urethane Foams"; *J. Cell. Plast.* **1965**, 1/1, 121-131.
- 2.97 Williams, J.L.; Stein, N.J. "Determination of Cloud Points of Nonionic Surfactants"; *J. Am. Oil Chem. Soc.* **1965**, 42, 1054-1056.
- 2.98 "Standard Test Method for Cloud Point of Nonionic Surfactants"; American Society for Testing and Materials, D 2024-65; ASTM: Philadelphia, 1992.
- 2.99 Scholten, H. G.; Schuhmann, J. G.; TenHoor, R. E. "Urethane Polyether Prepolymers and Foams - Influence of Chemical and Physical Variables on Reaction Behavior"; *J. Chem. Eng. Data* **1960**, 5/3, 395-400.
- 2.100 *Influence Of Catalysts On The Chemistry Of "One-Shot" Polyether Urethane Foams*; The Dow Chemical Company; Form No. 125-281-60.
- 2.101 Ferrigno, T. H. *Rigid Plastic Foams*; Reinhold: New York, 1963, 27-34.
- 2.102 Ryall, B.; Griffiths, P. G. "Some Developments in One-Shot, Semi-Rigid Polyurethane Foam Moulding"; *J. Cell. Plast.* **1970**, 6/5, 232-239.
- 2.103 Controlled polymerization is only half of it; Merck and Company, *J. Cell. Plast.* **1970**, 6/6, 257.
- 2.104 Willoughby, B.G. "Use of instrumental techniques for troubleshooting, control and development with adhesives, sealants and binders"; *Rub. World* **1982**, 187/3, 26-33.
- 2.105 Freitag, H.A.; Volland, A. "Flexible Polyurethane Molded Foam"; In *Polyurethane Handbook*; Oertel, G., Ed., Hanser: New York, 1985, 201-202.
- 2.106 Burchell, D.J.; Porter, J.R. "Rheological Analysis of Modulus Growth: A Probe for Determining the Strength of Reacting Urethane Systems"; *Proceedings of The SPI-32nd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989; 144-148.
- 2.107 *Dow Polyurethanes, Solid Technical Support for Flexible Foam Slabstock Producers*; The Dow Chemical Company; Form No. 109-925-389, 10.
- 2.108 Webb, D.D. "Urethane Systems Reactivity Measurement"; *Proceedings of The SPI-28th Annual Technical/Marketing Conference*, Technomic: Lancaster, Pa., 1984; 2-5.
- 2.109 Scott, K.W. "Giving good vibrations, A new examination of viscosity"; *Ureth. Tech.* **1988**, Aug./Sept.
- 2.110 Scott, K.W. "Polyurethane applications for the vibrating needle curemeter"; *Rub. World* **1990**, 202/6, 19-22.
- 2.111 Wright, P.; Cumming, A. P. C. *Solid Polyurethane Elastomers*; Gordon And Breach: New York, 1969, 68-70.
- 2.112 Sittig, M. *Amines, Nitriles and Isocyanates, Processes and Products*, 1969; Noyes Development Corporation: Park Ridge, New Jersey, 1969.
- 2.113 Ozaki, S. "Recent Advances In Isocyanate Chemistry"; *Chem. Rev.* **1972**, 72/5, 457-496.
- 2.114 Ranney, M. W. *Isocyanates Manufacture*; Noyes Data Corporation: Park Ridge, New Jersey, 1972.

- 2.115 Ulrich, H. *Introduction to Industrial Polymers*; Hanser: Munich, 1982, 83-84.
- 2.116 Eldib, I.A. "How to Make Polyurethanes"; *Hydrocarbon Proc. Petrol. Ref.* **1963**, 42/12, 121-127.
- 2.117 Chadwick, D. H.; Cleveland, T. H. "Isocyanates, Organic"; In *Kirk-Othmer Encyclopedia Of Chemical Technology, Third Edition*; John Wiley and Sons: New York, 1982; Vol. 13, 789-818.
- 2.118 Lunde, K. E.; Bratt, L. C. "Toluene Diisocyanates"; *Process Economics Program Report No. 1*; Stanford Research Institute: Menlo Park, California, 1963.
- 2.119 Bailey, M. E.; Kirss, V.; Spaunburgh, R. G. "Reactivity of Organic Isocyanates"; *Ind Eng. Chem.* **1956**, 48/4, 794-797.
- 2.120 Lenz, R.W. *Organic Chemistry of Synthetic High Polymers*; Interscience: New York, 1967, 180-185.
- 2.121 Bender, R. J. *Handbook of Foamed Plastics*; Lake Publishing Corporation: Libertyville, Illinois, 1965, 130.
- 2.122 McGinn, C. E.; Spaunburgh, R. C. "Relative Activation Energies Of Several Aryl Diisocyanates"; Symposium on Isocyanate Polymers, Paper No.38, *American Chemical Society Meeting, Atlantic City, New Jersey, September 1956*, 16/2.
- 2.123 Gmitter, G. T.; Gruber, E. E. "Effect of Ratio of Diisocyanate Isomers in Polyurethane Foams"; *SPE Journal* **1957**, 13/1, 27-31.
- 2.124 Berger, S. E.; Cataldo, F. L.; Dwyer, F. J.; Stone, H. "Toluene Diisocyanate 2, 6 - Isomer - Its Effect on Urethane Polymers"; *SPE Journal* **1961**, 17/2, 170-173.
- 2.125 Smith, C. H.; Petersen, C. A. "Effect of Diisocyanate Structure on Load-Bearing Properties of Flexible Urethane Foams"; *SPE Journal* **1962**, 18/4, 455-459.
- 2.126 Mispreuve, H.; Duff, A.; Gansow, M.; Fangareggi, A. "Recent Developments in Hot Moulding Polyurethane Flexible Foam Technology for Automotive Seating"; *J. Cell. Plast.* **1988**, 24/4, 348-358.
- 2.127 Nierzwichi W.; Walczynski, B. "A Study of Toluene Diisocyanate-Based Polyurethanes of Various Isomer Ratios"; *J. Appl. Polym. Sci.* **1990**, 41, 907-915.
- 2.128 Vargas, J. B.; Loefgren, B. C.; Kato, H. "Urethane Foams In Latin America - A Study In Contrasts"; *Proceedings of The SPI-18th Annual Urethane Division Technical Conference*; Technomic: Lancaster, Pa., 1972; 17-35.
- 2.129 Yen, Y. C. "Isocyanates, Supplement A and B, Part I"; *Process Economics Program Report No. 1-A*; Stanford Research Institute: Menlo Park, California, 1968-1973.
- 2.130 Twitchett, H.J. "Chemistry of the Production of Organic Isocyanates"; *Chem. Soc. Revs.* **1974**, 3, 209-230.
- 2.131 Chono, M.; Fukuoka, S.; Kohno, M. "A New Route To MDI Without Phosgene"; *Proceedings of the SPI-6th International Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983, 394-398.
- 2.132 *High-Performance Isocyanates for Polyurethanes*; The Dow Chemical Company; Form No. 109-799-86.
- 2.133 *Preparation of Prepolymers, Laboratory To Full-Scale Production*; The Dow Chemical Company; Form No. 109-00895-290-SAI.

- 2.134 Heiss, H.L.; Combs, F.P.; Gemeinhardt, P.G.; Saunders, J.H.; Hardy, E.E. "Influence of Acids and Bases on Preparation of Urethane Polymers"; *Ind. Eng. Chem.* **1959**, 51/8, 929-934.
- 2.135 Wall, J.R. "Continuous processing of urethane foam prepolymers"; *Chem. Eng. Prog.* **1961**, 57/10, 48-51.
- 2.136 Saunders, J.H.; Frisch, K.C. *Polyurethanes, Chemistry and Technology; Part II. Technology*; Interscience: New York, 1964, 8-43.
- 2.137 Martin, R. A.; Hoy, K. L.; Peterson, R. H. "Computer Simulation Of The Tolylene Diisocyanate-Polyol Reaction"; *Ind. Eng. Chem., Prod. Res. Dev.* **1967**, 6/4, 218-222.
- 2.138 Peebles, L.H. "Sequence Length Distribution in Segmented Block Copolymer"; *Macromol.* **1974**, 7/6, 872-881.
- 2.139 Wang, T.; Lyman, D.J. "The effect of reaction conditions on the urethane prepolymer formation"; *Polym. Bul.* **1992**, 27, 549-555.
- 2.140 Saunders, J.H.; Frisch, K.C. *Polyurethanes, Chemistry and Technology, Part II, Technology*; Interscience: New York, 1964, 8-49.
- 2.141 Gemeinhardt, P.G. "Section X- Flexible Urethane Foam"; In *Handbook of Foamed Plastics*; Bender, R.J., Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965, 173-208.
- 2.142 Zwolinski, L.M.; Frink, J.W. "High Resilience 'Cold -Molded' Urethane Foam"; *J. Cell. Plast.* **1972**, 8/1, 20-29.
- 2.143 Brydson, J.A. *Plastics Materials*; Butterworth Scientific: London, 1982, 709-712.
- 2.144 Hartley, F.D.; Cross, M.M.; Lord, F.W. "The Mechanism of Polyurethane Foam Formation"; In *Advances in Polyurethane Technology*; Buist, J.M.; Gudgeon, H., Eds.; Maclaren and Sons: London, 1968, 135-136.
- 2.145 Klempner, D.; Frisch, K.C. *Handbook of Polymeric Foams and Foam Technology*; Hanser: Munich, 1991, 53-54.
- 2.146 Patent U.S. 5,114,989, R.J. Elwell, R.A. Sewell, W.A. Lidy and J.A. Thoen to Dow Chemical Company, May 19, 1992.
- 2.147 Hogan, J. M.; Pearson C. J.; Rogers, T. H.; White, J. R. "Humidity Characteristics of HR and Hot Urethane Foams"; *J. Cell Plast.* **1973**, 9/5, 219-225.
- 2.148 Woods, G. W. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 118-120.
- 2.149 Burks, S.; Gutowsky, K.; Autenrieth, R. "Ultrasonic Rise and Adiabatic Temperature Evaluation (URATE) of Polyurethane Foams"; Paper No. 900729, *Proceedings of The SAE International Congress and Exposition, Detroit, Michigan, 1990*; SAE: Warrendale, Pennsylvania.
- 2.150 Ferrigno, T. H. "The Use of Extenders In Flexible Urethane Foams"; *SPE Journal* **1960**, June, 638-640.
- 2.151 Byall, R.D. "Flexible Urethane Foam"; paper presented at American Chemical Society Meeting, Rubber Chemistry Division, Oct. 20, 1965.
- 2.152 Reilly, A.F. "Urethane Slab Foam for Furniture and Automotive Markets"; *Chem. Eng. Prog.* **1967**, 63/5, 104-108.

- 2.153 Currier, V. "How to Compound High-Density Urethane Foams"; *Plast. Tech.* **1966**, 12/8, 35-37.
- 2.154 Doyle, E.N. *The Development and Use of Polyurethane Products*; McGraw-Hill: New York, 1971; 77-82.
- 2.155 Katz, H. S.; Milewski, J. V. *Hand Book of Fillers for Plastics*; Van Nostrand Reinhold: New York, 1987.
- 2.156 Tabor, R.L.; Hinze, K.J.; Priester, R.D.; Turner R.B. "The Compatibility of Water with Polyols"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 514-528.
- 2.157 Hersch, P. "Choosing and Using The Right Silicone Surfactant For Urethane Foams"; *Plast. Tech.* **1967**, 13/12, 49-53.
- 2.158 Bryant, R. M.; Stewart, H. F. "The Chemistry of Silicone Surfactants for Urethane Foams"; *J. Cell Plast.* **1973**, 9/2, 99-102.
- 2.159 Plumb, J.B.; Atherton, J.H. "Copolymers Containing Polysiloxane Blocks"; In *Block Copolymers*; Allport, D.C., Janes, W.H., Eds., John Wiley & Sons, New York, 1973, 305-353.
- 2.160 Brydson, J.A. "Silicones and Other Heat-resisting Polymers"; In *Plastics Materials*; Butterworth Scientific, London, 1982, 730-766.
- 2.161 Boudreau, R. J. "How Silicone Surfactants Affect Polyurethane Foams"; *Mod. Plast.* **1967**, Jan., 133-147.
- 2.162 Frey, J.H. "Design of a New Silicone Surfactant for Flexible Slabstock Polyurethane Foam"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 224-229.
- 2.163 Snow, S.A.; Fenton, W.N.; Owen, M.J. "The addition of Polyoxyethylene/polyoxypropylene block copolymers to silicone surfactant systems to improve the porosity of flexible polyurethane foam"; *J. Cell. Plast.* **1990**, 26/2, 172-182.
- 2.164 Burkhardt, G.; Schlons, H.-H.; Zellmer, V. "New Silicone Surfactant Technology for Flexible Polyester Polyurethane Foams"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 359-363.
- 2.165 Burkhardt, G.; Klietsch, J.; Zellmer, V. "New Surfactant for High Resiliency Moulded Polyurethane Foam Improves Processing"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 127-131.
- 2.166 Grabowski, W.; Desnier, M.C. "L-2100, a New Silicone Surfactant for Use in High Resilience Slabstock Foam"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 81-88.
- 2.167 Brune-Fischer, A.; Burkhardt, G.; Zellmer, V. "New Concepts in Designing Silicone Surfactants for HR-Molded Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 267-273.
- 2.168 Brune, A.; Klietsch, J.; Zellmer, V. "Design of New Stabilizers for HR-Moulded Foam"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 12.

- 2.169 Dahm, M. "The Role of Surfactants during Polyurethane Foam Formation"; In *Cellular Plastics, National Academy of Sciences-National Research Council Publication 1462*; 52-63 (1967).
- 2.170 Rossmy, G. R.; Kollmeier, H. J.; Lidy, W.; Schator, H.; Wiemann, M. "Cell-Opening in One-Shot Flexible Polyether Based Polyurethane Foams. The Role of Silicone Surfactant and its Foundation in the Chemistry of Foam Formation"; *J. Cell. Plast.* **1977**, 13/1, 26-35.
- 2.171 Woods, G. W. Flexible *Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 68-72.
- 2.172 Brecker, L. R. "Additives for plastics - polyurethane catalysts"; *Plast. Eng.* **1977**, March, 39-42.
- 2.173 Rusch, T. E.; Raden, D. S. "Chosing Urethane-Foam Catalysts", *Plast. Compd.* July/August **1980**, 61-74.
- 2.174 Listemann, M.L.; Wressell, A.L.; Lassila, K.R.; Klotz, H.C.; Johnson, G.L.; Savoca, A.C. "The Influence of Tertiary Amine Structure on Blow-to-Gel Selectivity"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 595-608.
- 2.175 Winkler, J. "Effects of Foaming Catalysts On Aging of Urethane Foams"; *SPE Journal* **1956**, 12/11, 23-26.
- 2.176 Alzner, B. G.; Frisch, K. C. "Effect of Catalysts on Urethane Foam Properties"; *Ind. Eng. Chem.* **1959**, 51/5, 715-716.
- 2.177 Gmitter, G.T.; Gruber, E.E.; Joseph, R.D. "Tertiary Amine Catalysts: How They Affect Foam Properties"; *SPE Journal* **1959**, 15/11, 957-960.
- 2.178 Patent U.S. 5,508,314, M. L. Listermann, K.R. Lassila, K.E. Minnich and A.C.L. Savoca to Air Products and Chemicals Inc., April 16,1996.
- 2.179 Burkhardt, G.; Kollmeier, H. J.; Schloens, H. H. "The Importance of Catalysts for the Formation of Flexible Polyurethane Foams"; *J. Cell. Plast.* **1984**, 20/1, 37-41.
- 2.180 Malwitz, N.; Manis, P. A.; Wong, S. W.; Frisch, K. C. "Amine Catalysis of Polyurethane Foams"; *Proceedings of the SPI-30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa.; 1986, 338-353.
- 2.181 Malwitz, N.; Kresta, J. E. "Amine Catalysis of the Aryl Isocyanate Reaction"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 826-836.
- 2.182 Baker, J. W.; Holdsworth, J. B. "The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part XIII. Kinetic Examination of the Reaction of Aryl Isocyanates with Methyl Alcohol"; *J. Chem. Soc.* **1947**, 713-726.
- 2.183 Farkas, A.; Strohm, P. F. "Mechanism Of The Amine - Catalyzed Reaction Of Isocyanates With Hydroxyl Compounds"; *Ind. Eng. Chem. Fund.* **1965**, 4/1, 32-38.
- 2.184 Anon. "Load-Bearing Properties of Flexible Urethane Foam"; *Plast. Tech.* **1962**, 8/4, 26-32.
- 2.185 Sandridge, R.L.; Gemeinhardt, P. G. ; Saunders, J.H. "Effect of Catalyst Concentrations on One-Shot Polyether Flexible Urethane Foams"; *SPE Trans.* **1963**, 3/2, 117-122.

- 2.186 Mack, G.P. "Effect of tin catalysts on physical properties of cellular urethane"; *Mod. Plast.* **1964**, 42/4, 148-160, 194.
- 2.187 Letts, J.B.; Gerkin, R.M.; Martineau, P. "Non-Corrosive, High Performance, Delayed Action Catalyst"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 174-181.
- 2.188 Diblitz, K.; Diblitz, C. "Influence of Acids on the Delayed-Action Characteristics of Amine Catalysts"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 619-624.
- 2.189 Derderian, E.J.; El Ghobary, H.; Esposito, G.; Muller, L.J-M. "Cell-Opening, Low Fugitivity, Delayed-Action Catalysts for HR Molded Foam"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 274-279.
- 2.190 Casati, F.M.H.; Arbir, F.W.; Raden, D.S. "Delayed Action Amine Catalysts For New Polyurethane Techniques"; *Proceedings of the SPI-27th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982, 35-48.
- 2.191 Casati, F.M.H.; Arbir, F.W.; Tylenda, E.J. "Influence Of Amine Catalysis On Processability And Physical Properties Of HR Molded Foams"; *Proceedings of the SPI-6th International Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983, 161-171.
- 2.192 Stepek, J.; Daoust, H. *Additives For Plastics*; Springer-Verlag: New York, 1983.
- 2.193 Miley, J. W.; Moore, P. D. "Reactive Polymeric Colorants For Polyurethane", *Proceedings Of The SPI-26th Annual Technical Conference*; Technomic: Lancaster, Pa., 1981; 83-86.
- 2.194 Moore, P. D.; Miley, J. W.; Bates, S. H.; "New Uses For Highly Miscible Liquid Polymeric Colorants In The Manufacture of Colored Urethane Systems"; *Proceedings of the SPI-27th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982; 255-261.
- 2.195 Bates, S. H.; Miley, J. W. "Polyol-Bound Colorants Solve Polyurethane Color Problems"; *Proceedings Of The SPI-30th Annual Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1986; 160-165.
- 2.196 Bates, S. H.; Moore, P. D.; Miley, J. W. "The Advantages of a Color System for Polyurethanes Using Polyol-Bound Colorants"; *Proceedings of The SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 916-921.
- 2.197 Miley, J. "Polymeric colorants"; *Pure & Appl. Chem.* **1996**, 68/7, 1423-1428.
- 2.198 Vielee, R.C.; Haney, T.V. "Polyurethanes"; In *Coloring of Plastics*; Webber, T.G., Ed., Wiley-Interscience: New York, 1979, 191-204.
- 2.199 Davis, A.; Sims, D. *Weathering Of Polymers*; Applied Science: London, 1983, 222-237.
- 2.200 Beachell, H. C.; Ngoc Son, C. P. "Color Formation In Polyurethanes"; *J. Appl. Polym. Sci.* **1963**, 7, 2217-2237.
- 2.201 Nevskii, L.V.; Tarakanov, O.G. "Discoloration in polyurethanes under the action of light"; *Soviet Plast.* **1967**, 9, 47-48, (translation of Plast. Massy., 9, 1966).
- 2.202 Bieneman, R. A. "Polyurethane Seamless Flooring"; In *Polyurethane Technology*, Interscience Publishers: New York, 1969, 230-231.

- 2.203 Bellettini, A.G.; Harrison, J.R. "Protection of Polyurethanes against UltraViolet Light"; *Cell. Polm.* **1984**, 3, 241-247.
- 2.204 Capocci, G. "Advances In The Light Stabilization Of Polyurethanes"; *Proceedings of The SPI-30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986; 220-227.
- 2.205 Rabek, J.F. *Photostabilization Of Polymers*; Elsevier: London, 1990.
- 2.206 Valentine, C.; Craig, T.A.; Hager, S.L. "Inhibition of the Discoloration of Polyurethane Foam Caused by Ultraviolet light"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 149-155.
- 2.207 Sutton, R.G.; Steever, J.A. "Upgrading The Long Term Stability Of Polyurethanes By The Use Of Pigments" *J. Cell. Plast.* **1983**, 19/6, 372-374.
- 2.208 *Understanding Polymer Flammability*; The Dow Chemical Company; Form No. 101-222-83.
- 2.209 Lyons, J. W. *The Chemistry And Uses of Fire Retardants*; Robert Krieger Publishing: Malabar, Florida, 1987.
- 2.210 Babiec, J. S.; Pitts, J. J.; Ridenour, W. L.; Turley, R. J. "Flame-Retarding Flexible PU Foam"; *Plast. Tech.* **1975**, June, 47-50.
- 2.211 Patent U.S. 3,635,821, K. Treadwell to M&T Chemicals Inc., January 18, 1972.
- 2.212 Patent U.S. 3,810,851, D. S. Cobbledick and A.J. Norman to Gencorp Inc., May 14, 1974.
- 2.213 Patent U.S. 3,876,571, D.S. Cobbledick and A.J. Norman to The General Tire and Rubber Company, April 8, 1975.
- 2.214 Patent U.S. 3,884,849, R.A. Molbert to The General Tire and Rubber Company, May 20, 1975.
- 2.215 Patent U.S. 3,925,266, H.J. Fabris and E.M. Maxey to The General Tire and Rubber Company, December 9, 1975.
- 2.216 Patent U.S. 3,931,062, D.S. Cobbledick to The General Tire and Rubber Company, January 6, 1976.
- 2.217 Stone, H. "Flexible Polyurethane Foams, Flammability - Problems And Progress"; *Proceedings of the 1978 Fire Retardant Chemicals Association Meeting, Houston, Texas*, March 12-15, Fire Retardant Chemicals Association: Westport, CT., 1978, 257-273.
- 2.218 Woods, G.W. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 88.
- 2.219 Grace, O.M.; Mericle, R.E.; Taylor, J.D. "Melamine Modified Polyurethane Foam"; *J. Cell. Plast.* **1985**, 21/5, 311-317.
- 2.220 Natoli, F.S.; Puig, J.E.; O'Connor, J.M.; Chandalia, K.B. "Novel Polyol System for Flame Retarded Flexible Foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 762-765.
- 2.221 Wujcik, S.E.; Smiecinski, T.M.; Lane, G.F.; Christman, D.L. "Polyurethane Flexible Slabstock Foam Requirements to Meet Furniture Flammability Tests"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 672-677.

- 2.222 Bhatnagar, V. M. *Fire Retardant Formulations Handbook, Volume 1, Progress in Fire Retardancy Series*; Technomic: Westport, Connecticut, 1972.
- 2.223 *Handbook Of Flame Retardant Chemicals And Fire Testing Services*; Technomic: Lancaster, Pa., 1992.
- 2.224 Kuryla, W.C.; Papa, A.J. *Flame Retardancy of Polymeric Materials, Vol. 3*; Marcel Dekker: New York, 1975, 1-133.
- 2.225 Darby, R.T.; Kaplan, A.M. "Fungal Susceptibility of Polyurethanes"; *Appl. Microbiol.* **1968**, 16/6, 900-905.
- 2.226 Kapan, A.M.; Darby, R.T.; Greenberger, M.; Rogers, M.R. "Microbial Deterioration of Polyurethane Systems"; *Dev. Ind. Microbiol.* **1968**, 9, 201-217.
- 2.227 Rei, N.M. "Polyurethanes And Fungal Attack: Susceptibility And Protection"; *J. Coated Fab.* **1978**, 8, 21-32.
- 2.228 Tamborini, S. M.; Mahoney, C. J.; McEntee, T. C. "Manifestations of Microbiological Growth on Urethane Foam"; *Proceedings of The SPI-27th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982; 308-313.
- 2.229 Baseman, A. L. "Antimicrobial Agents for Plastics"; *Plast. Tech.* **1966**, No. 9, 33-37.
- 2.230 Patarcity, R.; Stern, E.; Murthy, U. "Reactive Antimicrobial Agents For Urethane Foams"; *Proceedings of The SPI-6th International Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1983, 142-144.
- 2.231 Brophy, J.F. "Innovative Use of Antimicrobials In Creating New Market Opportunities"; *Proceedings of The SPI-29th Annual Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1985, 224-229.
- 2.232 Battice, D.R.; Hales, M.G. "A New Technology For Producing Stabilized Foams Having Antimicrobial Activity"; *Proceedings of The SPI-29th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1985, 108-112.
- 2.233 Patent U.S. 4,618,630, T.M.Knobel, E.E. Kennedy and M.A. Walker to The Dow Chemical Company, October 21, 1986.
- 2.234 Sweet, F. H.; Knobel, T. M.; Walker, M. K.; Thompson, C. P. "Protection of Electrostatic Discharge (ESD) Sensitive Devices with Urethane Foams"; *J. Cell. Plast.* **1986**, 22/2, 139-146.
- 2.235 *STATURE II, Static Control Additive For Electrostatic Discharge Control In Polyurethane Applications*; The Dow Chemical Company; Form No. 109-968.
- 2.236 Kopsheva, L.M.; Shamov, I.V.; Tarakanov, O.G. "Dependence of the mechanical properties of flexible polyurethane foams on the compatibility of components"; *J. Appl. Chem. USSR. Translated from Zh. Prikl. Khim. (Leningrad)* 1984, 57/6, 1358-1361.
- 2.237 White, K.B.; Largent, B.; Jirka, L.; Bailey, B. "Low Cost Compatibilizers for Waste Stream Polyester Polyols"; *J. Cell. Plast.* **1986**, 22/3, 331-339.
- 2.238 Hager, S.L.; Craig, T.A.; Artavia, L.D.; Macosko, C.W.; Jorgenson, M.W. "Interfacial Mixing of Urethane Foam Chemicals"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 529-534.

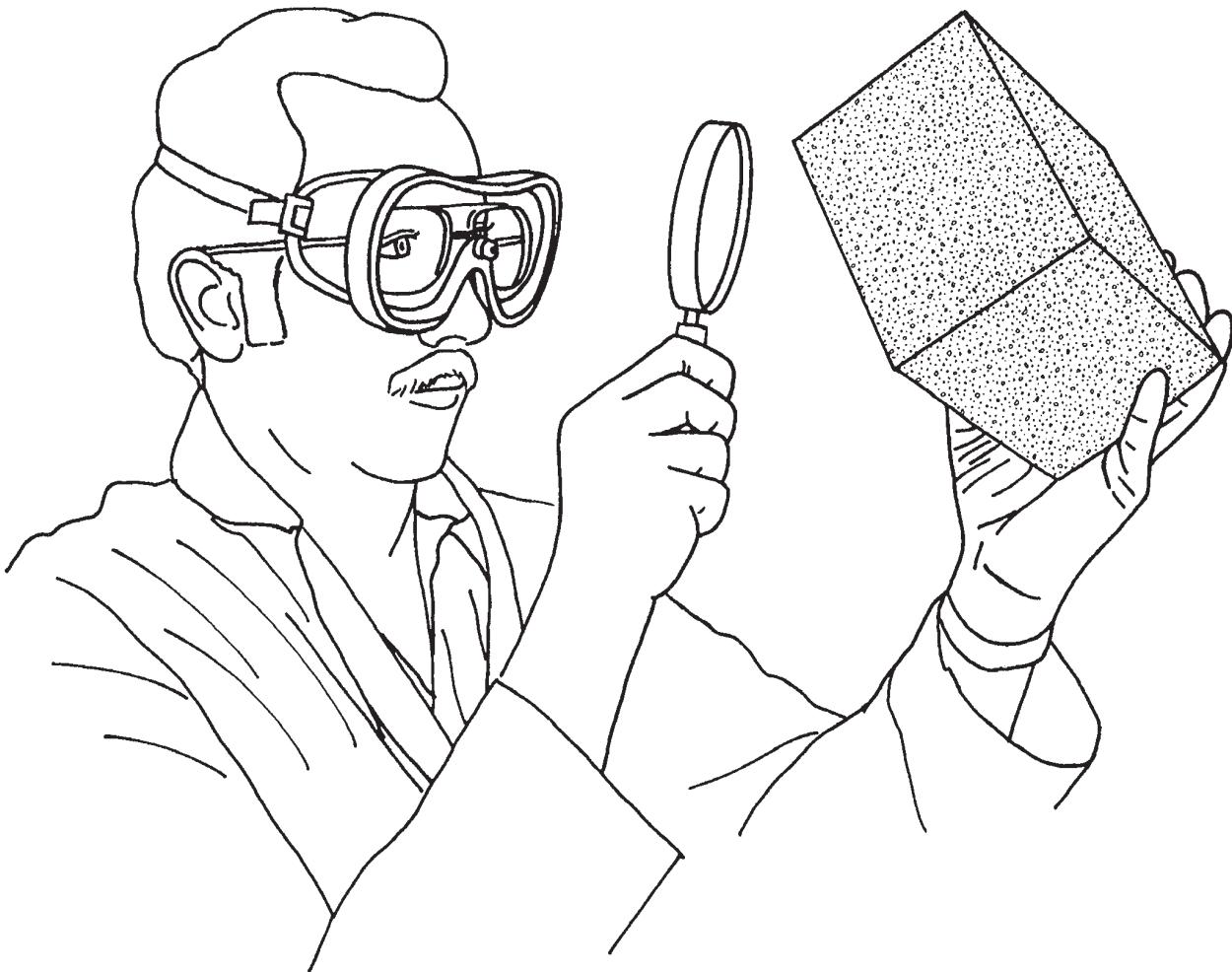
- 2.239 Patent U.S. 4,246,364, C.E. Koehler, T.R. McClellan and P.L. Murray to The Upjohn Company, January 20, 1981.
- 2.240 Patent U.S. 4,444,916, L.L. Grube and C.J. Horner to GAF Corporation, April 24, 1984.
- 2.241 Patent U.S. 4,529,744, R.J. Wood to Stephan Company, July 16, 1985.
- 2.242 Patent U.S. 4,579,877, A.B. Goel and T.A. Tufts to Ashland Oil Incorporated, April 1, 1986.
- 2.243 Patent U.S. 3,929,730, P.U. Graefe, V.J. Gajewski and I.A. Jimenez to Inter-Polymer Research Corporation, December 30, 1975.
- 2.244 Patent U.S. 4,585,803, D.L. Nelson, R.J. Matijega, and D.P. Miller to The Dow Chemical Company, April 29, 1986.
- 2.245 Patent U.S. 5,126,421, W. Majewski, H. Khalil and J. Wypych to Tremco Ltd., June 30, 1992.
- 2.246 Patent U.S. 5,104,904, K.T. Glynn and E.N. Doyle to Crowley Chemical Company, April 14, 1992.
- 2.247 Wang, D.S.T. "Plasticizers in Rigid Polyurethane Foam"; *J. Cell. Plast.* **1979**, 15/3, 144-151, 162.
- 2.248 Patent U.S. 3,993,576, B.G. Barron to The Dow Chemical Company, November 23, 1976.
- 2.249 Patent U.S. 4,485,031, F. Olstowski and R.D. Peffley to The Dow Chemical Company, November 27, 1984.
- 2.248 Patent U.S. 4,485,032, F. Olstowski and R.D. Peffley to The Dow Chemical Company, November 27, 1984.
- 2.249 Patent U.S. 4,981,877, R. Carswell to The Dow Chemical Company, January 1, 1991.
- 2.252 Klesper, E. "Application Of Volatile Organic Liquids for Expanding Flexible Urethane Foam"; *Rubber Age* **1958**, Oct., 84-87.
- 2.253 Burt, J.G.; Brizzolara, D.F. "Auxiliary Blowing Agents for Flexible Polyurethane Foams"; *Proceedings of The SPI-18th Annual Technical Conference; Technomic*: Lancaster, Pa., 1975, 35-39.
- 2.254 Sayad, R.S.; Williams, K.W. "Methylene Chloride Urethane Grade As A Viable Auxiliary Blowing Agent In Flexible Slabstock Foam"; *Proceedings of The SPI-24th Annual Urethane Division Technical Conference*; Technomic: Lancaster, Pa., 1978, 1-8.
- 2.255 Sayad, R. S.; Williams, K. W. "Flexible PU Foamers: There is an Alternative To Fluorocarbon Blowing Agents"; *Plast. Tech.* **1979**, June, 71-74.
- 2.256 *Handbook for Reducing and Eliminating Chlorofluorocarbons in Flexible Polyurethane Foams*; United States Environmental Protection Agency, 21A-4002, April 1991.
- 2.257 Patent U.S. 5,120,771, G.D. Walmsley to Hickory Springs Manufacturing Company, June 9, 1992.

- 2.258 Graff, G. "Advantages claimed for acetone as a foam agent"; *Mod. Plast.* **1993**, 70/4, 32-36.
- 2.259 Patent U.S. 4,906,672, H. Stone, S. Lichvar, C.W. Bredbenner, R. Rupp and E. Minnich to PMC Incorporated, March 6, 1990.
- 2.260 Patent U.S. 5,081,162 P.V. Farkas and J.A. Duley to The Woodbridge Foam Company, January 14, 1992.
- 2.261 Patent U.S. 5,120,770, E.N. Doyle and S. Carson, June 9, 1992.
- 2.262 Fiorentini, C.; Taverna, M.; Griffith, T.; Collins, B. "Latest Manufacturing Solutions for Slabstock Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 12-16.
- 2.263 Eiben, R.G.; Sulzbach, H.M.; Ferrand, J.T.; Radovich, D.A. "High-Quality Flexible Slabstock Foam using Liquid Carbon Dioxide as an Auxiliary Blowing Agent"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 70-73.
- 2.264 Fiorentini, C; Taverna, M.; Griffiths, T.; Collins, B. "Liquid-Carbon Dioxide-Blown Slabstock Foams: Industrial Results"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 491-496.
- 2.265 Eiben, R.G. "Blowing Flexible Slabstock with Liquid Carbonic Acid: Progress with Technology"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 31.
- 2.266 Noakes, C.W.; Casagrande, G. "Liquid CO₂ Blown Foam for Automotive Flexible Moulding"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 11.
- 2.267 Taverna, M.; Corradi, P. "Liquid-Carbon-Dioxide-Blown Moulded Foams: Latest Developments for an Industrial Application"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 10.
- 2.268 Taverna, M.; Meloth, H.; Griffiths, T. "Two Years of Industrial Experience with Liquid CO₂-Blown Slabstock Foams"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 164-168.
- 2.269 Patent U.S. 5,030,664, R. Franklin, W.J. Parr, G. Fesman and B.A. Jacobs to Akzo N.V., July 9, 1991.
- 2.270 Bradford, L.; Franklin, R.; Williams, B. "From CFC to CBA-A Viable Alternative?"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 668-671.
- 2.271 Lichtenberg, F. W., Ed. *CFCs and the Polyurethane Industry: A Compilation of Technical Publications, 1986-1988*; Technomic: Lancaster, Pa., 1988.
- 2.272 *Eliminating CFCs in Foam Plastics*; The Society of the Plastics Industry; 1989.
- 2.273 Lichtenberg, F.W., Ed. *CFCs and the Polyurethane Industry: Volume 2, A Compilation of Technical Publications, 1988-1989*; Technomic: Lancaster, Pa., 1990.
- 2.274 Lichtenberg, F.W., Ed. *CFCs and the Polyurethane Industry: Volume 3, A Compilation of Technical Publications, 1990*; Technomic: Lancaster, Pa., 1990.
- 2.275 *AEROTHENE TT For Urethane Foam Blowing*; The Dow Chemical Company; Form No. 100-6446-89-SMG.

- 2.276 Methven, J. M. "Foams and Blowing Agents"; *Rapra Review Reports* **1990**, 3/1, 1, 5-33.
- 2.277 Zwolinski, L.M. "CFC Alternatives Development Status"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 23-24.
- 2.278 Dwyer, F.J.; Knopeck, G.M.; Zwolinski, L.M. "CFC Alternates Emissions in Thermoset Foam Production"; *Proceedings of The SPI-33rd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 400-406.
- 2.279 Decaire, B.R.; Pham, H.T.; Richard, R.G.; Shankland, I.R. "Blowing Agents: The Next Generation"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 2-11.
- 2.280 White, L. "Foam Industry ahead in ODS phase-out: global warming next on agenda"; *Urethanes Tech.* **1996**, 13/4, 42.
- 2.281 *Dow Methylene Chloride Urethane Grade: The Tested Blowing Agent*; The Dow Chemical Company; Form No. 109-5445-80.

Chapter 3

Flexible Foam Fundamentals



The final properties of a flexible polyurethane foam depend both on the geometry of the cells and the properties of the polymer contained within the foam's structural elements. This chapter will discuss how a foam is formed, grows and stabilizes to give a useful final product. The chapter will also introduce some powerful investigative analytical tools that are useful in studying the characteristics of the final product.

Chapter 3

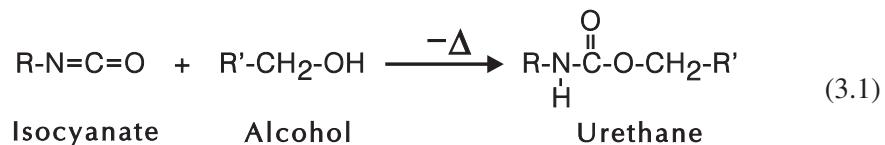
Flexible Foam Fundamentals

R. Herrington, R. Turner, W. Lidy

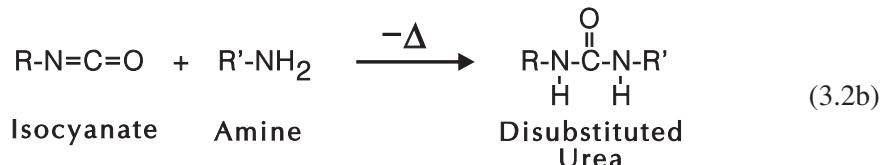
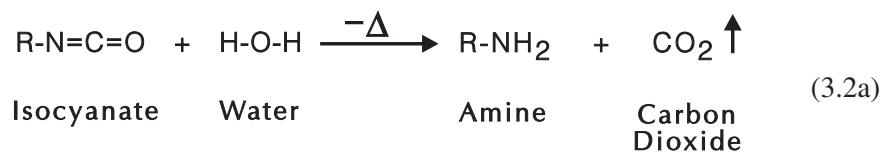
The major markets for flexible polyurethane foams are as cushioning materials in furniture, bedding, carpet underlay, automotive and packaging applications. With a broad range of available load-bearing capacity and resiliency, these foams offer degrees of comfort and protection not approached by any other single cushioning material. Flexible polyurethane foams can be molded to shape or produced in large bunstock form for later cutting and fabrication. High mechanical strength properties allow these foams to endure rigorous fabrication processes. In addition, modern-day flexible polyurethane foams are resistant to moisture, odor formation and normal cleaning procedures.

One goal in the study of foam fundamentals is to learn to control and extend the limits of foam properties. The properties of a polyurethane foam are known to result from both the geometry of the cells and the properties of the polymer. To aid in understanding the contribution of each factor, this chapter will discuss foam formation, cell-window opening and will review our current understanding of flexible polyurethane foam morphology.

Formation of a flexible polyurethane foam is an intricate process employing unique hardware, multiple ingredients and at least two simultaneous reactions. The urethane forming reaction occurs between the isocyanate and the polyol as shown simply in Equation 3.1.



This is a simple addition reaction which, when extended to polyfunctional reactants, provides a direct route to cross-linked polymers. To make a foam, the polyurethane polymer is conveniently expanded or blown by the *in situ* formation of carbon dioxide gas. The gas is produced by the reaction of an isocyanate group with water.



The amine molecule formed in this reaction further reacts with an additional isocyanate group to form a urea. When the starting isocyanate molecule is polyfunctional, this initial urea structure is substituted with additional reactive groups that provide another pathway for polymer growth.

Successful preparation of a foam from these reactions requires the formation, growth and stabilization of gas bubbles within the reacting medium.

FORMATION AND STRUCTURE OF FOAMS

BUBBLE INITIATION

Foams are three-dimensional agglomerations of gas bubbles, separated from each other by thin sections of the host medium. For finished open-celled

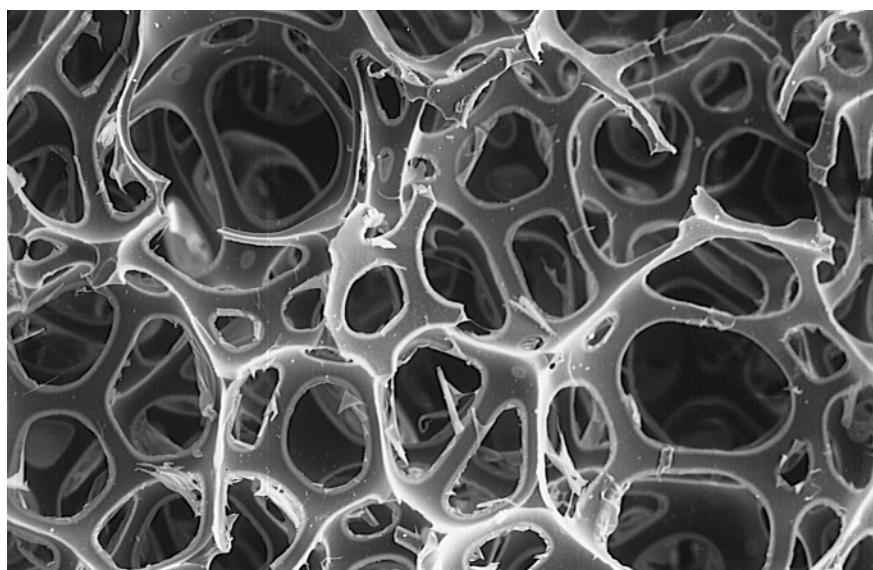


Figure 3.1 Open-Celled Flexible Polyurethane Foam at 50X Magnification

flexible polyurethane foam like that shown in Figure 3.1, the void areas are artifacts of expanded gas bubbles that were introduced into the reacting medium early in its existence.

The thin structures separating the bubble spaces are the polymer formed from the various reactions. In classical discussions of foam, physical chemists identify cell-walls and struts as lamellae and Plateau borders. Polyurethane foam chemists usually call them windows and struts. Foam can be further characterized as having a very large surface area and a widely variable cellular structure.

The development of bubbles within a liquid is called nucleation. For polyurethane foams, the gas contained within those bubbles has several potential sources:

- Dissolved gases in the liquid reactants,
- Low-boiling liquids purposely added into the system as blowing agents,
- Gases such as carbon dioxide produced by the reactants, and
- Gases released from thermally decomposable additives in the formulation.

In addition, air or other gases may be purposely entrained into the system by mechanical mixers or frothing devices. The number and size of any entrained bubbles play an important part in foam performance, since gas from the above sources may preferentially diffuse into these sites.

The fundamental understanding of bubble dynamics began with the works of Young^{3.1} and Laplace^{3.2} in the early nineteenth century. Plateau is also credited with a major share of our knowledge about foams.^{3.3} An excellent review of bubble dynamics has been given by Bikerman.^{3.4}

Conceptually, foams can be described with either a dispersion or a condensation model. In a dispersion model, the gas would be present in a large separate phase such as in the head space of the vessel shown in Figure 3.2.

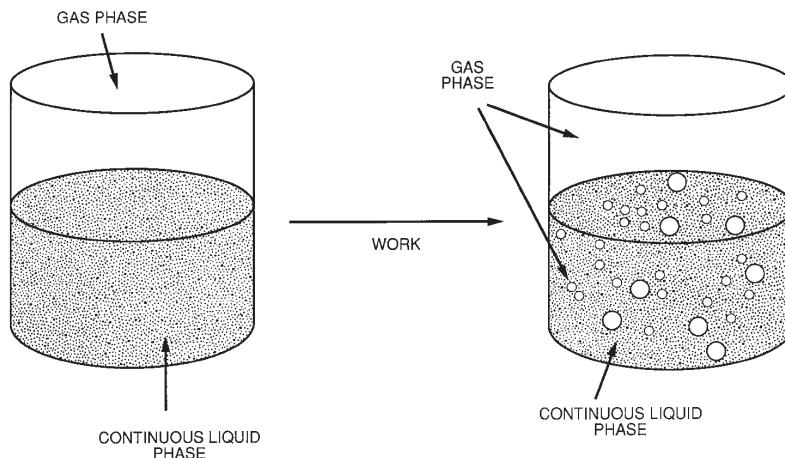


Figure 3.2 Dispersion Model for Foam Preparation

With sufficient added work, aggregate molecules of the gas can be entrained and dispersed uniformly throughout the continuous liquid phase. A common example would be the meringue topping on a lemon pie (meringue is the French word for the foam formed by whipping air into a mixture of egg whites and sugar). In a condensation model, soluble gas molecules are forced to condense to form a bubble. Figure 3.3 depicts gas molecules present as solute dissolved in a continuous liquid phase.

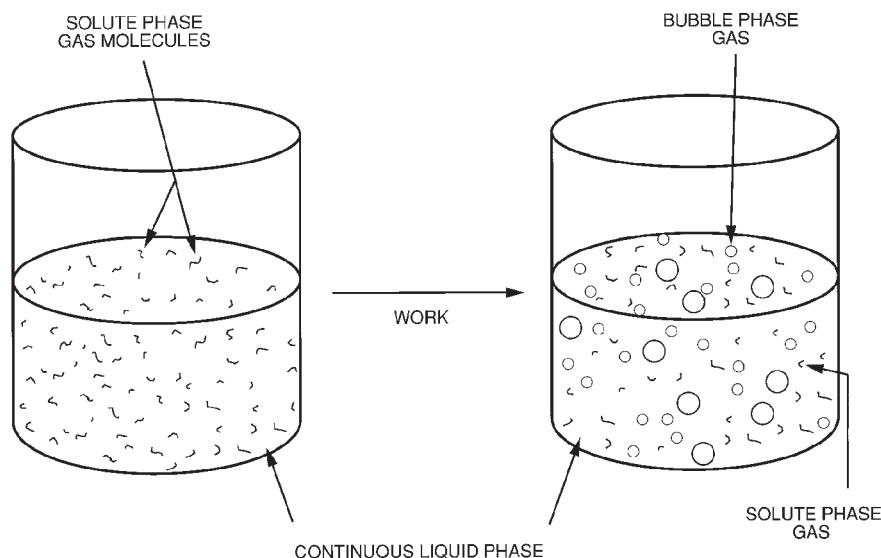


Figure 3.3 Condensation Model for Foam Formation

Again, with added work, the soluble gas molecules of a sufficiently supersaturated liquid may be caused to aggregate and condense into a bubble within the continuous liquid phase. An interesting apparent example of this model is the foam that forms on a glass of beer.

The nucleation phenomenon, like all physical events, requires an input of energy before the desired event will occur. A bubble of carbon dioxide in a liquid will differ from an equal number of gas molecules in solution by possession of enough surface energy to produce that bubble as a new phase. Foams can therefore be characterized as thermodynamically unstable until such time as other events, e.g., polymer gellation, provide permanent stabilization.

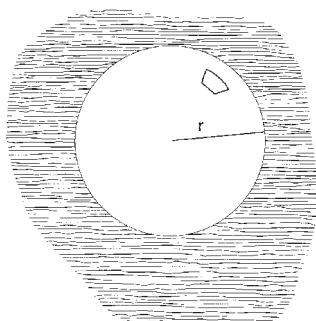


Figure 3.4
A Bubble with
Radius r

Figure 3.4 shows a bubble of radius r in a liquid with surface tension γ . To make that bubble, work, W , equal to $4\pi r^2$ against that surface tension must be performed. For self-nucleation, this work must be supplied solely by the environment surrounding the spot where the bubble will appear.

$$W = 4\pi r^2 \gamma \quad [\text{dyne cm}] \quad (3.3)$$

Note: Such work is easily introduced by the physical forces used to produce foams by the dispersion model above. Such forces may or may not be present in condensation models.

The total weight, w, of gas with density ρ in a bubble is given by:

$$w = \frac{4}{3} \pi r^3 \rho \quad [g] \quad (3.4)$$

The total elevation of free energy when gas molecules are transferred from supersaturated solution into a bubble can be expressed as ΔF . For the formation of one gram of bubbles, it follows that the energy requirement (E) is:

$$E = \frac{4}{3} \pi r^3 \rho \Delta F \quad [\text{dyne cm}] \quad (3.5)$$

For a bubble to form spontaneously, the energy associated with that event must exceed the work necessary to form the bubble or:

$$\text{Energy Requirement (E)} > \text{Work Needed (W)} \quad (3.6)$$

or,

$$\frac{4}{3} \pi r^3 \rho \Delta F > 4\pi r^2 \gamma \quad (3.7)$$

which simplifies to:

$$r\rho \Delta F > 3\gamma \quad (3.8)$$

Further manipulation shows that the necessary increase in free energy will have the following relationship to surface tension (γ), bubble radius (r), and gas density (ρ):

$$\Delta F > \frac{3\gamma}{r\rho} \quad \left[\frac{\text{dyne cm}}{g} \right] \quad (3.9)$$

$$\Delta F > \frac{k}{r} \quad \text{when } k = \frac{3\gamma}{\rho} \quad (3.10)$$

where k is a physical property constant. Note that as r approaches zero, ΔF approaches infinity.

If we assume that freshly formed, self-nucleated bubbles are extremely small, then spontaneous formation of those bubbles is unlikely unless energy is supplied from another source.

Applying Equation 3.9 to the case of nucleating a carbon dioxide bubble in a polyol is instructive.

Carbon dioxide gas taken at standard conditions (25°C, 1 atm), a best case for this example, has a density of 0.00198 grams per cubic centimeter. Polyols typically have a surface tension on the order of 30 dynes per centimeter. Assuming that freshly nucleated bubbles have a radius on the order of 1×10^{-5} centimeter gives the following estimation of required free energy:

$$\Delta F > \frac{3\gamma}{r\rho} \quad \left[\frac{\text{dyne cm}}{\text{g}} \right] \quad (3.11)$$

$$\Delta F > \frac{3 \times 30}{0.00001 \times 0.00198} \quad \left[\frac{\text{dyne cm}}{\text{g}} \right] \quad (3.12)$$

$$\Delta F > 45.5 \times 10^8 \quad \left[\frac{\text{dyne cm}}{\text{g}} \right] \quad (3.13)$$

or roughly 455 Joules per gram of bubbles.

Spontaneous formation of a bubble is unlikely unless energy is supplied from another source. The impossibility of self-nucleating carbon dioxide from a supersaturated solution of polyol and toluene diisocyanate was eloquently demonstrated experimentally by Kanner and Decker.^{3.5}

Using the apparatus shown in Figure 3.5 and with the aid of still and motion picture photography, they were able to demonstrate that self-nucleation was absent over a range of conditions more favorable for nucleation than those normally found in a polyurethane foam system. Bubble introduction was found to be due solely to physical mixing of air into the liquid; and, if properly stabilized by surfactant, such admixed air was more than sufficient to account for all of the cells present in the final foam.

Their observations also showed that, throughout the expansion of a foam, new smaller bubbles (such as might arise from self-nucleation) did not appear. Growth for the initial volume of bubbles was attributed to the diffusion of carbon dioxide gas into the existing bubbles. The possibility of a surfactant sufficiently lowering the surface tension component of Equation 3.9 to allow for bubble self-nucleation was discounted by these authors.

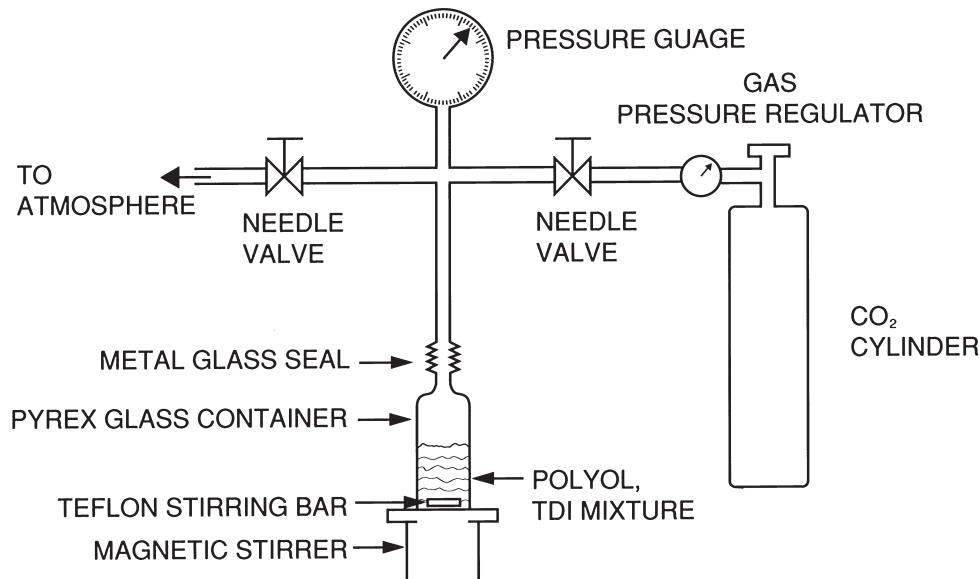


Figure 3.5 Apparatus for Bubble Formation Studies (Redrawn from Ref. 3.5)

As detailed above, to disperse a volume of gas in a unit volume of liquid requires the expenditure of an increment of work equal to the product of the liquid surface tension times the interfacial area produced.

$$\Delta F = \gamma A \quad \left[\frac{\text{dyne cm}}{\text{g}} \right] \quad (3.14)$$

According to the classical theories of Young (1805) and Laplace (1806), for that bubble to be stable within the liquid requires a differential gas pressure given by:

$$P_b - P_l = \Delta P = \frac{2\gamma}{r_c} \quad \left[\frac{\text{dyne}}{\text{cm}^2} \right] \quad (3.15)$$

where P_b is the pressure in the gas bubble, P_l is the pressure in the liquid phase, γ the liquid surface tension and r_c is a critical bubble radius unique for each foam system. For carbon dioxide in a polyol/toluene diisocyanate mixture, Kanner and Decker found the critical radius to be approximately 2.4×10^{-5} centimeters.

Solving Equation 3.15 for the effect of surface tension gives:

$$\gamma = \left[\frac{\Delta P r_c}{2} \right] \quad \left[\frac{\text{dyne}}{\text{cm}} \right] \quad (3.16)$$

and combining with Equation 3.14 above gives:

$$\gamma = \frac{\Delta P r_c}{2} = \frac{\Delta F}{A} \quad \left[\frac{\text{dyne}}{\text{cm}} \right] \quad (3.17)$$

Simply stated, lowering the surface tension of a system (by addition of a surfactant, for example) will reduce the work needed to disperse a gas in the system and also favor the formation of smaller bubbles.

From Equation 3.16 it can also be deduced that, for a bubble to grow larger, there must exist a pressure difference ΔP of a magnitude greater than 2 times the surface tension divided by the bubble radius.

That is, for bubble growth:

$$\Delta P > \frac{2\gamma}{r} \quad \left[\frac{\text{dyne}}{\text{cm}^2} \right] \quad (3.18)$$



In real polyurethane foams, this ΔP blowing stress comes from the exothermic gas-producing reactions occurring in the continuous liquid phase.

La Mer has reviewed how the introduction of various interfaces within the gas saturated liquid phase drastically lowers the work of nucleation.^{3.6} Various nucleating aids and events have been observed. Examples would include sharp pressure drops as in a high-pressure impingement mixing head, finely dispersed silicone oils and even finely dispersed particulates.

Since nucleating aids are not universally successful, some authors, notably Baumhakel, argue that the gases involved in nucleation come solely from gas loading of the initial reaction components.^{3,7} Such loading will include gas from:

- Dissolved gas loading of the polyol and isocyanate during storage,
- Entrainment of bubbles during the liquids handling and mixing process (work provided by mechanical energy input).

Dissolved gases are defined as those gas molecules present as a ‘solute’ phase in a polyol, isocyanate or other liquid formulation ingredients. The maximum amount of a given gas that a liquid will absorb at standard conditions (1 atmosphere and 25°C) is termed the Bunsen Coefficient.^{3,8} Most polyether polyols exhibit a Bunsen Coefficient in the range of 6-10 volume percent.^{3,9}

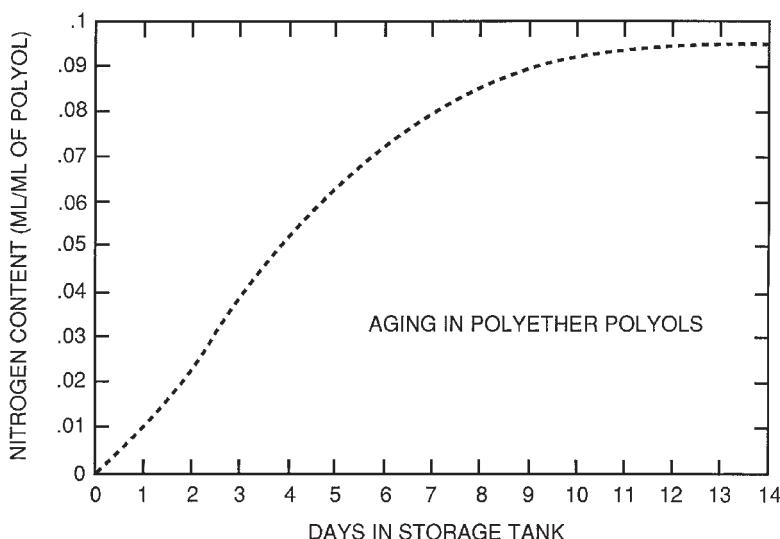


Figure 3.6 Gas Content of Polyol Varies with Storage History

Figure 3.6 illustrates that the actual degree of loading of dissolved gas such as nitrogen into a polyol (or isocyanate) is a significant variable related to storage history. Without allowing sufficient time for freshly produced raw materials to absorb a loading of nitrogen, foam cell-size and stability problems are known to result.^{3,10} The amount of dissolved gas in an isocyanate is reported to vary widely and to be a function of pad gas pressure.^{3,11-3,12} Excessive amounts of dissolved gas in the isocyanate are reported to lead to foam collapse.^{3,13-3,14}

Problems have also been encountered when excessive amounts of entrained gas are allowed to form in viscous component streams. Entrained gas can be helpful in proper nucleation of a foam mixture. The amount of entrained gas that can be tolerated depends on the formulation, the metering system, the mixer geometry and the desired final foam cell-structure. If the amount of gas becomes excessive; metering problems can result, pea holes can form, density can vary and in severe cases, total collapse of the foam may occur.^{3,15-3,16}

Walmsley described how gas sources were important for proper nucleation.^{3,17} In the initial stages of a polyurethane foam reaction, the ingredients are thoroughly mixed by various mechanical devices. In low pressure machines like that conceptualized in Figure 3.7, the work supplied by the rotating agitator is more than sufficient to entrain air bubbles into the mixture. In actual production of slabstock foam, it is common to bleed controlled amounts of air purposely into the mix head.^{3,18-3,19} Typical air injection rates are on the order of 0.5 scf/hr per 100 pounds per minute of total mixture throughput. Many modern slabstock foam machines are equipped with mixing heads in which some individual high-pressure streams are injected into a slowly stirring polyol stream.

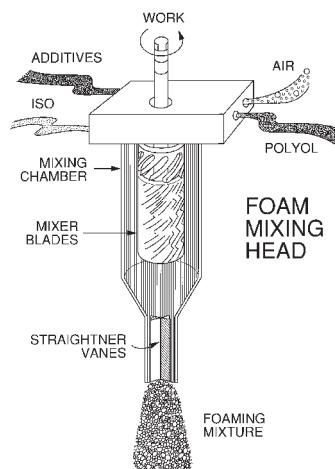


Figure 3.7 Essentials of a Low Pressure Mixing Head

With proper shear conditions, nucleation of bubbles by gases dissolved in the reactants will occur at the trailing edges of the mixer blades, as illustrated in Figure 3.8. These events occur well before any appreciable concentration of dissolved carbon dioxide gas is produced by chemical reaction.

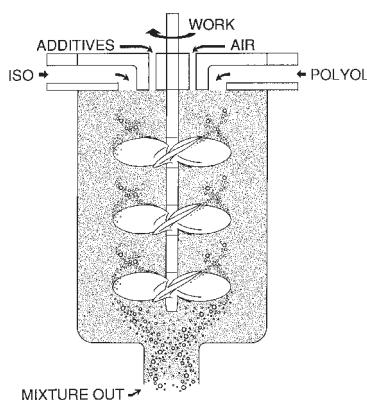


Figure 3.8
Nucleation of Bubbles at
Trailing Edges of Mixer

For the case of the typical high-pressure impingement mixing head in Figure 3.9, there is no rotating agitator and thus no possibility of mechanically entraining gas. The reactants are fed into a small mixing chamber through two or more opposing nozzles. The nozzles are sized such that the sharp pressure drop across them causes the liquid streams to be accelerated to velocities of several hundred feet per second. It has been shown that the Reynolds number of each impinging stream is the major criterion for varying mixing quality.^{3,20} In this case the sole source of nucleation bubbles is the gas dissolved in the initial reactants. As these gases pass through the constricting orifices, some of the energy conversion in going from a high-pressure stream to a fast-moving low-pressure stream goes into the work necessary to form gas bubbles in the liquid.^{3,21} Reviews of this complex phenomenon have been presented.^{3,22-3,27}

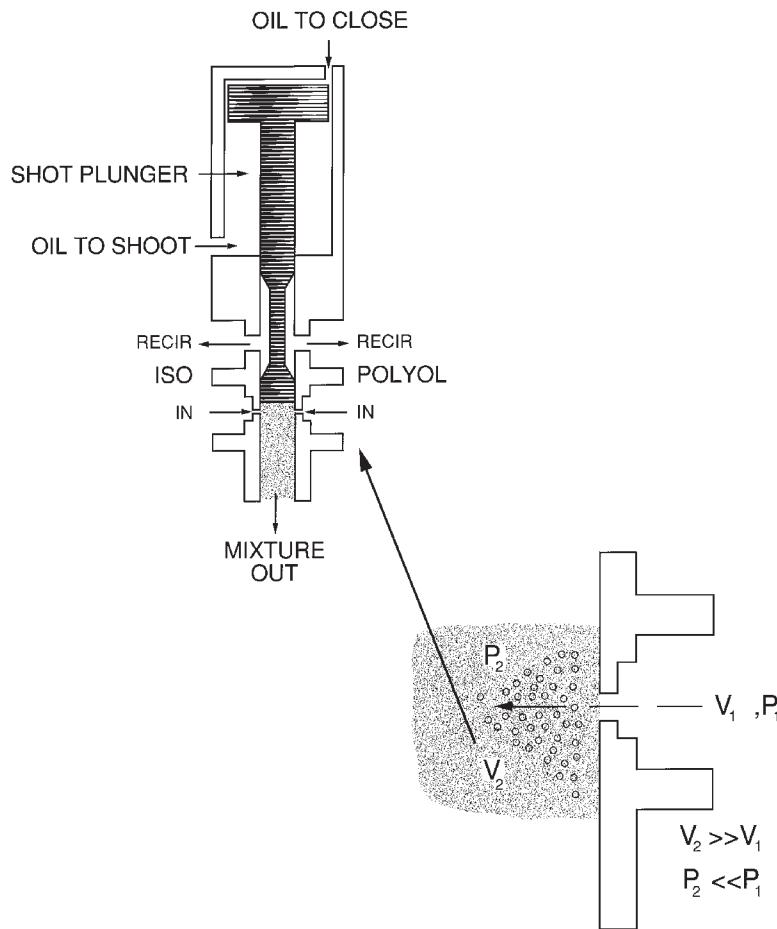


Figure 3.9 Sharp Pressure Drop Nucleates Bubbles

Typical data relating dissolved nitrogen content of a polyol to cell-count in the final foam is presented in Table 3.1.

Table 3.1 Dissolved Gas Impacts Cell-Count In Slabstock Foam

| Gas Content ml gas/ml polyol | Linear Count Cells/cm | Cubic Count* Cells/cm ³ |
|---------------------------------|--------------------------|---------------------------------------|
| 0.035 | 12 | 1728 |
| 0.046 | 15 | 3375 |
| 0.050 | 18 | 5832 |
| 0.058 | 22 | 10,648 |
| 0.072 | 23 | 12,167 |

* A calculated number.

It is interesting to note the major increases in cell-count resulting from apparently small changes in dissolved gas content. Bessette and Sundstrom have shown that for a given volume of foam, a larger number of cells results in a more viscous, more stable foam.^{3.28} The impact of cell-count on foam physical properties has been widely discussed.^{3.29-3.36}

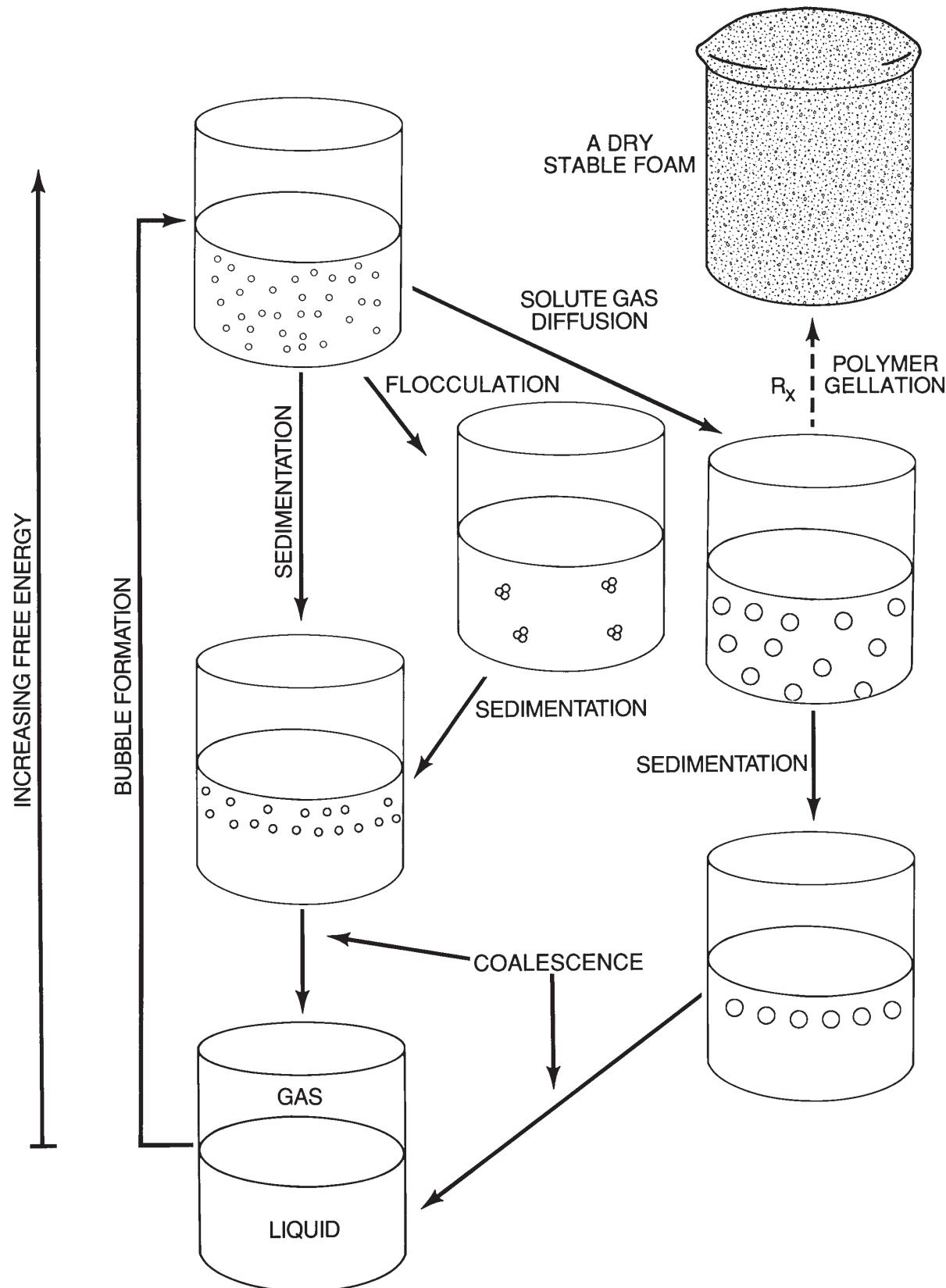


Figure 3.10 Possible Fates of a Foamed System

BUBBLE GROWTH

The production of spherical bubbles in a desired liquid is only the first step in arriving at a commercially useful foam. The initial mixture of reaction components has a low viscosity, which would result in an unstable foam without input of additional energy. Figure 3.10 conceptualizes the possible fates of a foam system.

This figure illustrates that foams are thermodynamically unstable, and unless permanent stabilization occurs soon after formation, foam disintegrates. In polyurethane foams, the energy for bubble growth comes from the exothermic and gas-producing reactions. Factors promoting bubble expansion include the production of carbon dioxide gas, the volume expansion work provided by an increasing temperature and bubble coalescence.

An important consequence of the existence of a free surface energy in gas bubbles is the presence of a pressure difference across the curved gas-liquid interface. This pressure difference under a concave curved meniscus gives rise to the well known capillary elevation effect on a liquid in a small tube. If the curved liquid surface fully encloses a volume of gas, a bubble results. The pressure excess of the gas in the bubble is given by the LaPlace equation:

$$\Delta P = \frac{2\gamma}{r_c} \quad \left[\frac{\text{dyne}}{\text{cm}^2} \right] \quad (3.19)$$

where γ is the surface tension of the liquid and r_c the critical radius of the bubble.

From this equation, it is evident that the pressure inside a bubble is inversely proportional to the radius of the bubble. In real foams there is always a distribution of bubble sizes, hence the pressures in different bubbles will not be the same. This will lead to the diffusion of gas molecules from regions of higher pressure (the small bubbles) to regions of lower pressure (the large bubbles). The rate at which diffusion proceeds will be proportional to the pressure difference, the permeability and the thickness of the liquid film separating bubbles of unequal size. Therefore, all bubbles will grow or shrink depending on their diameter and the diameter of the bubbles in their environment. Initially, each large bubble is surrounded by many smaller ones and one concept for bubble growth would be the diffusion of gas from the smaller to the larger bubbles. A simplified case of one large and one small bubble is presented in Figure 3.11.

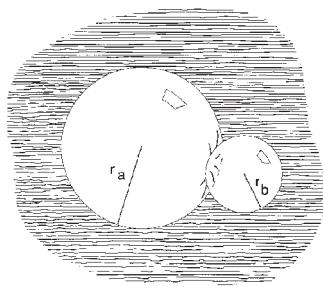


Figure 3.11 Two Different Size Bubbles

The pressure difference between the gas in a small bubble and that of an adjacent larger bubble is given by:

$$\Delta P = P_b - P_a = 2\gamma \left[\frac{1}{r_b} - \frac{1}{r_a} \right] \quad \left[\frac{\text{dynes}}{\text{cm}^2} \right] \quad (3.20)$$

where r_b is the radius of the small bubble and r_a is the radius of the large bubble. Again γ is the surface tension of the liquid.

The radius of the large bubble, r_a , will be many times as large as that of the small bubble, r_b , and, for a first approximation, the term $1/r_a$ may be neglected. The pressure difference causing gas diffusion is then proportional to the pressure excess in the small bubble. The rate at which a small bubble shrinks and disappears is then dependent mainly on its own radius and the permeability of the gas through the liquid separating adjacent bubbles.

The net observation in a static system is that, with time, the average bubble size in a polydisperse system will increase, while the total number of bubbles will decrease. A common example of this event can be found in a bubble bath. The scientific validity of this conclusion is exemplified in Figure 3.12, taken from the work of Clark and Blackman.^{3,37}

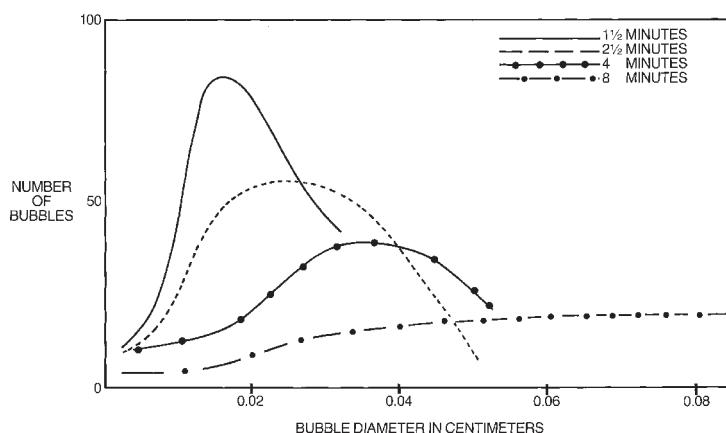


Figure 3.12 Increasing Polydispersity of 5% Soap Solution

Similar data were presented in pictorial form by Smith.^{3,38} Frensdorff reported the same phenomena in a model polyurethane foam system.^{3,39} For actual polyurethane-based foams, there is argument that diffusion between bubbles is not a major factor in bubble growth.^{3,40} That mechanism is expected to be very slow compared with the rate of gas diffusion from the gas saturated liquid phase into the bubbles.

From Equation 3.19 it can be deduced that low values of γ (the liquid surface tension) favor low pressure differences between bubbles of different sizes. Lowering system surface tension can therefore be expected to lead to better bubble stability and smaller average cell-size.

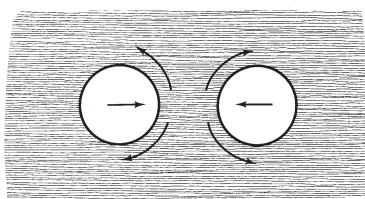
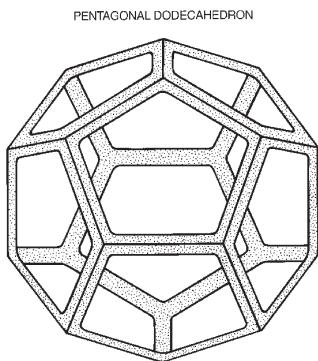


Figure 3.13
Two Bubbles Approaching
in a Viscous
Liquid Phase.

Viscosity of the moving liquid should affect the rate at which the liquid layer between two bubbles thins. Ideally, the viscosity of a thick section of liquid would be low enough to allow the bubbles to come together quickly and then be high enough as a thin film to overcome coalescence. If the thin film viscosity can be made great enough, coalescence would not occur at all.

BUBBLE PACKING



With continued reaction, the bubbles in a polyurethane foam system will grow. As the volume fraction occupied by the bubbles exceeds 74%, the bubbles lose their spherical shape and begin distorting into multi-sided polyhedra. Matzke has reviewed over three hundred years of literature debating the theoretically preferred and the actually observed polyhedra shapes in real foams.^{3,41} Early polyurethane researchers described these polyhedra as being approximately the pentagonal dodecahedron shape.^{3,42} Pure structures of that type have twelve five-sided membranes and would not be expected to account for all available physical space. Real polyurethane foams also show some four-and-six sided cells and may be better approximated by Lord Kelvin's fourteen-faced tetrakaidecahedron space filling models.^{3,43-3,44} A comparison of the real and approximated geometries is given in Figure 3.14.

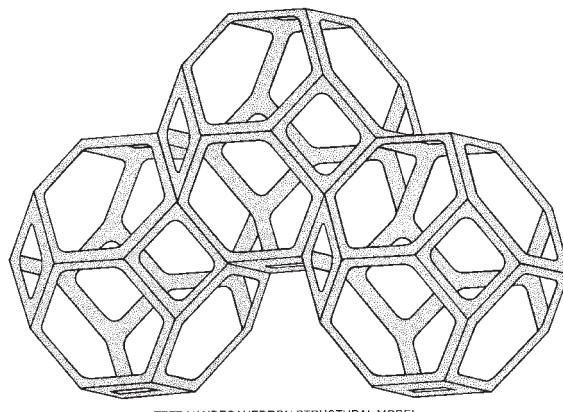
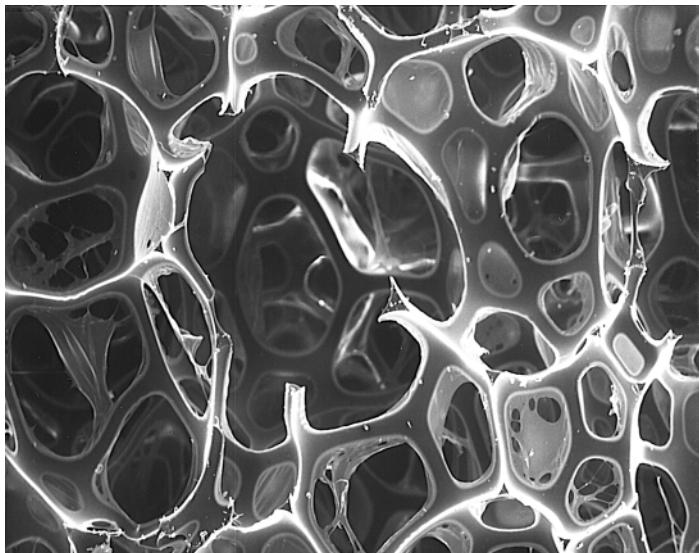


Figure 3.14 Real and Approximated Foam Geometries

Actual counts of the number of faces-per-cell closely match the 14 predicted by Ducharte.^{3,45} A distribution of actual cell sizes is normally noted.

Bubble stability during growth is a complex function of surfactant effects, rate of gas evolution, viscosity, pressures and the presence of cell-disrupting agents. As the growing spherical cells are squeezed into polyhedra, the liquid phase is initially redistributed between the tetrahedral interstices and the bubble surfaces. With continued cell-volume growth, cell-wall thinning takes place and polymer is drained from the lamellae into unique structural features known as Plateau borders (see Figure 3.15).

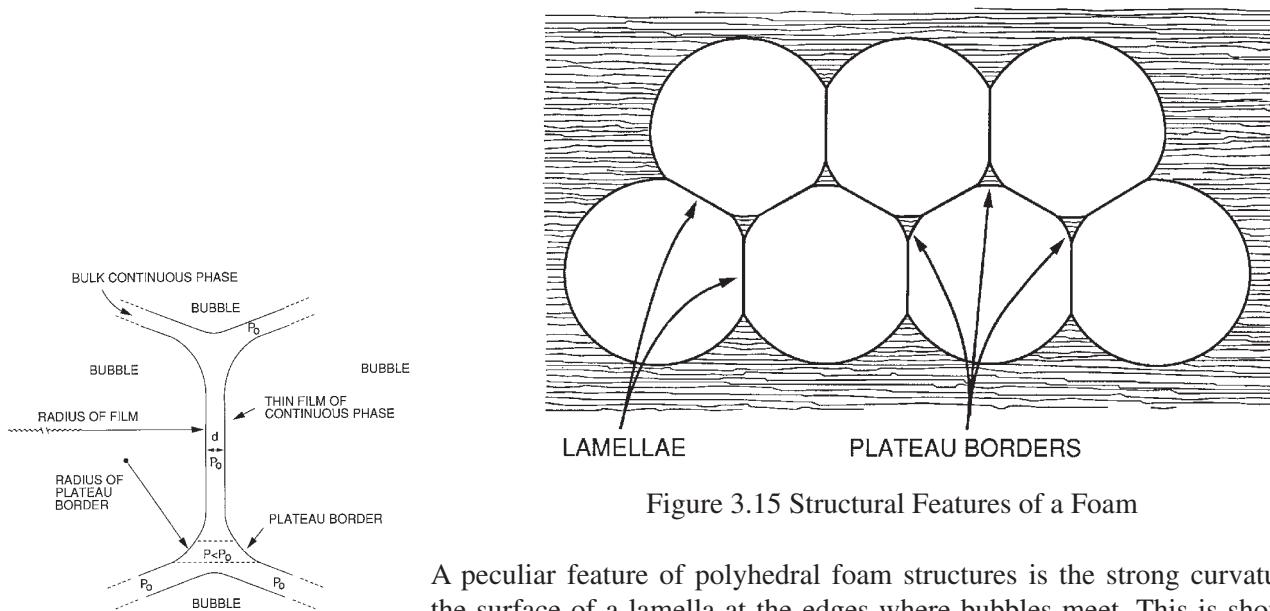


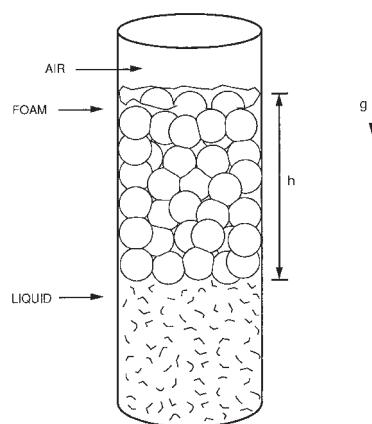
Figure 3.15 Structural Features of a Foam

A peculiar feature of polyhedral foam structures is the strong curvature of the surface of a lamella at the edges where bubbles meet. This is shown in the more detailed drawing of Figure 3.16. According to the fundamental equation of Young and LaPlace, the pressure in the liquid inside these edges should be lower than in the liquid of the bubble walls. As was first pointed out by Plateau, this pressure difference will produce a suction exerted upon the liquid in the cell-walls. This action causes a thinning of the cell-walls as mass moves from the walls into the Plateau border area. Therefore, in foams, thinning of the cell-windows is promoted by three factors; gravity, capillary suction into Plateau borders and foam volume expansion. The effects of these forces may be additive in some parts of a lamella and opposite in other parts.

To compare the relative contributions of gravity and Plateau border suction on drainage of lamellae into struts, consider Figure 3.17 and the following analysis.

For a foam h centimeters high, the pressure in the capillary between adjacent bubbles will be $981h$ dynes/cm². To a first approximation, the pressure due to Plateau border suction is given by the surface tension of the liquid divided by the r_{PB} radius of curvature at Plateau's border, or:

Figure 3.17 Gravity Drainage in a Simple Foam System



$$P_g = \text{Gravity} \times \text{Height} \quad (3.21)$$

$$P_g = 981h \quad [\text{dynes}] \quad (3.22)$$

$$P_{PB} = \frac{\gamma}{r_{PB}} \quad [\text{dynes}] \quad (3.23)$$

The ratio of pressures due to Plateau borders and gravity would then be:

$$\frac{P_{PB}}{P_g} = \frac{\gamma}{r_{PB}} \cdot \frac{1}{981h} \quad (3.24)$$

To convert these pressure expressions into comparative flow rates would require an accurate knowledge of the geometry of the capillary system in which flow is occurring. Since this knowledge is not available and is quite probably dynamic in nature, the following expression for comparative flow rates is offered:

$$\frac{Flow_{PB}}{Flow_g} = \frac{k}{r_{PB}} \quad (3.25)$$

where k is a constant (or quite probably a dynamic variable) reduced from the liquid variables of density and viscosity and also from the uncertain and probably dynamic geometric factors associated with the capillary.

Then, as the bubbles continue to grow, the radius of curvature at Plateau's border will approach zero, which on a comparative basis drives the flow due to Plateau's border to infinity.

$$\frac{Flow_{PB}}{Flow_g} = \frac{k}{r_{PB}} \quad \text{as } r_{PB} \rightarrow 0 \quad (3.26)$$

then,

$$\frac{Flow_{PB}}{Flow_g} \rightarrow \infty \quad (3.27)$$

Thus drainage, as a result of gravity, Plateau's borders and cell-volume expansion pull reacting polymer from the windows and struts into the Plateau border areas. The net result is a continuous thinning of the film in the windows. Prior to permanent stabilization by polymer gellation, the rate at which a film thins will be diminished by film viscosity and self-healing phenomena.

The means by which foams stabilize themselves and are more persistent than might be expected from consideration of the above drainage forces is a much debated subject. The lack of understanding arises in part from the experimental and calculational difficulties in elucidating the intimate details of the molecular events occurring in foams. Kitchener and Cooper have reviewed the five major theories of foam stabilization. Four of those theories can be reasonably applied to flexible polyurethane foams. Table 3.2 lists the major theories of foam stabilization.^{3.46}

Table 3.2 Major Theories of Foam Stabilization

| Theory By | Date | Teaching | Ref. |
|--------------------|------|--------------------|------|
| Plateau | 1869 | Surface Viscosity | 3.47 |
| Marangoni | 1871 | Surface Elasticity | 3.48 |
| Gibbs | 1878 | Film Elasticity | 3.49 |
| Ewers & Sutherland | 1952 | Surface Transport | 3.50 |

The various theories are largely similar and complementary. They vary at the detail level. Implicit in each theory is the assumption that rupture of a thinning window is preceded by a pronounced local thinning at some spot on the film. This localized thinning may be the result of drainage or the action of a sudden force, such as a thermal, pressure or vibrational shock.

Localized thinning in a film will result in an expansion of the surface in that area. With that event will come a dilution of the locally absorbed surfactant. The expanded film element will thus possess a higher non-equilibrium surface tension. See Figure 3.18 for a visual representation of this effect.

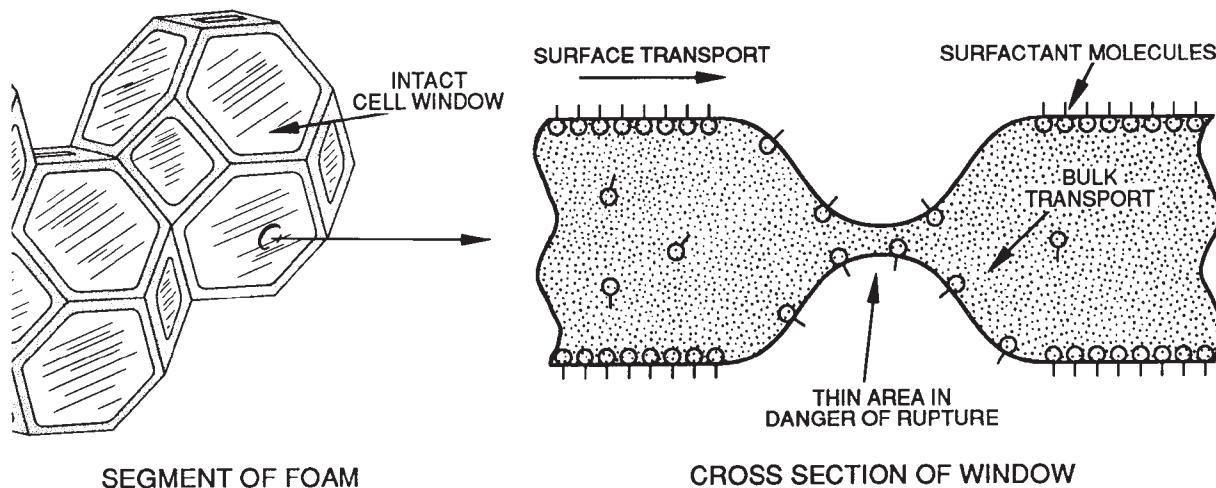


Figure 3.18 Thinning in a Cell-Window

The existence of a surface tension gradient brings several conceptual film repair mechanisms into effect. One mechanism, referred to as “Gibbs Elasticity,” is somewhat analogous to the behavior of a stretched rubber band. In that sense, the surface tension gradient operates to pull the film together again. This effect, expressed in various ways by Gibbs, Marangoni and Plateau, serves to maintain the film at a uniform thickness and thus delay eventual rupture.

Ewers and Sutherland observed that the existence of a surface tension gradient might bring about a second stabilizing mechanism. They reasoned that surfactant molecules absorbed in the undisturbed film surface would diffuse into the disturbed area. During that movement, the surfactant molecules would carry with them an underlying layer of the base liquid that would serve to increase the thickness of the thinned area and thus delay rupture. For further discussion of the various stabilization theories, the reader is directed to the reviews provided by Bikerman and by Kitchener and Cooper.

Summary

Figure 3.19 offers a summarizing ideal model for nucleation and bubble growth in polyurethane foams.

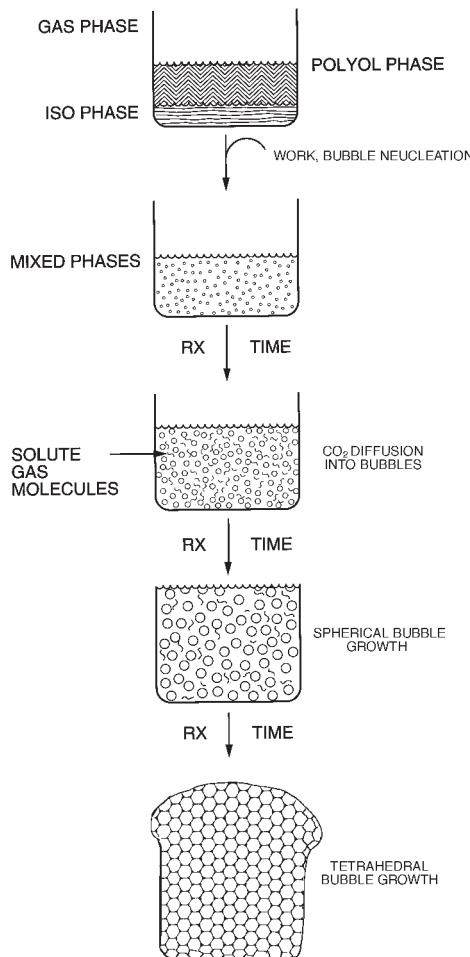


Figure 3.19 Model for Bubble Nucleation and Growth

Cells in the final polyurethane foam are produced by gas diffusion into bubbles that are nucleated or stirred into the system at the time of mixing. The eventual size of the cells can be related to the total amount of blowing agent available, the exotherm and the degree of stabilization (as by a surfactant). The total number of cells produced is governed by the dissolved gas content and the amount of gas stirred in.

Ultimate stabilization of the polyhedral framework occurs as a result of the chemical reactions that occur up to the point of polymer gellation. At the point of “gellation”, all film movement and expansion except that induced by outside physical forces (and leading to anisotropy) ceases. At this point the foam may or may not possess the population of open-cells necessary to make it a commercially viable product.

CELL-OPENING

In the production of flexible polyurethane foams it is desirable to have a high population of cell-windows rupture through a natural balance of the various physical and chemical forces. If this happens near the chemical gel point region of the reacting polymer system, a stable nonshrinking foam may result. When enough windows are open, the foam will have less pneumatic character and will be more suitable for comfort cushioning applications. It has also been postulated that a more completely open-cell foam will have better fatigue characteristics.^{3,51} As Figure 3.20 indicates, cell-opening is a very complex and formulation dependent phenomenon.

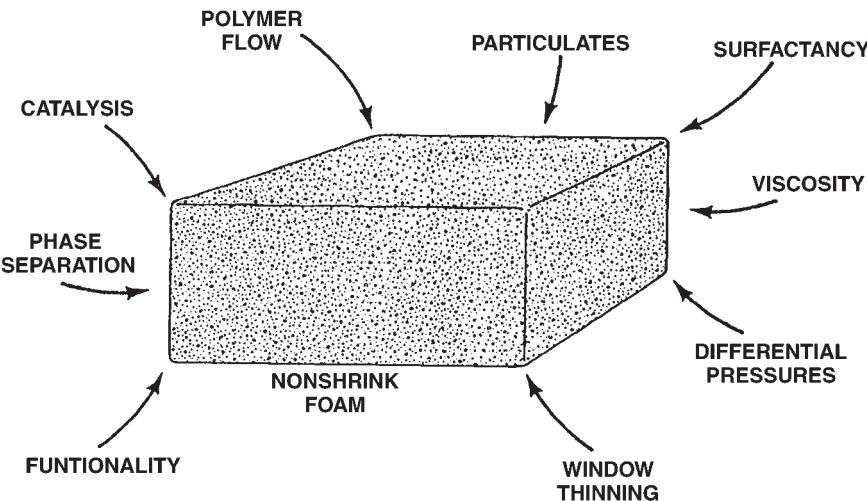


Figure 3.20 Cell-Opening Influences

Some of the major theories taught in the literature include that cell-opening is a result of steam formation,^{3,52} urea precipitation,^{3,53} balanced catalysis^{3,54} or due in part to some particle effects.^{3,55} The literature also teaches that surfactants, through their influence on bubble nucleation and stability are important contributors to controlled cell-opening.^{3,56-3,59} The importance of viscosity in controlling the drainage of polymer from the cell-windows has also been discussed.^{3,39, 3,60} It has also been reported that foam cells can be opened by the precisely timed application of a physical shock.^{3,61-3,62}

The classical concept regarding the cell-opening event in flexible foams has been reviewed by many authors (see Saunders and Frisch, Reference 3.63). Conceptually the opening of cells would occur to a large extent just as the foam reaches its full rise. At that time, the foamed polymer would have reached a high level of viscosity with a very low level of elasticity. The high viscosity would not permit the foam structural elements to flow fast enough to expand and relieve the still-increasing cell-gas pressure. Low elasticity in the cell-window membranes would likewise prohibit reversible stretching of the cell-windows. Under such conditions, the cell-window membranes burst, leaving an interconnected open-celled network. The polymer in the cell-struts must have enough strength to endure this event and prevent splits or catastrophic foam collapse. Attaining this ideal natural balance is a complex task due to the large number of formulation and equipment variables in common use.

Shrinkage in a flexible foam results when a large population of foam cells with intact windows remains at the end of foam manufacture. Just after production, such cells are filled with hot, pressurized carbon dioxide gas. As the foam cools, two things happen: the internal gas pressure diminishes; and the carbon dioxide diffuses out of the cells roughly fifteen times faster than air diffuses into the cells.^{3.39, 3.64-3.65} The net result is a partial vacuum in the cell which, when taken over a population of closed-cells, causes the foam to shrink and lose physical dimensions.

A unique method for the automatic detection of the cell-opening event has been described.^{3.66}

CELL-OPENING IN CONVENTIONAL SLABSTOCK AND HOT-MOLDED FOAMS

A more accurate understanding of the actual cell-opening mechanism in conventional slabstock and hot-molded foams began with the work of Rossmy, Kollmeir, Lidy and their co-workers.^{3.52-3.53,3.67-3.68} In detailed experiments, they found that a high polymer molecular weight was not present at the observed time of actual cell-opening. Shortly before cell-opening, infrared spectroscopy showed only negligible formation of urethane bonds and a sudden appearance of a strong urea related absorption. Coinciding with that event, it was also found that a visible phase separation occurred in the bulk liquid. The macro phase separation was identified as the precipitation of an agglomerated polyurea phase and that event was noted to momentarily increase the viscosity of the bulk liquid to a level consistent with the onset of a chemical gel. Later studies with the small angle X-ray technique revealed that the macro-phase separation was also accompanied by a micro phase separation that was attributed to the formation of bidentate hydrogen bonded urea hard domains. Further, cell-opening was noted to occur only after a critical amount of these hard domains had formed.

It is not totally clear how these urea phase separations induce cell-opening. At that point in the reaction, the gel-like consistency of the bulk liquid would reduce its elasticity and further film thinning from bubble expansion may not be favored. The presence of a particulate phase may allow film rupture to proceed through classical mechanisms. Silicone surfactants are helpful in moderating the cell-opening effects of urea precipitation giving the polyhedral framework time to build sufficient covalent network strength to resist collapse.

In practical terms the degree of cell-openness can be regulated by adjusting the catalyst package. If, at the time of cell-window rupture, the struts have not attained sufficient mechanical strength, film rupture will spread. If the rupture stops within a few inches, the resulting defect is called a split. If it proceeds unchecked, the foam may totally collapse. Conceptually, a pinhole in one window of each cell should be enough to prevent shrinkage. Such a foam however, would have an undesirable pneumatic (shock absorber like) feel in response to compression and recovery. Between these extremes, Figure 3.21 shows how variations in the gellation catalyst result in more or less open-celled foam.

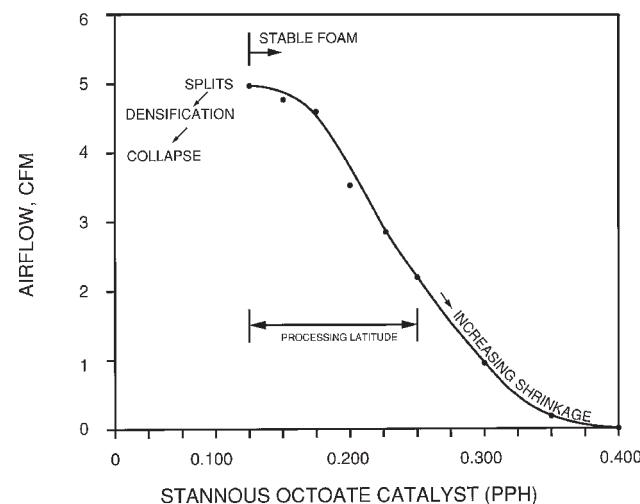


Figure 3.21 Effect of Catalyst on Openness in Slabstock Foam

CELL-OPENING IN HIGH RESILIENCY FOAMS

The higher reactivity ingredients used in HR slabstock and molded foams make these foams more susceptible to having closed-cells and shrinkage. During foam rise, the primary-hydroxyl-capped-polyols and the cross-linkers compete successfully with the water resulting in higher levels of urethane and urea bond (and thus molecular weight) formation. The bidentate hydrogen bonded urea structures form to a lesser degree and appear only as a microphase. The macrophase separation of urea domain agglomerates does not occur and thus that potential cell-opening mechanism is not available. In molded foams, cell-opening due to continuing volume expansion is limited due to the restricted volume of the mold cavity. Cell-opening in HR foams is thus more dependent on one of the chemical methods list in Table 3.3.

Table 3.3
Methods for Chemically Influencing Cell-Opening

- Filled Polyols
 - Polyurea Dispersions
 - SAN Copolymer Polyol
 - PIPA Dispersions
- TDI/Polymeric MDI Blends
- Additives
 - VORANOL 4053 Polyol
 - VORANOL CP-1421 Polyol
 - High MW EO/PO Diols
 - High Functional EO/PO Compounds
 - High MW Polyethylene Glycols
 - Fumed Silica
 - Silicone Fluids

Each of these technologies can be demonstrated to be effective in one or another foam formulation but, none is universally successful across the broad range of high resiliency foams produced commercially. Many molded foam producers feel that overall foam moldability is better with a tight formulation than with a more open one. One consequence of running a tight formulation is the danger of excessive foam shrinkage if the cell-walls are not adequately opened by crushing. The most common methods of crushing are:

- Passing the foam through narrow-gapped rollers,
- Subjecting the foam to the reduced pressure of a vacuum chamber, and
- The precisely timed release of internal pressure from the mold (commonly called the “TPR” technology).^{3.61-3.62}

Though successful in overcoming shrinkage, mechanical crushing represents an additional labor and capital cost to the foam producer. Figure 3.22 shows that the mechanical force applied to crush open the cell-windows may also damage the main structural elements (the struts) of the foam.

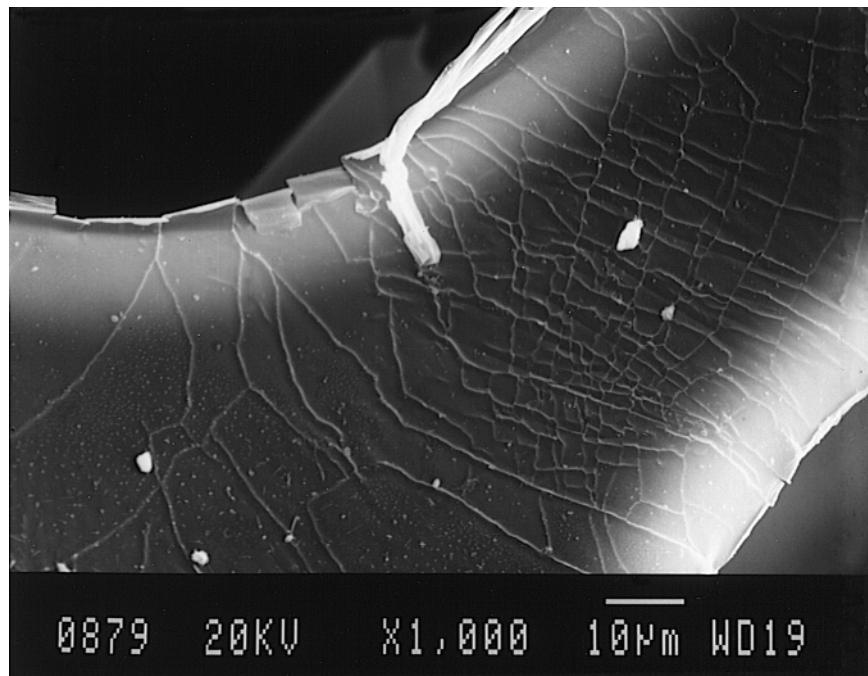


Figure 3.22 SEM Micrograph of Strut from Mechanically Crushed HR Foam

The figure provides a close-up view of a single strut with open cell-windows occupying the upper left and lower right corners. Torn fragments of the window membrane are visible near the edge of the strut. Notice how the tear lines in the window fragments continue on into the body of the strut. More discussion of this observation is provided in the morphology section below. One conceptual basis for designing a more naturally cell-opening foam system is presented below.

Viscosity Influence on Cell-Opening

Thinning of cell-windows is caused by foam volume expansion and the flow of reacting polymer in those windows into the Plateau border regions. This flow of material and thus the rate of window thinning can be expressed conceptually as:

$$\text{Flow} \propto \frac{k}{\mu} \quad (3.28)$$

where μ is the viscosity, and k is a dynamic variable related to the pressure difference between the window and Plateau's border and the geometric factors defining the capillary flow channel. Thus for any system, thinning of the cell-windows will be inversely proportional to viscosity of the draining polymer. In an ideal foam system, polymer viscosity would remain low while the foam was rising and then increase rapidly as the foam approached maximum height. Through proper control of polymer viscosity growth one should be able to control the cell-opening event in actual foam systems.

The measurement of dynamic viscosity in a rising foam system is experimentally difficult. Some success has been reported in References 3.69-3.71. Typical data from this type of experimentation is shown in Figure 3.23.

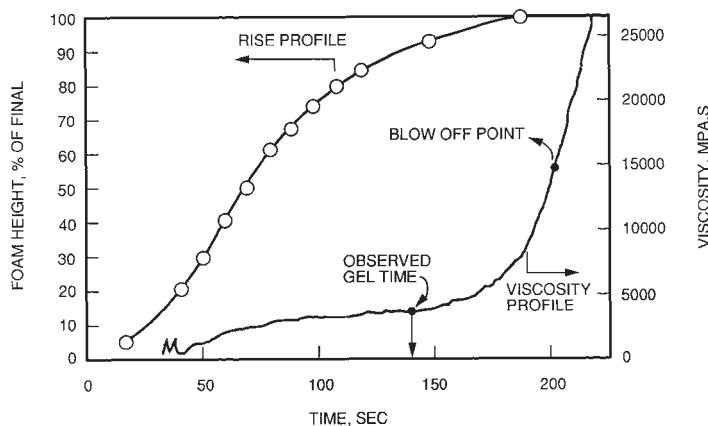


Figure 3.23 Typical Viscosity and Rise Profiles for Flexible Foam

In this experiment it was found that the foam rose and increased in viscosity with time. As the reaction proceeded and the foam approached maximum height, viscosity increases rapidly and the polymer could be observed to pass through an apparent gel point (measured by string time).

The attainment and timing of gellation is expected to have a pronounced effect on cell-opening. Conceptually the continuous phase of a foam can be present in one of the three states depicted in Figure 3.24.

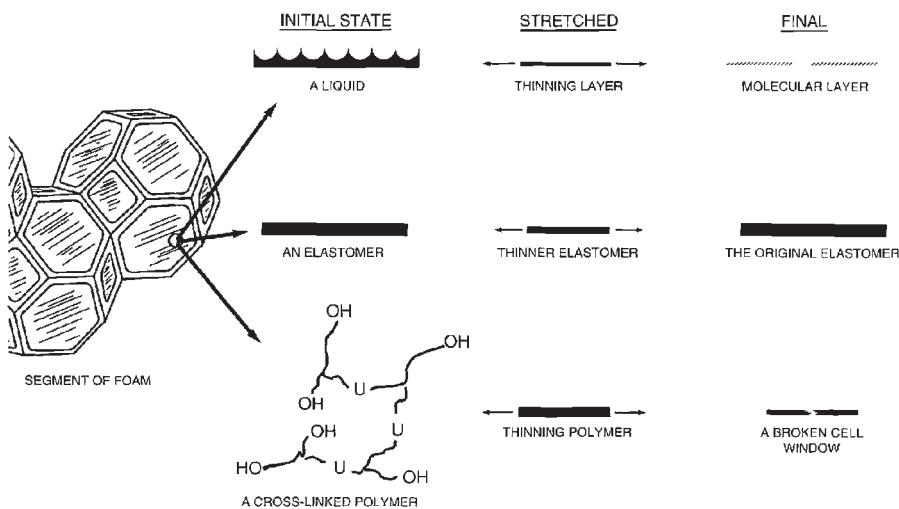


Figure 3.24 Conceptual States For Continuous Phase Of A Foam

If the material is a liquid, the drainage forces will thin the material down to a molecular (black film) layer before final rupture. With sufficient time, all membranes in a liquid foam will rupture and the foam will be destroyed.

If the continuous phase of a foam is elastomeric in nature, then the thinning membranes may be able to stretch and avoid rupture. Such nonruptured cell-membranes will cause shrinkage as the foam cools.

A sufficiently cross-linked thin film will break when stretched if the viscosity is too high for adequate flow and the molecular weight is still too low for ultimate strength.

If the timing of these conditions falls at or near the completion of the blowing reaction, a stable foam may result. An idealized profile for a rising foam is presented in Figure 3.25.

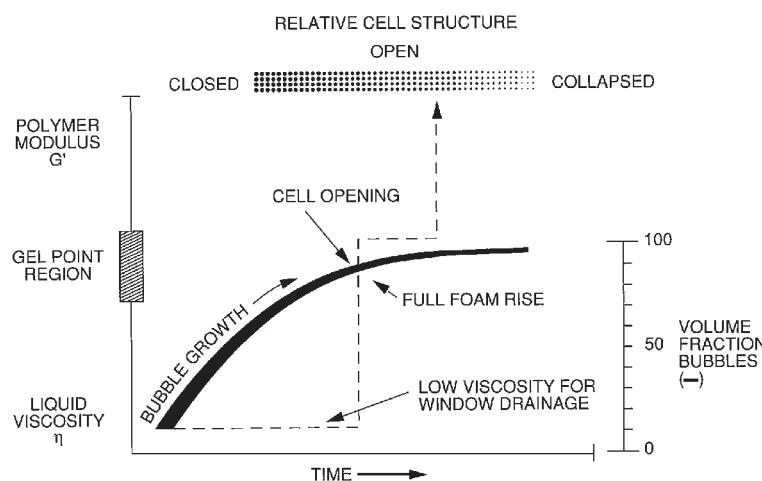


Figure 3.25 Idealized Gel and Rise Profile

As the reaction begins, viscosity of the mixture is low, allowing for bubble growth. As the bubbles grow and approach 74% volume fraction, polyhedral cells form and window drainage begins. Drainage is aided by a still low system viscosity. As the volume fraction occupied by the bubbles approaches 95-98 percent, it would be desirable for the system viscosity to increase rapidly to a level consistent with polymer gellation. As the internal cell-gas pressure continued to increase, cell-window rupture would occur. Some finite time in the gel point region may be needed to allow time for each individual cell-window to rupture. It is postulated that the window opening would begin at the outside edge of the foam and progress inward. After cell-opening, the system should rapidly approach final cure so that the foam part can be demolded and further processed in a timely manner.

Closed-Cell Concept

Figure 3.26 proposes a profile for a foam system resulting in closed-cells.

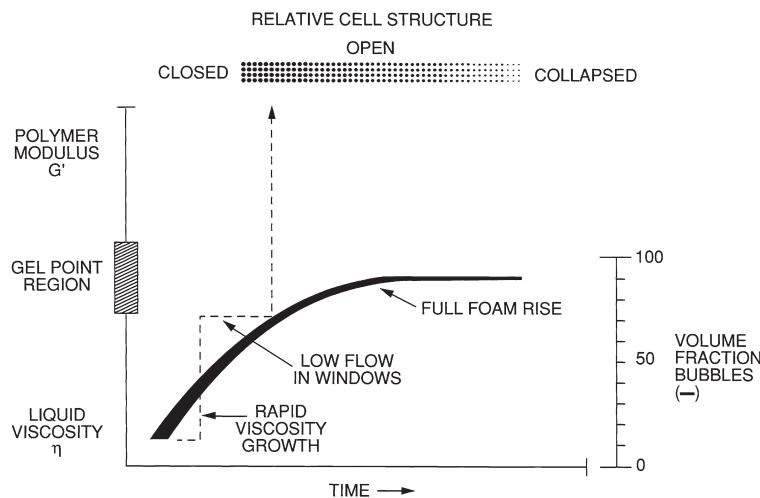


Figure 3.26 Profile for a Closed-Cell Foam

If the foam gels too early, the results can be higher-than-optimum foam density and shrinkage after the foam cools down. In this case, the rapid onset of molecular weight build gives a polymer strong enough to expand reversibly and tough enough to resist membrane rupture.

Catalysis Effects

There are many ways to change the viscosity growth profile of a reacting foam system. Figure 3.27 conceptualizes the results of varying the level of gellation catalysts.

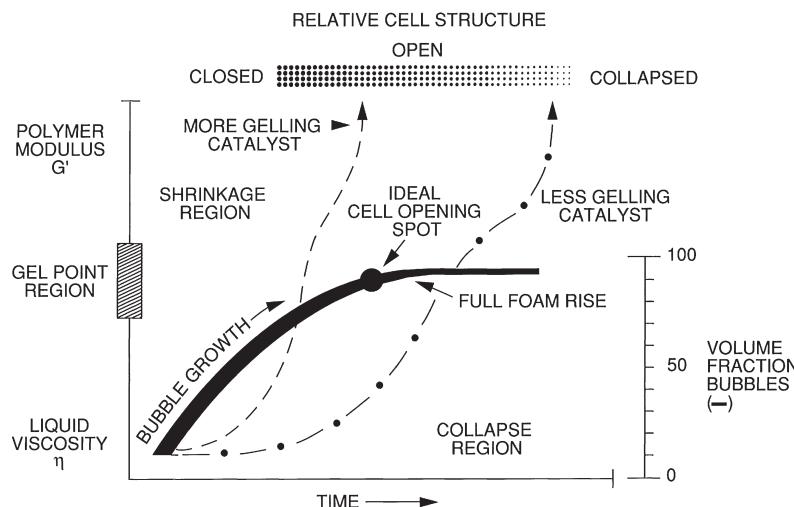


Figure 3.27 Catalysis Effects on Cell-Opening

If a foam contains too little gellation catalyst, the bubbles will expand and the windows will thin to the point of rupture before the polymer has reached gel point and partial or even total foam collapse will result. With excessive catalysis, the polymer becomes too tough to allow membrane rupture and shrinkage results. Experimental verification of this concept is presented in Figure 3.28.

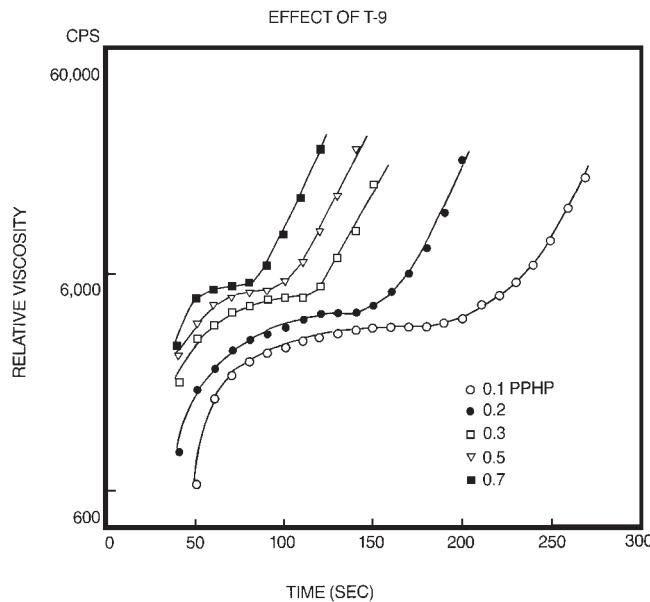


Figure 3.28 Catalyst Effects in a Typical Hot-Molded Foam

In this hot-molded foam formulation, the expected increase in polymer viscosity with increasing concentration of gellation catalyst was found. Another verification of this concept is found in the HR foam data presented in Figure 3.29.

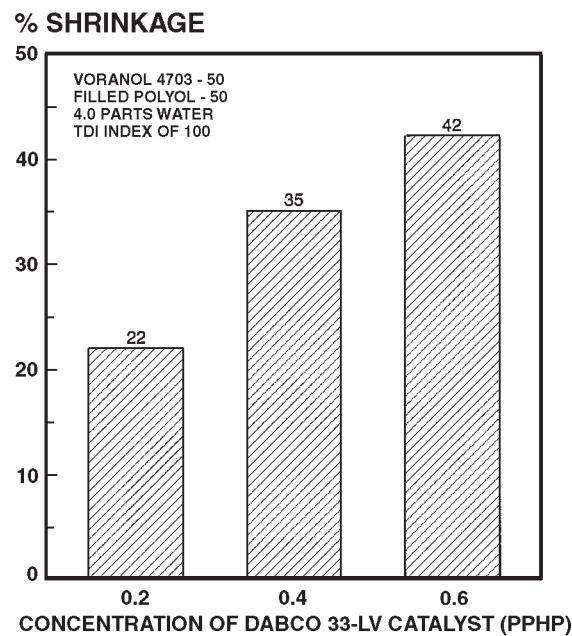


Figure 3.29 Catalyst Effects in HR Molded Foam

In the above experiment HR molded foams were prepared without crushing and the shrinkage measured after 24 hours. The only gellation catalyst present in the formulation was DABCO 33-LV and its concentration was varied through the indicated range. The resultant shrinkage numbers are consistent with the above theory.

Functionality Effects

Another way of altering time to gel point is by varying functionality of the reactants. Figure 3.30 illustrates the expected results of varying for example, polyol functionality over a wide range.

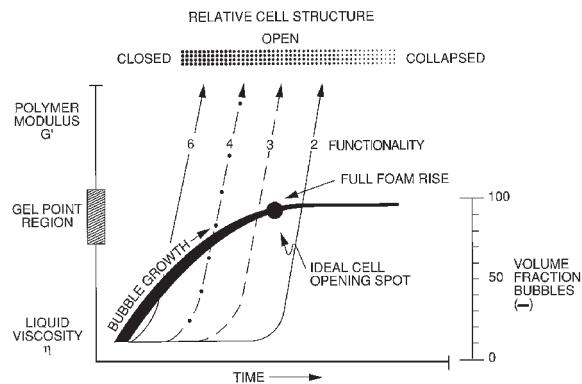


Figure 3.30 Functionality Effects on Cell-Opening

A logical extension of this concept would be the possibility of blending various functionality polyols to reach the optimum cell-opening point for a given foam production scenario. Data for the experimental verification of this concept is presented in Figure 3.31.

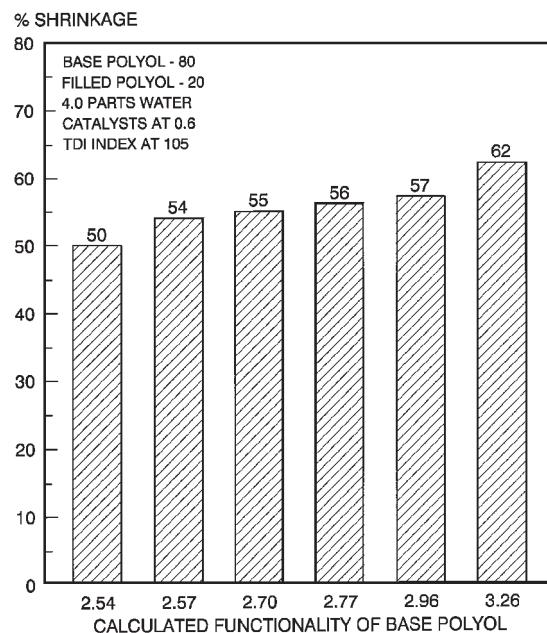


Figure 3.31 Functionality Effects in HR Molded Foam

To acquire the above data, HR molded foams were prepared from a constant formulation, varying only the functionality of the base polyol. Functionality was varied across the indicated range and all other compositional features of the base polyol were controlled tightly. The observed trend is a slight increase in foam shrinkage as functionality of the base polyol increased.

Reactivity Effects

A final concept for reaching optimum cell-opening would be to control the growth of viscosity through polyol reactivity. For a given functionality, polyol reactivity is controlled by the level of primary hydroxyl capping. Figure 3.32 conceptualizes the expected results from the two extremes of hydroxyl content.

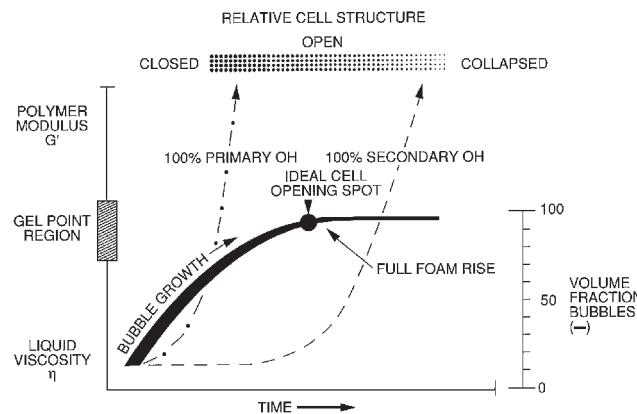


Figure 3.32 Primary Hydroxyl Effects on Cell-Opening

Again it appears plausible that these features of a polyol could be used in designing or blending to an optimum level of cell-opening. Experimental verification of this effect is shown in Figure 3.33.

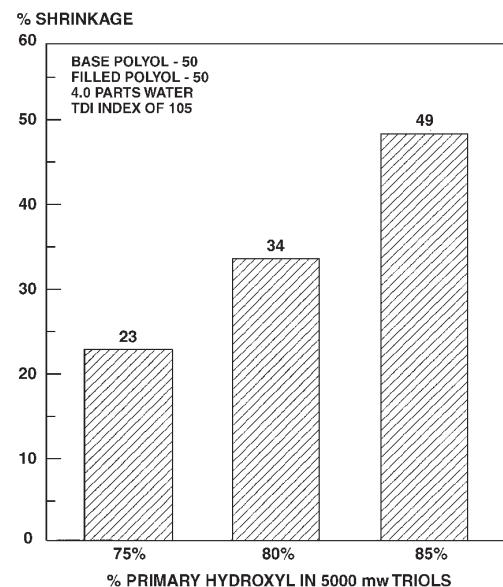


Figure 3.33 Shrinkage in HR Foams Varies with Primary Hydroxyl Content

In the above experiment, all formulation and process variables except the base polyol were held constant. Shrinkage varied in direct relation to percentage of primary hydroxyl.

Summary

The cell-opening process in a flexible polyurethane foam is a complex physical/chemical event influenced in various foam systems by;

- The kinetics of the chemical reactions,
- The kinetics of cell growth,
- The type and concentration of surfactant,
- The morphology of the thinning cell-window membranes,
- Phase separation,
- The presence of cell-disrupting agents, and
- The contribution from physical stresses, as in mechanical or vacuum crushing.

A proper combination of these factors at the right moment in a foam's history leads to the desired open-celled flexible foam. More discussion of cell-opening mechanisms can be found in References 3.72-3.73.

MORPHOLOGY

The final mechanical properties of a flexible foam depend both on the macroscopic cell geometry and on the morphology of the polymer contained within the foam's structural elements. Numerous reviews of cell geometry effects on foam physical properties can be found in the literature.^{3.29-3.36} The following discussion of polymer morphology effects is condensed from the published literature.^{3.74-3.88}

Figure 3.34 illustrates how the several reactions occurring during manufacture of an unfilled conventional slabstock polyurethane foam lead to the formation of a polymer with a multiphase molecular morphology. The existence of a heterogeneous phase-separated morphology in polyurethanes was suggested as early as 1966.^{3.89} It is generally conceptualized that this morphology consist of discrete hard-segment domains dispersed within a continuous soft polymer phase.

The kinetics of these reactions have been followed and it was found that in the early stages of a slabstock foam, the water-isocyanate reaction proceeds much faster than the polyol-isocyanate reaction.^{3.53,3.94-3.95} This is due in part to the low reactivity of the secondary hydroxyls present in most slabstock grade polyols. This disparity in reaction rates leads to the formation of polyurea oligomers that continue to grow in size until by virtue of a complimentary symmetry and the ability to form strong hydrogen bonds, the oligomers segregate into domains that phase separate from the continuous liquid phase.^{3.87-3.88} A detailed review of hydrogen bonding events in polyurethanes is available.^{3.86}

In the lower portion of Figure 3.34, the hard-domains are represented by the clustered thick lines. These features are tied into the matrix by covalent attachment to polymer chains that are shown fading off into the continuous phase.

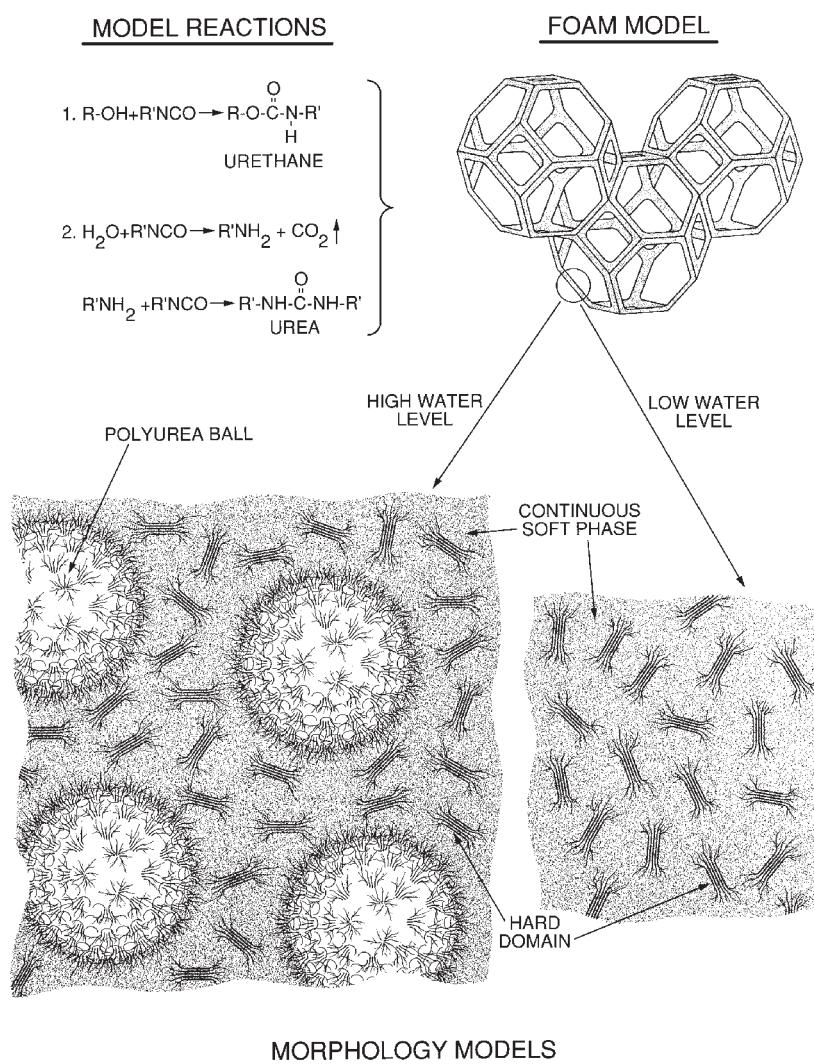


Figure 3.34 Conceptual Representation of Polyphase Structure in Conventional Slabstock Polyurethane Foams

At comparatively low formulation water levels, the water is completely soluble in the mixed formulation and reacts with the isocyanate to form urea species that are initially totally in solution. At a certain concentration and/or molecular weight, these species suddenly separate out as the discrete hard-domain phases indicated in the lower right-hand portion of Figure 3.34.

With sufficiently high concentrations of water in the formulation, a third phase, consisting of agglomerated polyurea hard-domains (the polyurea balls indicated in the lower left-hand portion of Figure 3.34) will be present.

These features arise when the concentration of water in the formulation exceeds the solubility of water in the polyol/isocyanate/additives blend. At that point, discrete, stable droplets of water are formed in the mixture.^{3,87} With continuing reaction, these areas of locally high water concentration give rise to locally high urea oligomer concentrations which, once a certain molecular weight is reached, separate into the macrophase urea agglomerates.^{3,88}

The continuous soft-phase polymer results when the polyol-isocyanate reaction proceeds past the chemical gel point. The covalent links between the soft-phase and the polyurea hard-segment domains are urethane bonds.

Evidence for the existence of this polyphase structure in polyurethane slabstock foams was first reported by Lidy, et al^{3,96} and later confirmed by Turner and Wilkes.^{3,81}

The macrophase polyurea agglomerates (the urea balls) are not found in typical high-resiliency foams. In HR foams, the primary-hydroxyl capped polyol and low molecular weight cross-linker successfully compete with the water in isocyanate consuming reactions. Typically, the water is also totally soluble in the polyol/isocyanate/additives blend. Thus, the urea oligomers that are formed are much more uniformly dispersed in the continuous phase. The polyol reacts earlier with the isocyanate to give prepolymer species that react further with the water and the isocyanate groups contained in the growing hard-segments to couple these segments with the continuous phase and further prevent agglomeration and macrophase separation. The cross-linker molecules also react into the hard-segments to further build molecular weight and disrupt the symmetry so that hydrogen bonding between hard-segment groups is hindered.

An additional reinforcing phase may be present if the foam has been formulated to contain particulate fillers. Variations in this polyphase morphology can be expected to account for the wide range of bulk physical properties attainable in flexible polyurethane foams. For example, when the water level is increased, the size of both the hard-segment domains and the urea precipitates should increase. Both structures will contribute to an increase in load-bearing capacity of the foam. It is postulated however, that there may be differences in the efficiency and permanence of load enhancement between the two structures.^{3,81} Clearly, a thorough understanding of polymer morphology will aid the polyurethane chemist in designing better performing foams.

PHYSICAL INVESTIGATIONS OF FOAM MORPHOLOGY

Some of the investigative tools used in deriving the above described morphological features will be discussed in detail below.

Foam Samples for Morphology Studies

Conventional slabstock foams were produced at the laboratory scale using the semiautomatic box foaming machine shown in Reference 3.91. All formulation ingredients except the isocyanate were weighed into a metal mixing cup and subjected to a 30-second premix. Isocyanate was weighed into a disposable beaker and transferred to the mixing cup immediately prior to a 5-second 1200-rpm mix cycle. The mixed components were then quickly poured into a box and allowed to foam under free-rise conditions.

After cure, samples were cut from prime interior areas of the foam for analysis.

A series of four foams was made in which the water content was varied from 2 to 5 parts per hundred parts polyol. Isocyanate index was held constant at 110 and all other formulation ingredients were held constant. The actual formulations used are summarized in Table 3.4.

Table 3.4 Formulations for Morphology Studies

| Foam Number | 1 | 2 | 3 | 4 |
|----------------------|--------|--------|--------|--------|
| Formulation | | | | |
| VORANOL 3100 Polyol | 100.00 | 100.00 | 100.00 | 100.00 |
| Water | 2.00 | 3.00 | 4.00 | 5.00 |
| BF-2370 Surfactant | 1.00 | 1.00 | 1.00 | 1.00 |
| DABCO 33-LV Catalyst | 0.30 | 0.30 | 0.30 | 0.30 |
| T-9 Catalyst | 0.15 | 0.15 | 0.15 | 0.15 |
| TDI (110 Index) | 30.79 | 41.43 | 52.06 | 62.70 |

A calculated average degree of chain extension and weight percent hard segment is presented in Table 3.5. The calculations are based on a theoretical complete reaction of the water, polyol and isocyanate but do not consider the 10% excess toluene diisocyanate.

Table 3.5 Calculated Foam Composition

| Foam No. | Water pphp | Hard-Segment Wt% | Average Chain Extension Ratio, A |
|----------|------------|------------------|----------------------------------|
| 1 | 2 | 21 | 32 |
| 2 | 3 | 26 | 43 |
| 3 | 4 | 30 | 54 |
| 4 | 5 | 34 | 65 |

Samples from these foams were used in obtaining most of the example data presented below.

Fourier Transform Infrared Spectroscopy

Infrared spectroscopy has been useful in studying the formation and structure of polyurethane foams.^{3.92-3.100} Fourier Transform infrared spectroscopy has been particularly useful in studying the time-related aspects of foam reaction kinetics and morphology development.^{3.101-3.103} A full discussion of the Fourier Transform IR analysis of the foams in Table 3.4 has been presented by Harthcock.^{3.104} Among his findings are; complications in assignment of all absorbance bands, and an increase in urea-related absorbances as foam formulation water level was increased.

Dynamic Mechanical Spectroscopy

Dynamic mechanical spectroscopy (DMS) measures the ability of a viscoelastic material to store and dissipate mechanical energy. Ideally two extreme types of behavior are possible; that of the elastic solid with a definite shape that is altered by external forces, but returns to its original shape upon removal of the forces, and that of the viscous liquid which has no definite shape and which flows irreversibly under the action of external forces. Real materials have behavior/properties that are intermediate between these two extremes. The experimental procedure involves subjecting the specimen to an alternating sinusoidal strain and simultaneously measuring the stress. The resultant stress will typically be out of phase with the applied strain by the phase angle delta indicated in Figure 3.35.

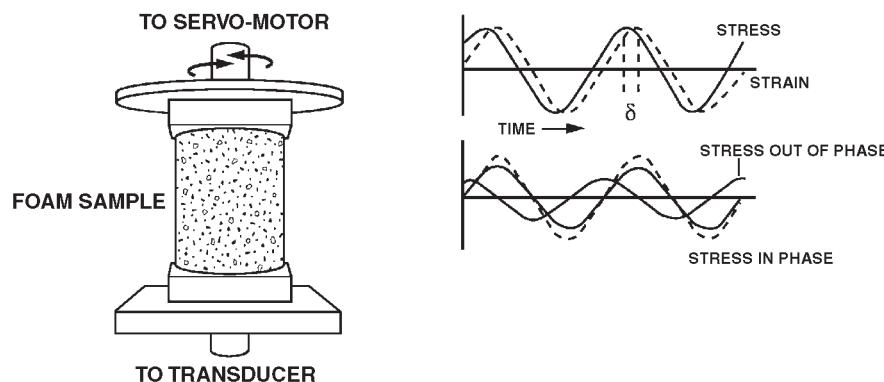


Figure 3.35 Dynamic Mechanical Spectrometer Concept

The response of multiphase polymers to the induced strain over the temperature range of investigation provides information as to the stiffness of the polymer and the degree of phase separation in the specimen. Two excellent instructional reviews on the use of this technique with polyurethanes are available.^{3.105-3.106}

For the above foams, DMS was used to locate the soft-segment glass transition, to observe the modulus - temperature behavior and to look for the presence of other thermal transitions. The experiments were conducted on a Rheometrics Model RDS-7700 dynamic mechanical spectrometer. Foams were tested in a parallel plate mode using cylindrical samples cut with a high-speed cork borer. Sample dimensions were 25 millimeters diameter by

25 millimeters high. Foam samples were subjected to an oscillatory shear deformation at a frequency of 1 Hertz and an initial strain rate of approximately 1 %. Data were collected over the temperature range of -160 to 300°C at 5°C intervals. Temperatures were allowed to equilibrate for two minutes before each reading was taken. Typical test duration times were 5 hours for each sample.

The DMS spectra for the above foams are presented in composite Figure 3.36.

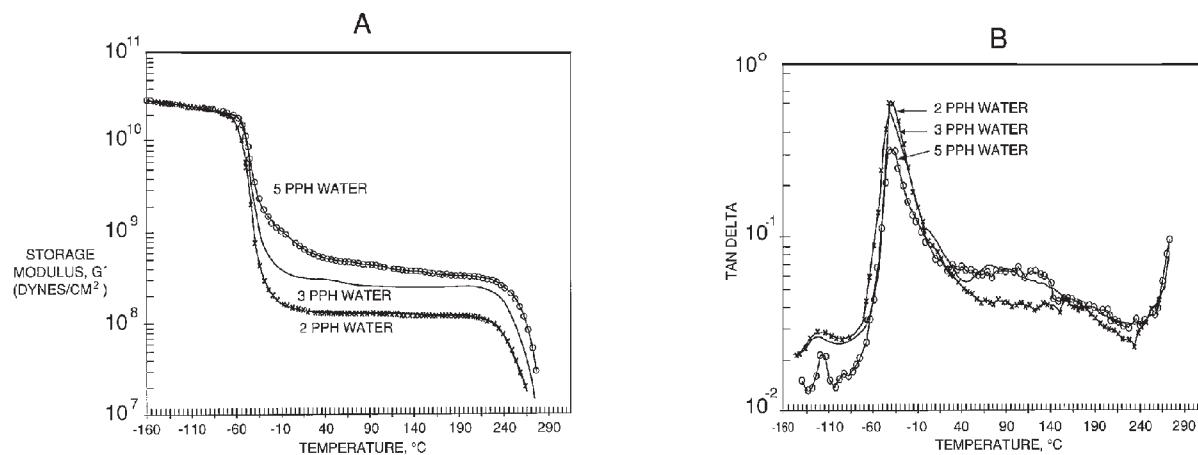


Figure 3.36 DMS Spectra for Foams of This Study

Both versions of the DMS spectra are similar to those found for relatively soft solid polyurethane elastomers. The storage modulus G' is a measure of polymer stiffness. At low temperatures, molecular movement is essentially frozen, modulus is high and the polymers have nearly perfect elasticity. Tan delta is at a minimum indicating that nearly all the energy stored in deforming the sample is recovered when the stress is removed. Each of the curves reveals a sharp transition from a glassy state to a rubbery state around -40°C. This transition has been assigned to the onset of molecular motion in the continuous soft-segment phase of the sample. In this region, modulus decreases sharply with a corresponding sharp increase in tan delta.

The maximum in the tan delta curve is generally quoted as the soft-segment glass transition temperature.

The position of the glass transition temperature for polyurethane polymers has been related to the molecular weight of the pure soft-segment^{3.107-3.113} with upscale shifts resulting from the chain immobilizing effects of a second phase.^{3.107, 3.110, 3.114-3.116} Then follows a rubbery plateau extending to the temperature range normally assigned to the dissociation of the microdomains of polyurea hard blocks.^{3.117-3.118} This leads to a further decrease in modulus, followed by sample degradation. Figure 3.36 also reveals that an increased water level increases the modulus of the polymer. Presumably, with increased water - isocyanate reactions, greater amounts of polyurea-rich phase are formed. With little or no inclusion into the soft polyol phase, these

additional polyurea units go to the filler-like polyurea microphases and produce a rise in system modulus.

The observation that the foam polymers exhibit fairly flat, temperature-insensitive moduli offers indirect support for the presence of a virtual as well as a covalent cross-linked network. Additionally, observation of the position, sharpness, intensity and insensitivity of the glass transition argues for a well-segregated domain structure with little phase mixing.

The curve in Figure 3.36B is the tan delta curve. It is a mathematical ratio of the energy lost relative to the energy recovered during each strain cycle. In perfect systems, all input energy is returned and the value of tan delta would be zero. In imperfect systems, as more input energy is lost, the tan delta function approaches infinity. In polyurethane foams the energy loss will occur as heat loss due to hysteresis in the polymer. An approximate range for tan delta in polyurethane foams would be 0.01 to 1.0.

The application of DMS and related techniques to the study of flexible polyurethane foams is a fairly new endeavor.^{3,78, 3.119-3.120} This technique has routinely been used to characterize linear and cross-linked polyurethane elastomers. References 3.121-3.124 were also helpful in interpreting the foam data. By comparison, it can be concluded that, despite the possibilities for formation of a more complex morphology, polyurethane foam behavior is strikingly similar to that of polyurethane elastomers.

Differential Scanning Calorimetry

Complimentary differential scanning calorimetry (DSC) data were collected on the foam series to confirm the soft-segment glass transition temperatures and to note other thermal responses in the foams. The experiments were conducted on a Mettler Model TA3000 instrument. Scans were conducted at 10°C per minute over the range of -120 to 350°C. Typical scans are presented in Figure 3.37.

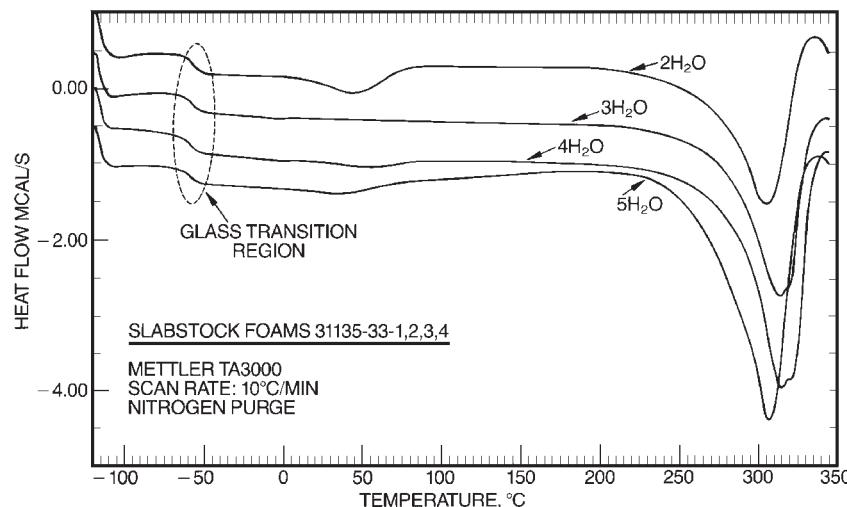


Figure 3.37 Composite DSC Scans for Flexible Slabstock Foam

The DSC experiments gave glass transition values that are slightly lower than those obtained from the DMS spectra. This small difference may be due to the kinetic differences arising from the different scanning rates. Table 3.6 is a summary of the various thermal transitions observed in both the DMS and DSC scans.

Table 3.6 Thermal Transition Summary

| Foam | Water pphp | T _g (°C) DMS* | T _g (°C) DSC* | T _g (Hard)(°C) DMS** |
|------|---------------|-----------------------------|-----------------------------|------------------------------------|
| 1 | 2 | -40 | -57.6 | 235 |
| 2 | 3 | -38 | -57.2 | 245 |
| 3 | 4 | -38 | -58.3 | 243 |
| 4 | 5 | -41 | -58.3 | 250 |

*Value is based on a peak in tan delta curve
**Value is the apparent hard-segment softening temperature

Scanning Electron Microscopy

For purposes of comparison, the scanning electron microscope (SEM) can be used to study the cellular structure of a foam.^{3,125} Typical micrographs for the foams of this study are shown in Figure 3.38. In general, it can be said that

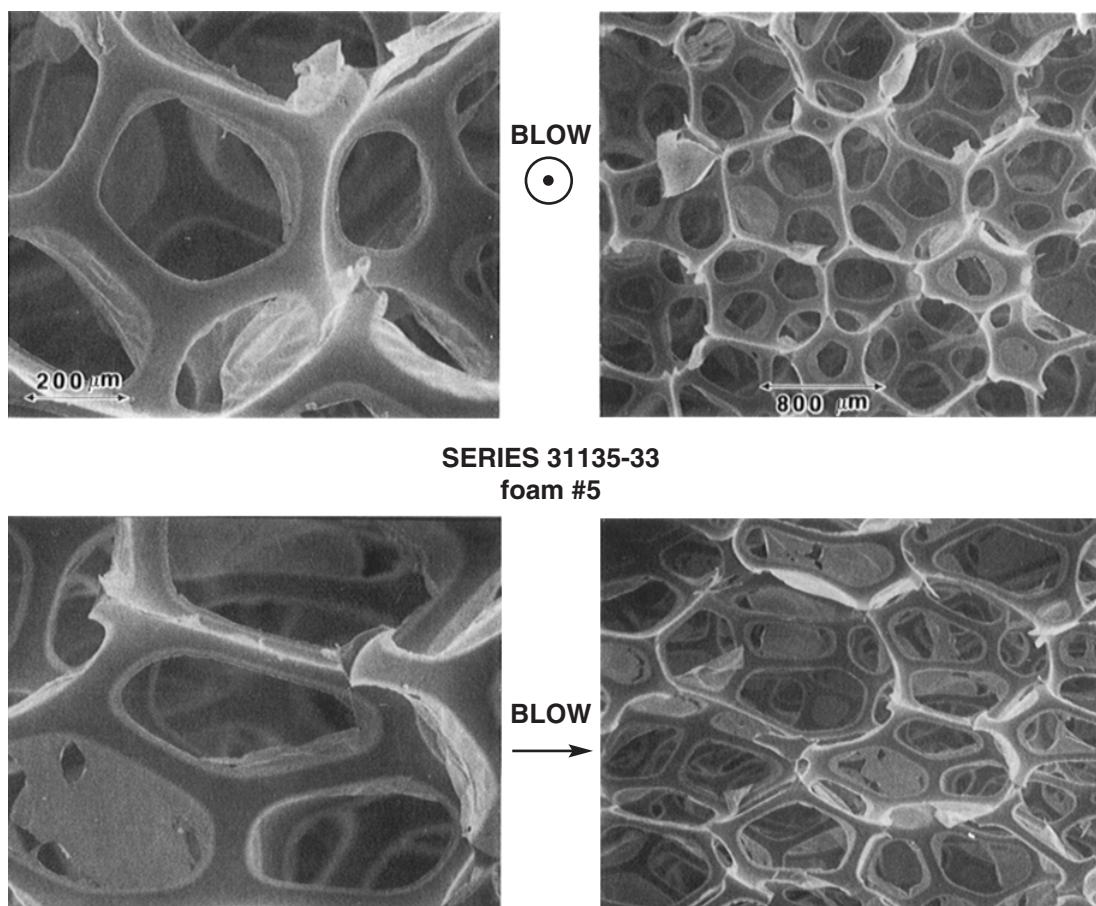


Figure 3.38 Typical SEM Micrographs for Foams of this Study

the foams consist largely of interconnected void areas within a fibrous-appearing continuous solid phase. From such photographic data, one could estimate a population of intact closed-cell windows or even gain clues as to the method of cell-window opening in various foam systems.

For the foams in Figure 3.38, the two different views clearly show an inherent structural anisotropy when the foams are viewed perpendicular to the direction of foam rise. The consequence of this anisotropic feature has long been recognized in the observation that foam bulk properties, such as load bearing, can be influenced simply by the way a sample is cut from a larger bun.^{3.126-3.127} An example of the utility of using SEM for cell opening studies is given in Figure 3.39.

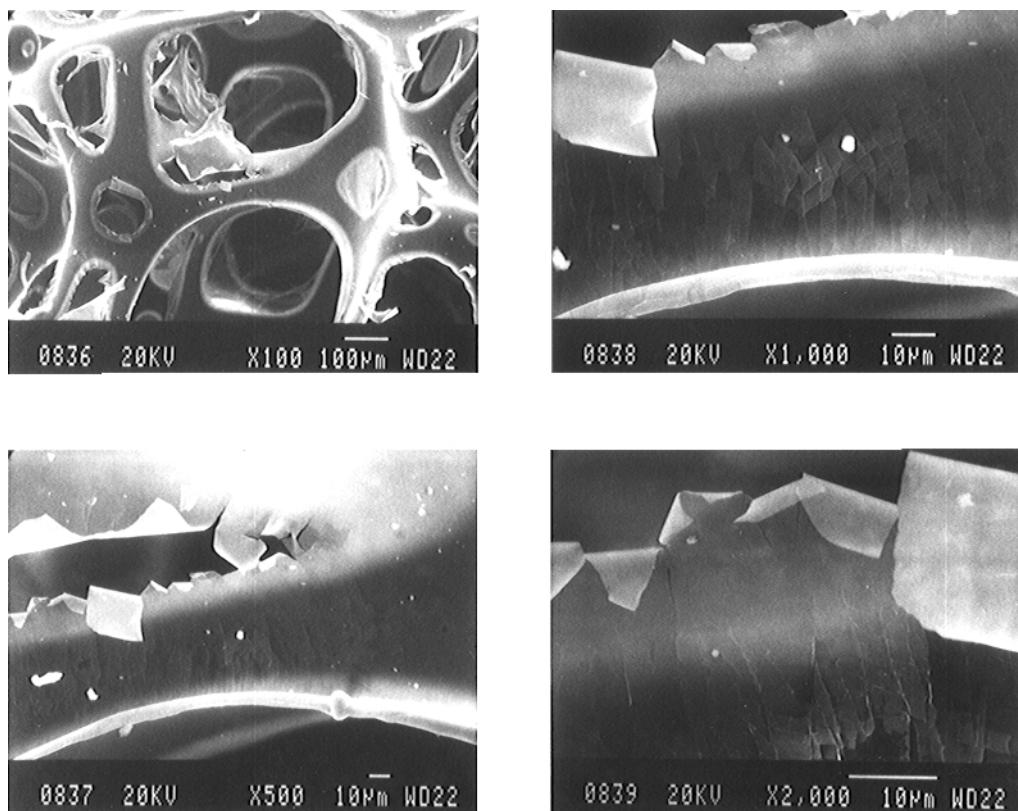


Figure 3.39 Evidence of Cell-Opening Events in HR Molded Foams

The foam of this example was a typical low-density HR molded foam based on the copolymer polyol and all-TDI technology. As typical of foams produced for the North American auto industry, this foam had been formulated to run tight for production safety and was given a thorough mechanical crush after demold to avoid shrinkage. In the 100X view, the remaining window fragments suggest a brittle fracture type of window opening event. Successively higher magnifications show that cracks in the windows propagated on into the struts. Figure 3.40 presents a more detailed cross-sectional view of a strut from the same foam.

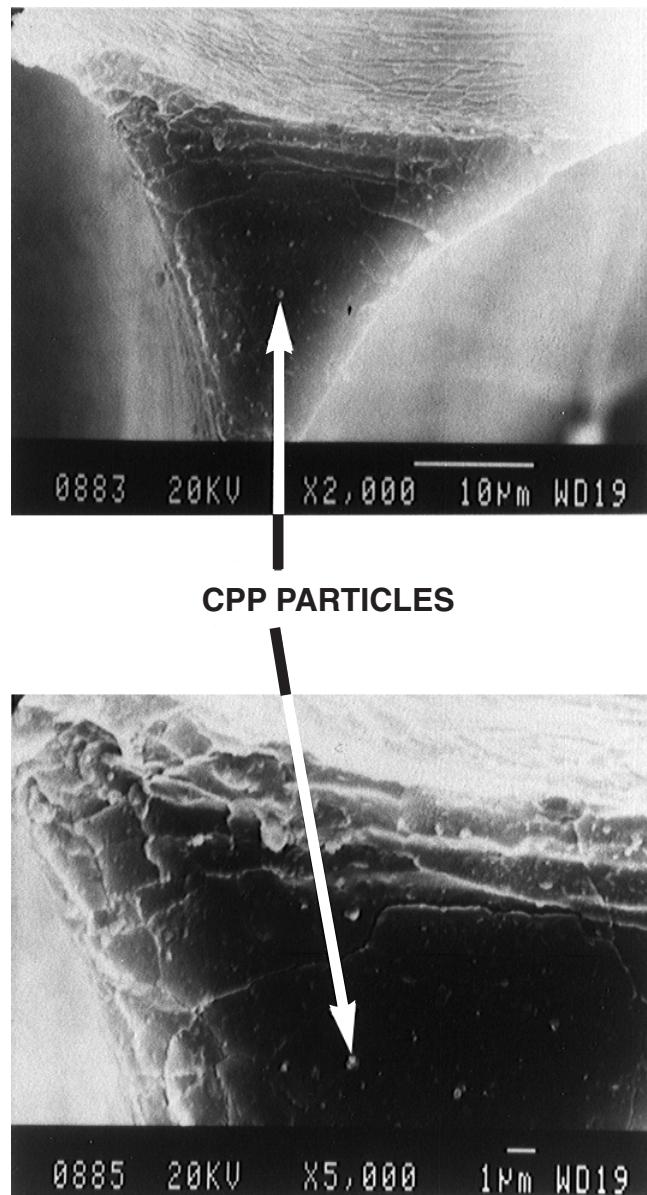


Figure 3.40 Detailed Views of Foam Strut

These views confirm the structural damage arising from mechanical crushing. Fatigue performance in such a foam could be expected to be poor. Another feature visible in Figure 3.40 is the presence of copolymer polyol particles. Figure 3.41 is an artist concept drawing of the top photo in Figure 3.40. SEM allows a useful study of the role such particles may play in cell window opening and in overall property enhancement.

Optical microscopy has also been successfully used to study the detail features of flexible polyurethane foams.^{3.91, 3.128-3.135}

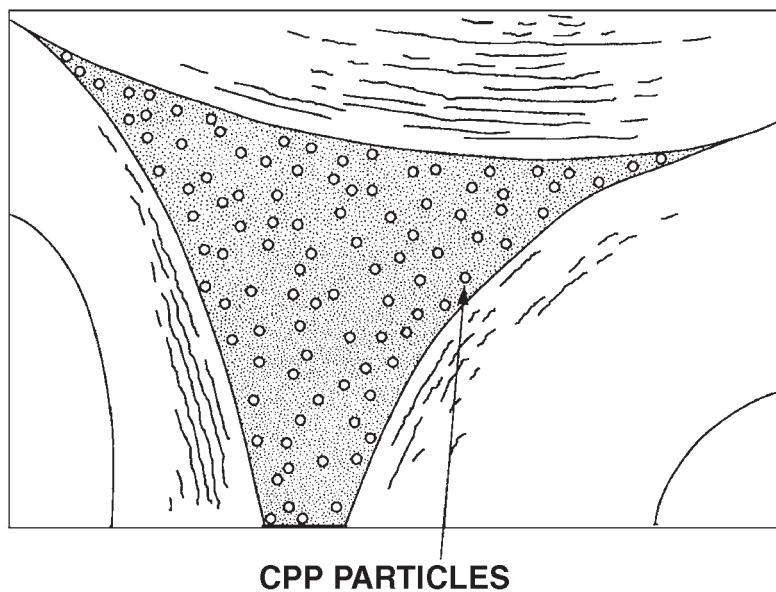


Figure 3.41 Copolymer Polyol Particles Found Within The Foam Struts

Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) allows the observation of materials at magnifications from 10,000 to 50,000X. For this study a JEOL 100C Analytical TEM operating at an accelerating voltage of 80 KV and a magnification of 10,000X was used. The foam samples were prepared by fitting small samples of foam into capsules and imbedding the capsule in epoxy resin. A vacuum pump was utilized to remove entrained air from the sample. The capsules were cured at 60°C for 8 hours. The composite was then cooled to -80°C and sliced into sections approximately 120 nanometers (1200 angstroms) thick using a Sorvall MT-2 ultramicrotome. For the TEM analysis such sections were mounted on a 300-mesh copper grid. Figures 3.42 through 3.45 show the TEM micrographs for the slabstock foams of this study.

The micrograph for Foam 1, the lowest water content, shows a diffuse grainy texture, but no distinct precipitated features. The grainy texture is not visible in the surrounding epoxy matrix and is presumed to arise from features, e.g., the hard-segment domains, smaller than the thickness of the specimen. The micrograph for Foam 2 (Figure 3.43) shows what are believed to be aggregations based principally on precipitated polyurea-rich regions. In the micrograph, distinct white and dark areas can be seen. The whitish areas are believed to be regions of lower electron dense material, e.g., the continuous soft-phase. It is the darker electron dense regions that are believed to be precipitated polyurea. These regions average roughly 3000 angstroms in diameter and are randomly dispersed in both isolated and agglomerated groups. Close examination shows these dense regions are surrounded by lighter white regions implying that this phase is discontinuous. Collectively the TEM micrographs show that as water level increases, the number, but not the size of polyurea precipitates increases.



Figure 3.42 TEM Micrograph - Foam 1



Figure 3.43 TEM Micrograph - Foam 2



Figure 3.44 TEM Micrograph - Foam 3



Figure 3.45 TEM Micrograph - Foam 4

Figure 3.46 presents an artist concept drawing of an edge-on view of the prepared samples from Foams 1 and 4.

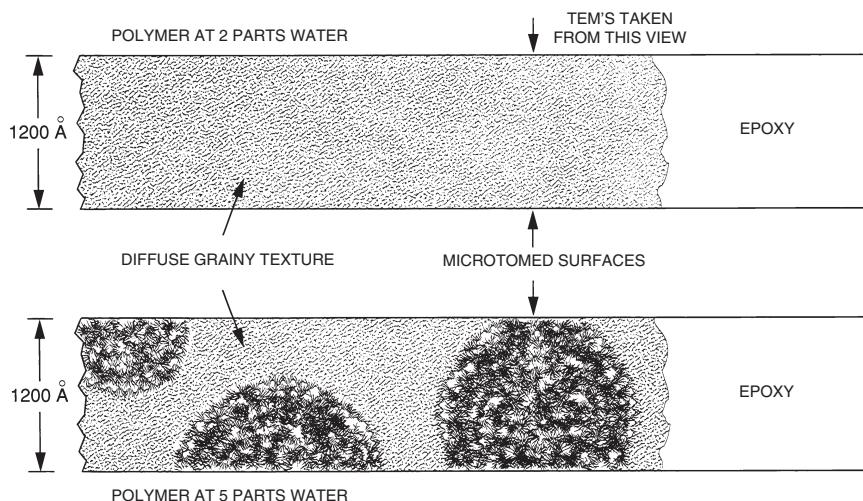


Figure 3.46 Artist Concept Of Features Visible
In Figures 3.42 and 3.45

Figure 3.47 presents micrographs from another recent work^{3.88} comparing the features of a conventional slabstock foam to those for an HR type slabstock foam prepared at the same water level (4.0 parts).

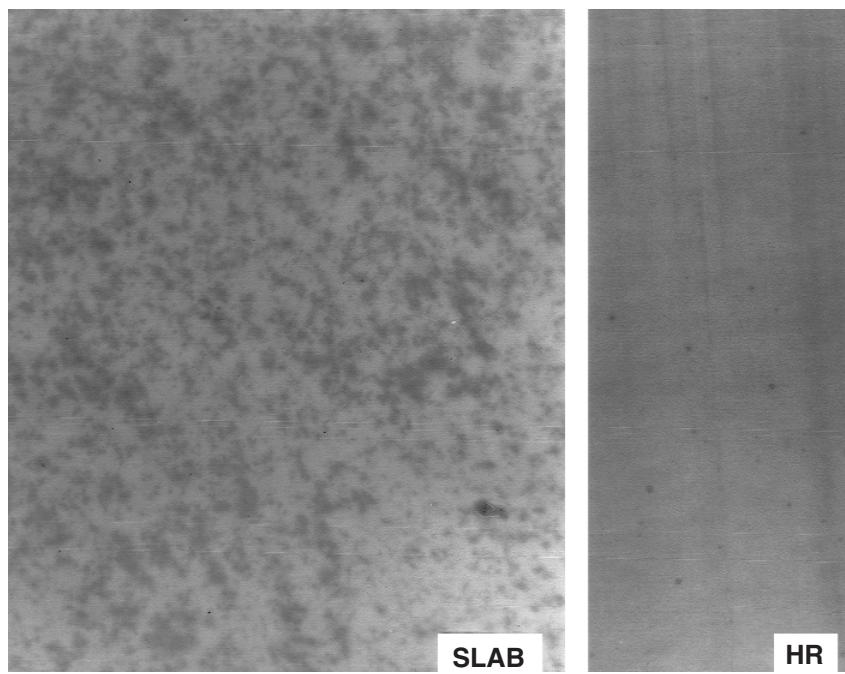


Figure 3.47 TEM Micrographs for Conventional
and HR Type Slabstock Foams

Note that the macrophase polyurea precipitates are present in the conventional foam, but are absent in the HR foam.

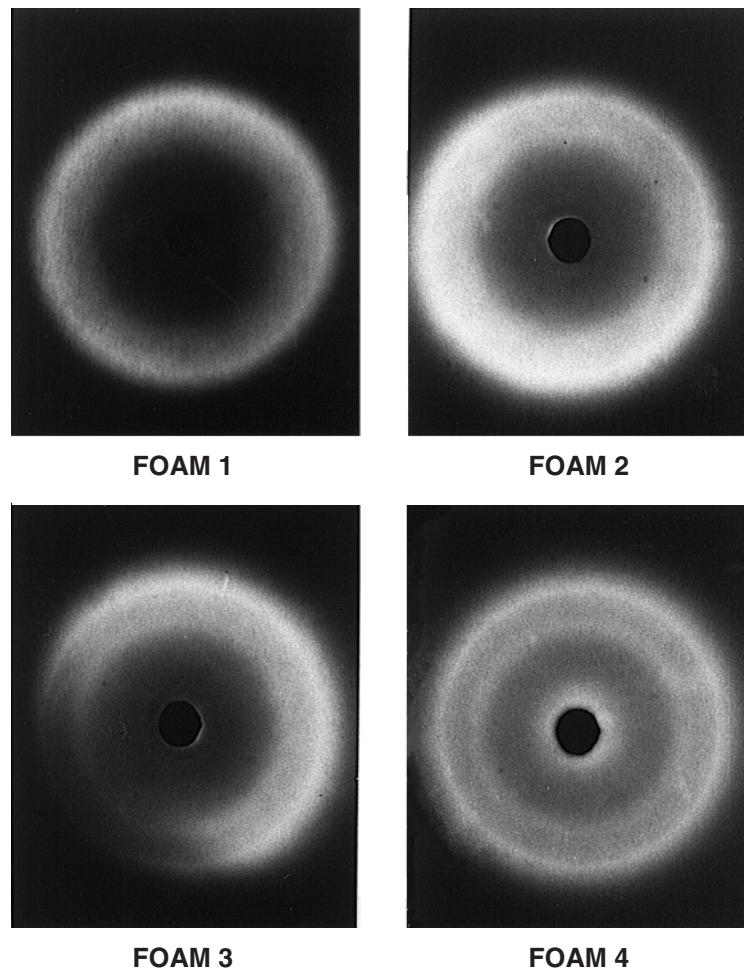


Figure 3.48 X-ray Diffraction Patterns For Slabstock Foams

Wide-Angle X-ray Scattering

Wide-angle X-ray scattering (WAXS) patterns were obtained for the foams to note the possible presence of any sharp rings due to crystalline ordering. The patterns were taken in a standard Statton camera under vacuum and at a sample-to-film distance of 8 centimeters. The X-ray source was a Philips tabletop X-ray generator model PW1720 equipped with a fine-focus tube. The radiation was nickel-filtered Cu K α with a wavelength of 0.154 nanometers. Foam samples were cut approximately 10 millimeters thick and compressed to less than 2 millimeters for the WAXS runs. Exposure times were 10 to 20 hours, depending on foam density and expected hard-segment content. Diffraction patterns for the four foams are shown in composite Figure 3.48.

All of the foams show a diffuse halo and what appears to be a diffraction peak at about 0.45 nanometers. A second peak appears at about 0.59 nanometers. The peaks appear to sharpen with increased hard-segment content and are clearly too distinct to arise from maxima in the amorphous halos. Attempts to sharpen the diffraction peaks by heat annealing were not successful.

The peak spacings mentioned above are consistent with the results of other published studies on polyurethane - ureas with noncrystalline hard-segments.^{3,121, 3,136-3,137} From all the studies mentioned above, it is concluded that the diffuse halo in all the foams can be attributed to short-range ordering in the hard-segment domains. The 0.45 and 0.59 nanometer peaks are taken as an indicator of increasing order in the hard-segments. The true origin of these peaks is still unknown and is believed to arise from noncrystalline ordering in the hard-segments as a result of hydrogen bonding. In other work, similar peaks observed in polyurethane elastomers were attributed to paracrystalline ordering.^{3,138-3,140}

Small-Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) can be used to gain information about the average size of hard, electron dense domains within polymer materials.^{3,141} In a typical experimental setup shown in Figure 3.49, incoming radiation interacts with electrons of the polymeric matrix and is either absorbed or scattered. In an ideal system, the scattered radiation reaches maxima which can be related to differences in the electron density of the matrix and thus to the chemical composition of the scattering phases. In real systems however, mixing of phases tends to homogenize the sample, yielding a somewhat uniform intensity reduction as a function of the scattering angle. Analysis of the scattering intensity can, nevertheless, provide information on the domain size, interfacial thicknesses and total content of hard-segments.

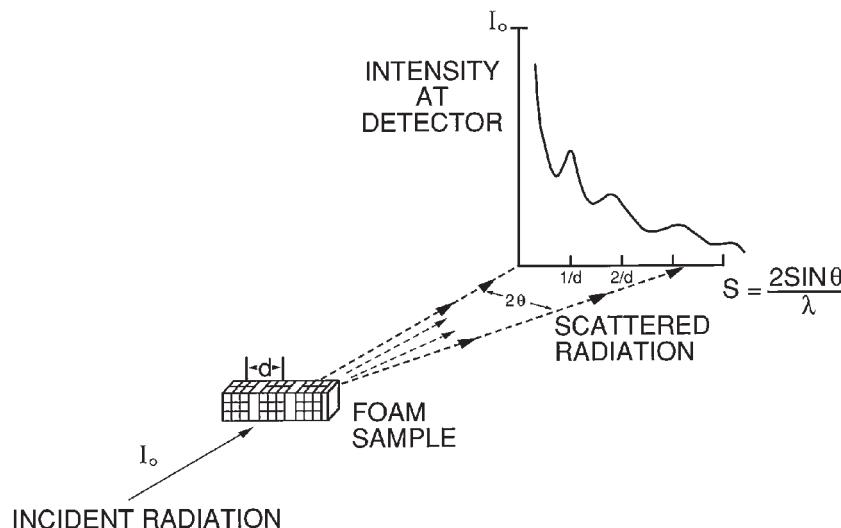


Figure 3.49 Small-Angle X-ray Concept

Our initial work with SAXS was done using the Oak Ridge National Laboratory 10-Meter SAXS camera. This instrument features a rotating anode X-ray source, crystal monochromatization of the incident beam, pinhole collimation and a two-dimensional position-sensitive detector. A copper anode was used and the incident beam was monochromized to Cu K α radiation. Details regarding use of the ORNL 10-Meter SAXS camera are

given in Reference 3.142. More recently, SAXS analysis has been done with in-house equipment.^{3,83}

Foam samples approximately 10 millimeters thick were compressed along the blow axis to about 6 millimeters thick for these experiments. To avoid any possible effects from particle anisotropy, care was taken to align the foam samples so that the incident beam would be parallel to the blow direction. Figure 3.50 and Tables 3.7 and 3.8 show the data collected from the SAXS experiments.

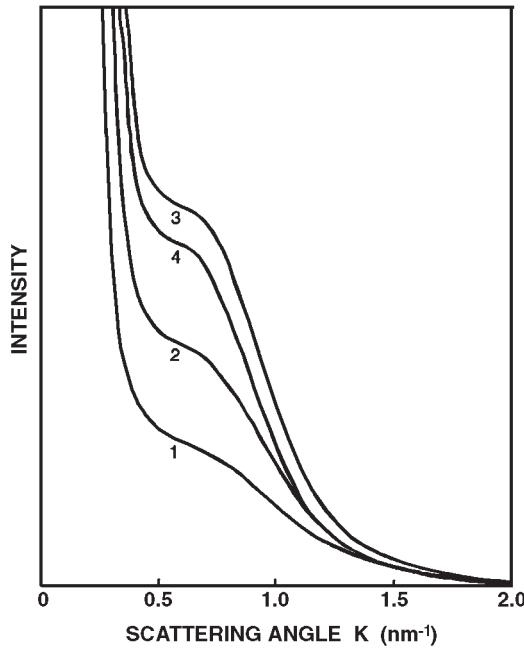


Figure 3.50 SAXS Curves for Foams of This Study

The curves are corrected relative intensities, which are the result of standard X-ray data manipulations involving background subtraction, zero-angle extrapolation, tail fitting and smoothing. Each of the scattering curves has a shoulder that appears at approximately the same angle for each foam sample. Each of these shoulders can be thought of as an interference or correlation peak that is not completely resolved because it occurs at low scattering angles and is quite diffuse. The 2-to-100 nanometer (20-1000 angstroms) morphological features that give rise to SAXS events are typically not expected to be of uniform shape, or to be separated by consistent distances. As a result, sharp peaks are generally not seen in these experiments.

By applying Bragg's law to the shoulders of the curves, an estimate of the center-to-center (interdomain) distance between scattering features is obtained. Table 3.7 summarizes the calculated data.

Table 3.7 Interdomain Spacing

| Foam No. | Water pphp | D via Bragg's Law (Angstroms) | R via 3-D Corr. (Angstroms) | X via 1-D Corr. (Angstroms) |
|---|------------|-------------------------------|-----------------------------|-----------------------------|
| 1 | 2 | 89 | 69 | 66 |
| 2 | 3 | 94 | 73 | 67 |
| 3 | 4 | 94 | 77 | 69 |
| 4 | 5 | 96 | 72 | 71 |
| R = First Maximum in 3-D Correlation Function | | | | |
| X = First Maximum in 1-D Correlation Function | | | | |

The R and X values in Table 3.7 are alternative estimates of interdomain spacing taken from Armistead's more precise correlation function analyses.^{3,82} Two possible spacings are calculated on the basis of differences in assumed geometrical factors. The conclusion from these data is that there are hard-segment domains in these foams and that the center-to-center spacing of these domains is on the order of 65 to 95 angstroms.

Figure 3.51 helps to visualize the differences in the spacing of the hard domains detected by SAXS with the spacing of polyurea aggregates detected in the TEM work.

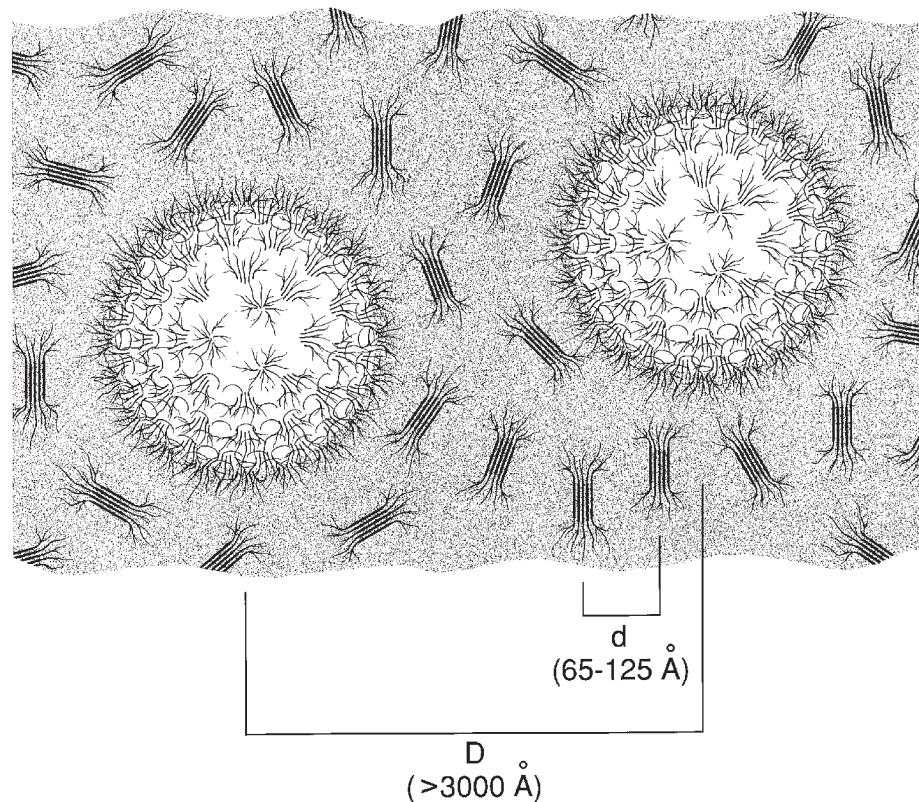


Figure 3.51 Comparative Spacings For Morphological Features

A second comment on the scattering profiles in Figure 3.50 is that the measured intensity increases with water content. Armistead showed this observation to be consistent with that predicted from SAXS theory applied to ideal two-phase systems.^{3,79} The anomaly of Foams 3 and 4 being transposed is thought to arise from the data normalization procedures. Those procedures assumed that a comparable mass of sample was exposed to the beam. Uncertainty in knowing how much material was actually exposed to the X-ray beam may account for the observed result.

Table 3.8 Diffuse Boundary Thickness for Slab Foam

| Foam | Water pphp | σ (Angstroms) |
|------|------------|----------------------|
| 1 | 2 | 2.3 |
| 2 | 3 | 4.0 |
| 3 | 4 | 5.1 |
| 4 | 5 | 5.2 |

The thicknesses of the diffuse boundary between hard and soft-segments were determined by analysis of deviations from Porod's law (see Reference 3.143 for details). That analysis gives an interfacial thickness parameter, σ (in angstroms), which is the half width of the assumed Gaussian distribution over which the phases are mixed at the interfaces. Integration of a corrected scattering curve is used to calculate a total scattering, which is related back to the degree of phase segregation. The results of the Porod law analyses are summarized in Table 3.8.

Foam 1 shows a σ value of 2.3 angstroms, and these values are seen to increase with hard-segment content up to a value of 5.2 angstroms for Foam 4. The reverse trend might be expected on the basis of an argument for formation of larger, better-ordered domains with increasing hard-segment content. The observed trend, however, indicates that the lengths of the chain-extended hard-segments are likely to be more polydisperse with increasing water content and that improved ordering at the interface may not be as possible with such asymmetric hard-segments. In any case, it can be concluded that the hard-segment domains are reasonably well segregated from the soft-phase.

In recent years, advances in small-angle X-ray technology have made it possible to conduct dynamic SAXS experiments during the formation of a flexible foam. This allows the study of the kinetics of hard-domain formation and phase separation. McClusky and co-workers studied the kinetics of microphase separation in TDI-based slabstock and HR foams.^{3,144} In conventional slabstock foams, they found that the microphase separation event coincided with the formation of bidentate urea, the viscosity increase and the cell-opening event. In HR type foams, they found that the microphase separation gave rise to a more intense scattering pattern than that observed in the conventional foam. Similar data for an all-MDI based HR foam was presented by Elwell, et al.^{3,145}

Summary

Figure 3.52 presents a summarizing model for the various events leading to a flexible polyurethane foam.

CURRENT MODEL FOR FOAM FORMULATION

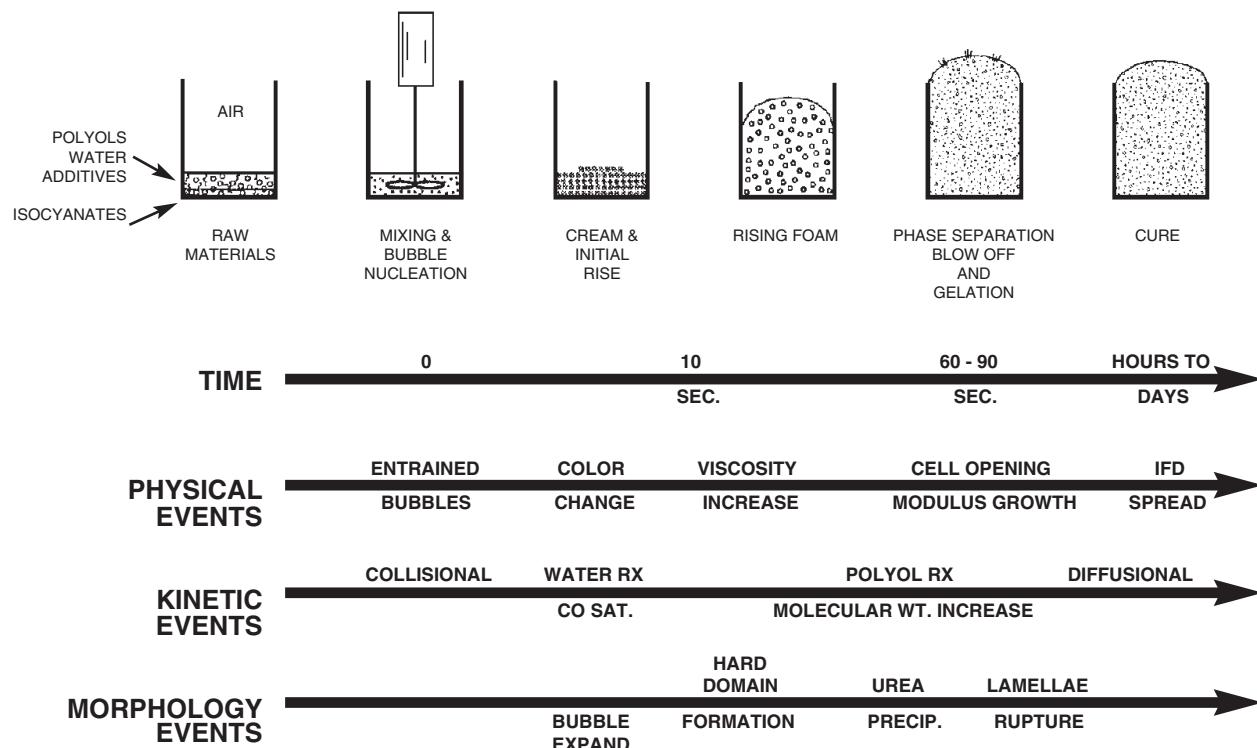


Figure 3.52 Summarizing Model For Foam Formation

Cells in the final foam are produced by gas diffusion into bubbles that are nucleated into the system at the time of mixing. The bubbles grow to a final size controlled by the amount of blowing agent available, the exotherm and the degree of bubble stabilization. Polymer morphology developments and mechanical factors govern the degree of cell-openness in the final foam. Geometric and morphological factors account for the wide range of physical properties available in flexible polyurethane foams.

The investigative tools described above were useful in reaching an understanding of the morphological structure of flexible polyurethane foams. Such knowledge will be invaluable in efforts to extend the performance characteristics of foams.

From the study above it can be concluded that simple TDI-based flexible slabstock foams have a morphology consisting of:

- A soft-segment phase,
- A hard-segment or microdomain phase, and
- With high enough water levels, a precipitated polyurea discontinuous phase.

A simplified model of these morphological structures is presented in Figure 3.53. While further work in this area is ongoing, this model should serve as a good base upon which to develop a more refined understanding of the structure property relationships in flexible polyurethane foams.

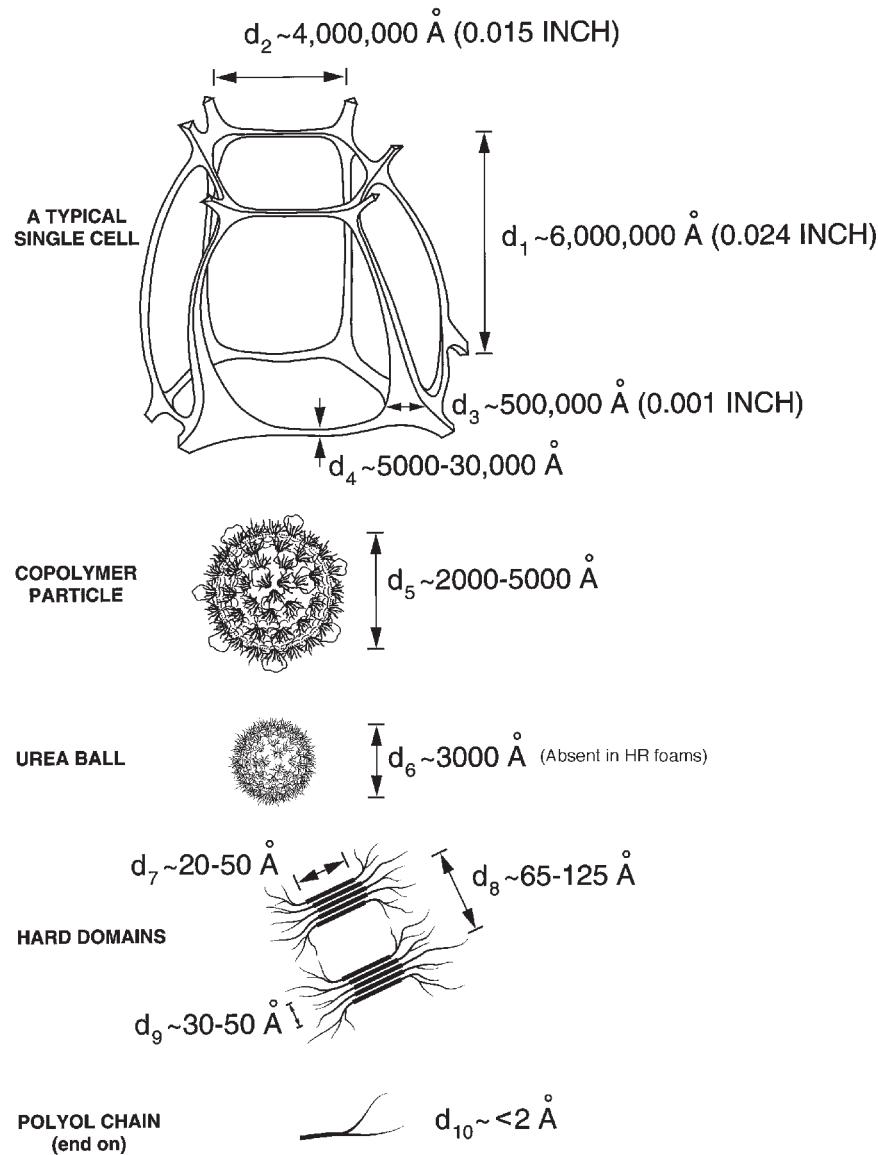


Figure 3.53 Simplified Model for the Morphological Features Found in Flexible Polyurethane Foams

References

- 3.1 Young, T. Phil. Trans. Royal Soc. (London) **1805**, 95, 65-87.
- 3.2 Laplace, P. S. Traite de Mecanique Celeste Vol. 4; Courcier: Paris, 1806.
- 3.3 Plateau, J. *Mem. Acad. Roy. Sci. Belgique* 1849, 23, 2nd series.
- 3.4 Bikerman, J. J. *Foams: Theory and Industrial Applications*; Reinhold: New York, 1953.
- 3.5 Kanner, B.; Decker, T. G. "Urethane Foam Formation - Role of the Silicone Surfactant"; *J. Cell. Plast.* **1969**, 5/1, 32-39.
- 3.6 LaMer, V. K. "Nucleation in Phase Transitions"; *Ind. Eng. Chem.* **1952**, 44, 1270-1277.
- 3.7 Baumhakel, R. "Influence of Stirring Velocity and Air Loading on the Formation of Flexible Urethane Foams"; *J. Cell. Plast.* **1972**, 8/6, 304-310.
- 3.8 Bunsen, R. "Ueber das Gesetz der Gas absorption"; *Ann.* **1855**, 93, 1-50.
- 3.9 Woods, G. W. *Flexible Polyurethane Foams, Chem. Tech.*; Applied Science: New Jersey, 1982, 142.
- 3.10 Saunders, J. H. "The Formation Of Urethane Foams"; *Rubber Chem. and Tech.* **1960**, 33, 1293-1322.
- 3.11 Walmsley, G. D. "The Production Chemist and Flexible Urethane Foam Technology"; *J. Cell. Plast.* **1965**, 1/1, 97-100.
- 3.12 Woods, G. W. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 98.
- 3.13 Buist, J. M. "Polyurethane Foams: Basic Equipment for Producing Flexible and Rigid Foams"; *Proceedings International Rubber Conference*, Washington, D.C., November 8-13, 1959, 9-20.
- 3.14 Buist, J. M.; Hurd, R.; Lowe, A. "Polyurethane Foams: Methods of Production, Properties and Applications"; *Chem. and Ind.* **1960**, 1544-1558.
- 3.15 Gemeinhardt, P. G. "Flexible Urethane Foam"; *In Handbook Of Foamed Plastics*; Bender, R. J., Ed.; Lake Publishing Corp.: Libertyville, Illinois, 1965, 215.
- 3.16 Hook, T.K. "Chemical Engineering in Urethane Foam Molding"; *Chem. Eng. Prog.* **1967**, 63/6, 94-100.
- 3.17 Walmsley, G. D. "The Production Chemist and Flexible Urethane Foam Technology"; *J. Cell. Plast.* **1965**, 1/1, 97-100.
- 3.18 Agabeg, R. C. "Intermediates For Polyurethane Foams"; In *Polyurethane Foams*; Healy, T. T., Ed.: Cliffe Books: London, 1963, 15.
- 3.19 Buist, J. M.; Gudgeon, H. *Advances in Polyurethane Technology*; Maclaren and Sons: London, 1968, 181.
- 3.20 Castro, J. M.; Romagnoli, J. A. "Analysis Of The Reaction Injection Moulding (RIM) Process"; In *Developments In Plastics Technology - 2*; Whelan, A.; Craft, J. L., Eds.; Applied Science Publishers: London, 1985, 49.

- 3.21 Blackwell, J. B. "Processing Equipment for Cellular Polyurethanes"; In *Developments with Thermosetting Plastics*; Whelan, A.; Brydson, J. A., Eds.; John Wiley and Sons: New York, 1975, 102-103.
- 3.22 Jackson, R. "The Formation and Coalescence of Drops and Bubbles in Liquids"; *Chem. Engr.* **1964**, 178, 107-118.
- 3.23 Uhlmann, D. R.; Chalmers, B. "The Energetics Of Nucleation"; *Ind. Eng. Chem.* **1965**, 57/9, 19-31.
- 3.24 Kumar, R.; Kuloor, N. R. "The Formation Of Bubbles And Drops"; In *Advances In Chemical Engineering*, Vol. **8**; Academic Press: New York, 1970, 255-363.
- 3.25 Holl, J. W. "Nuclei and Cavitation"; *J. Basic Eng.* **1970**, 92, 681-688.
- 3.26 Clift, R.; Grace, J. R.; Weber, M. E. *Bubbles, Drops and Particles*; Academic Press: New York, 1978.
- 3.27 Lubetkin, S.D. "The Fundamentals of Bubble Evolution"; *Chem. Soc. Rev.* **1995**, 24/4, 243-250.
- 3.28 Bessette, M.D.; Sundstrom, D. W. "Rheology of Model Polyurethane Foams"; *Polym. Proc. Eng.* **1985**, 3(1&2), 25-35.
- 3.29 Jones, R. E.; Fesman, G. "Air Flow Measurement and Its Relations to Cell Structure, Physical Properties, and Processability for Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 200-216.
- 3.30 Harding, R. H. "Morphologies of Cellular Materials" In *Resinography of Cellular Plastics*; ASTM STP 414, 1967.
- 3.31 Blair, E. A. "Cell Structure and Physical Properties of Elastomeric Cellular Plastics"; In *Resinography of Cellular Plastics*; ASTM STP 414, 1967.
- 3.32 Buist, J. M.; Ball, G. W.; Woods, G. "Flexible Foam: Manufacture and Properties"; In *Advances in Polyurethane Technology*; Buist, J. M., Gudgeon, H., Ed.; Maclarens and Sons: London, 1968, 152-154.
- 3.33 Meinecke, E. A.; Clark, R. C. *Mechanical Properties of Polymeric Foams*; Technomic: Conn., 1972.
- 3.34 Baumhakel, R. "Influence of Stirring Velocity and Air Loading on the Formation of Flexible Urethane Foams"; *J. Cell. Plast.* **1972**, 8/6, 304-310.
- 3.35 van Leuwen, B. G.; Powell, D. G.; Puig, J. E.; Natoli, F. S. "Physical and Chemical Approaches to Ideal Cushioning Foams"; In *Advances in Urethane Science and Technology Vol. II*; Technomic: Westport, Conn., 1973, 173-202.
- 3.36 Berlin, A. A.; Shutov, F. A.; Zhitinkina, A. K. *Foam Based On Reactive Oligomers*; Technomic: Westport, Conn., 1982, 85-87.
- 3.37 Clark, N. O.; Blackman, M. "The Degree Of Dispersion Of The Gas Phase In Foam"; *Trans. Faraday Soc.* **1948**, 44, 1-7.
- 3.38 Smith, C. S. "Some Elementary Principles Of Polycrystalline Microstructure"; *Met. Rev.* **1964**, 9/33, 1-51.
- 3.39 Frensdorff, H.K. "Polyurethane Foams; Stability, Collapse, Shrinkage"; *Rubber Age* **1958**, August, 812-818.

- 3.40 Owen, M. J.; Kendrick, T. C. "The Surface Chemistry of Polyurethane Foam Formation, II. The Role of Surface Elasticity"; *J. Colloid Interface Sci.* 1967, 24, 141-150.
- 3.41 Matzke, E. B. "The Three-Dimensional Shape Of Bubbles In Foam -An Analysis Of The Role Of Surface Forces In Three-Dimensional Cell Shape Determinations"; *Amer. Jour. Bot.* **1946**, 33/1, 58-80.
- 3.42 Jones, R. E.; Fesman, G. "Air Flow Measurement and Its Relations to Cell Structure, Physical Properties, and Processability for Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 200-216.
- 3.43 Kelvin, Lord "On the division of space with minimum partional area"; *Phil. Mag.* **1887**, 5s24: 503-514.
- 3.44 Kelvin, Lord "On the homogeneous division of space"; *Proc. Roy. Soc. London* **1894**, 55, 1-16.
- 3.45 Duchartre, P. *Elements de botanique*, Paris, 1867.
- 3.46 Kitchener, J. A.; Cooper, C. F. "Current Concepts in the Theory of Foams"; *Quarterly Reviews (London)* **1959**, 13/1, 71-97.
- 3.47 Plateau, J. *Mem. Acad. Roy. Sci. Belgique* **1869**, 37, 49.
- 3.48 Marangoni, C. *Nuovo Cimento* **1871**, (2), 5-6, 239.
- 3.49 Gibbs, J. W. *Collected Works Vol. I.*; Longmans Green: New York, 1928.
- 3.50 Ewers, W. E.; Sutherland, K. L. "The Role of Surface Transport In The Stability and Breakdown Of Foams"; *Austral. J. Sci. Res.* **1952**, A, 5, 697-710.
- 3.51 Blair, E. A. "Cell Structure and Physical Properties of Elastomeric Cellular Plastics"; In *Resinography of Cellular Plastics*; ASTM STP 414, 1967, 84-95.
- 3.52 Rossmy, G. R; Kollmeier, H. J.; Lidy, W.; Schator, H.; Wiemann, M. "Cell-Opening in One-Shot Flexible Polyether Based Polyurethane Foams. The Role of Silicone Surfactant and its Foundation in the Chemistry of Foam Formation"; *J. Cell. Plast.* **1977**, 13/1, 26-35.
- 3.53 Kollmeier, H. J.; Burkhardt, G; Klietsch, J.; Lammerting, H. "Reaction Sequences in High-Resilience Foam"; *Plast. Cmpd.* **1985**, July/August, 64-74.
- 3.54 Petrella, R. G.; Kushner, S. A. "Cell Opening Catalysts"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 186-190.
- 3.55 Patten, W.; Seefried, C. G., Jr.; Whitman, R. D. "Polymer-Polyols in the Development of High Resiliency Foams"; *J. Cell. Plast.* **1974**, 10/6, 276-282.
- 3.56 Boudreau, R. J. "How Silicone Surfactants Affect Polyurethane Foams"; *Mod. Plast.* **1967**, January, 133-138, 143-147, 234-240.
- 3.57 Dahm, M. "The Role of Surfactants during Polyurethane Foam Formation"; In *Cellular Plastics, National Academy of Sciences-National Research Council Publication 1462*; 52-63 (1967).
- 3.58 Schwarz, E. G. "Silicone Surfactants for Urethane Foams: Mechanism, Performance, and Applications"; In *Applied Polymer Symposia, No. 14: Silicone Technology*; John Wiley and Sons: New York, **1970**, 71-93.

- 3.59 Battice, D. R.; Lopes, W. J. "New Cell Opening Surfactants for Molded High Resiliency Polyurethane Foam"; *J. Cell. Plast.* **1987**, 23/2, 158-167.
- 3.60 Turner, R. B.; Nichols, J. B.; Kuklies, R. A. "The Influence of Viscosity in Cell Opening of Flexible Molded Foams"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988; 18-21.
- 3.61 Patent U.S. 4,579,700, K.D. Cavender to Union Carbide Corporation, April 1, 1986.
- 3.62 Cavender, K. D. "Novel Cell Opening Technology for HR Molded Foam"; *J. Cell. Plast.* **1986**, 22/3, 222-234.
- 3.63 Saunders, J. H.; Frisch, K. C. *Polyurethanes, Chemistry and Technology, Part I, Chemistry*; Robert Krieger: New York, 1978, 250-255.
- 3.64 Ostrogorsky, A. G.; Glicksman, L. R. "Rapid, Steady-State Measurement of the Effective Diffusion Coefficient of Gases in Closed-Cell Foams"; *Trans. ASME J. Heat Trans.* **1988**, 110, 500-506.
- 3.65 Foreman, P. J. "Automation of permeation measurement and its role in monitoring the ageing of cellular foams"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 268-273.
- 3.66 Miller, T. E.; Schmidt, D. L. "Methods For Detecting Cell Opening and Rate-Of-Rise In Flexible Foams"; *J. Cell. Plast.* **1983**, 19/5, 326-332.
- 3.67 Rossmy, G.R.; Kollmeier, H.J.; Lidy, W.; Schator, H.; Wiemann, M. "New Aspects in the Chemistry and Physics in the Formation of Flexible Polyurethane Foam"; *Proceedings of International Conference on Cellular and Non-Cellular Polyurethanes, Strasbourg, France, June, 1980*; Carl Hanser Verlag: Munich, Germany, 1980, 634-646.
- 3.68 Rossmy, G.R.; Kollmeier, H.J.; Lidy, W.; Schator, H.; Wiemann, M. "Mechanism of the Stabilization of Flexible Polyether Polyurethane Foams by Silicone-Based Surfactants"; *J. Cell. Plast.* **1981**, 17/6, 319-327.
- 3.69 Kostrzewski, W.; Lindt, J. T. "Flow Characterization Of A Chemically Blown Polymeric Foam III"; *J. Polym. Eng.* **1986**, 6/1-4, 187-199.
- 3.70 Burchell, D. J.; Porter, J. R. "Rheological Analysis of Modulus Growth: A Probe for Determining the Strength of Reacting Urethane Systems"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989; 144-148.
- 3.71 Horacek, H. "CIM of combustion-modified slabstock foam"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 90-93.
- 3.72 Artavia, L.D.; Macosko, C.W. "Polyurethane flexible foam formation"; In *Low Density Cellular Plastics*; Hilyard, N.C.; Cunningham, A.; Eds., Chapman & Hall: London, 1994, 47-55.
- 3.73 Yasunaga, K.; Neff, R.; Macosko, C.W. "Study of Air Flow Control in Flexible Polyurethane Foam"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 362-370.
- 3.74 Seefried, C. G., Jr.; Whitman, R. D.; Pollart, D. F. "Influence of Polymer Structure on High Resiliency Urethane Foams"; *J. Cell. Plast.* **1974**, 10/4, 171-180.
- 3.75 Noshay, A.; McGrath, J. E. *Block Copolymers, Overview And Critical Survey*; Academic Press: New York 1977, 365-389.

- 3.76 Gibson, P. E.; Vallance, M. A.; Cooper, S. L. "Morphology and Properties of Polyurethane Block Copolymers"; In *Developments In Block Copolymers-1*; Goodman, I., Ed., Applied Science Publishers: London, 1982, 217-259.
- 3.77 Wilkes, G. L.; Abouzahr, S.; Radovich, D. "Small Angle X-ray Scattering from Polyurethane Foams of Different Composition: An Analytical Method for Better Understanding Their Fine Structure"; *J. Cell. Plast.* **1983**, 19/4, 248-254.
- 3.78 Turner, R. B.; Spell, H. L.; Wilkes, G.L. "Dynamic Mechanical Spectroscopy Study of Flexible Urethane Foam"; *Proceedings of the SPI-28th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1984; 244-247.
- 3.79 Armistead, J. P. "Morphology of Water-Blown Flexible Polyurethane Foams"; MS Thesis, Virginia Polytechnic Institute and State University, Nov. 1985.
- 3.80 Abouzahr, A.; Wilkes, G. L. "Segmented Copolymers with Emphasis on Segmented Polyurethanes"; In *Processing Structure And Properties Of Block Copolymers*; Folkes, M. J., Ed., Elsevier Applied Science Publishers: London, 1985, 165-207.
- 3.81 Turner, R. B.; Wilkes, G. L. "Structure Vs. Properties of Flexible Urethane Foams Used in the Home Furnishing Industry (Polymer-Morphology)"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 935-940.
- 3.82 Armistead, J. P.; Wilkes, G.L.; Turner, R. B. "Morphology of Water Blown Flexible Polyurethane Foams"; *J. Appl. Polym. Sci.* **1988**, 35, 601-629.
- 3.83 Creswick, M. W.; Lee, K. D.; Turner, R.B.; Huber, L. M. "Urea Domain Structure in Polyurethane Foams"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988; 11-17.
- 3.84 Artavia, L.D.; Macosko, C.W.; Priester, R.D.; Schrock, A.K.; Turner, R.B. "An Integrated View of Reactive Urethane Foaming"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 509-518.
- 3.85 Artavia, L.D.; Macosko, C.W. "Polyurethane flexible foam formation"; In *Low Density Cellular Plastics*; Hilyard, N.C.; Cunningham, A.; Eds., Chapman & Hall: London, 1994, 22-55.
- 3.86 Priester, R.D.; Turner, R.B. "The morphology of flexible polyurethane matrix polymers", In *Low Density Cellular Plastics*; Hilyard, N.C.; Cunningham, A.; Eds., Chapman & Hall: London, 1994, Chapter 4.
- 3.87 Lidy, W.A. "The Polyurethane Flexible Slabstock Foaming Process. Chemistry and Physics Standards and Testing"; *UTECH '96-Processing Workshop 3*; Crain Communications: London, 1996.
- 3.88 Lidy, W.A.; Rightor, E.; Phan Thanh, H.; Cadolle, D. "New Insight into the Chemical and Morphological Differences Between Slab and High Resilient Foam Elastomers"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 119-135.
- 3.89 Cooper, S. L.; Tobolsky, A. V. "Properties of Linear Elastomeric Polyurethanes"; *J. Appl. Polym. Sci.* **1966**, 10, 1837-1844.
- 3.90 Cangelosi, F.; Shaw, M. T. "A Review Of Hydrogen Bonding In Solid Polymers: Structural Relationships, Analysis, And Importance"; *Polym. Plast. Technol. Eng.* **1983**, 21/1, 13-98.

- 3.91 Dow Polyurethanes: Technical Resources for Flexible Molded Foam Producers; The Dow Chemical Company; Form No. 194-924-589 SMG, 3.
- 3.92 Merten, R.; Lauerer, D.; Dahm, M. "IR Spectroscopic Studies of Urethane Foam Formation"; *J. Cell. Plast.* **1968**, 4/7, 262-275.
- 3.93 Rossmy, G. R.; Kollmeier, H. J.; Lidy, W.; Schator, H.; Wiemann, M. "Cell Opening in One-Shot Flexible Polyether Based Polyurethane Foams. The Role of Silicone Surfactant and Its Foundation in the Chemistry of Foam Formation"; *J. Cell. Plast.* **1977**, 13/1, 26-35.
- 3.94 Hauptmann, G.; Dorner, K. H.; Hocker, H.; Pfisterer, G. "Chemical and Physical Processes in the Manufacture of Flexible Polyurethane Foams"; *Proceedings of International Conference on Cellular and Non-Cellular Polyurethanes, Strasbourg, France, June, 1980*; Carl Hanser Verlag: Munich, Germany, 1980, 617-634.
- 3.95 Bailey, F. E.; Critchfield, F. E. "Chemical Reaction Sequence in the Formation of Water-Blown Urethane Foam"; *J. Cell. Plast.* **1981**, 17/6, 333-339.
- 3.96 Lidy, W.A.; Phan Thanh, H.; Cadole, D.; an unpublished presentation at the 1984 Gordon Conference on foams.
- 3.97 Menges, G.; Schwesig, H.; Hahn, H. "Quantitative Determination of Reaction during PUR Foam Formation"; *Org. Coat. Plast. Chem.* **1981**, 44, 229-233.
- 3.98 Cole, K. C.; Van Gheluwe, P. "Flexible Polyurethane Foam. I. FTIR Analysis of Residual Isocyanate," *J. Appl. Polym. Sci.* **1987**, 34, 396-407
- 3.99 Van Gheluwe, P.; Cole, K. C.; Hebrard, M. J.; Leroux, J. "Attenuated Total Reflectance Infrared Spectroscopic Analysis of High Index Foams"; *J. Cell. Plast.* **1987**, 23/1, 73-85.
- 3.100 Artavia, L. D.; Macosko, C. W. "Foam Kinetics"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 554-561.
- 3.101 Cole, K. C.; Van Gheluwe, P.; Dueck, C. L.; Martineau, P.; Leroux, J. "Thermal and FT-IR Analysis of the Polyurethane Foaming Reaction: The Effect of the Isocyanate Index"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988; 2-10.
- 3.102 Priester, R. D.; McClusky, J. V.; O'Neill, R. E.; Turner, R. B.; Harthcock, M. A.; Davis, B. L. "FT-IR A Probe into The Reaction Kinetics and Morphology Development of Urethane Foams"; *J. Cell. Plast.* **1990**, 26/4, 346-367.
- 3.103 Elwell, M.J.; Ryan, A.J.; Grunbauer, H.J.M.; Van Lieshout, H.C. "In-Situ Studies of Structure Development during the Reactive Processing of Model Flexible Polyurethane Foam Systems Using FT-IR Spectroscopy, Synchrotron SAXS, and Rheoogy"; *Macromol.* **1996**, 29/8, 2960-2968.
- 3.104 Harthcock, M. A. "FTIR Study Of Slabstock Polyurethane (Urea) Foams and Their Corresponding Compression Molded Plaques (Preliminary Report)"; Appendix A3 In *Morphology of Water-Blown Flexible Polyurethane Foams*; Armistead, J. P., MS Thesis, Virginia Polytechnic Institute and State University, Nov. 1985, 220-235.
- 3.105 Fuest, R. W.; Palinkas, R. L. "Engineering properties of castable urethanes"; *Conference Papers, UTECH 88*: Crain Communications: London, 1988, 32-35.

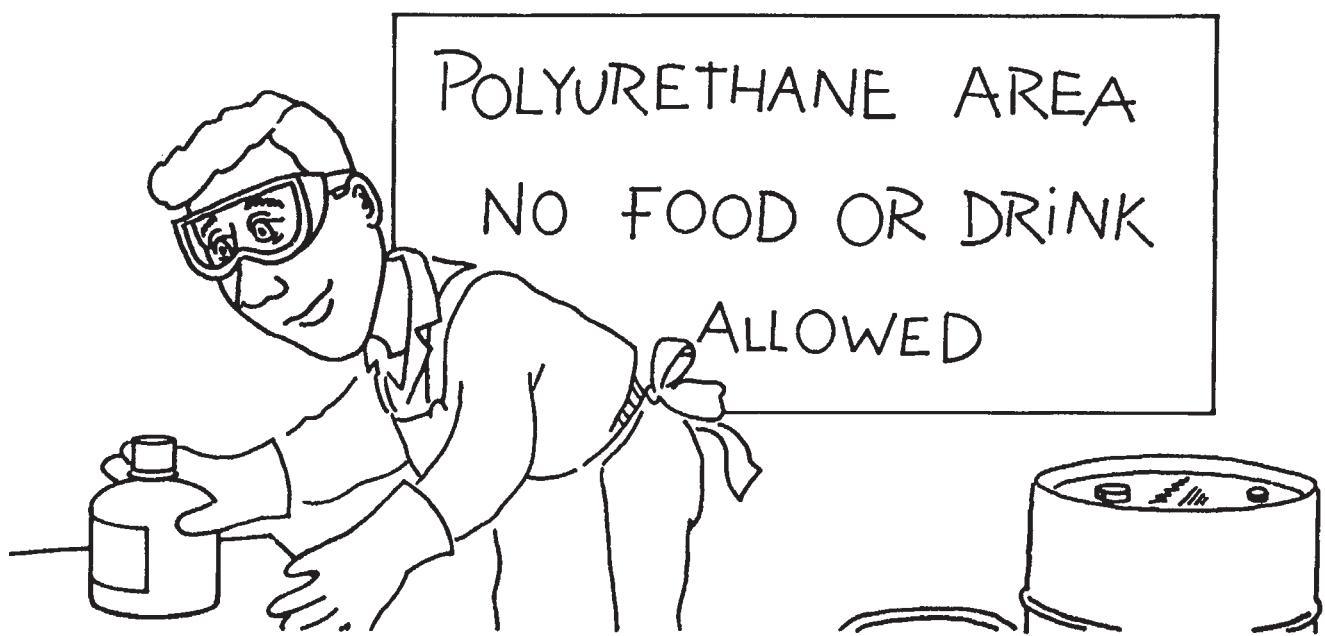
- 3.106 Clift, S. M. "Understanding the Dynamic Properties of Polyurethane Cast Elastomers"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 547-553.
- 3.107 Whitman, R. D.; Faucher, J. A.; Reding, F. P. "Urethane Foam Properties Related To The Fundamental Polymer Molecular Structure"; *Proceedings of the SPI-7th Annual Technical Conference*; The Society of the Plastics Industry, New York, 1963; Section 2-C, 1-8.
- 3.108 Darr, W. C.; Gemeinhardt, P. G.; Saunders, J. H. "Effect Of Molecular Structure On Properties Of Highly Cross-Linked Urethane Polymers"; *Ind. Eng. Chem. Prod. Res. Dev.* **1963**, 2, 194-199.
- 3.109 Seefried, C. G.; Koleske, J. V.; Critchfield, F. E. "Thermoplastic Urethane Elastomers. I. Effects of Soft Segment Variations"; *J. Appl. Polym. Sci.* **1975**, 19, 2493-2502.
- 3.110 Seefried, C. G.; Koleske, J. V.; Critchfield, F. E. "Thermoplastic Urethane Elastomers. II. Effects of Variations in Hard-Segment Concentration"; *J. Appl. Polym. Sci.* **1975**, 19, 2503-2513.
- 3.111 Redman, R. P. "Developments In Polyurethane Elastomers"; In *Developments In Polyurethane-1*; Buist, J. M., Ed., Applied Science Publishers: London, 1978, 47.
- 3.112 Patent U.S. 4,843,138, J. H. Tazewell et al to Firestone Tire and Rubber et al, June 27, 1989.
- 3.113 Gilch, H.; Rath, W. "Moisture Curing PU Hot Melt Adhesives"; *Conference Papers, UTECH 90*; Crain Communications: London 1990, 179-184.
- 3.114 Illinger, J. L.; Schneider, N. S. "Low Temperature Dynamic Mechanical Properties of Polyurethane-Polyester Block Copolymers"; *Polym. Eng. Sci.* **1972**, 12/1, 25-29.
- 3.115 Work, J. L. "Morphological Interpretation of the Dynamic Mechanical Properties of Some $(AB)_n$ Urea-b-urethane Copolymers"; *Macromol.* **1976**, 9/5, 759-763.
- 3.116 Christenson, C. P.; Harthcock, M. A.; Meadows, M. D.; Spell, H. L.; Howard, W. L.; Creswick, M. W.; Guerra, R. E.; Turner, R. B. "Model MDI/Butanediol Polyurethanes: Molecular Structure, Morphology, Physical and Mechanical Properties"; *J. Polym. Sci.: Part B: Polym. Phys.* **1986**, 24, 1401-1439.
- 3.117 Harrell, L. L. "Segmented Polyurethanes. Properties as a Function of Segment Size and Distribution"; *Macromol.* **1969**, 2/6, 607-612.
- 3.118 Lee, H. S.; Hsu, S. L. "An Analysis of Phase Separation Kinetics of Model Polyurethanes"; *Macromol.* **1989**, 22/3, 1100-1105.
- 3.119 Neff, R.; Macosko, C.W. "A Parallel-Plate Rheometer for the Study of Modulus Development and Cell Opening in Flexible Polyurethane Foam"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 386-392.
- 3.120 Neff, R.; Macosko, C.W. "A Model for Modulus Development in Flexible Polyurethane Foam"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 344-352.

- 3.121 Paik Sung, C. S.; Hu, C. B.; Wu, C. S. "Properties of Segmented Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate. 1. Thermal Transitions, X-ray Studies, and Comparison with Segmented Poly(urethanes)"; *Macromol.* **1980**, 13/1, 111-116.
- 3.122 Paik Sung, C. S.; Smith, T. W.; Sung, N. H. "Properties of Segmented Polyether Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate. 2. Infrared and Mechanical Studies"; *Macromol.* 1980, 13/1, 117-121.
- 3.123 Wang, C. B.; Cooper, S. L. "Morphology and Properties of Segmented Polyether Polyurethaneureas"; *Macromol.* **1983**, 16/ 5, 775-786.
- 3.124 Tyagi, D. *Structure-Property Relationships In Segmented Copolymers*; Ph.D. Thesis, Virginia Polytechnic Institute and State University, Chemical Engineering Dept., 1985.
- 3.125 Brumfield, H. L.; Estill, W. B. "Characterization of Foam Structure by Use of the Scanning Electron Microscope"; *J. Cell. Plast.* **1969**, 5/4, 212-220.
- 3.126 Kanakkanatt, S. V. "Mechanical Anisotropy of Open-Cell Foams"; *J. Cell. Plast.* **1973**, 9/1, 50-53.
- 3.127 Hilyard, N. C. *Mechanics of Cellular Plastics*; Macmillian: New York, 1982; 107.
- 3.128 Rhodes, M. B. "Applicable Technique of Optical Microscopy for Polyurethane Investigations"; *Cellular and Noncellular Polyurethanes, International Conference, Strasbourg, France, June, 1980*; Carl Hansen Verlag: Munich, Germany, 1980, 803-819.
- 3.129 Rhodes, M. B.; Khaykin, B. "Foam Characterization and Quantitative Stereology"; *Langmuir* **1986**, 2/5, 643-649.
- 3.130 Rhodes, M. B. "Under close scrutiny. Gaining by optical microscopy"; *Ureth. Tech.* **1988**, 5/3, 29-32.
- 3.131 Rhodes, M. B. "Microscopic Look Reveals Foam Structure"; *Rub. Plast. News* **1988**, 18/3, 27-28.
- 3.132 Rhodes, M. B.; Khaykin, B. "Multiple Stereological Parameter Characterization of Cellular Structures"; *Proceedings of The SPI-32nd Annual Polyurethane Technical/Marketing Conference*; Technomic, Lancaster, Pa, 1989; 178-182.
- 3.133 Chaffanjon, P.; Verhelst, G. "An Automated Image Analysis Method for the Characterisation of Flexible Foam Cellular Structure"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 545-552.
- 3.134 Rhodes, M.B. "Image Analysis as Applied to the Characterization of the Cellular Structure in Urethane Foams"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 548-551.
- 3.135 Reimann, K.A.; Iglehart, M.L.; Jourdan, J.S.; Ajbani, M.; Wujcik, S.E. "Cell Size Determination in Flexible Urethane Foams"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 112-118.
- 3.136 Chang, Y. P.; Wilkes, G. L. "Superstructure in Segmented Polyether-Urethanes"; *J. Polym. Sci. Phys. Ed.* **1975**, 13, 455-476.
- 3.137 Schneider, N. S.; Paik Sung, C. S.; Matton, R. W.; Illinger, J. L. "Thermal Transition Behavior of Polyurethanes Based on Toluene Diisocyanate"; *Macromol.* **1975**, 8/1, 62-67.

- 3.138 Bonart, R.; Morbitzer, L.; Hentze, G. "X-ray Investigations Concerning the Physical Structure of Cross-Linking in Urethane Elastomers. II. Butanediol As Chain Extender"; *J. Macromol. Sci. Phys.* **1969**, B3(2), 337-356.
- 3.139 Bonart, R.; Morbitzer, L.; Muller, E. H. "X-ray Investigations Concerning the Physical Structure of Cross-Linking in Urethane Elastomers. III. Common Structure Principles for Extensions with Aliphatic Diamines and Diols"; *J. Macromol. Sci. Phys.* **1974**, B9(3), 447-461.
- 3.140 Blackwell, J.; Gardner, K. H. "Structure of the hard segments in polyurethane elastomers"; *Polym.* **1979**, 20, 13-17.
- 3.141 Clough, S. B.; Schneider, N. S.; King, A. O. "Small-Angle X-ray Scattering from Polyurethane Elastomers"; *J. Macromol. Sci. Phys.* **1968**, B2(4), 641-648.
- 3.142 NCSASR. *User Notes for the 10-Meter SAXS Instrument*; ORNL: Oak Ridge, Tennessee, 1983.
- 3.143 Koberstein, J. T.; Morra, B.; Stein, R. S. "The Determination of Diffuse-Boundary Thicknesses of Polymers by Small-Angle X-ray Scattering"; *J. Appl. Cryst.* **1980**, 13, 34-45.
- 3.144 McClusky, J.V.; Priester, R.D.; Willkomm, W.R.; Heaney, M.D.; Capel, M.A. "The Use of FT-IR and Dynamic SAXS to Provide an Improved Understanding of the Matrix Formation and Viscosity Build of Flexible Polyurethane Foams"; *Proceedings of The Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 507-516.
- 3.145 Elwell, M.J.; Ryan, A.J.; Grunbauer, H.J.M.; Van Lieshout, H.C.; Lidy, W. "Structure development via FT-IR spectroscopy, synchrotron SAXS and rheology during the reactive processing of flexible polyurethane foam"; *Plast. Rub. Comp. Proc. Appl.* **1995**, 23/4, 265-276.

Chapter 4

Safety



The versatility of polyurethanes has made them the material of choice for many applications. To minimize potential risks in working with polyurethane chemicals and products, this chapter and the accompanying references should be studied thoroughly.

Chapter 4

Safety

R. Herrington, R. Morgan, J. Beckerdite

This section establishes methods for the safe handling of polyurethane chemicals, provides guidelines for the proper handling of hazardous materials, outlines the procedures for disposal of chemical wastes generated, and establishes methods for containment and cleanup of spills.

The reader is also encouraged to study the more detailed works found in References 4.1- 4.7.

HANDLING PRECAUTIONS SUMMARY

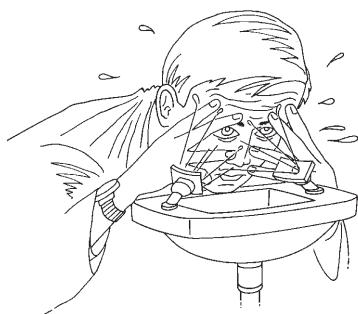
To minimize the hazards associated with the handling, use and storage of polyurethane chemicals and polymers, the following precautions and recommendations should be observed:

- Always wear the proper protective equipment.
- Never work alone when using or handling reactive chemicals.
- DO NOT inhale vapors, mists or dusts.
- Avoid skin and eye contact with all formulation chemicals.
- Handle freshly polymerized parts with care. Be aware of the potential hazards of vapors and of the heat of reaction/cure.
- DO NOT stack fresh polyurethane buns. Insulation of the heat can cause spontaneous combustion.
- Equip foam storage areas with sprinkler systems.
- Keep adequate quantities of isocyanate neutralizer available for quick decontamination of work areas in the event of spills or leaks.
- Never expose isocyanate in containers to water, amines or other reactive chemicals.
- Never expose polyurethane chemicals in closed containers to elevated temperatures.
- Never expose a polyurethane foam to an open flame or high-heat source.

HEALTH AND INDUSTRIAL HYGIENE

Refer to current Material Safety Data Sheets for the specific chemicals used in your process for safe handling procedures. Also follow the manufacturers' recommendations for protective clothing and other chemical handling precautions.

POLYOLS



These materials are typically mild irritants to eyes and skin and are very low in acute oral toxicity. Despite their relatively innocuous characteristics, they should be handled with appropriate caution and skin and eye contact should be avoided. Eye protection should be worn when polyols are handled. Polyols should be removed from the skin with soap and water. Eyes contacted with polyols should be flushed with large amounts of flowing water.

If other chemicals are blended into a polyol, the ventilation and handling requirements should conform to those for the most hazardous chemical in the blend.

ISOCYANATES AND PREPOLYMERS

These materials can be hazardous unless specific safety precautions are understood and practiced. Specific safe handling and disposal information should be obtained from suppliers.



Chemical worker's goggles should be worn when handling isocyanates. All isocyanate work areas should be equipped with an eyewash. If an isocyanate contacts the eyes, first aid must be administered immediately. The eyes should be held open while flushing with a continuous low-pressure stream of water for at least 15 minutes. Seek medical care immediately.

Repeated or prolonged skin contact may cause irritation, blistering, dermatitis or skin sensitization. It may also result in respiratory sensitization. In the event of direct contact with the skin, use a safety shower immediately, removing all clothing and shoes while washing. Wash the affected skin thoroughly, using plenty of water and a mild soap. Contaminated clothing should not be worn again until laundered. Leather items such as shoes, belts or watchbands should be destroyed.

Isocyanates are not likely to be swallowed in normal industrial operations and are low in oral toxicity, but some materials may burn the tissues of the mouth, throat and stomach if swallowed. In the event an isocyanate is ingested do not induce vomiting. Seek medical attention immediately.

Isocyanate vapors and mists are irritating to the nose, throat and lungs. Even brief exposures may cause irritation, difficult breathing and coughing. Toluene diisocyanate (TDI) has a relatively high vapor pressure at ambient temperatures and a vapor density six times that of air. Thus, open containers



or any use that releases TDI to the atmosphere will result in a relatively high concentration of TDI vapor which does not disperse easily. Sensitization to isocyanates may result from excessive exposure, and any subsequent exposure to very low concentrations might provoke an allergic reaction with symptoms like asthma. Isocyanates must always be handled in properly ventilated areas. Appropriate respirators must be worn whenever there is any possibility of exposure to vapors. If inhalation of isocyanate vapors occurs, the affected person should be moved promptly to a well-ventilated and uncontaminated area and all contaminated clothing should be removed quickly. Call a physician immediately.

The methylenediphenyl diisocyanate (MDI) based isocyanates have a lower vapor pressure and do not become airborne readily at room temperature. Aerosol or mists of these isocyanates are easily formed and should be treated with the same concerns discussed above.

SYSTEMS

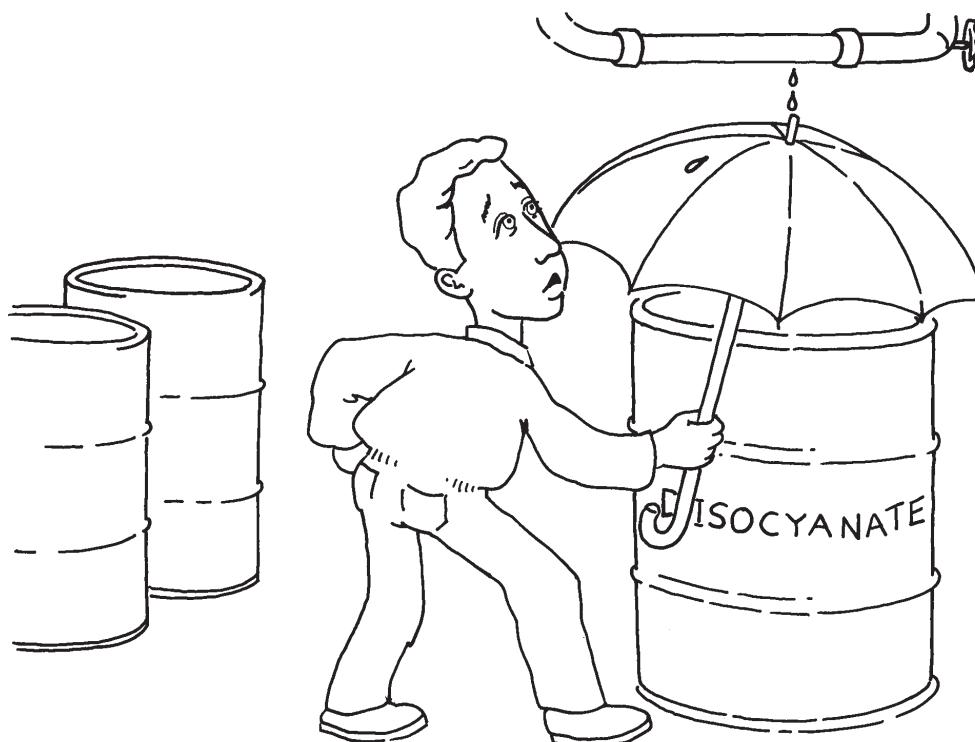
The polyol side of a system is typically not as hazardous as the isocyanate side; however, care and caution are recommended. Formulated polyol sides often contain volatile blowing agents or catalysts such as amines which may pose hazards under certain conditions. Good ventilation and proper handling precautions should be used as prescribed by the Material Safety Data sheets for these materials. If systems contain low-boiling fluorocarbons, they must not be stored at temperatures that may cause pressure buildup and cause containers to rupture.

The isocyanate side of a system is hazardous. Different systems may use different isocyanates. The most common isocyanates are based on MDI or TDI. These isocyanates may be present in different versions such as prepolymers, polymeric or crude materials. They should all be treated with equal respect because they are isocyanate products. Since inhalation may be

the most common route of exposure (skin contact being second), one must be aware of the product's vapor pressure. The various isocyanate products will have a vapor hazard in direct proportion to the amount of free monomer (TDI or MDI) present. Use at elevated temperatures will increase the vapor hazard.

OTHER RAW MATERIALS

Many other additives, such as surfactants, fillers, flame retardants, pigments and catalysts are used in various polyurethane applications. Each has its own profile of hazards and recommended safety precautions. It is essential that users contact their suppliers for specific instructions on the safe handling, use, storage and disposal of each of these products.



REACTIVE CHEMICALS

POLYOLS

Most polyols are low in volatility and have flash points (Pensky-Martens Closed Cup Test) in the range of 300-500°F (148-260°C). They are classified as Class IIIB Combustible Liquids. Being organic materials, they will burn under fire conditions to liberate water and carbon dioxide and when insufficient oxygen is present, some carbon (soot) and carbon monoxide.

See the manufacturers recommendations for fire fighting procedures. Polyols have no known explosion potential. However, as with all organic substances, if heated to decomposition in a confined area, they may generate sufficient volatiles to be an explosion hazard.

ISOCYANATES

Most commercial isocyanates have a high flash point and are classified as Class IIIB combustible liquids. However, they may burn in the presence of an existing fire or high heat source and adequate oxygen. The low volatility of isocyanates normally minimizes the potential hazard of explosion. However, under fire conditions in which a large concentration of isocyanate vapor may be generated, an explosion could occur.

Carbon dioxide or dry chemical extinguishers are effective for fighting fires. Water spray in large quantity is effective for large areas. Fire fighters must wear self-contained breathing apparatus to protect against nitrogen dioxide vapors as well as isocyanate fumes.

The most common causes of deterioration in the quality of isocyanates are exposures to water and heat. Careful consideration must be given to the steps necessary to prevent such exposures.

In contact with water, isocyanates react readily, producing heat and forming carbon dioxide and insoluble ureas. The pressure created by the evolved heat and carbon dioxide may be sufficient to rupture a closed container. Contact with formulations containing reactive hydrogen groups can produce more violent reactions. To protect isocyanates from atmospheric moisture contamination, all containers and equipment to be used should be carefully cleaned and purged with a dry, inert gas. Nitrogen that is also free of oil and dust is preferred.

Isocyanates should be stored in the appropriate temperature range to avoid freezing. If freezing occurs, follow the manufacturers recommendations for restoring the product to a useable state. High storage temperatures should be avoided since discoloration and dimerization may occur. At temperatures above 200°F (93°C), isocyanates may trimerize in an exothermic reaction to form isocyanurates, carbodiimides and carbon dioxide. These reactions may create a pressure hazard in closed vessels.

Isocyanates are incompatible with acids, bases, metal compounds such as copper, zinc, tin, or their alloys (including brass, bronze or galvanized materials), and organometallic catalysts such as mercury and tin compounds. Strong bases, such as sodium and potassium hydroxide or alkoxides, will catalyze the rapid formation of isocyanurates and carbodiimides. Normally, the trimerization reaction occurs first, furnishing heat to cause the carbodiimide reaction to occur. This second reaction liberates carbon dioxide and forms a solid or a foam that can only be removed from the vessel or line by mechanical means.

Avoid contamination of isocyanates by such compounds as alcohols, glycols, phenols, amines, amides and acid anhydrides. Such compounds react readily with isocyanates to form their corresponding addition products.

CATALYSTS

Many liquid amine catalysts have Open Cup flash points in the range of 20 to 115°F (-7 to 46°C) and are classified, depending on flash point, as flammable or combustible liquids. Because of their volatility and flammability, therefore, amine catalysts should be considered fire hazards.

BLOWING AGENTS

Although fluorocarbon blowing agents are generally considered nonflammable, they can, when heated to decomposition, generate quantities of carbonyl chloride (phosgene) and carbonyl fluoride. In addition, when confined and subjected to high temperatures, fluorocarbon blowing agents may also present a serious pressure hazard.

Like fluorocarbons, methylene chloride has neither a flash point nor a fire point as reported by any of the standard test methods. However, when heated to decomposition it will produce a variety of potentially hazardous materials such as hydrochloric acid, chlorine, carbon dioxide and carbon monoxide.

SPILLS

Current Material Safety Data Sheets (MSDS) for chemicals used should be referenced for information about safe spill, leak and disposal procedures. In the event of a spill or leak, expert advice can be obtained 24 hours a day from:

In the USA
Call CHEMTRAC
1-800-424-9300

In Canada
Call CANUTEC
1-613-996-6666

In Europe
Call Dow In Terneuzen
00-31-115-694-982

Isocyanate Spill Cleanup Protective Equipment

- Self-Contained Breathing Apparatus
- Chemical Protective Suit
- Chemical Protective Boots
- Chemical Protective Gloves



ISOCYANATES

Isocyanate spills and leaks should be contained and cleaned up only by properly trained and equipped personnel. All others should promptly leave the contaminated area. Protective equipment should include self-contained breathing apparatus and impervious clothings, footwear and gloves. An approved respiratory protective device MUST be worn whenever there is any possibility of exposure to concentrations of isocyanate vapors exceeding the O.S.H.A. permissible exposure limit ceiling of 0.02 ppm, or the 0.005 ppm time weighted average (TWA) threshold limit value.

All leaks and spills should be contained immediately to prevent contamination of the surrounding area. If the source of the leak is a damaged or leaking drum, immediately remove the drum to a well-ventilated, isolated area or outdoors. Carefully transfer the contents to a clean, leak-free, dry container. The damaged container should then be decontaminated and destroyed so it can't be reused. If the source of the leak is a damaged storage or holding tank, plug the container with a rubber or wooden plug. Then transfer the contents into a leak-free tank. Make sure the damaged storage tank is thoroughly cleaned before permanent repairs are attempted.

Sawdust (or other absorbent materials) and a liquid neutralizer are both used in cleanup procedures. A suitable liquid neutralizer consists of 5 percent aqueous ammonia (or sodium carbonate) and 1-2% detergent in water.

The area should be ventilated, if possible. Any standing pools of isocyanate should be pumped into closed top, not sealed containers for disposal. Cover

the remaining isocyanate with sawdust and then physically remove it to a suitable container for further decontamination and disposal. The spill area should be treated with the liquid neutralizer mixture. This liquid should be removed with more absorbent material. Final decontamination may be accomplished by spraying the spill site with large quantities of water. Move the containers to a safe location before proceeding with decontamination. Enough liquid neutralizer should be added to the containers to wet the sawdust thoroughly. All of these containers should be covered, but not sealed, for a period of 48 hours.

All sawdust should be kept wet with water to decrease the possibility of fire. During the reaction time, the containers should be placed in a well-ventilated area. After 48 hours, the containers may be closed but not tightly sealed, and further processed for disposal. The tools and equipment used must be decontaminated or properly disposed of.

If possible, prevent isocyanate from entering drains, since reaction with water may cause blockage. Checks should be made to determine that no residual active isocyanate adheres to the ground surface. If it does, then re-decontamination is necessary. The area can be declared safe and reoccupied after satisfactory air samples have been taken.

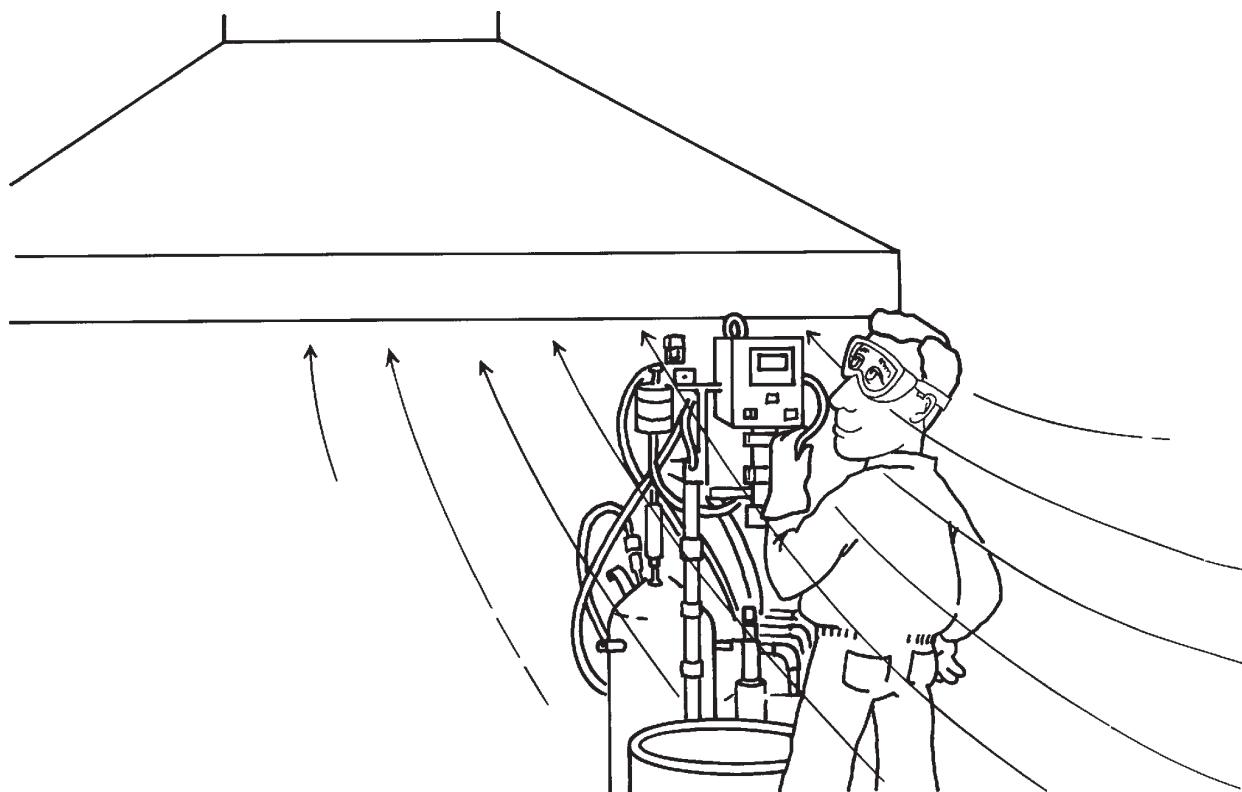
POLYOLS

Small spills on hard surfaces can be absorbed with sawdust and then swept up for disposal. Large spills should be diked and the material pumped into drums or vacuum trucks for disposal. Personnel engaged in cleanup should wear appropriate skin and eye protection.



VENTILATION

One risk in the use of isocyanates arises from inhalation of their vapors. During any activity using any isocyanates, it is essential to maintain adequate mechanical ventilation of the work area. If vapor concentrations cannot be controlled below exposure guidelines via ventilation, respiratory protection must be worn.



WASTE DISPOSAL

Only thoroughly trained and properly equipped personnel should be permitted to participate in disposal operations.

Waste isocyanates and waste polyols should be widely separated. All applicable federal, state and local regulations and ordinances must be followed. General guidelines for disposal of containers and waste chemicals from polyurethane operations can be found in References 4.8-4.9.

General liquid wastes comprise primarily the isocyanates, the polyols and auxiliary chemicals associated with them in the foam-making process. These may occur, for example, in the form of residues in empty drums or as unusable materials.

Solid waste polyurethanes are usually disposed of by incineration or landfill. Reuse, rebonding and recycling are also sometimes appropriate disposal methods.

ISOCYANATE WASTES

Disposal of liquid isocyanate wastes may be done in several ways, depending largely on the scale of operation. One method is reaction with waste polyol to make a low quality foam, which may then be incinerated. Another is to react the isocyanate, generally in small quantities, with isocyanate neutralizer and then incinerate. Be certain that all disposal procedures are conducted in strict compliance with all applicable federal, state and local regulations and ordinances. Mixing isocyanate with sawdust in plastic containers is an appropriate disposal method, but 48 hours must be allowed for reaction of the moisture in the sawdust with the isocyanate before the containers are closed (not tightly) and delivered to an incinerator.

POLYOL WASTES

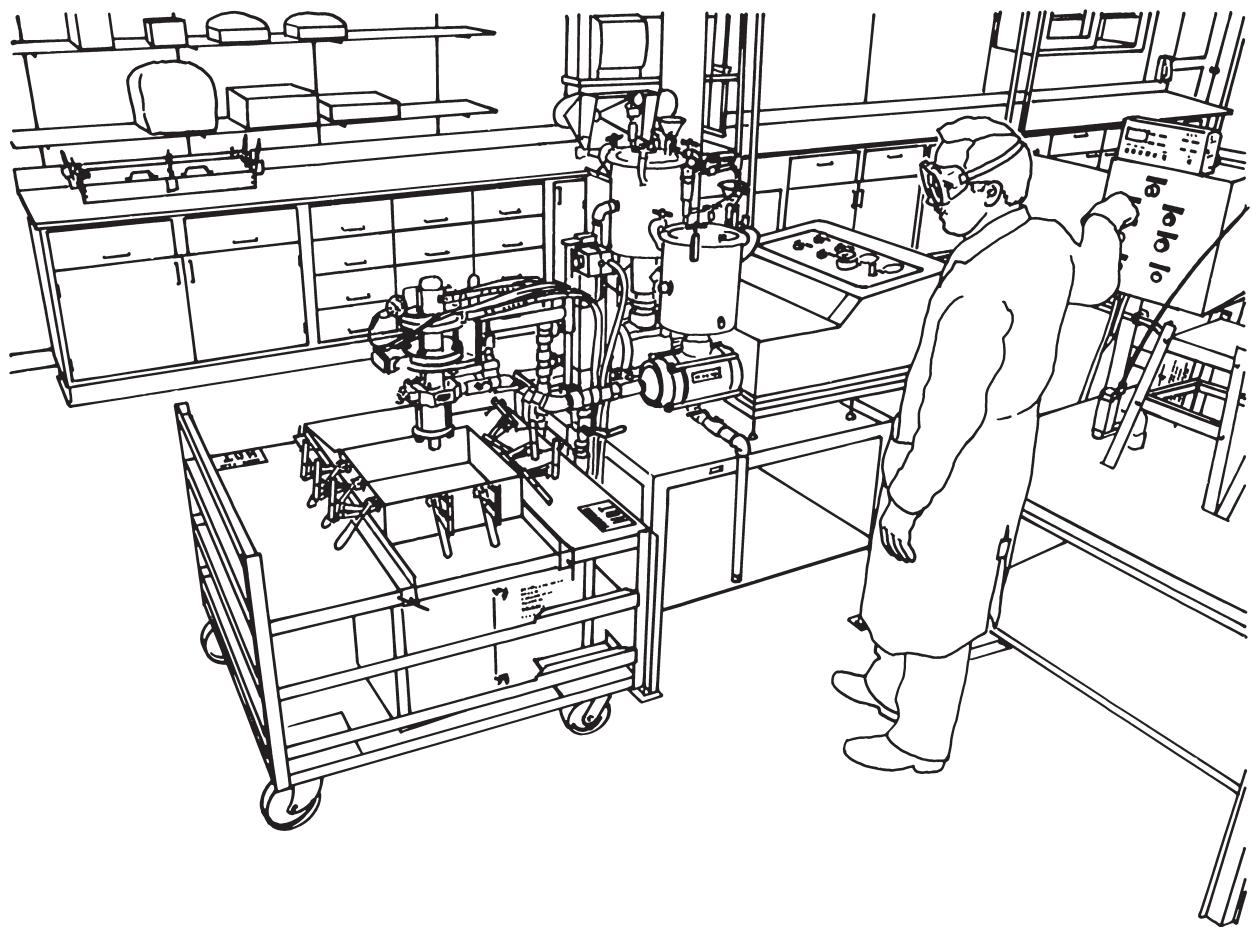
Polyols are preferably disposed of by burning in a suitable high temperature, low smoke producing incinerator in accordance with all applicable local, state and federal regulations.

References

- 4.1 Precautions for the Proper Usage of Polyurethanes, Polyisocyanates, and Related Materials; The Upjohn Company, 1981; Technical Bulletin 107, second edition.
- 4.2 *Safe Handling and Storage of VORANOL Polyether Polyols for Flexible Foams*; The Dow Chemical Company; Form No. 109-933-1188.
- 4.3 *Safe Handling and Storage of MDI-Based Isocyanates, Pure, Modified and Polymeric*; The Dow Chemical Company; Form No. 109-01224-295.
- 4.4 *Recommendations for the Handling of Toluene Diisocyanate (TDI)*; Technical Bulletin No. 1; Revised November 1980, compiled by the International Isocyanate Institute, Inc.
- 4.5 *Recommendations for the Handling of 4,4' Diphenylmethane Diisocyanate MDI Monomeric and Polymeric*; Technical Bulletin No. 4; December 1982 Edition, compiled by the International Isocyanate Institute, Inc.: Parsippany, NJ.
- 4.6 *Safe Handling and Storage of VORANATE T-80 Toluene Diisocyanates*; The Dow Chemical Company; Form No. 109-01243.
- 4.7 *Safe Handling and Storage of VORANATE Specialty Isocyanates*; The Dow Chemical Company; Form No. 109-546.
- 4.8 *Drum Handling Information Kit*; The Society of the Plastics Industry: New York, 1988.
- 4.9 Bastian, C. "Environmental Impact and Disposal of TDI and MDI"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 346-351.

Chapter 5

Flexible Foam Preparation



Development of flexible polyurethane foams proceeds through three stages: cup foaming, box foaming and machine foaming. Shown above is a laboratory-scale bench-top foam machine.

Chapter 5

Flexible Foam Preparation

**R. Herrington, K. Hinze, J. Porter, K. Skaggs, S. Burks,
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In this chapter, the basic principles and methods of preparing a flexible polyurethane foam are described. The chapter covers the general concept and provides some details as to how a concept might progress from the simplest hand or cup-foam mixes to the technique of box-foaming and ultimately to foam machine processing.

Most polyurethanes are processed quite differently from the other major plastic materials. The majority of thermoplastic materials are polymerized in large chemical factories and then sold to another processor as polymer granules, e.g., polyethylene pellets. These are then converted to useful end products by one of the thermoplastic processing techniques, which may include heating, shaping under pressure and then cooling and packaging. The properties of the plastic thus produced are almost entirely dependent upon the properties of the base polymer purchased from a chemical manufacturer. The polymerization of polyurethanes is more often carried out by independent outside processors, who often possess enough skill to achieve wide variations in the properties of products made from just a few base resins. In addition to providing the raw chemicals, the chemical manufacturer is often required to provide advice, technical information and even manpower assistance in helping the processor reach the desired products.

FOAM RECIPES

The number of variables in the formation of polyurethane foams is unlimited. Clearly, the development or selection of recipes that give high quality results at minimum cost is not simple. The task requires not only a knowledge of polyurethane chemistry, but also skill in the operation of dispensing machines of various types, and in the technology and art of evaluating the final product. Over the roughly 40-year commercial history of polyurethanes, many successful methods for producing foam have been developed and recorded in the literature. Many of the best foam recipes are

commercially available from Dow or other suppliers as fully formulated chemical systems. Such systems are often attractive to manufacturers who, because of volume requirements, in-house technical limitations, equipment or other restraints, feel a need to limit their involvement to the final mixing and distribution of the polyurethane materials.

FOAM PRODUCTION

The chemical reaction between a polyol and an isocyanate begins immediately when the two ingredients are mixed in the presence of suitable catalysts. Once started, the polymerization is exothermic to completion. Whichever method of mixing and dispensing is used, certain basic requirements for satisfactory foam production apply. These include the items shown in Table 5.1 and further discussed below.

Table 5.1 Basic Requirements for
Foam Production

- Temperature Conditioning
- Accurate Metering or Weighing
- Freedom from Contaminants
- Effective Mixing
- Curing Environment

TEMPERATURE CONDITIONING

The viscosity, density and chemical reactivity of polyols and isocyanates vary with temperature. Controlling the temperature of the components is therefore essential to the reproducible processing of polyurethane foams. For laboratory work at the cup or box-foam scale, this normally necessitates bringing sufficient stocks of chemicals into the lab a day or more before the actual time of foaming. This will allow the chemicals to equilibrate with the ambient lab temperature. In some cases, more precise control of component temperature may be justified. The use of excessively hot components can lead to inconsistencies in formulated foam recipes.^{5.1}

The effects of temperature variation on the polyurethane reaction may be complex. In most reaction mixtures, simultaneous and sequential chemical reactions take place. The various chemical reactions may be affected, to a different extent, by a change in component temperature. Variable product quality may be one result of uncontrolled temperature variations. Examples of changes in both foam processing and physical properties are given in References 5.2-5.4.

ACCURATE METERING

To make a foam, the conditioned chemicals must be mixed together in the proportions required by the formulation. Cup or box foaming allows for the weighing of components in the correct proportions. Most dispensing machines require the use of metering pumps to feed the components to a mixer in the correct proportions and at the required rate. Many types of metering systems are available and the reader is directed to References 5.5-5.11 for excellent reviews of the subject. As with any complex machinery, best results come from well maintained and operated equipment.

EFFECTIVE MIXING

One of the most critical factors affecting foam production is the effective mixing of multiple components. These components are often of widely varying viscosity. Incomplete mixing can produce foam that has both cosmetic and physical deficiencies.

CURING

In general, polyurethanes do not develop their ultimate properties until some hours or days after initial mixing. Many foams cure satisfactorily and develop properties simply through storage at room temperature. Other systems may benefit from a post-cure heating cycle. The optimum processing and curing conditions must be investigated for each type of flexible foam.

FREEDOM FROM CONTAMINATION

Defects in polyurethane foams are often eventually linked to contaminants. Contamination is defined as the presence of any unintended foreign material in the foam preparation system. Some historically known contaminants are discussed below.

General Contaminants

During the roughly 40 year history of polyurethane commercial production, contamination effects from many (often surprising) sources have been recorded. Some of these are listed below:

- Particulate dirt in the system or falling into the rising foam.
- Liquid drips into the rising foam, onto substrates or onto mold surfaces prior to foam dispensing.
- Residual material remaining in systems from previous runs.
- Residual acids or bases in raw materials.
- Activated carbon fines from treated water supplies.
- Incomplete removal of solvents or detergents used in cleaning equipment.
- Buildup of rust or scale in machinery components (especially in tanks containing amines).

- Pipe dope or cutting oils used in fabrication and installation of new lines.
- Silicone- or Molybdenum-based greases.
- Use of copper, brass or zinc in lines carrying amines or amine/polyol blends.
- Use of plastic syringes in dispensing chemicals.
- Oil or water in compressed air or nitrogen supplies.
- Use of rubber hoses for polyol transfer lines. Only high-quality, plastic-lined or metal hoses should be used.
- Water/glycol from heat exchanger leaks.
- Hydraulic oils from mixing head leaks.
- Dioctyl phthalate (DOP) from seals or equipment flushing.
- Drifting aerosols of oil or wax.
- Lubricants/greases in new pumps and valves.

An example of the effect selected contaminants can have is given in Figure 5.1.

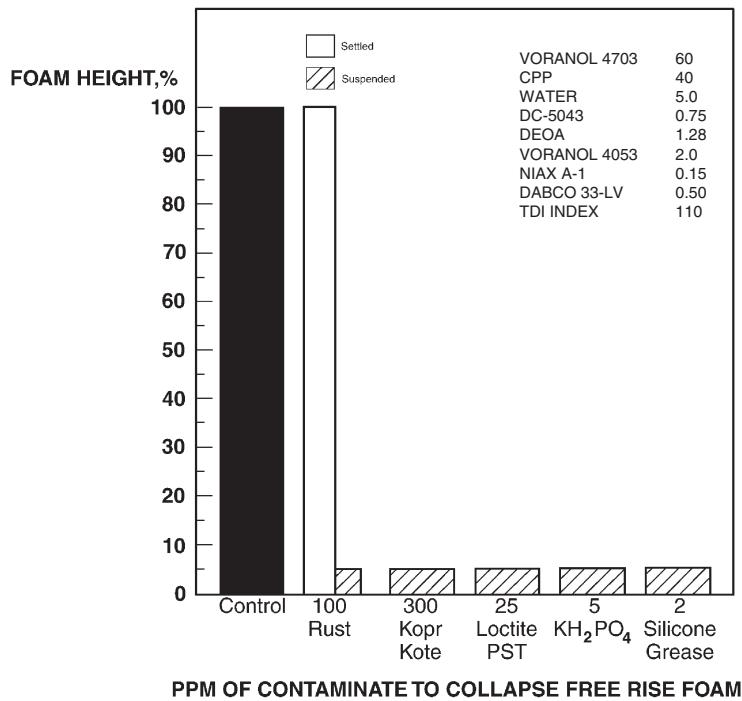


Figure 5.1 Contamination Study in Low-Density HR Foam

The figure compares what minimum level of five specific contaminants would be needed to cause total collapse of a free-rise HR foam of the indicated formulation. To obtain the data, polyol masterbatches were prepared, spiked with a contaminant, and then used to prepare free-rise cup foams in the normal manner. The rust was obtained from natural sources. Kopr-Kote and Loctite PST are commercial pipe dope compounds.

Monobasic potassium phosphate was introduced by first dissolving the solid crystals in water. The silicone grease was a common laboratory grade of stop-cock grease.

The experimental observation was that the foams would rise to a maximum height and then collapse. Two parts per million of silicone stop-cock grease was sufficient to cause boiling with no foam rise. It should be emphasized that such results are highly formulation dependent. A greater or lower concentration of contaminants may be needed to cause processing or physical property problems in other formulations.

Problems have also been encountered when excessive amounts of entrained air are allowed to form in viscous polyol streams. Entrained air is helpful to a certain degree in proper nucleation of a foam mixture. The amount of entrained air that can be tolerated depends on the formulation, the metering system, the mixer geometry and the desired final foam cell-structure. If the amount of air becomes excessive, metering problems can result, pea holes can form and in severe cases, total foam collapse can occur.^{5,12} For best results, it is recommended that the amount of air entrained due to material handling be minimized. Some operating situations that may lead to excessive entrained air include:

- Transferring polyol from a drum carelessly.
- The absence of a return dip pipe in polyol tanks. With a dip pipe, the polyol stream does not have to fall through a vapor space when the tank is loaded or recirculated.
- Formation of a vortex (e.g., from excessive stirring) in feed tanks.
- Leaking seals on the suction side of feed pumps.
- Leaking seals on mechanical mixing heads.
- Too large or too long a discharge nozzle or hose.
- Splash during lay-down of the foam mixture.

Dissolved Gases

A definition for dissolved gases is: those molecules of gas present as a “solute” phase in a polyol or isocyanate. Figure 5.2 helps to differentiate dissolved gases from the entrained air mentioned above.

Normally the dissolved gases in a polyol are limited to oxygen and nitrogen, and problems arise when suitable concentrations are not present. Many hydrocarbons are soluble in polyol. During foam preparation, volatilization of the hydrocarbon can produce excessive gas concentrations that lead to the formation of pea holes in the final foam.

The amount of dissolved air in an isocyanate is reported to vary widely and to be a function of pad gas pressure.^{5,13-5,14} Excessive amounts of dissolved gas in the isocyanate are reported to lead to foam collapse.^{5,15-5,16}

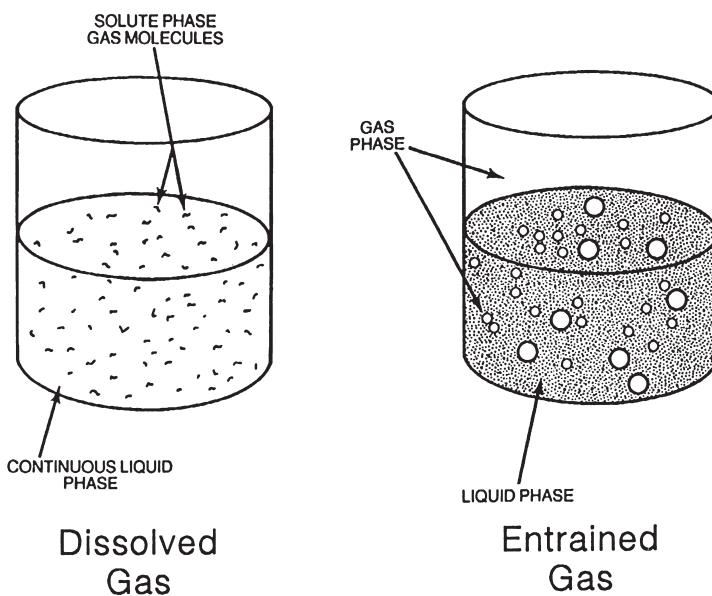


Figure 5.2 A Conceptual Comparison of Dissolved and Entrained Gas

Peroxides

Polyether polyols are easily oxidized.^{5.17} The existence of hydroperoxides and their decomposition products in polyols has been reported.^{5.18-5.20} An analytical procedure for the measurement of peroxide content in polyols is available.^{5.21} Hydroperoxides arising from oxidative degradation of polyether polyols have a half-life of only several minutes at elevated polyol temperatures.^{5.22} Thus, it is possible that the absence of peroxides in freshly prepared polyols that have been dewatered at high temperature, is not necessarily an indication that oxidation has not occurred. The decomposition products of polyether-based hydroperoxides have been shown to cause a loss of reactivity in foam formulations.

At normal storage and handling temperatures, significant concentrations of peroxides can build up with time. Engineering controls to preclude oxygen exposure and/or antioxidant additive technologies are necessary to ensure consistent product performance. It is noted that low parts per million (e.g., less than 10) concentration of peroxides in polyol has a detrimental effect on polyol reactivity and foaming behavior.^{5.23} Similar problems result with copolymer polyols containing residual peroxide-based grafting catalyst.^{5.24} Oxidation of the tin catalyst by peroxide is the most commonly reported problem.

Trace concentrations of peroxides in isocyanates or isocyanate prepolymers can lead to the formation of color bodies.^{5.25} Degradation of surfactant performance has also been linked to the presence of peroxides.

Water

An important consideration in handling, storing and conditioning polyurethane chemicals is to avoid contamination with water or atmospheric moisture. Most polyols used in foam production are somewhat hygroscopic. Storage containers should be designed and operated to avoid any such exposure. In machinery tanks, this is usually done by blanketing the contents with a small overpressure of dry nitrogen. If the dry nitrogen is allowed to continuously flush through leaking tank seals, the water content of a formulated polyol can be undesirably reduced. Condensation of moisture on tank walls can occur if a wet pad gas is used. Precise control of the water content is important because small variations in water content often have a major effect on the properties of the final product.

Simple inorganic salts introduced via domestic water supplies have been found to influence foam processing and properties. Foam discoloration has been linked to the presence of iron ions in the water supply.

SCALES OF FOAM PRODUCTION

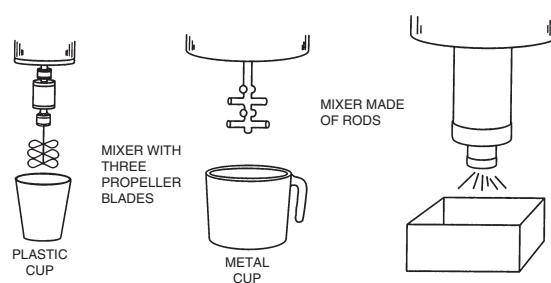
Foam-making reactions are generally carried out at one of the three scales detailed in Table 5.2.

Table 5.2 Stages of Foam Production

| Foaming Scale | Nominal Requirements | | |
|---------------|----------------------|-----------|----------|
| | Personnel | Materials | Time |
| Cup-Foamer | 1 | 1 gal | 1 day |
| Box-Foamer | 1 | 1-5 gal | 1 day |
| Machine | variable | 5-55 gal | 1-5 days |

For a given foam formulation, the different scales of mixing are known to produce foams of different cell-sizes. Figure 5.3 illustrates this result using data from a HR molded foam study.

To obtain these data, one large masterbatch of a typical low-density HR molded foam formulation was made up and distributed among the three foam-making stations. All foams were then prepared on the same day using a consistent procedure. The number of cells increased with successively larger scales of mixing. Mixer rpm also varied from 1200 for the cup-foamer, to 3600 for the box-foamer and finally 5000 for the Admiral 150 machine. From the cup-foamer to the machine foam, cell-count was more than doubled. Figure 5.4 illustrates how the foam physical properties changed with increasing cell-count. These observations relating to cell-count and resultant physical properties are consistent with those widely reported in the literature.^{5,26-5,33}



CELLS PER CUBIC CENTIMETER

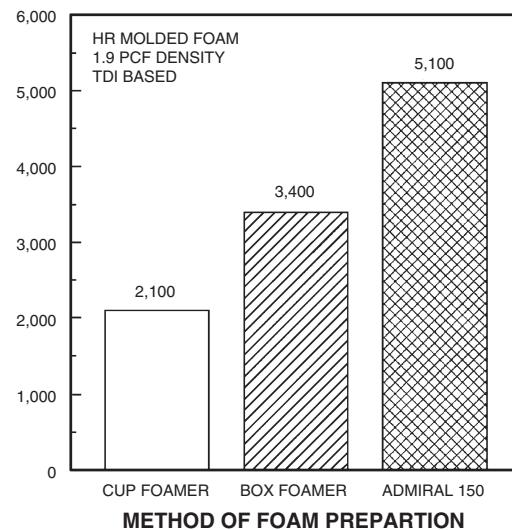


Figure 5.3 Effect of Mixing Scale on Cell-Size

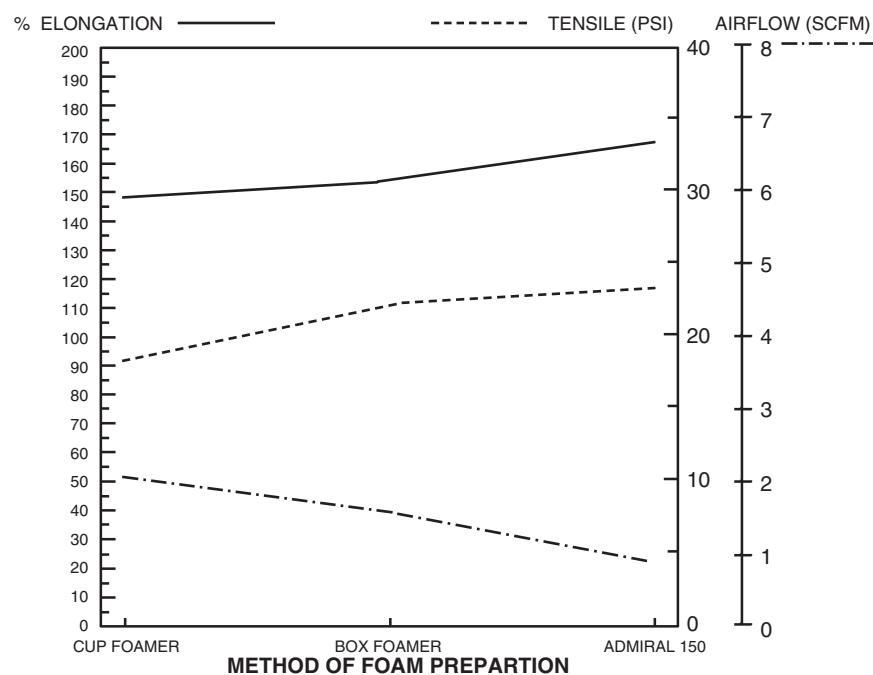


Figure 5.4 Effect of Cell-Count on Physical Properties

LABORATORY-SCALE CUP-FOAMING

Small-scale hand-mixed preparation of foams has been shown to be of value in production as well as the laboratory for fast and approximate evaluations of foaming systems. An example of a laboratory cup-foaming situation is shown in Figure 5.5. With care, reasonably reproducible results can be obtained. Some of the useful functions hand mixing can perform are:

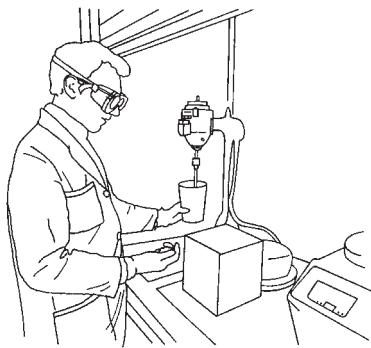


Figure 5.5
Laboratory-Scale Cup-Foaming

- Evaluating raw materials in existing formulations.
- Checking the approximate cream and rise time of a formulation before a large machine run is made.
- Determining levels of catalysts, additives, blowing agents, etc., in new formulations.
- Checking the efficiency of silicone surfactants.
- Checking catalyst stability and activity.
- Checking for suspected contamination of raw materials.
- Training new personnel in formulation variables.

Generally, hand-mixed foams are prepared as free-rise buns. With practice, satisfactory prototype molded parts can be made. To obtain data most useful to production, hand-mixed components should be handled in essentially the same manner as in production. For instance, if in production the polyol is preblended in a masterbatch with water, catalyst, etc., the same masterbatch should be prepared for hand mixes. Controlled experiments have shown significant differences in processing and foam properties between polyol masterbatches and freshly blended and foamed components. Regardless of the care and expertise employed in preparing hand-mixed foams, there are differences in processing and foam properties of these small foams compared to analogous formulations prepared in larger box-foaming equipment and production machines. Several factors including mass effects, heat effects and mixing shear effects are believed to be responsible for these differences. Hand-mixed cup foams should therefore be used only as first approximations of formulation processing and properties.

TYPICAL EXPERIMENTAL PROCEDURE

The following procedure and Figure 5.6 are given as an example of how to prepare a hand-mixed cup foam. Modifications of this procedure are common, depending on particular needs and size of foam desired. Other methods of cup-foam preparation can be found in References 5.34 and 5.35.

Equipment and Supplies:

- Laboratory mechanical or electrical stirrer with blade mixer and variable-speed mixing in the desired rpm range.
- One-quart-capacity cylindrical paper cups or plastic disposable beakers.
- Syringes or other means of dispensing 0.1 to 10 gram quantities of catalysts, surfactants, additives, etc.

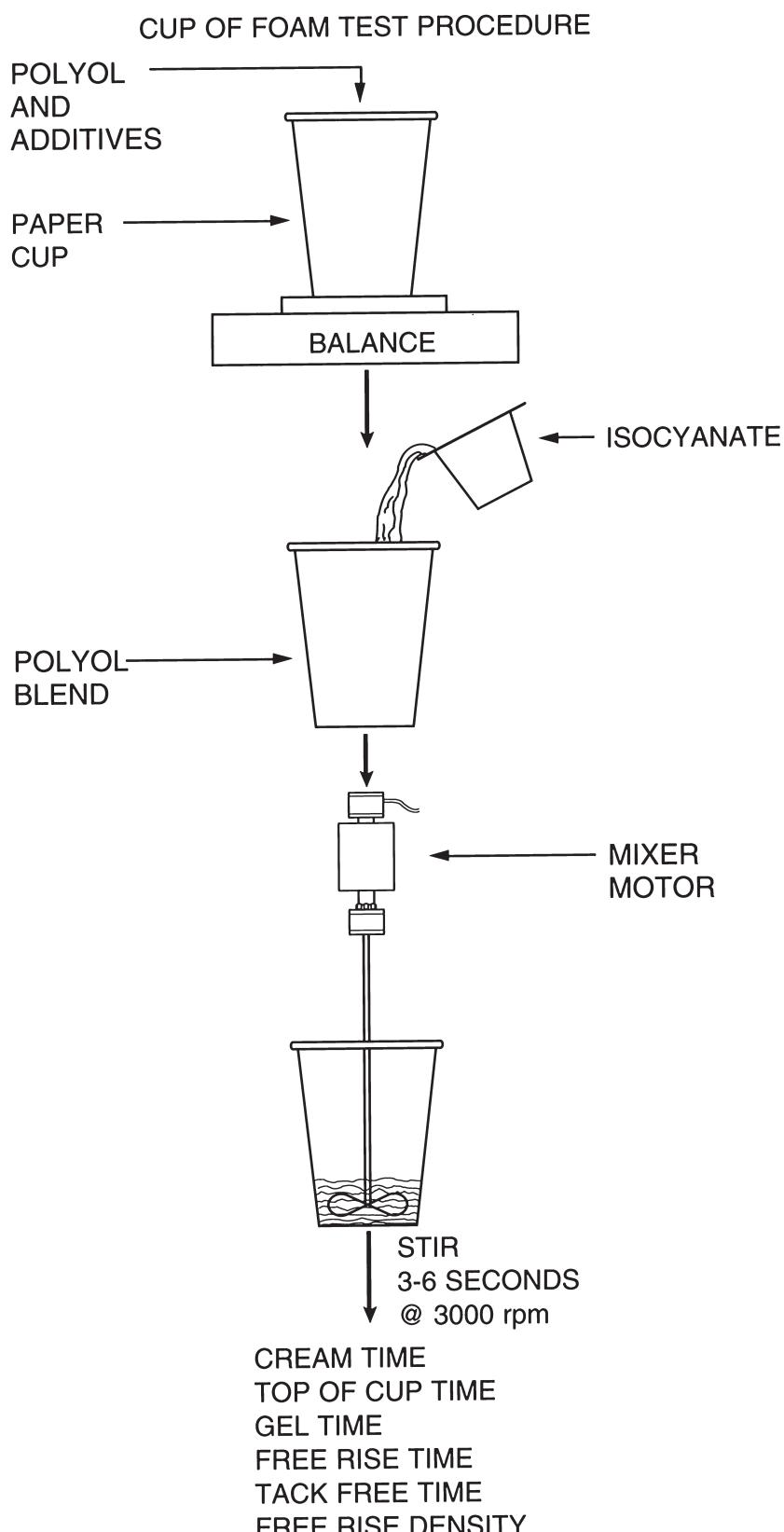


Figure 5.6 Steps of the Cup-Foaming Procedure

- Stopwatch or other timing device.
- Cardboard boxes or other containers of suitable size to hold the foam being prepared.
- Laboratory balances.
- Miscellaneous sizes of glass or plastic bottles to hold formulation components.
- Methylene chloride or other solvent for cleaning mixer.

NOTE: Hand-mix foam operations should be carried out in a laboratory fume hood. Operators should wear appropriate protective equipment such as lab coat, chemical workers goggles and protective gloves. To obtain reproducible cream, rise and gel times, it is recommended that all foam components be maintained at a controlled starting temperature. For comparison purposes, a control foam should be made.

Procedure:

1. Weigh out the polyol (generally 100-200 gram charges) into a suitable mixing container.
2. Weigh out the required amount of isocyanate into a disposable beaker.
3. Add water, catalysts and other ingredients to the polyol using syringes or by weight. Mix thoroughly for 10 to 30 seconds.
4. Add tin catalyst if needed and mix again.
5. Add isocyanate and mix again for 3 to 5 seconds depending on cream time.
6. Pour mixture into suitable box or mold.
7. Record cream, rise and gel times.
8. Clean stirrer with desired solvent.

The quantities of foam produced can be varied along with the exact technique used. Any number of different additives can be incorporated and tested for gross effect on properties and processing. If the foam is to be tested, it should be allowed to cure over night at room temperature. Cure may be accelerated by placing the foam in an oven at 250 °F (121 °C) for 30 minutes. Molded foams may be prepared by pouring the mixed formulation into small prototype molds. Heat-curing of hand-mixed cup foams should be the same as for actual or anticipated production cycles.

Recent refinements to the traditional types of cup-foam procedure are discussed in References 5.36-5.37. Reductions in the procedural and equipment variability have been shown to improve the accuracy and reliability of a simple cup foam test.^{5.36} Reference 5.37 further discusses the statistical accuracy of the cup foam test and demonstrates the further improvements available through use of an ultrasonic foam rise sensor and computer processing of the raw data.

LABORATORY BOX-FOAMS

Another useful tool in flexible foam formulation development is the laboratory box-foam machine. With the box-foaming procedure, a foam block suitable for physical property testing can be produced with from 500 to 1000 grams of polyol. The smallest development-size flexible slabstock foam machine would require from 150 to 300 pounds of polyol to produce a foam block suitable for sampling for foam physical property testing. Due to the small volume of raw materials used and wastes generated with the laboratory box-foam machine, it has become vital to foam research and development.

LABORATORY BOX-FOAM MACHINE

A suitable laboratory box-foam machine consists of at least an 8-horsepower electric motor equipped with a clutch and brake mechanism to allow for the instantaneous start and stop of the agitator. Several agitator designs may be used, but the pin type is the most common. The electric motor is mounted on a frame inside a fume hood. A typical layout for a box-foaming station is shown in Figure 5.7. The frame is equipped with two nitrogen-actuated pistons, attached to a ram plate suitable for holding the mixing cup. During

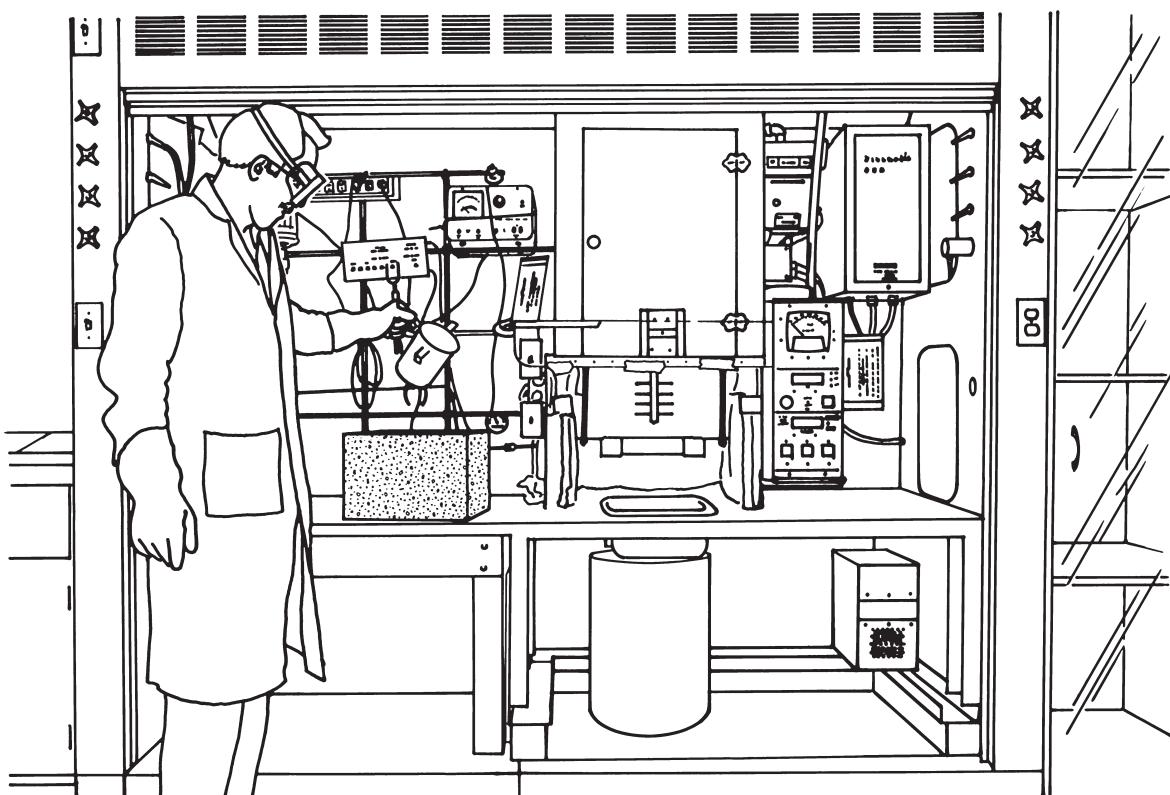


Figure 5.7 Typical Box-Foaming Station

the mixing cycle the pistons raise the mixing cup over the agitator and hold the cup against a gasket to prevent splashing of the liquid components. The mixing cup is equipped with a handle and with a collar to hold the cup in position in the ram plate. The agitator and mixing cup are constructed of stainless steel.

The laboratory box-foam machine is also equipped with an electronic controller with three semiautomatic mixing cycles. The controller allows the operator to preset the mixing time and agitator speed of each of the three cycles. The controller also starts a timer at the end of the second mix cycle to allow the operator to determine the cream and rise time of the foam formulation. The three cycles are referred to as:

Cycle 1—PREMIX CYCLE
Cycle 2—ISOCYANATE MIX
Cycle 3—SOLVENT WASH CYCLE

LABORATORY BOX-FOAMING EQUIPMENT

Other equipment necessary for producing laboratory box-foams are:

- Single pan electronic balance with a capacity of at least 4000 grams and readability of at least 0.1 grams (the balance must be located in the fume hood if the isocyanate is to be measured gravimetrically).
- Disposable plastic beaker suitable for holding the isocyanate to be used in the formulation when gravimetric addition is used or large graduated cylinder for the isocyanate if volumetric addition is used.
- Other plastic beakers, pasteur pipettes or syringes, either glass or plastic suitable for dispensing the water, auxiliary blowing agents, surfactant, amine catalyst, tin catalyst and other additives.
- Wood or fiberboard boxes measuring 15" x 15" x 12" for pouring slabstock foam formulations. The boxes are lined with white paper (coated side down) or polyethylene bags. Metal molds measuring up to 17" x 17" x 6" may also be used. The molds should be coated with an appropriate mold-release compound.
- One gallon or smaller container suitable for transferring the polyol into the mixing cup.
- A second fume hood or ventilated foam-block storage cabinet suitable for storage of fresh foam blocks that are giving off isocyanate or other vapors.
- A supply of solvent for cleaning residual polymer from the agitator and mixing cup.
- A 5-gallon plastic bucket suitable for holding the waste solvent wash.

LABORATORY BOX-FOAMING PROCEDURE

The mixing operation and the transfer of all chemicals should be carried out in a fume hood. The operator should wear the appropriate protective equipment such as a lab coat, chemical workers goggles and protective gloves. All ingredients used in the formulation should be allowed to equilibrate at room temperature before use. The formulation is prepared in the following sequence:

1. Make sure that the box foamer is ready for operation and set the desired mixing time and agitator speed for the three cycles.

2. Dispense the desired weight or volume of isocyanate into a disposable plastic beaker or glass graduated cylinder.
3. Place the mixing cup on the electronic balance and weigh in the desired amount of polyol, auxiliary blowing agent, water, silicone surfactant, amine catalyst(s), tin catalyst and other additives.

Note: For repeated usage of water, amine catalyst and silicone surfactant at the same predetermined levels, a masterbatch of these ingredients is recommended for the consistency and convenience. If the tin catalyst is added gravimetrically, a freshly prepared 10 weight percent solution in dry polyol can be used.
4. Place the mixing cup in the ram plate and mix for 15 to 30 seconds at 1800 to 2300 rpm using the PREMIX CYCLE.
5. Add the isocyanate to the mixing cup.
6. Mix the formulation using the ISOCYANATE MIX CYCLE for 3 to 5 seconds at 1800 to 2300 rpm.
7. As soon as the ram plate comes down after the ISOCYANATE MIX CYCLE, carefully pour the mixture into the lined box or waxed mold. Note and record the cream time of the foam.
8. Add methylene chloride or other solvent to the mixing cup until it is about 1/3 full.
9. Place the mixing cup in the ram plate and agitate the solvent with the SOLVENT WASH CYCLE at about 600 rpm for about 30 seconds.
10. At some point after step 7 the foam should reach maximum rise and blow-off if it is open. Note the rise time and record it.
11. At the completion of Cycle 3, place the solvent wash in the waste solvent wash container and clean all residual polymer from the apparatus before the next foam is prepared.
12. Place the foam in a ventilated storage area and leave it there until it is cured.
13. When finished foaming, clean all equipment and place waste materials in the proper location in accordance with the appropriate waste disposal regulations.
14. After the foam blocks are completely cured, remove blocks from the paper or plastic liners and submit them to the testing lab for physical property testing.

Other methods of box-foam preparation are described in References 5.38 and 5.39.

MACHINE-MADE FOAM

The first technology and machinery for preparing flexible foams were developed in Germany by Bayer. Today, numerous companies offer specialized equipment for all applications of polyurethane chemistry. A historical review of advances in polyurethane machinery is available.^{5,40} A suitable dispensing machine will have the following elements:^{5,41-5,44}

- Tanks properly sized and constructed to hold the various foam chemicals safely and exclude moisture or other contaminants.
- Temperature control systems capable of maintaining the components at plus or minus 5°F (3°C) within the process set points.
- Ratio control scenarios for each component as well as total throughput control.
- Selectable pour or shot times.
- Adequate mixing with capability to vary mixing parameters over a wide range.
- A laminar flow pattern out of the mix head.

Polyurethane foams are made almost exclusively by the one-shot process. In this process, the raw materials are either metered separately to a mix head or are preblended into a polyol-and-compatible-additives masterbatch or an isocyanate-and-compatible-additives masterbatch. The two masterbatches are then metered to a mixer.

METERING UNITS

Most dispensing machines can be classified as either low-pressure or high-pressure, depending on the liquid pressure developed in the lines and the type of mix-head used. The essential features of a dispensing machine are shown in Figure 5.8

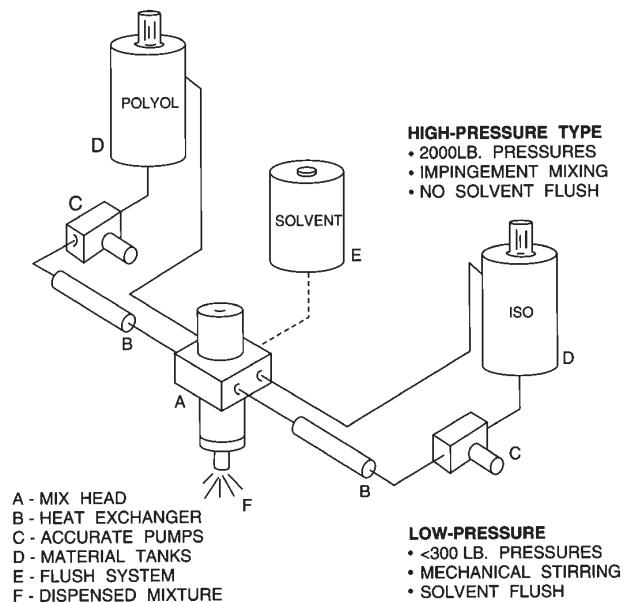


Figure 5.8 Essentials for a Dispensing Machine

For low-pressure systems, variable-speed electrically driven gear pumps are most commonly used. Many other types of pumps can be used, but the general criterion is that less than about 300 psig of internal line pressure is developed.

High-pressure systems are developed with electrically driven piston pumps or, more recently, with hydraulically driven cylinders. These pumps typically transfer material to the mix head at pressures in the range of 1500 to 3000 psig. With either system, accuracy is extremely important and it is essential that the metering unit be calibrated routinely.^{5.45-5.46}

MIXING HEADS

The mixing head is often taken to be the heart of any polyurethane dispensing machine. Success or failure with a given chemical system can often be influenced by the adequacy of mixing.

Mix heads can be classified as recirculating or nonrecirculating. In a recirculating head, the components are circulated from the feed tank through the head and back to the tank. The recirculating type head is essential for good performance in most commercial molding operations. Most slabstock foam lines use nonrecirculating heads. With these heads, material is delivered, injected, mixed and dispensed for controlled times without returning to the tanks.

In low-pressure machines, all the mixing must be done by the mechanical mixer. The mixer imparts high-shear energy by close tolerances between the mixing element and the surrounding barrel. Mixer speeds are normally varied in the range of 2000 to 6000 rpm. Supplemental technology for the control of foam cell-size by injection of air directly into the mixing chamber has been described.^{5.47-5.48} Typical air injection rates are on the order of 0.5 scf/hr per 100 pounds per minute of total mixture throughput. One disadvantage of low-pressure machines is that a solvent must be used to flush the mixer. The historically used chlorinated solvents are now being replaced by more environmentally acceptable materials.^{5.49-5.54} A self-cleaning, solvent-free, mixing head has been developed.^{5.55}

In high-pressure machines, the reactants are fed into a mixing chamber through two or more opposing nozzles. The nozzles are sized to produce a sharp pressure drop which causes the liquid streams to be accelerated to velocities of about 450 feet/second. The impingement of these streams into each other is sufficiently effective to cause a level of mixing. High-pressure impingement mixers are self-cleaning by design.^{5.56}

Conceptual examples and discussion of both the stirring and impingement-mixing types of mix head were presented in Chapter 3. The influence of other foam machine variables and problems frequently encountered in the use of foam dispensing machines is discussed in References 5.57-5.62. Specific recommendations for setting up and checking out a new dispensing machine are given in References 5.63-5.64. One technique to judge mixing efficiency is to pour a free-rise foam, allow it to cure and then cut it open for

inspection. If poor mixing or severe lead/lag problems are suspected, the presence of unreacted isocyanate in a foam can be confirmed with a qualitative spot test. The test is taken from an idea in Reference 5.65. The photos presented in Figure 5.9 will aid the test description.

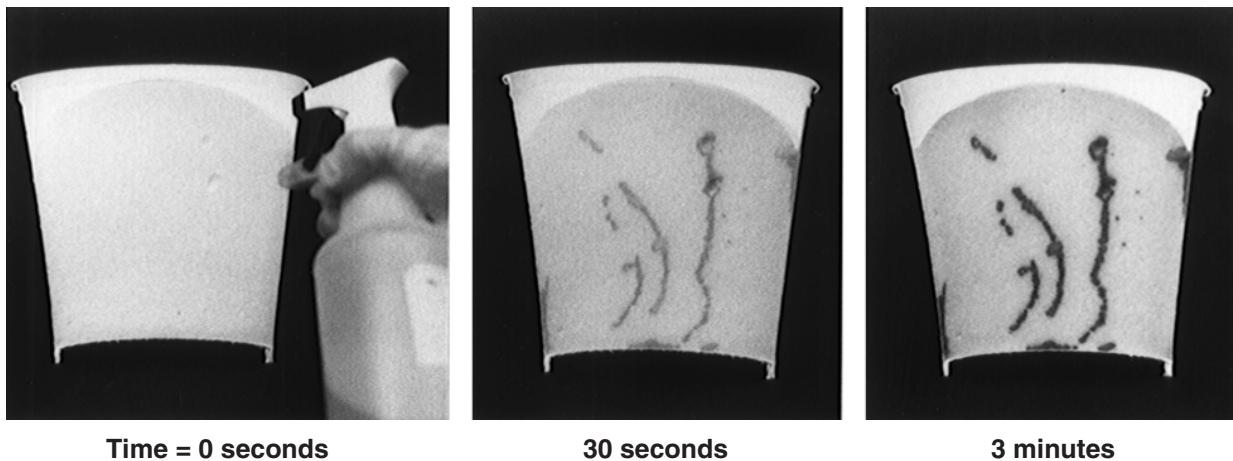


Figure 5.9 Spot Test for Presence of Unreacted Isocyanate In a Foam

The first photo in Figure 5.9 shows a solution of three percent hydrogen peroxide in water being sprayed on the cut surface of a freshly prepared foam. This foam was especially prepared for this example and was allowed to have isocyanate wet spots and mixing lines. Hydrogen peroxide reacts with any free isocyanate to give a strong color body. After 30-seconds of exposure, isocyanate-rich areas were beginning to show. With longer exposure, the isocyanate-rich areas would take on a darkbrown coloration.

COMMERCIAL FOAM PROCESSES

Flexible foams are made commercially by a variety of manufacturing processes. Typical block flow diagrams for slabstock and molded foam processes are presented in Reference 5.66. Detailed descriptions of the processes for making slabstock, molded and carpet foams are presented below.

SLABSTOCK PRODUCTION

More than half of the flexible polyurethane foam now produced is in the form of slabstock foam buns. Slabstock foam is relatively high in demand because of its wide application and large volume usage. Most foams are made on continuous foam machines, although discontinuous box-foaming is a viable approach in less-developed countries or for low-volume specialty grades of foam.

Commercial Box-Foaming

The commercial box-foamers are basically scaled-up versions of the laboratory box-foamers described earlier. A typical hardware configuration is shown in Figure 5.10. These versatile and inexpensive machines include an electrically controllable mechanical stirrer, which is usually mounted on a metal frame with a vertically movable platform for the mixing container. The machines may also be equipped with timing devices and variable-speed mixing control. The design of the mixer is very critical, and many types, including the vortexless type, have been designed. The foam mixture is poured into an open wooden or metal box of any suitable dimensions. The box is constructed so that the four sides are hinged on the bottom piece, which is fitted with casters for ease of movement. The mixing procedure is generally the same as that used for laboratory box-foam machines.

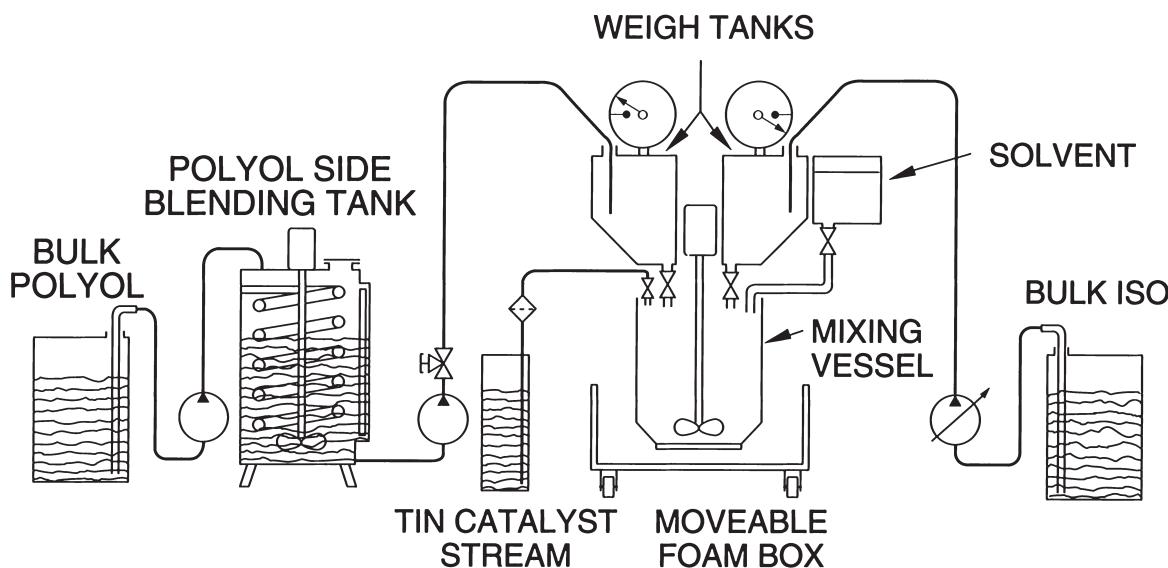


Figure 5.10 Typical Configuration for a Discontinuous Commercial Box-Foaming Machine

Continuous Foam Machines

Foam machines are classified as either high or low-pressure machines. The pressure at which the isocyanate and polyol streams are metered into the mixing head determines the classification of the machine.

On a low-pressure machine, the streams are metered into a large mixing chamber under low pressure (<300 psig). The components are effectively mixed with a large, high-shear stirrer operating at 2000-6000 rpm. Good mixing has to be achieved by the stirrer.

On a high-pressure machine, the streams are metered under high-pressure (300-3000 psig) into a small mixing chamber, which is equipped with a small inefficient stirrer. The mixing is achieved by the impingement of the components under high velocity through nozzles in the small-volume mixing chamber.

Most machines of either type use electrically driven metering pumps. The high-pressure machines use gear pumps, diaphragm pumps or piston pumps. Other types of pumps, such as turbine pumps or screw pumps, may be used to feed the metering pump or to recirculate the components. Some slabstock foam machines have recirculation for all components going from the storage tanks through adjustable metering pumps to the mixing head and back to the storage tanks. Heat exchangers for cooling are normally situated on the way to the mixing head.

To ensure accurate and safe production, a commercial production machine is also equipped with an instrument panel to measure, control and record the flow of components and their temperatures and pressures. Most of these machines use flow meters to monitor the actual flow rate of the liquid components. The flow-rate signal can be fed back electronically to adjust the pump drive speed and maintain a preset flow rate. Many modern machines may be programmed to maintain and adjust both the overall output and the ratios of the chemical components. Flow meters, downstream from the metering pumps, monitor the flow rates and transmit electrical pulses to a microprocessor, where the ratios of the signals are compared with the preset figure. Differences are used to adjust the pump drive speed until the desired ratios and output are obtained.

The number of separate streams metered to the mixing head will depend on the total output of the machine. It only becomes practical to meter the minor chemical additives, such as water, catalysts and surfactants, when the total output of the machine is greater than 200 pounds per minute. Large commercial machines can have outputs of up to 1100 pounds per minute and may have separate metered streams for polyol, copolymer polyol, toluene diisocyanate, water, amine catalyst, silicone surfactant, stannous octoate catalyst, physical blowing agents, fire-retardant additive and dye or coloring agent.

In the absence of individual streams for each liquid component, some of the components may be combined. Both the polyol and toluene diisocyanate run tanks are filled from drums or bulk storage tanks. The physical blowing agents are normally added directly to the mixing head, but in the absence of such facilities the blowing agents are blended with the polyol. Other components, such as copolymer polyol, fire-retardant additives and dyes, can also be blended with the polyol. The water and amine catalyst can be added in a stream, which may be combined with a nonhydrolyzable silicone surfactant. The stannous octoate must be added in a separate stream, but it may be added as a 10-50% solution in dry polyol for metering efficiency. Both water and amine catalyst(s) react with stannous octoate and therefore should not be mixed together.

Apart from the principle of mixing, the construction of both the high and low-pressure machines is the same. Other typical parts of a continuous slabstock foam machine include an inclined or angled pour plate and a moving conveyor provided with sidewalls. The conveyor may be angled to permit pouring higher buns than would be possible on a flat conveyor. Paper feed-in and take-off equipment are provided to line the bottom and sidewalls

of the conveyor with brown paper or a polyethylene film. The conveyor and mixing head are located in a ventilated tunnel fitted for exhausting vapors given off during the foaming process. Cutting equipment is located at the end of the tunnel to cut the foam buns into lengths that can then be moved to the bun cure area by conveyors, lift trucks, or overhead cranes.

Calibration

After the appropriate temperatures are attained by recirculation through heat exchangers, each stream is calibrated in turn so that the final throughput of the streams is within 1% error of the theoretical or calculated values.

Conventional Crowned-Block Process

Figure 5.11 shows the profile of a rising foam bun, which will help explain why conventional foam buns have a crowned or domeshaped top. As the foam mixture leaves the mixing head, it is clear or slightly cloudy when conventional polyols are used. The mixing head or dispensing hose is traversed across the conveyor to distribute material as uniformly as possible. The conveyor and side support walls are lined with paper or plastic film moving at the same speed as the conveyor. As soon as reaction becomes visible, the material is said to be creaming and the cream line is the distance from the head to the start of creaming. The creaming liquid layer is about $\frac{3}{4}$ inch thick. Within 1-2 minutes it will rise to a height of about 40-50 inches. As the foam begins to rise, the sidewall paper exerts a frictional drag on the foam. This drag causes the foam near the sidewall to rise more slowly than the foam in the center of the bun, thus resulting in a crown shape. The foam reaches maximum height and “health bubbles” appear, which indicate cell-wall rupture and release of the gas which caused the foam rise. A slight amount of sigh-back occurs shortly after that point, which reduces the crown somewhat. After 5-10 minutes the foam is cured enough to be cut and handled. A post-cure time of at least 24 hours is required for the foam to reach its ultimate hardness.

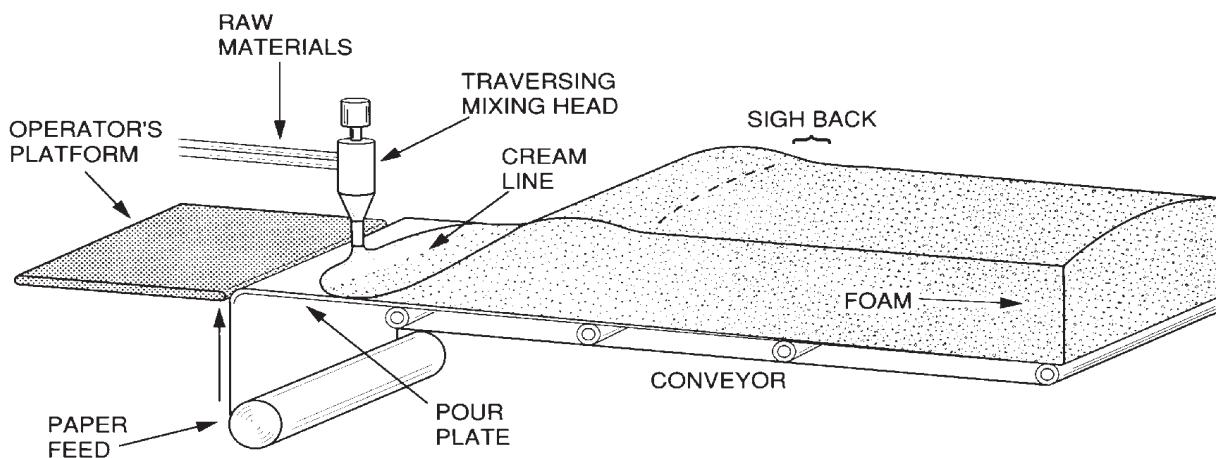


Figure 5.11 Conventional Crown-Block Process (Sidewalls Omitted for Clarity)

Rectangular Block Processes

Foam buns made by the method described above will always have a crowned or domed top surface. Over the years, a variety of slabstock foam machine designs have evolved. The reason for this was that buns with a more rectangular shape reduced trim losses when the foam was cut into finished shapes. A domed foam block produces relatively high amounts of scrap foam since the mattress cores and cushions which are fabricated from these buns are mostly rectangular in shape. It has been estimated that ten percent more prime foam can be obtained from a rectangular block process than from a conventional crowned-block process. Four different systems for making rectangular blocks have been developed.

Draka and Petzetakis Processes. These two rectangular block processes are quite similar. Figure 5.12 shows the Draka modification to the conventional system. In this modification, an extra polyethylene film is added between the sidewall paper and the foam. During the foam rise, this film is pulled upward. The film is parallel to the foam surface and prevents the foam from sticking to the side paper. By eliminating friction at the sidewall, the sides of the block rise to the same height as the center of the bun, thus producing a rectangular bun.^{5,67}

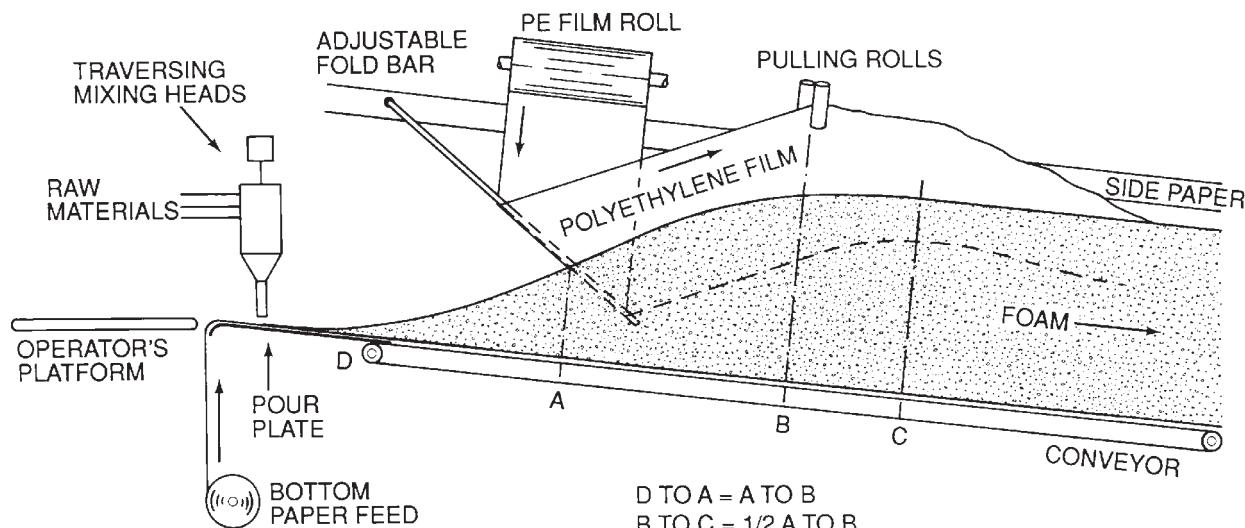


Figure 5.12 Draka and Petzetakis Process

Position (A), where the polyethylene film is fed in between the sidepaper and the foam, and the position of the pulling rolls (B) relative to the location of the cream line (D) and the full-rise point (C), are rather critical as well as the distance between A and B. As a rule, distance D-A should be equal to distance A-B, and both should be about twice as long as distance B-C. These relationships, however, are influenced by the block height as well as the rise profile of the foam. Improper setting of the various points will result in domed top or side splits. Other important variables are the film width, the speed of the pulling rolls and the distance between the pulling rolls and the foam surface.^{5,68-5,69}

All of these variables make this process more complicated and more difficult to handle than a conventional one. An added disadvantage is that the polyethylene film can be used only once, thus increasing production costs. The maximum block height that can be handled with the Draka and Petzetakis systems is usually about 40 inches.^{5.70}

Hennecke, Planiblock and Econo Foam Processes. These three systems use the same principle for making rectangular blocks, but the details differ. The Hennecke and Planiblock systems are designed for retrofitting on existing foam lines, while the Econo Foam system is a complete new line. The basics of these processes are shown in Figure 5.13. Both processes use an apparatus to squeeze the top surface of the rising foam bun so that it is uniform across the conveyor. Immediately after the cream line, paper (or a nonporous film) is fed on top of the foam. The paper or film is pressed on the foam surface by means of weighted or spring-loaded pressure-regulating members (A). These pressure elements, which can be metal or wooden plates or bars, are positioned on top of the foam bun from the cream line to a few feet past the full-rise point. In order to allow the gases generated during the foaming process to escape, a spiked roller perforates the paper at point (B). After the last pressure element, the paper is peeled off and rewound.

With these processes, rectangular blocks can be made that have the additional advantage of having hardly any top skin. A serious disadvantage is that the top surface of the bun cannot be observed during the rise and gel periods. This can lead to more waste or scrap foam in the case of mechanical or human error.^{5.68-5.70}

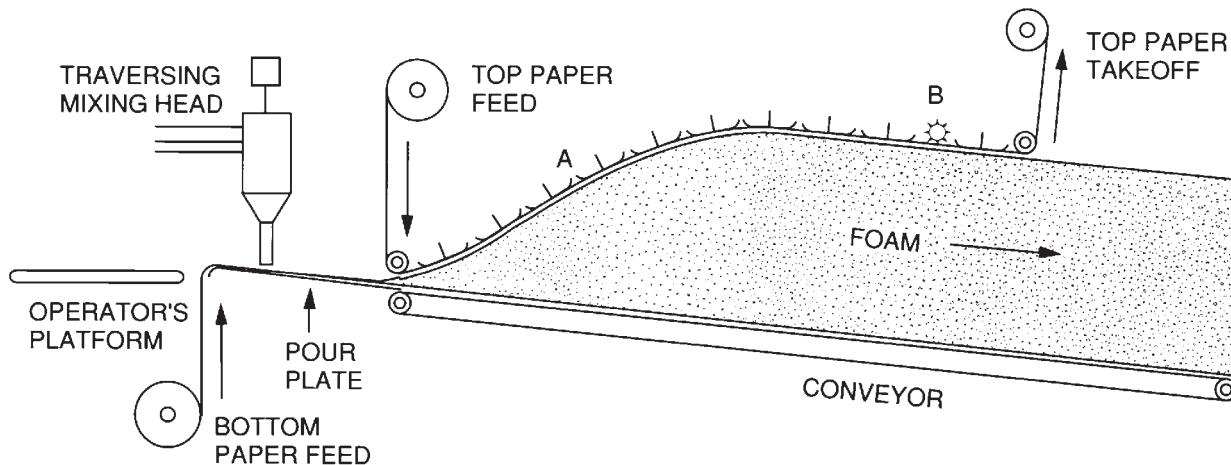


Figure 5.13 Hennecke, Planiblock and Econo Foam Processes

Maxfoam Process. Probably the most popular rectangular bun process is the Maxfoam process (Figure 5.14), which works in an entirely different way.^{5.71-5.75}

Instead of using a reciprocating traverse, the mixing head is fixed and the liquid coming from the head is fed into the bottom of a trough where it slowly begins to react. The reacting mass flows over the forward edge of the

trough onto the bottom paper, which is sliding on an inclined fall plate. On the newer versions of this machine the fall-plate is made up of five sections hinged together at the pivot points shown in the figure. The angle of each fall-plate section can be changed by raising or lowering the height of the pivot points. The last section, which meets the horizontal conveyor, can be lowered all the way to horizontal. By changing the configuration of the fall-plate sections, the rise profile of the foam formulation can be matched. The foam, which expands downward, reaches the horizontal conveyor as a fully expanded slab. When the fall-plate sections are properly adjusted, the reacting foaming mass flowing out of the trough is evenly distributed between the sidewalls. The surface of the slab will follow the side paper on a horizontal line at the same level as the top of the foam expanding from the trough, thus producing a flat-topped block. Improper adjustment of the fall-plate sections will result in a foam block with either a slightly domed top or with "ears" on the top corners of the block.^{5.68-5.69}

The total length of the machine is reduced by about 25%; thus, since the conveyor is horizontal, the height of the machine is almost halved. The amounts of surfactant, amine catalyst and stannous octoate can be reduced considerably, so that substantial savings in the cost of raw materials can be achieved.^{5.70}

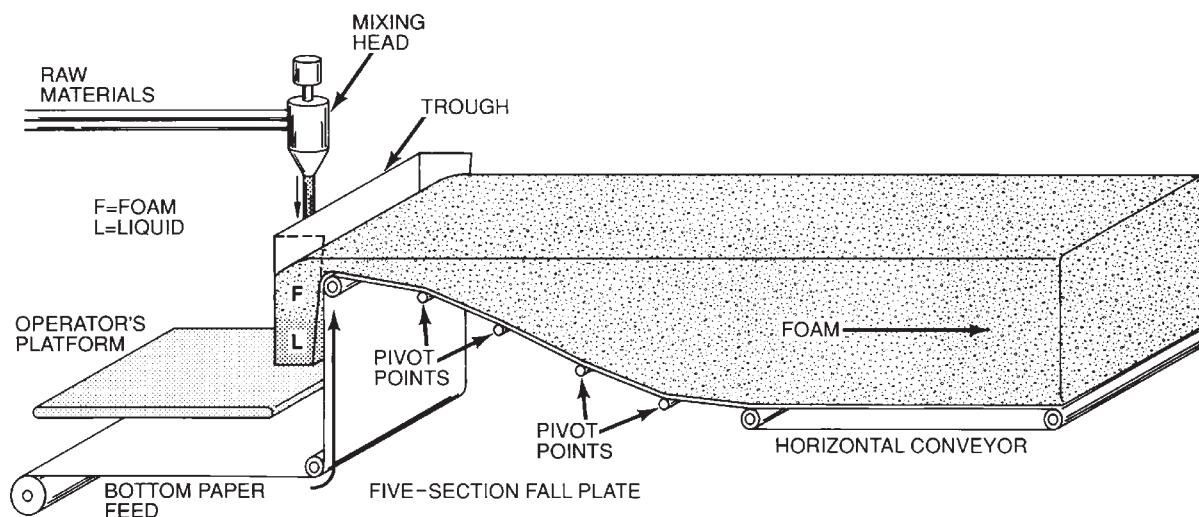


Figure 5.14 Maxfoam Process

Vertifoam Process. Most flexible slabstock foam is made by one of the horizontal foaming processes described above. All of these continuous processes require the use of machines with high outputs in order to obtain large blocks, which yield a low scrap rate when fabricated into cushioning. The high outputs require faster and longer conveyors, and machines over 300 feet in length are common. The size of the foam production machine is thus dictated by the size of the buns required and not by the rate of production needed to meet demand. The larger the machine, the more

expensive it is to vent and heat or air-condition. The Vertifoam process, patented^{5.76-5.77} and licensed throughout the world by Hyman International of England, overcomes this problem.

In the Vertifoam process, illustrated in Figure 5.15, the foam reaction mixture is introduced at the bottom of a totally enclosed expansion chamber. This chamber is lined with brown paper and/or polyethylene film, both of which are drawn upwards at a controlled rate depending on the pressure in the chamber, the foam formulation and the rate of production. The rheology of the foam reaction process combined with the effect of gravity ensures a stable, uniform foaming front and prevents the mixing of the still-liquid reacting mixture with older partially gelled foam. Thus, foam blocks with the required large cross-section may be made at relatively low outputs. Since the machine is much smaller than horizontal machines making similar-sized foam blocks, there are major operational savings. Other advantages from the use of vertical foaming are that blocks made in this way do not have dense top and bottom skins. Also, more of the chemicals used are converted to usable foam and the foam produced is of uniform density and structure.^{5.78-5.83}

The major disadvantage is that mechanical or operator error can not be observed in the foam until about 5 minutes of run time has elapsed. For most foam grades, a narrower processing latitude can be expected.

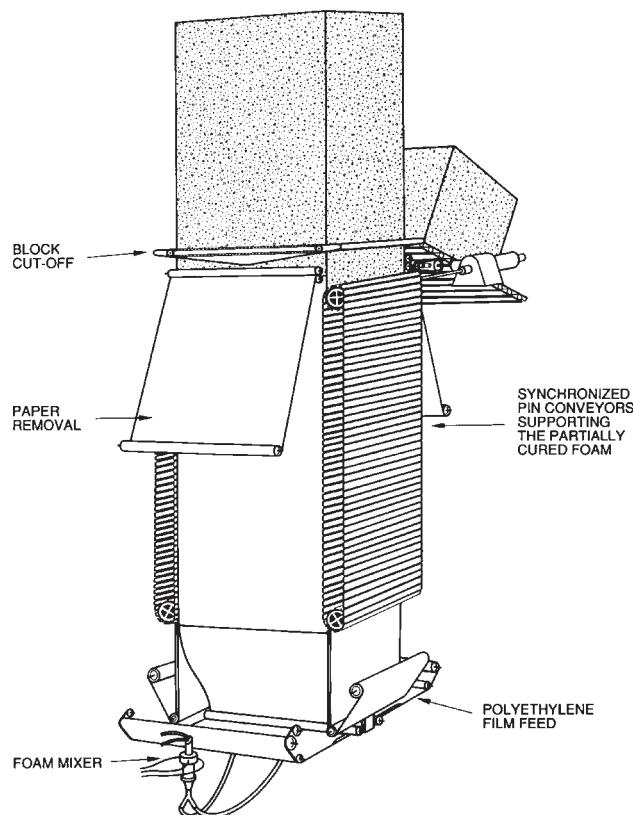


Figure 5.15 Vertifoam Process

ABA Elimination Processes

In addition to the machines described above, several new processes have been developed recently to aid in the elimination of traditional auxiliary blowing agents (ABAs). These processes fall into three categories:

- Mechanical Cooling.
- Reduced Pressure.
- Liquid CO₂.

Mechanical Cooling

In this process, the foam blocks are purposely cooled shortly after production in order to remove the heat generated during the exothermic foam reaction. The basic process consists of one or a series of cooling chambers/devices over which the foam passes after completing its rise.^{5.84-5.87} At that time the hot gases and any volatile components are removed and the foam is cooled to a lower temperature. The preferred cooling method is to draw ambient air through the foam. The exhaust gases can be treated in a carbon bed to remove trace impurities before being discharged to the atmosphere.

The two major advantages of this method are that force cooled foam blocks can be handled quickly after production and that the short thermal history leads to excellent hardness uniformity. The fundamentals of forced cooling have been studied and described in detail.^{5.88}

This method has gained acceptance in the United States but only limited success in other global areas.

Foaming Under Reduced Pressure

The concept of using a reduced pressure atmosphere to aid in the foaming of a polymer system was commercially used for the preparation of artificial sponges from natural rubber in the 1940s.^{5.89} Laboratory experiments applying the technique to flexible polyurethane foam were reported in 1958.^{5.90} Detailed process engineering studies for scaling-up the concept were reported by Porteous and Wallis.^{5.91-5.93} Further developed jointly by Recticel^{5.94-5.96} and Beamech^{5.97} in Europe, this technology is now enjoying commercial success.^{5.98-5.99} The technique has also been applied to commercial scale box-foaming operations.^{5.100-5.102}

The principle of this approach is that foaming is based on volume expansion of a blowing gas, and the volume of that gas is influenced by the temperature and pressure of the surrounding atmosphere. By dropping the surrounding pressure, one can generate a larger volume of gas from the same amount of reactants and thus reduce the density of the final foam.

One of the essential features of the Variable Pressure Foaming (VPF) technology is the encapsulation of the complete conveyor section of the machine (including trough and fall plates in the case of Maxfoam) in an airtight enclosure. Figure 5.16 shows a schematic view of a VPF machine lay-out. In order to allow full continuous production, the airtight enclosure is

divided in two sections. A process enclosure and an airlock enclosure. At the start, the whole enclosure is under controlled pressure. Once the desired length of foam is produced, an automatic cut-off saw cuts off a long foam block. That block is then transported at high-speed into the airlock enclosure which is then closed and restored to ambient pressure while foaming continues under a controlled reduced pressure in the process enclosure. The airlock door can then be opened to transport the block into the cure rack. The airlock enclosure is then returned to the process enclosure pressure before the next foam block arrives.

The advantage of this approach is that working under controlled conditions, the foam density can be adjusted and foam grades that are difficult or impossible to make on other equipment can be produced. The physical properties of the resulting foams are in general excellent.

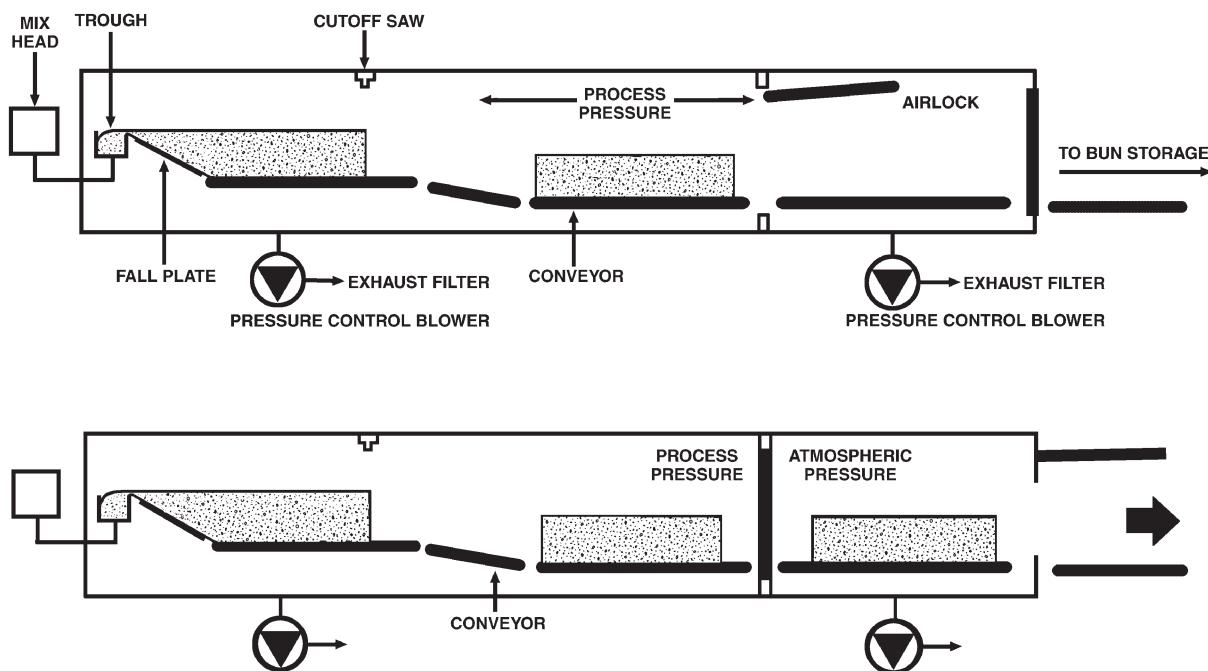


Figure 5.16 Schematic of Variable Pressure Foaming

The disadvantages are that this process requires a high-level of expertise, is relatively capital intensive and some foam grades remain difficult to produce under the reduced pressure conditions.

Liquid Carbon Dioxide (CO_2) Addition

Liquid CO_2 is a logical blowing agent to consider when replacing other blowing agents. It is a cheap, available, well known chemical compound derived from existing industrial processes. Its use supplements the carbon dioxide gas already generated by the water/isocyanate reaction.^{5.103-5.105}

However, CO_2 must be maintained in the liquid form during the early stages of the foaming process. During the mixing of the components it tends to

rapidly leave the liquid phase but gets trapped in the viscous media and tends to expand it. The first rapid expansion produces a frothy blend that can be laid on a slabstock conveyor.

Problems arise in mainly three areas:

- Pre-mixing of a precise amount of CO₂ into the formulation.
- Thorough mixing of the components to avoid unmixed gas bubbles.
- Lay-down of the mixture on the conveyor to avoid pin holes.

To address these challenges, at least three separate approaches have been developed by different machine manufacturers: Cannon (Italy),^{5.106-5.109} Hennecke (Germany)^{5.110-5.112} and Beamech (UK).^{5.113} Figure 5.17 shows a simplified schematic drawing of Cannon's CarDio process.

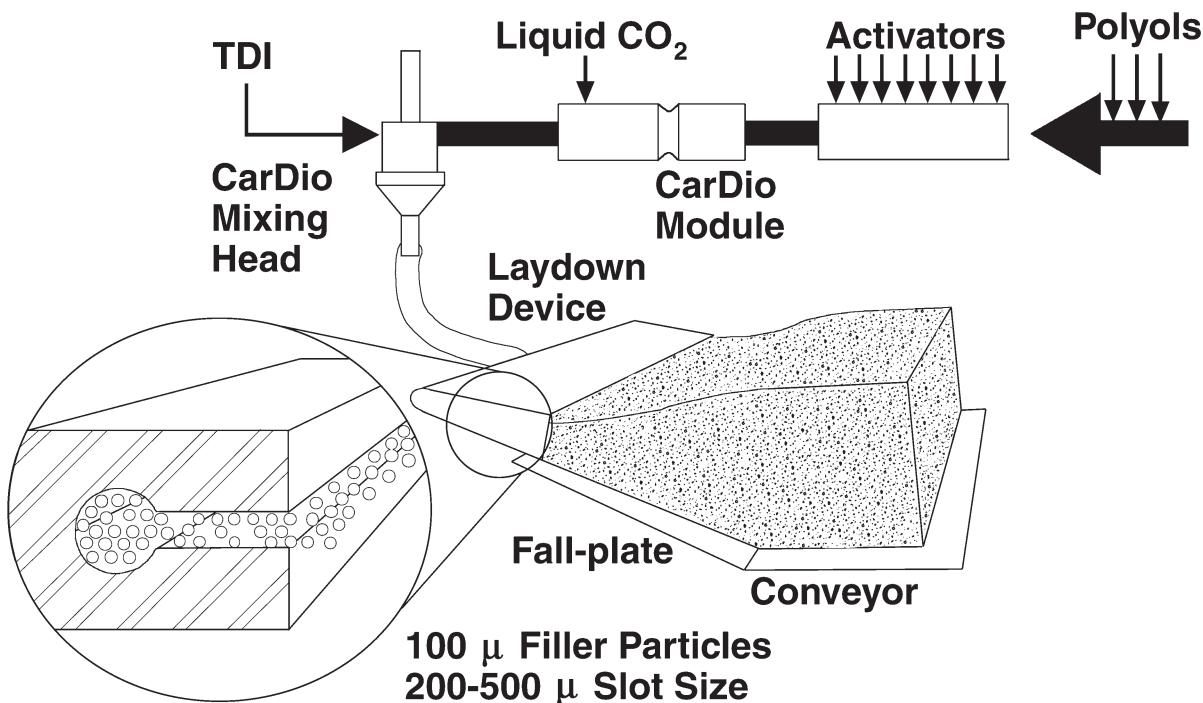


Figure 5.17 Schematic of Cannon CarDio Max Machine

Although most of the chemicals used in the process are conventional, development work is taking place to fine-tune product offerings to improve process efficiency. All these processes have in common the fact that hardness control is critical so that grafted polyols are necessary to produce the higher loadbearing grades.

A detailed comparison of the variable pressure and liquid carbon dioxide processes has been presented.^{5.114}

MOLDED FOAM

Automotive Seat Cushions

Most of the seating cushions used in automobiles today are made from either hot or HR-molded foam. A small percentage are cut from slabstock foam buns.^{5.115-5.117} The wide diversity and intricate shapes involved in this application lend themselves to successful molding of foam. With the appropriate selection of starting isocyanate and polyol and with selective use of additives it is possible to form flexible molded foams meeting widely differing product application specifications. Another advantage of molding foam is the foaming in place of reinforcements or otherwise producing foams with multiple zones of hardness.

In the typical molding operation, a mold is preheated and waxed with a mold-release agent. A predetermined amount of a foam system is poured into the mold, then the lid is closed and locked, and the ingredients foam into the shape of the mold. After the part is cured, it is stripped from the mold and the process can be repeated.^{5.118-5.124} Success at molding foam in a reduced pressure atmosphere has been reported.^{5.125-5.127}

Preheating of the molds is necessary for several reasons. The overall density of a molded part can be affected by mold surface temperature. If the surfaces are cold or at uneven temperatures, the heat from the exothermic reactions may dissipate unevenly and result in nonuniform skin density. Preheating also helps to complete the reactions at the outer skins and thus reduces the cure time. Warm mold surfaces are necessary to evaporate carrier solvents introduced during the mold-release application step.

Because molding is inherently a batch operation, commercial molding machines are designed for intermittent operation. Valves are arranged so that raw materials can be recirculated between shots to help ensure uniform composition in the dispensed mix. Throughput rates for molding machines are generally lower than those of slabstock machines. The actual output must be carefully sized to supply the necessary amount of material to the mold before the mixture begins to foam.

The two major molding techniques in the polyurethane industry are the hot-cure and the cold-cure (or HR) processes. The hot-cure molding process was commercially established over 30 years ago. Formulations for hot-molded foam are similar to that of conventional slabstock foam except for use of lightly ethylene-oxide-capped polyols and slightly different catalyst packages. Significant external heat is applied to the mold after filling in order to obtain sufficient surface cure of the foam to allow its early removal from the mold.

The cold-cure or HR molding process is derived from the original hot molding and is designed to utilize much less externally applied energy. To accomplish this, polyol manufacturers build a more reactive molecule so that the reactions proceed faster and less overall cure energy is needed; e.g.,

lower oven temperatures. The essential differences between hot and HR molding are summarized in Table 5.3. Detailed discussions of other processing and physical property differences are available.^{5.128-129}

Table 5.3 Hot-Cure and HR-Molding Technologies

| | Hot-Cure | HR |
|--|------------------------------|---|
| Isocyanate | 80/20 TDI | 80/20 TDI Blends w/MDI Polymeric MDI MDI prepolymers |
| Polyol Molecular Weight EO-Capped Copolymer Polyol | 2800-3500 Yes Optional | 4500-6500 Yes Optional |
| Cure Oven Temperature | 180-300°C 356-572°F | 75--200°C 165-392°F |
| Postcuring | No | Optional |
| Mold Temperature at Pour | 25-45°C 77-113°F | 50-70°C 122-158°F |

Foam Molding Lines

A typical foam molding line will consist of many functional parts. The larger portions of floor space will be taken up by conveying systems for the molds, ovens and related finished-foam handling systems. Conveyors for moving the foam molds from station to station can be of any number of layouts. Long racetrack-style designs are still as common as the newer, smaller and more specialized carousel lines like that shown in Figure 5.18. In most (but not all) cases, the mold moves under the mixing head to receive a charge of foam. It is common to find the mixing head mounted on a robot or other computerized pour bridge for purposes of optimizing pour pattern for each individual mold cavity. Technology has also been developed for using dedicated high-pressure mixing heads on stationary molds.

The molds are usually made of cast aluminum in two parts with provision for mechanically opening and closing the lid. For shorter production runs, sheet metal or sprayed metal tooling may be viable alternatives.^{5.130-5.131} Nonmetallic molds have also proven useful in less demanding applications.^{5.132-5.134} A critical comparison of alternative mold making materials is available.^{5.135}

For hot-cure foams, the molds are generally thin (6-10 mm) and lightly constructed. The lids are liberally drilled with holes to prevent air trapping and pressure buildup in the mold. HR and specialty molded foam molds are generally of heavier, more precise construction. The molds should be constructed to withstand up to 30 psig internal pressure. To build the pressure, the parting line seals should be made as tight as possible with

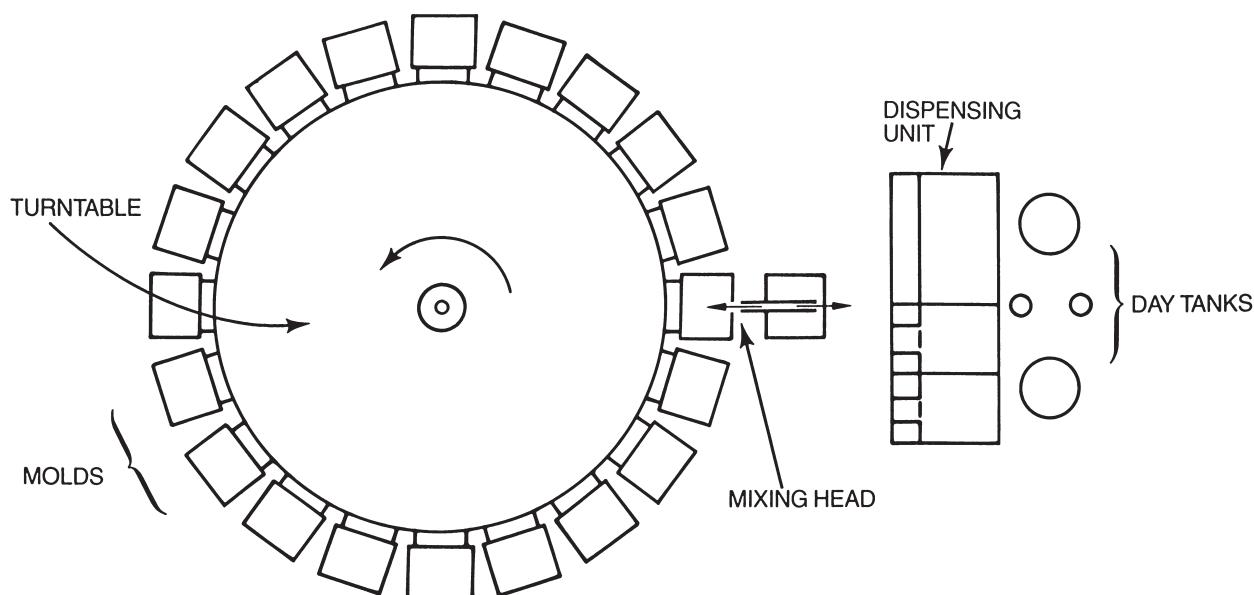


Figure 5.18 Carousel Molding Line

strong clamps. Since these foams are prone to collapse with untimely pressure relief, venting must be carefully controlled.

A proper initial mold temperature is critical for the production of cosmetically acceptable foam surface skins. For hot-molded foams, temperatures around 100°F (37°C) are preferred. If the mold is cooler than about 77°F (25°C), an undesirable densified layer of skin will form. When the mold gets too hot, the skin becomes exceedingly thin and fragile. HR foams vary widely in chemistry, with some systems requiring only ambient temperature molds, while other systems perform best with initial mold temperatures in the range of 140-160°F (60-71°C). At excessive temperatures, HR foams exhibit cosmetic surface and subsurface defects. With either chemistry, the molds should be sized to allow for about 2% shrinkage of the final molded part.

Most semiflexible foam processes run best when the mold temperature is carefully controlled in the range of 85-110°F (29-43°C). Beyond these limits, foam flowability and internal mold pressure problems occur.

Mold-Releases

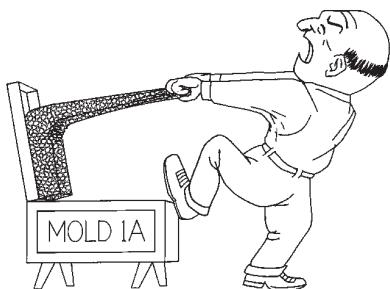


Figure 5.19 The Need for Mold-Release Agents

Figure 5.19 emphasizes that without a purposely applied mold-release, removal of a foam part from a mold would be very difficult. Polyurethanes make excellent adhesives. The principal mold-release agents used are commercial blends of various natural and synthetic waxes. The exact composition is chosen so that the melting point of the wax is slightly below the stripping temperature of a given foam line. The release agent is thus a solid during the pour and gelation parts of the cycle. As the mold approaches the demolding temperature, the release agent becomes liquid and allows the foam to be easily stripped from the mold. This type of hot wax mixture gives optimum release properties, but must be renewed after each molding. In

some cases it is desirable to use a film-forming mold release that can go with the part in order to serve as a protective or decorative coating for the finished product (e.g., toys).

Mold-releases can be characterized as either water or solvent-based. Detailed review articles can be found at References 5.136-5.142. Recent developments in water-based systems are reported in References 5.143-5.153.

Hot-Cure Molding

A typical layout for a hot-cure molding line is shown in Figure 5.20. The molding line is in essence a drag-chain conveyor moving molds from one operating station to another.^{5.154} The process begins with the molds entering the preheat oven, where they are typically heated to 104-122°F (40-43°C); epoxy molds are heated slightly higher.

After exiting the preheat oven, the molds proceed via conveyor to the pour station. An exhaust system with its inlet near the pour conveyor removes vapors from the area. The residence time at the pour station is sufficient to charge the molds and allow the foam to cream. The reaction mixture can be dispensed into the molds as a puddle or by strip pouring as required for optimum mold filling characteristics. The molds are normally closed automatically as they are conveyed to the radiant oven. The foam dispensing machine may feed one or two mixing heads suspended from booms, robots or other pour bridges. The polyol and isocyanate are transferred from bulk storage to day tanks, which are usually an integral part of the dispensing unit. Water, catalyst and surfactant are normally stored in separate day tanks. Precision pumps feed the components to the mixing head, and the components are normally recirculated between pours. The mixing head may be either the low or high-pressure type.

In the radiant section of the oven, the molds are heated to an internal surface temperature of about 250°F (121°C). The remainder of the curing oven is heated with hot air. At the end of curing, the molds are opened automatically and the foam is removed. The molds are then cleaned, sprayed with fresh mold-release and fitted with the required inserts and wires. From there the molds travel through a cooling and conditioning station to bring them back to the proper pour temperature. The stripping, waxing and cooling areas are also under ventilation. A typical molding cycle for a hot-cure line is given in Table 5.4.

Table 5.4 Hot-Cure Molding Cycle

| Process Steps | Time(Minutes) |
|----------------|---------------|
| Preheat | 3.0 |
| Pour | 0.5 |
| Cure | 15.0 |
| Demold and Wax | 6.0 |
| Cool | 5.5 |
| Total | 30.0 |

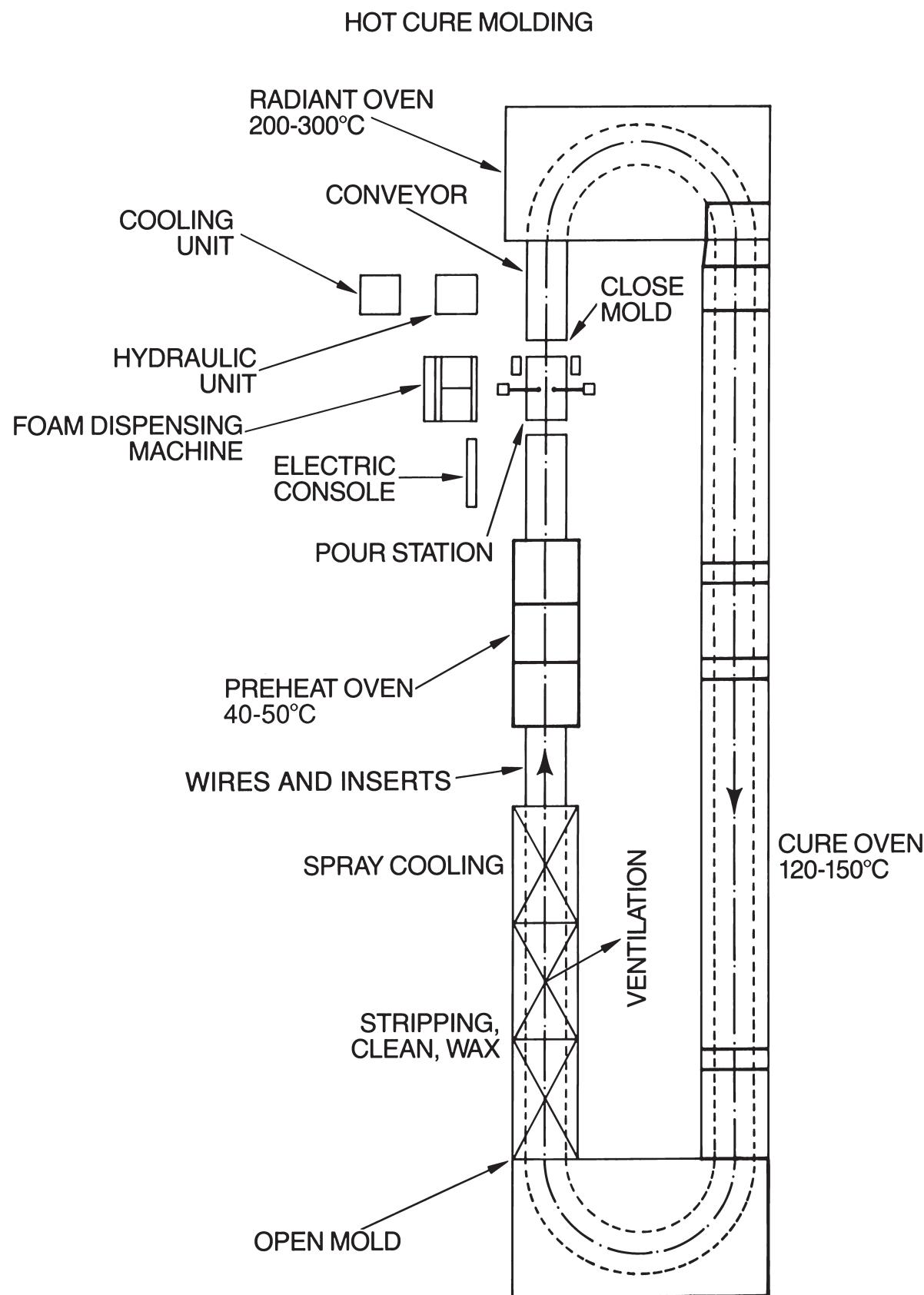


Figure 5.20 Typical Hot-Cure Molding Line

HR Molding

Foam formulations that cure at lower temperatures are the basis of most HR-foam processes. Various formulations exist that require no or greatly reduced heating cycles. With many systems, curing ovens are not needed and low mold temperatures allow the molds to be lined with ABS, PVC or upholstered skins, thus allowing the production of finished parts in a single process. The cycle time of most HR cold-cure moldings is approximately half that of hot-cure. This results in shorter, simpler conveyor lines and reduced equipment costs. Figure 5.21 illustrates a typical racetrack-style molding line for HR seating foam. More complex designs are also used.^{5,155}

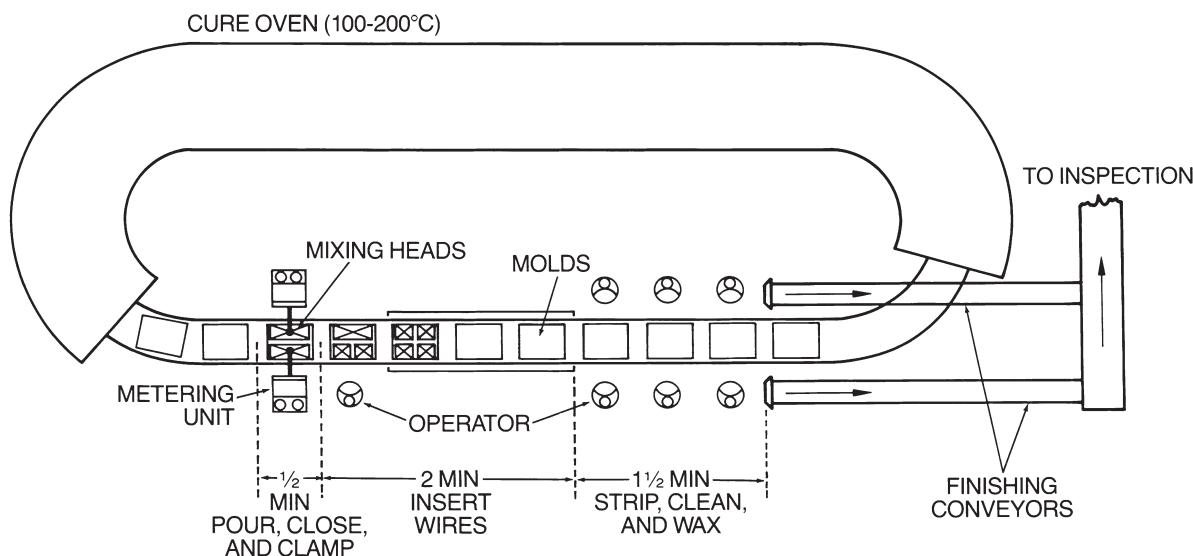


Figure 5.21 Racetrack-Style Molding Line

Depending on the foam system, the formulated ingredients are mixed and dispensed into waxed molds conditioned to a temperature in the range of 120-160°F (49-71°C). The molds proceed along any of various designs of conveyor systems, which are usually equipped for automatic closing and locking of the lids. In the case where auxiliary heat input is desired, as in low-density seating foam, the mold then enters a curing oven of sufficient temperature to bring the internal mold surface temperature up to the range of 170-200°F (77-93°C). After a mold residence time of 3 to 10-minutes, the mold is opened and the part is removed, either mechanically or by hand. The mold then proceeds through cleaning, waxing and other preparation stations before returning to the pour station. In contrast to open-celled hot-molded foam, most HR foams contain closed-cells that must be mechanically opened by means of a press, air injection, roller crushers, or by the vacuum crushing technique.

Specialty Molded Foams

These foams include the semiflexible, semirigid and integral-skin types of foams more fully defined in Chapter 12. In general, semiflexible molded

foams are used in instrument panels, arm rests, console covers, door panels and other foam parts found in automobile interiors.

In a typical semiflexible foam molding operation, a vinyl skin would be placed in the bottom of a waxed, temperature controlled, cure mold. Then the mold is fitted with a structural insert and foam is then dispensed into the mold in either a open or closed-mold process. The foam fills the cavity between the vinyl and the insert and provides both adhesion and cushioning properties. After curing, the composite part is demolded and subjected to additional trim and fabrication steps before shipment to the final customer.

CARPET BACKING

In the manufacture of tufted carpet, an adhesive backing is required to anchor the tufts. This backing is most commonly applied in two separate coatings. The first, known as the precoat, is driven into the back-stitch of the carpet to achieve penetration of the yarn bundles, with encapsulation of each fiber as the optimal target. The second coating is known as the adhesive or laminate coat. The purpose of the laminate coat is to adhere a secondary fabric, most commonly a woven polypropylene material, to the body of the carpet. Since the two coatings serve different purposes, it should not be a surprise that the formulations and polymers are different as well. A lower volume backing system, known as unitary, incorporates increased weights of precoat and a second coating, but does not utilize a secondary fabric on the outer surface. Unitary products are typically targeted at higher performance applications and command a premium price. It should be noted however, that unitary carpets are known to have a higher level of field installation problems than laminate products.

The most popular carpet backing systems are based on Styrene-Butadiene (SB) latexes, which give good tuft-lock at low cost. Another backing approach is the application of a resilient foam backing over the anchor coat. Foamed materials used for this backing are PVC plastisols, polyurethanes, EVA and latex. Although polyurethane raw materials are more expensive than latex, advantages in processing physical properties and durability cause polyurethanes to be the foam of choice.^{5,156} A processing advantage is lower energy consumption due to lower operating temperatures of the curing ovens. In latex foams, large amounts of water must be evaporated; this need is not present in polyurethane foams.

Significant research has been done to evaluate the field performance of THE ENHANCER polyurethane attached cushion. The attached cushion improves appearance retention of the carpet by reducing the energy absorbed by the carpet face during use. Studies have shown improvements of up to double the appearance rating when comparing the same carpet face with and without cushion at equivalent traffic counts. This translates into a longer life cycle for carpets incorporating an attached cushion, compensating for the additional cost of the backing. An obvious secondary advantage to attached cushion is improved walking comfort. Extensive studies on various aspects of comfort and comfort retention reveal important differences between cushioned and non-cushioned carpet, and between comfort imparted by high

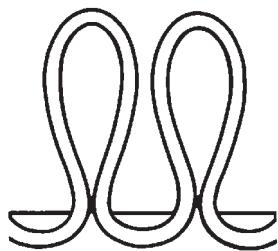


Figure 5.22 Tufts with Primary Backing

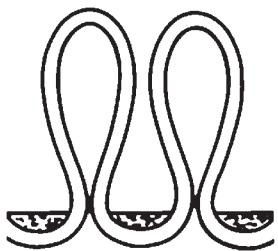


Figure 5.23 Tuft-Lock with Secondary Backing

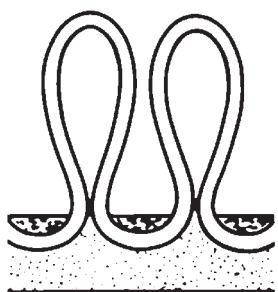


Figure 5.24 Tuft-Lock with Secondary Backing and Mechanically Frothed Foam

face weight and that imparted by an attached cushion. For example, it has been shown that on a carpet construction with a low (22 oz/sq. yd.) face weight with an attached cushion has greater comfort after 1 million foot trafficks than a higher face weight (28 oz/sq. yd.) version of the same did when it was new and untrafficked. In research focused on the ergonomic issues of energy expenditure and balance, again, polyurethane attached cushion was shown to be the backing of choice. A low level loop carpet face with an 18 lb/cu. ft. attached polyurethane cushion was found to result in a 24% reduction in the energy expenditure of the soleus leg muscle as compared to hard tile surfaces during walking evaluations. Such technical foundations may ultimately lead to quantification of reduced fatigue or improved productivity by office workers in areas where attached polyurethane carpet is installed.

Figures 5.22, 5.23 and 5.24 show tufted carpet with precoat backing and foam backing.

Production

Two types of production procedures are used in continuous polyurethane foam application: direct coating and reverse coating. Direct coating may use a spraying or a mechanical frothing process. Calcium carbonate is frequently used as a mineral filler for cost reduction and viscosity improvement. Additionally, hydrated alumina may be incorporated into carpet backing formulations, primarily as a modifier to ignition resistance. These fillers are generally 30 to 70 weight percent of the final foam. The filler is incorporated into the polyol and homogenized to a “compound” with the aid of high-shear blenders. The reaction partners are most commonly MDI and MDI prepolymers that are liquid at room temperatures. Metering and mixing of the components are carried out continuously with gear pumps and agitated mix heads.

Spraying Processes

This system, originally patented by ICI in the 1950s, in use for many years, has all but disappeared from commercial use in recent years. As shown in Figure 5.25, the process is characterized by the use of a high-speed traversing spray to distribute a highly reactive foam mixture directly onto the back of untreated tufted carpet. The carpet is carried through the foam application and curing tunnel on tenter pins that are shielded from the spray application. The reactivity of the foaming mixture is adjusted to allow from about 15 to 25% of the applied mixture to penetrate the base of the tufts and the primary backing of the carpet. This gives a stable carpet structure with good tuft-lock. The foam thickness is controlled by adjusting the amount of foam mixture deposited and by the rate of travel of the carpet through the application zone. An additional minor degree of thickness control is given by the embossing roll. This process gives a unique product with a tough, abrasion-resistant integral skin, the thickness of which is controlled mainly by adjusting the initial level of infrared surface heating in the curing oven. The foam is blown and the polymer is stiffened by the reaction between water and isocyanate. A disadvantage of the direct spray process is the tendency of the foam surface to reproduce the texture and the faults of the

primary backing and tufting. The foam back is therefore embossed, soon after the foam surface becomes tack-free, by use of an engraved roller at 266-302°F (130-150°C). The problems included inconsistent gauge and high ventilation requirements.

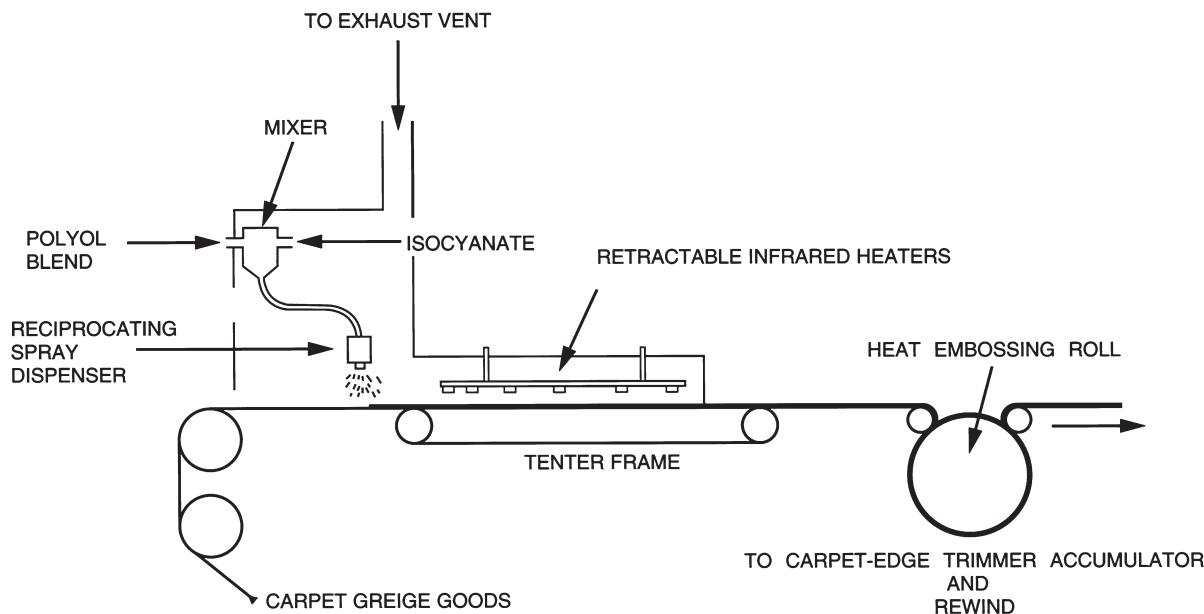


Figure 5.25 Spraying Process for Applying Foam Backing

Mechanical-Frothing Process

One of the primary advantages of this process is its use of modified latex foam backing equipment with the addition of metering units for the polyurethane components. An Oakes brand mixer froths three or more separately metered streams, including: a polyol/catalyst/surfactant/filler mixture, an isocyanate (usually a MDI prepolymer) and air.

Dow has a patent for this process that was issued in 1974.^{5.157} Dow licenses this and other patented technologies for polyurethane carpet backing to carpet mills to run THE ENHANCER carpet backing.

Oakes Mixer. The Oakes mixer (Figure 5.26) consists of a rear stator, a rotor and a front stator.^{5.158} The internal faces of the stator members and both faces of the rotor are provided with concentric rows of blades. The two stators are bolted together and appropriately supported with the rotor mounted on a revolving shaft between the stators. The rows of rotor blades mesh with the rows of stator blades, with ample clearance between. The materials to be mixed enter the mixing head at the center of the rear stator and flow radial between the blades to the outer periphery of the rotor. After flowing across the annular cavity between the rotor and the stators, the mixture again flows radial between the blades on the front stator to the center where the material is piped in-line to the next point in the process system or discharged to the point of use. Catalysts or other materials may be added through injection ports at various stages of the mixing cycle. Because

of the unique design of the Oakes mixer, materials flowing through the mixing head are subjected to an intense shearing and cutting action, brought about by the interaction of the rotating and stationary blades. The design of the Oakes mixer is such that all the material travels the same tortuous flow path and thus receives completely uniform mixing. The Oakes mixer works on a small product volume at any given instant and achieves extremely high efficiency in applying the power consumed to the mixing process. This efficiency results in relatively low power consumption in relation to the product flows obtained.

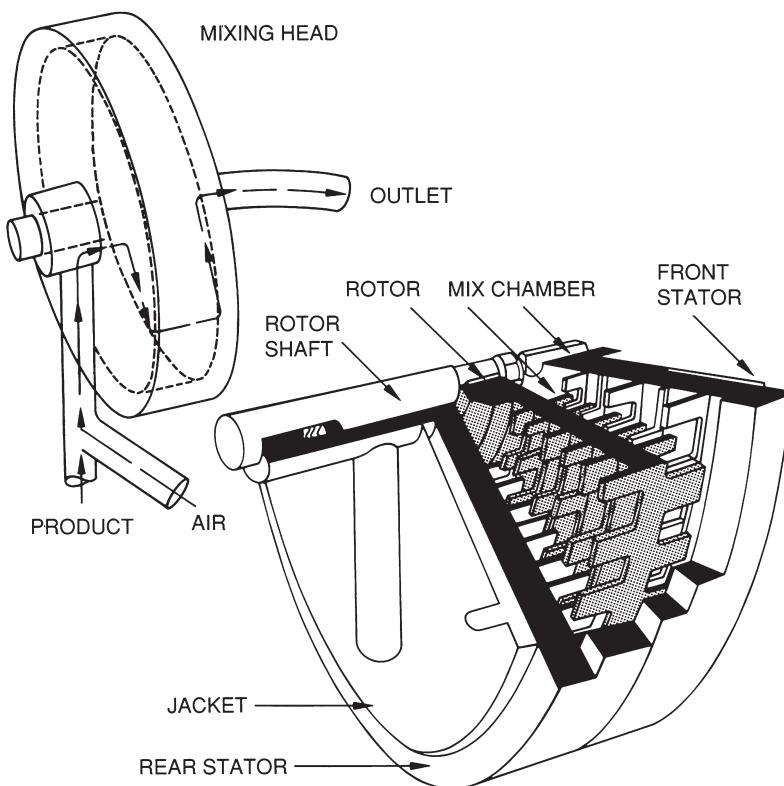


Figure 5.26 Oakes Mixer

Coating the Carpet

As shown in Figure 5.27, the carpet is attached, with the backing up, to a tenter frame conveying system that continuously moves the carpet through the coating and curing process at approximately 25 to 70 feet per minute. A filled, and potentially frothed, polyurethane precoat is first applied. The precoat is delivered to the back of the carpet via a traversing hose. A blade-over-bedplate or blade-over-roll applicator scrapes the precoat into the backing, splaying open the carpet tufts to allow the necessary penetration to lock in the fibers. The precoat layer may be partially cured before the foam is applied. Next, the froth from the Oakes mixer is deposited on the carpet back by a second traversing hose. The foam is smoothed to the desired thickness by a doctor bar. With some styles of carpet, a fabric (woven polypropylene or nonwoven felt) is applied to the curing polyurethane just before it enters the oven. The carpet then moves into a hot-air oven for curing at temperatures below 350°F. The carpet may then make a second

pass through the oven to complete curing. At this time, the finished carpet will often have topical treatments applied to the face or backing. It is then inspected, rolled up, wrapped in polyethylene and made ready for shipping.

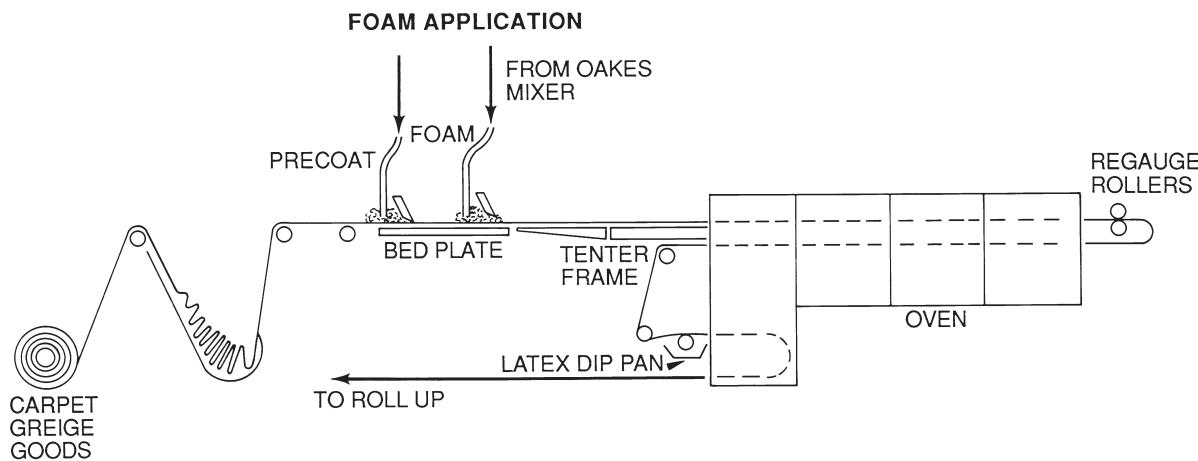


Figure 5.27 Mechanical-Frothing Process

Reverse-Coating

In a second type of coating system, the reverse-coating system, is shown in Figure 5.28. Textile Rubber and Chemical Company (Dalton, Georgia) detailed this process in a 1979 patent.^{5.159} In this system, a low-pressure mix head is used to deliver the foam to a conveyor belt.^{5.160} In this foam system, a small amount of water is added as a blowing agent. The reaction mixture, delivered from the traversing mix head, is applied directly to the conveyor belt. A suitable application system is used to spread the foam to the desired thickness. The conveyor belt with the foam travels over several sets of heated platens to increase the reaction rate. The carpet, which has been dried, is layered onto the still liquid mass and heated, whereupon bonding takes place under expansion. Because the carpet is laid into the foam, the precoat layer must be applied as a separate step. The coated carpet is removed from the release carrier, cooled and trimmed. Then it goes to the fabricating area for inspection.

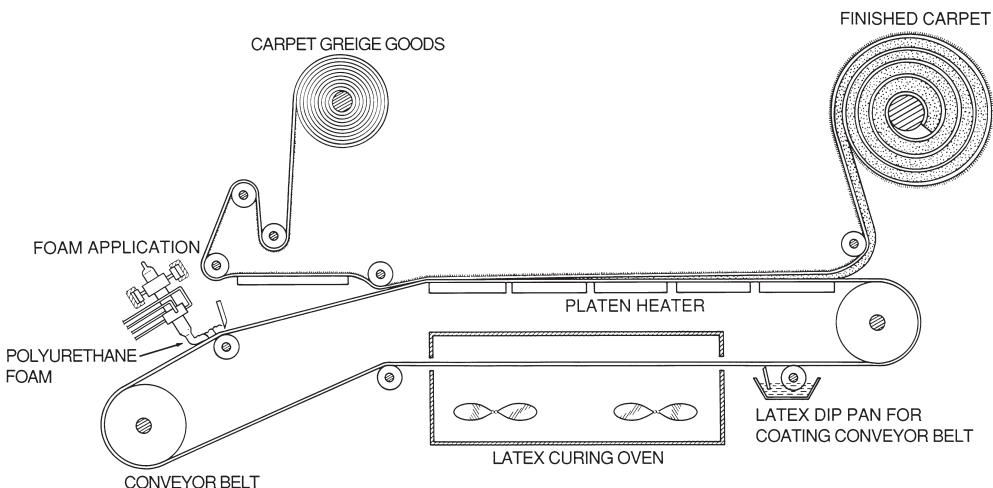


Figure 5.28 Reverse-Coating Process

References

- 5.1 Patent U.S. 5,292,778, K.J. Van Veen and G.R. Blair to Woodbridge Foam Corporation, March 8, 1994.
- 5.2 Gemeinhardt, P.G. "Flexible Urethane Foam"; In *Handbook Of Foamed Plastics*; Bender, R.J., Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965; 210.
- 5.3 Wolfe, H.W. "Designing High Resilience Molded Foams"; *Proceedings of the 3rd SPI International Cellular Plastics Conference*; Technomic: Lancaster, Pa., 1972, 451-464.
- 5.4 Frink, J.W.; Dwyer, F.J. "Advances In High-Resilience Urethane Foam Molding"; *Proceedings of the 3rd SPI International Cellular Plastics Conference*; Technomic: Lancaster, Pa., 1972, 467-477.
- 5.5 Buist, J.M. "Polyurethane Foams, Basic Equipment for Producing Flexible and Rigid Foams"; *Proceedings of the International Rubber Conference*, Washington, D.C., November, 1959; American Chemical Society, 1959; 9-20.
- 5.6 Brabandt, H., In *Handbook of Foamed Plastics*; Bender, R.J., Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965; 26-34.
- 5.7 Blackwell, J.B. "Processing Equipment for Cellular Polyurethanes"; In *Developments with Thermosetting Plastics*; Whelan, A.; Brydson, J.A.; Eds.; John Wiley and Sons: New York, 1975; 96-109.
- 5.8 Blackwell, J.B.; Rubatto, R. "Developments In Polyurethane Machinery"; In *Developments In Polyurethane I*; Buist, J.M., Ed.; Applied Science Publishers: London, 1978, 223-252.
- 5.9 Sweeny, F.M. *Introduction To Reaction Injection Molding*; Technomic: Westport, Conn., 1979, 77-126.
- 5.10 Knipp, U.; Becker, W.E. "Equipment"; In *Reaction Injection Molding*; Becker, W.E.; Ed.; Van Nostrand Reinhold: New York, 1979; 243-253.
- 5.11 Boden, H.; Schulte, K.; Wintz, H.; In *Polyurethane Handbook*; Oertel, G.; Ed.; Hanser: New York, 1985; 134-142.
- 5.12 Gemeinhardt, P.G.; In *Handbook Of Foamed Plastics*; Bender, R.J., Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965; 215.
- 5.13 Walmsley, G.D. "The Production Chemist and Flexible Urethane Foam Technology"; *J. Cell. Plast.* **1965**, 1/1, 97-100.
- 5.14 Woods, G.W. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 98, 142.
- 5.15 Buist, J.M. "Polyurethane Foams: Basic Equipment for Producing Flexible and Rigid Foams"; *Proceedings International Rubber Conference*, Washington, D.C., November 813, 1959, 9-20.
- 5.16 Buist, J.M.; Hurd, R.; Lowe, A. "Polyurethane Foams: Methods of Production, Properties and Applications"; *Chem. And Ind.* **1960**, 1544-1558.
- 5.17 Scott, G. *Atmospheric Oxidation And Antioxidants*; Elsevier Publishing: New York, 1965, 339.
- 5.18 St. Pierre, L.E.; Price, C.C. "The Room Temperature Polymerization of Propylene Oxide"; *J. Amer. Chem. Soc.* **78**, July Sept., 1956, 3432-3436.

- 5.19 Lloyd, W.G. "Inhibition of Polyglycol Autoxidation"; *J. Chem. Eng. Data* **1961**, 6/4, 541.
- 5.20 Capocci, G. "Advances In The Light Stabilization Of Polyurethanes"; *Proceedings of the 30th Annual Polyurethane Technical/Marketing Conference*, Oct. 1986; Technomic: Lancaster, Pa., 1986; 220-227.
- 5.21 David D.J.; Staley, H.B. *Analytical Chemistry Of The Polyurethanes*; Robert Krieger: New York, 1979, 294.
- 5.22 Lloyd, W.G. "The Low Temperature Autoxidation of Diethylene Glycol"; *J. Am. Chem. Soc* **1956**, 78,72-75.
- 5.23 Newton, R.A. "Propylene Oxide Polymers and Higher 1,2-Epoxy Polymers". In *Encyclopedia of Chemical Technology, Third Edition*; John Wiley and Sons: New York, 1982; Vol. 18, 637.
- 5.24 Kuryla, W.C.; Critchfield, F.E.; Platt, L.W.; Stamberger, P. "Polymer/Polyols, a New Class of Polyurethane Intermediates"; *J. Cell. Plast.* **1966**, 2/2, 84-96.
- 5.25 Layton, R.F.; Knecht, L.A. "Further Investigation of the Colorimetric Reaction between Aromatic Isocyanates and Peroxy Compounds"; *Anal. Chem.* **1971**, 43/6, 794-797.
- 5.26 Jones, R.E.; Fesman, G. "Air Flow Measurement and Its Relations to Cell Structure, Physical Properties, and Processability for Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 200-216.
- 5.27 Harding, R.H. "Morphologies of Cellular Materials"; In *Resinography of Cellular Plastics*; ASTM STP 414, 1967, 3-18.
- 5.28 Blair, E.A. "Cell Structure and Physical Properties of Elastomeric Cellular Plastics"; In *Resinography of Cellular Plastics*, ASTM STP 414, 1967, 84-95.
- 5.29 Buist, J.M.; Ball, G.W.; Woods, G. "Flexible Foam: Manufacture and Properties"; In *Advances in Polyurethane Technology*; Buist, J.M.; Gudgeon, H.; Eds., Maclaren and Sons: London, 1968, 152-154.
- 5.30 Meinecke, E.A.; Clark, R.C. *Mechanical Properties of Polymeric Foams*; Technomic: Conn., 1972.
- 5.31 Baumhakel, R. "Influence of Stirring Velocity and Air Loading on the Formation of Flexible Urethane Foams"; *J. Cell. Plast.* **1972**, 8/6, 304-310.
- 5.32 van Leuwen, B.G.; Powell, D.G.; Puig, J.E.; Natoli, F.S. "Physical and Chemical Approaches to Ideal Cushioning Foams"; In *Advances in Urethane Science and Technology*; Technomic: Conn., 1973; Vol. 2, 153-182.
- 5.33 Berlin, A.A.; Shutov, F.A.; Zhitinkina, A.K. *Foam Based On Reactive Oligomers*; Technomic: Westport, Conn., 1982, 85-87.
- 5.34 Rusch, T.E.; Raden, D.S. "Choosing Urethane-foam catalysts"; *Plast. Compd.* **1980**, July/August, 61-74.
- 5.35 Wooler, A.M. "Novel Small Scale Procedures for Initial Formulation Selection in the Development of Polyurethane Foams"; *Cell. Polym.* **1989**, 8, 296-320.
- 5.36 "Free Rise Cup Foam Test"; Dow Analytical Method DOWM 100531-TE890, January 31, 1989.

- 5.37 Burks, S.; Autenrieth, R.; Gutowsky, K. "Ultrasonic Rise and Adiabatic Temperature Evaluation (URATE) of Polyurethane Foams"; *Proceedings of the SPI33rd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 297-305.
- 5.38 Rosemund, W.R.; Sanders, M.R. "The Use of Silicone Surfactants and Amine Catalysts To Vary Processing and Properties of Various Urethane Foam Systems"; *J. Cell. Plast.* **1977**, 13/3, 182-193.
- 5.39 Motte, P.; Regnault, J. "Automated Bench Foam Test Equipment"; *Proceedings of the SPI32nd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 691-692.
- 5.40 Davis, B. "Machinery marches on From simplicity to sophistication"; *Urethanes Tech.* **1987**, March, 28-38.
- 5.41 Neary, W.J. "What to Look for In Urethane Foam Machinery"; *Plast. Tech.* **1965**, 11/3, 50-53.
- 5.42 Lerner, A.; Coen, R. "How To Buy Equipment For Foam Processing"; *Plast. Tech.* **1966**, July, 97-99.
- 5.43 Bowyer, R.L. "Special Production Equipment For Factory Production Lines"; In *International Progress In Urethanes, Volume 1*, Frisch, K.C.; Hernandez, A.; Eds; Technomic: Westport, Conn., 1977; 272-285.
- 5.44 *How To Buy A RIM Machine*; Gusmer-Admiral, Inc.: Lakewood, New Jersey, 1996.
- 5.45 Jennings, R. "Control Urethane Reaction For Quality Parts"; *Plast. Tech.* **1969**, 15/3, 43-46.
- 5.46 Schlueter, K. "Process Regulation for Polyurethane Machines"; *J. Cell. Plast.* **1981**, 17/1, 51-58.
- 5.47 Agabeg, R.C. "Intermediates For Polyurethane Foams"; In *Polyurethane Foams*; Healy, T.T., Ed.; Cliffe Books: London, 1963, 15.
- 5.48 Buist, J.M.; Gudgeon, H. *Advances in Polyurethane Technology*; Maclaren and Sons: London, 1968, 181.
- 5.49 Bedoit, W.C. "Foam Machine Operator Safety"; *J. Cell. Plast.* **1975**, 11/2, 79-86.
- 5.50 *Neutra-Flush*, product brochure, The Brulin Corporation, 1993.
- 5.51 Jackson, H.L.; Gallagher, R.J. "DBE purges polyurethane equipment without methylene chloride risks"; *Elast.* **1990**, 122/10, 56-60.
- 5.52 Editorial, "P-Series Glycol Ethers And Acetates Aid In Foam Clean-Up Applications"; *Urethane Plastics and Products* **1987**, 17/9, 34.
- 5.53 Editorial, "Flushing residues is easier - and safer"; *Urethanes Tech.* **1995**, 11/6, 42.
- 5.54 Ramey, J.S.; Porter, R.A. "Softening Aid, Flushing Agent, Viscosity Reducer: A Study of Plasticizers for Polyurethanes"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 216-223.
- 5.55 Lewis, G.D. "Solvent Free Mechanical Mixing"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 171-175.
- 5.56 Stengard, R.A. "High-Pressure Impingement Mixing—Route to Faster, Better PU Parts"; *Plast. Tech.* **1974**, 20/7, 41-44.

- 5.57 Gmitter, G.; Jaul, E. "Formulating and Processing factors in One-Shot Urethane Foam Production"; *Plast. Tech.* **1963**, 9/7, 28-33.
- 5.58 Brabandt, H. "Problems Frequently Encountered In The Use Of Machines For Processing Multi-Component Foams"; *Plast. Design Proc.* **1964**, 4/9, 22-25.
- 5.59 Hook, T.K. "Chemical Engineering in Urethane Foam Molding"; *Chem. Eng. Prog.* **1967**, 63/6, 94-100.
- 5.60 Stewart, S.A. "The Influence Of Foam Machine Variables On Physical Properties Of Urethane Foam"; *Proceedings of the 2nd SPI International Cellular Plastics Conference*; Technomic: Westport, Conn., 1968, Section 2F, 1-4.
- 5.61 Brabandt, H.; In *Handbook Of Foamed Plastics*; Bender, R.J.; Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965, 34.
- 5.62 Fruzzetti, R.E.; Hogan, J.M.; Murray, F.J.; White, J.R. "Factors Affecting the Quality of Impingement Mixed RIM Urethanes"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1977, Paper No. 770839; SAE: Warrendale, Pennsylvania.
- 5.63 Coen, R. "Six Steps to Setting Up and Checking Out a PU Foam Machine"; *Plast. Tech.* 1967, 13/7, 43-45.
- 5.64 Bodine, L.; Suarez, L. "Troubleshooting Guide For Urethane Processors"; *Plast. Tech.* 1971, 17/8, 36-37.
- 5.65 Layton, R.F.; Knecht, L.A. "Further Investigation of the Colorimetric Reaction between Aromatic Isocyanates and Peroxy Compounds"; *Anal. Chem.* **1971**, 43/6, 794-797.
- 5.66 Dworkin, D. "Urethane Foam Processing Techniques"; *SPE Journal* **1961**, Dec., 1269-1275.
- 5.67 Fisher, J. "A new development for the flexible polyurethane foam industry"; *Appl. Plast.* **1969**, March, 18-19.
- 5.68 Woods, George. *The ICI Polyurethane Book, (The Netherlands: ICI Polyurethanes)*; John Wiley & Sons: New York, 1987; 61-69.
- 5.69 Woods, George. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982; 140-149.
- 5.70 *Flexible Slabstock Polyurethane Foam*; Dow Chemical Europe; Form No. EU8727-E-7.79.
- 5.71 Editorial, "Improved production for flexible PU foam"; *Europlast. Month.* **1973**, 46/9, 71-72.
- 5.72 Editorial, "Material Savings a Key To PU Slab Process"; *Plast. Tech.* **1974**, 20/11, 9-10.
- 5.73 Webb, J.; Vreenegoor, N.C. "The Maxfoam Process for Foam Production"; *Proceedings of the SPI4th International Cellular Plastics Conference*; Society of The Plastics Industry: New York; 1976, 58-62.
- 5.74 Vreenegoor, N.C. "The Foamax process for making flat-top flexible polyurethane slabstock foams"; *Plast. Rub. Proc.* **1977**, 2/1, 30-32.
- 5.75 von Hassell, A. "Flat-Top Bun Lines: Which System for You"; *Plast. Tech.* **1978**, 24/12, 57-62.

- 5.76 Patent U.S. 4,504,429, A.C.M. Griffiths to Hyman International Ltd., March 12, 1985.
- 5.77 Patent U.S. 4,567,008, A.C.M. Griffiths to Hyman International Ltd., January 28, 1986.
- 5.78 Griffiths, T., Shreeve, P. "Vertifoam-Continuous Vertical Block Foam Process"; *Proceedings of the SPI6th International Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983, 76-79.
- 5.79 Poncet, J.A.A. "Methods And Devices For Continuously Producing Of Polyurethane Foam"; *Proceedings of the SPI-6th Internationnal Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983, 148-155.
- 5.80 Griffiths, A.C.M.; Shreeve, P. "Vertifoam Continuous Vertical Block Foam Process"; *Cell. Polym.* **1984**, 3, 195-204.
- 5.81 Poncet, J.A.A. "New Progress About An Economical Process Of Vertical Foaming"; *Proceedings of the SPI29th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1985, 236-239.
- 5.82 Webb, J.H.; Griffiths, A.C.M. "Flexible Polyurethane Foam Slabstock Manufacture Through The Next Decade"; *Proceedings of the SPI30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 62-66.
- 5.83 Griffiths, A.C.M. "Hypercure-Accelerated Curing of Flexible Polyurethane Slabstock For Better Control Over Foam Properties And A Safer Environment"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 922-925.
- 5.84 Patent U.S. 3,890,414, M.A. Ricciardi, D.J. Smudin, R.D. Wagner, M. Pcolinsky and J.E. Chaya, June 17, 1975.
- 5.85 Editorial, "New Ways to cool it"; *Urethanes Tech.* **1992**, August/September, 6.
- 5.86 Collins, B.; Fawley, C. "Cannon Enviro-Cure Equipment Applied to the Vertifoam and Maxfoam Processes"; *Proceedings of the Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 1993, 176-183.
- 5.87 Stone, H.; Reinink, E.; Lichvar, S.; Carlson, W.; Sikorsky, C. "The Rapid Cure Process - Industrial Experience, Engineering and Formulation Principles"; *Proceedings of the Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 1993, 270-278.
- 5.88 McAfee, C.D.; Wiltz, E.P.; Skorpenske, R.G.; Ridgway, D.H.; McClusky, J.V. "Understanding the Fundamentals of Forced Cooling in the Production of Blowing Agent Free Flexible Slabstock Polyurethane Foams"; *Proceedings of the Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 1993, 279-287.
- 5.89 Gould, L.P. "Cellular Rubbers"; In *Symposium On The Applications Of Synthetic Rubbers*; American Society For Testing Materials: Philadelphia, Pa., 1944, 90-103.
- 5.90 Klesper, E. "Application Of Volatile Organic Liquids for Expanding Flexible Urethane Foam"; *Rubber Age* **1958**, October, 84-87.
- 5.91 Porteous, A. *Improved Manufacture of Polyurethane Foams*, a Doctoral Thesis presented to the School of Engineering, Dartmouth College, Hanover, New Hampshire; May, 1967.

- 5.92 Porteous, A.; Wallis, G.B. "A Possible Means of Eliminating Supplementary Blowing Agents in Flexible Urethane Foam Production"; *Trans. Inst. Chem. Engr. London* **1967**, 45, CE276-CE283.
- 5.93 Porteous, A.; Wallis, G.B. "Vacuum Blowing of Flexible Urethane Foams"; *J. Cell. Plast.* **1968**, 4/11, 431-437.
- 5.94 Patent U.S. 5,194,453, L. Jourquin, E. DuPrez and R. Mortelmans to Recticel, Belgium, March 16, 1993.
- 5.95 Editorial "Novel reduced-pressure foaming for slabstock production"; *Urethanes Tech.* **1993**, April/May, 4.
- 5.96 Clockaerts, M.; Mortelmans, R. "Variable Pressure Foaming in Continuous Slabstock Production"; *Conference Papers, UTECH 94*; Crain Communications: London, 1990, Paper 34.
- 5.97 Blackwell, J.B.; Buckley, G. "The Manufacture of Flexible Polyurethane Foams by the Variable pressure Process V.P.F."; *Cell. Polym.* **1995**, 14/4, 311-330.
- 5.98 Smock, D. "Foamex develops new flexible urethane polymers"; *Plast. World* **1996**, 54/5, 12-13.
- 5.99 Editorial "Variable-Pressure Process Adds Flexibility to PUR Foaming"; *Plast. Tech.* **1966**, 42/6, 96.
- 5.100 Patent U.S. 5,182,313, by Scott Carson.
- 5.101 Ramazzotti, D.; Carson, S. "Controlled Environment Foaming"; *Proceedings Of The Polyurethanes 1994 Conference*; Technomic: Lancaster, Pa., 1994; 8-11.
- 5.102 *Foam One, Controlled Environment Foaming*; Product Brochure, The Edge-Sweets Company; Grand Rapids, Michigan.
- 5.103 Patent U.S. 4,906,672, H. Stone, S. Lichvar, C.W. Bredbenner, R. Rupp and E. Minnich to PMC, Inc., March 6, 1990.
- 5.104 Patent U.S. 5,081,162, P.V. Farkas and J.A. Duley to Woodbridge Foam Corporation, January 14, 1992.
- 5.105 Patent U.S. 5,120,770, E.N. Doyle and S. Carson, June 9, 1992.
- 5.106 Fiorentini, C.; Taverna, M.; Griffiths, T.; Collins, B. "Latest Manufacturing Solutions for Slabstock Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 12-16.
- 5.107 Fiorentini, C.; Taverna, M.; Griffiths, T.; Collins, B. "Liquid-Carbon-Dioxide-Blown Slabstock Foams: Industrial Results"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 491-496.
- 5.108 Taverna, M.; Corradi, P.; Meloth, H. "Foaming polyurethane with liquid carbon dioxide"; *Kunststoffe* **1996**, 86/6, 810-815.
- 5.109 Taverna, M.; Meloth, H.; Griffiths, T. "Two Years of Industrial Experience with Liquid CO₂-Blown Slabstock Foams"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 164-168.
- 5.110 Eiben, R.G.; Sulzbach, H.M.; Ferrand, J.T.; Radovich, D.A. "High-Quality Flexible Slabstock Foam using Liquid Carbon Dioxide as an Auxiliary Blowing Agent"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 70-73.

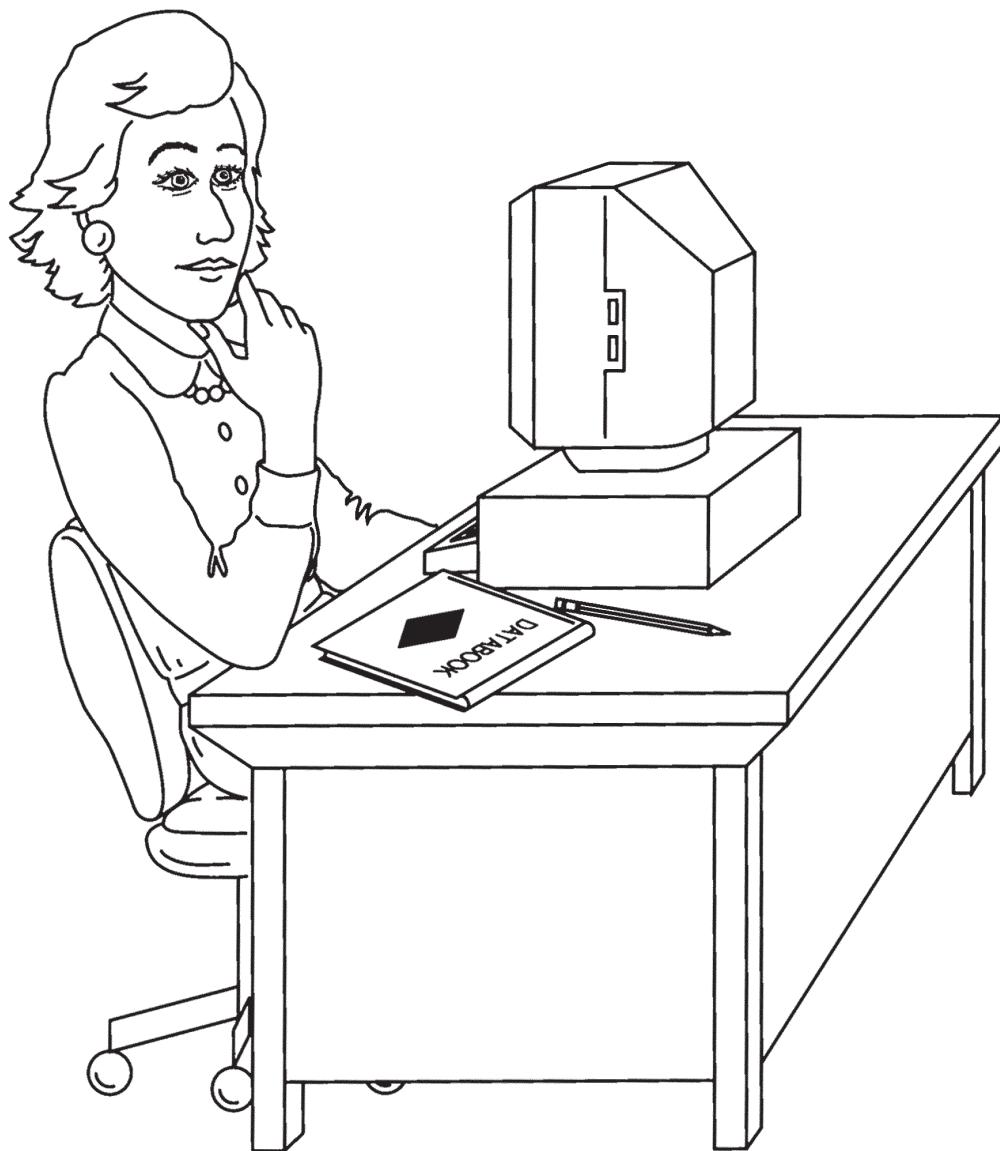
- 5.111 Eiben, R.G. "Blowing Flexible Slabstock with Liquid Carbonic Acid: Progress with Technology"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 31.
- 5.112 Kirschner, R.L.; Pisipati, J.S.; Ferrand, J.T.; Sulzbach, H.M. "NovaFlex - Technologies in the Slabstock Industries"; *Proceedings of the 1996 PFA Technical Program*; Polyurethane Foam Association: Wayne, New Jersey, 1996.
- 5.113 Blackwell, J.B.; Buckley, G.; Blackwell, B. "The Application of the CO₂ Process to the Major Methods of Continuous Flexible Slabstock Production"; *Proceedings of the 1996 SPI Conference*; Technomic: Lancaster, Pa., 1996, 136-143.
- 5.114 Blackwell, J.B.; Buckley, G.; Blackwell, S.W. "Comparison of the VPF and Liquid CO₂ Foaming Processes"; *Cell. Poly.* **1996**, 15/2, 105-116.
- 5.115 Potzsch, R. "Production of Automobile Seat Elements Out of PU-Flexible Block Foam"; *Proceedings of the SPI/FSK Polyurethanes World Congress, Aachen*; Technomic: Lancaster, Pa., 1987; 887-890.
- 5.116 Ubben, R. "Cutting machines for polyurethane flexible foam in the mattress, upholstery and automobile industry"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 145-148.
- 5.117 Schiffler, C. "The Application of Water Jet Technology in the Field of PU Foam"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996, Paper No. 20.
- 5.118 Dixon, S. "Polyurethane Foam Moulding"; *Brit. Plast.* **1963**, 36/1, 24-27.
- 5.119 Parkinson, J.C. "Moulding flexible polyurethane foam"; *Brit. Plast.* **1964**, 37/3, 146-147.
- 5.120 Gemeinhardt, P.G.; Reid, G.E.; Bingham, S.A.; Eakin, J.L.; Szabat, J.F. "Refinements in Molding One-Shot Flexible Polyether Urethane Foam"; *SPE Journal* **1964**, Apr., 357-362.
- 5.121 Buist, J.M.; Woods, G. "Moulding of Flexible Urethane Foam"; *Trans. Inst. Rubb. Ind.* **1965**, 41/1, T1-T23.
- 5.122 Zuckerman, J.L. "The Art of Molding Flexible Urethane Foam"; *SPE Journal* **1966**, May, 56-59.
- 5.123 Musgrave, I. "Modern Methods Of Molding Urethane Foams"; *Proceedings of the SPI 2nd International Cellular Plastics Conference*; Society of The Plastics Industry: New York, 1968, Section 5B, 18.
- 5.124 Naturman, L. "What You Should Know About Polyurethane Foam Molding"; *Plast. Tech* **1969**, 15/1, 44-46.
- 5.125 Patent U.S. 3,970,732, M.A. Slaats and D.E. Overton, July 20, 1976.
- 5.126 Brownbill, D. "New Equipment for cold-cure HR foam is faster, more efficient"; *Mod. Plast. Intl.* **1981**, 11/10, 28-31.
- 5.127 Patent U.S. 4,988,271, S. Kumasaka, S. Tada, K. Katsuki, O. Fujii, T. Yamamoto, R. Nagamine, M. Idel, Y. Sato and K. Ibata to Human Industry Corporation, January 29, 1991.
- 5.128 Knibbe, D.E. "A Chemical and Physical Comparison of Polyurethane Hot Cure and Cold Cure Moulding"; *J. Cell. Plast.* **1985**, 21/4, 264-268.

- 5.129 Lambach, J. L.; Gill, W.A. "Hot Foam Replacement with Non-CFC HR Foam"; *Proceedings of the SPI33rd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 165-171.
- 5.130 Nightingale, R.J. "Two low cost mould-making techniques for moulders and fabricators"; *Brit. Plast.* **1970**, August, 83-85.
- 5.131 Grant, L.J. "Metal Spray Tooling: A Low Cost Alternative for Polyurethane Molds"; *Proceedings of the SPI33rd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 120-124.
- 5.132 Stolton, R.E.; Wilkinson, W.V. "Epoxide resin moulds for forming and curing polyurethane foam by means of microwave energy"; *Intl. Plast. Eng.* **1964**, 4/10, 315-316.
- 5.133 Kosmala, J.; Tierney, J. "How to Make Molds for Plastic Furniture"; *SPE J.* **1970**, 26/11, 39-42.
- 5.134 Friedrich, H. "The Construction of Foam Molds from Epoxy Resins"; *Kunststoffe* **1976**, 66/4, 182-186.
- 5.135 Danien, W.R. "Choosing the right RIM tooling material"; *Plast. Design Forum* **1978**, 8/5, 51-55.
- 5.136 Green, H.L. "Practical Considerations Regarding Mold Release Agents for Urethane Foam"; *J. Cell. Plast.* **1969**, 5/3, 173-175.
- 5.137 Axel, F. "Mold Release Agents For Polyurethane Foams-New Trends and Developments"; In *International Progress In Urethanes*; Frisch, K.C.; Hernandez, A., Eds.; Technomic: Westport, Conn., 1975, 1, 286-291.
- 5.138 Kirkland, C. "The Mold Release Quandary: No Easy Answers For Molders"; *Plast. Tech.* **1980**, September, 65-70.
- 5.139 Collins, S.H. "Update: Additives that provide mold release"; *Plast. Cmpd.* **1983**, March/April, 38-44.
- 5.140 Cox, D.B. "The Role of Release Agents in Urethane Molding", In *Urethane Chemistry and Applications*; Edwards, K.M., Ed.; ACS Symposium Series 172, 1981, 565-573.
- 5.141 Lammerting, H. "Releasing details. Assortment of Agents now available"; *Uret. Tech.* **1986**, 3/1, 38-42.
- 5.142 Sherman, L.M. "Mold Releases, Cleaner and Safer Are the Watchwords"; *Plast. Tech.* **1995**, August, 42-45.
- 5.143 Andrews, G.D.; Wasilczyk, G.J. "Water-Based Mold Release Agents for Flexible Molded Applications", *Proceedings of the SPI31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988; 447-454.
- 5.144 Schroder, W. "Aqueous Release/System and Self-Releasing In-Mold-Coatings for Polyurethane-Foam-Systems"; *J. Elast. Plast.* **1988**, 20, 200-207.
- 5.145 Wochnowski, H. "Aqueous-Based Release Agents for Polyurethane Moulding"; *Kunststoffe* **1989**, 78/8, 680-683.
- 5.146 Block, H.H. "Aqueous Release Agents for the Processing of Polyurethane Systems"; *Kunststoffe* **1989**, 79/3, 240-242.

- 5.147 Fountas, G. "Water-based release agents offer solution to processors' CFC problems"; *Elastomerics* **1990**, 122/12, 30-31.
- 5.148 Moskowitz, M. "Water-based agents help molders clear the air"; *Plast. World* **1991**, 49/3, 103.
- 5.149 Andrew, G.D.; Swantek, D.J.; Diem, R.; Nollen, D. "Environmentally Friendly Release Agents for Molded Polyurethane"; *Proceedings of the Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 877-884.
- 5.150 Editorial "Aqueous mold release agents offer environmental benefits"; *Elastomerics* **1992**, 124/2, 29.
- 5.151 Thies, W. "The Smooth Changeover to Aqueous Release Agents at a Flexible Foam Plant"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994, Paper No. 15.
- 5.152 Michaeli, W.; Fleischer, D.; Colberg, M.; Ellinghaus, S. "Economical Application of Release Agent"; *Kunststoffe* **1996**, 86/6, 838-842.
- 5.153 Andrew, G.D.; Boyer, T.C.; Olari, J.R. "Unique Water Based Release Agents For Foam-To-Fabric Automotive Seat Applications"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 480-486.
- 5.154 Editorial "Advanced equipment-for the production of flexible foam cushions"; *Brit. Plast.* **1970**, August, 79.
- 5.155 Schiemann, L. "The Latest Process-Concepts for the Manufacture of High Quality Seating Systems"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996, Paper No. 13.
- 5.156 Editorial, "Mechanically foamed urethane moves into market for floorcovering backing"; *Mod. Plast. Int.* **1978**, Aug, 12-13.
- 5.157 Patent U.S. 3,821,130, B.G. Barron and J.R. Dunlap to the Dow Chemical Company, June 28, 1974.
- 5.158 Madge, E.W. *Latex Foam Rubber*; Interscience Publishers: New York, 1962, 78-79.
- 5.159 Patent U.S. 4,132,817, J.G. Tillotson to Textile Rubber and Chemical Company, January 2, 1979.
- 5.160 Ward, D. "Fresh Opportunities For Polyurethane Backing Process"; *Textile Month* **1980**, Sept., 23-26.

Chapter 6

Foam Calculations



This chapter is designed as an aid in making the calculations necessary to define flexible foam formulations and to calculate the raw material costs of those formulations. These calculations are easily done with any of the modern spread sheet-based computer programs.

Chapter 6

Foam Calculations

R. Herrington, K. Hock

This chapter discusses the basic calculations associated with flexible foam technology. First, calculation terms are defined. Next, basic foam-making calculations are given. The chapter ends with sample economic calculation methods.

DEFINITIONS AND EQUATIONS

For the purposes of this discussion, the following definitions apply:

A-Side: The isocyanate-containing material.

B-Side: The polyol-containing material, usually a blend of polyol, chain extenders, cross-linker, water, catalysts and surfactants.

Functionality: The functionality of a B-side foam ingredient is the number of isocyanate reactive sites on a molecule. For polyols, an average functionality is generally used.

$$\text{Average Functionality} = \frac{\text{total moles OH}}{\text{total moles polyol}} \quad (6.1)$$

Acid Number: A number arising from a wet analytical method to determine the amount of residual acidic material in a polyol. It is reported in the same units as hydroxyl number.

Hydroxyl Number (OH Number): A number arising from a wet analytical method for the hydroxyl content of a polyol; it is the milligrams of potassium hydroxide equivalent to the hydroxyl content in one gram of polyol or other hydroxyl compound.

$$OH\ Number = \frac{56.1 \times 1000}{Equivalent\ Weight} \quad (6.2)$$

where 56.1 is the atomic weight of potassium hydroxide and 1000 is the number of milligrams in one gram of sample. The OH number for each lot of polyol is provided by the manufacturer.

Polyols are sometimes characterized by quoting the weight percentage of hydroxyl groups. Conversion to hydroxyl number is accomplished by:

$$OH\ Number = 33 \times \% OH \quad (6.3)$$

where the number 33 is obtained by reduction of constants. For a mixture of polyols, the hydroxyl number of the mixture (OH_m) is given by:

$$OH_m = OH\ Number_A (Wt.\% Polyol\ A) + \\ OH\ Number_B (Wt.\% Polyol\ B) + \dots \quad (6.4)$$

Equivalent Weight of a Polyol: The weight of a compound per reactive site.

$$Equivalent\ Weight = \frac{Molecular\ Weight}{Functionality} \quad (6.5)$$

Since polyols have a molecular weight distribution, an average equivalent weight is calculated. These calculations are done using the product analyzed hydroxyl (OH) content and acid number:

$$Equivalent\ Weight = \frac{56.1 \times 1000}{OH\ Number + acid\ number} \quad (6.6)$$

For most polyols in use today, the acid number is very low and may be omitted. If the acid number is larger than about 1.0, it should be factored into the above equation.

Example: The lot analysis for a new batch of polyol indicates a OH Number of 54.2 and an acid number of 0.01. What is the polyol's equivalent weight?

$$Equivalent\ Weight = \frac{56.1 \times 1000}{54.2 + 0.01} \quad (6.7)$$

$$Equivalent\ Weight = 1035 \quad (6.8)$$

Equivalent Weight of a Polyol Blend: For foam systems based on a blend of polyols, the net equivalent weight can be calculated by using the result of Equation 6.4:

$$Equivalent\ Weight_{BLEND} = \frac{56.1 \times 1000}{OH\ Number + acid\ number} \quad (6.9)$$

where an acid number for the blend is calculated using the logic of Equation 6.4. Alternatively, the equivalent weight of a polyol blend is given by:

$$\text{Equivalent Weight}_{\text{BLEND}} = \frac{100}{\frac{\text{Wt. \% Polyol A}}{\text{Eq. Wt. Polyol A}} + \frac{\text{Wt. \% Polyol B}}{\text{Eq. Wt. Polyol B}}} + \dots \quad (6.10)$$

Equivalent Weight of an Isocyanate: The weight of an isocyanate compound per isocyanate site. This is calculated from the analyzed isocyanate (NCO) content.

$$\text{Equivalent Weight} = \frac{42 \times 100}{\% \text{ NCO}} \quad (6.11)$$

where 42 is the atomic weight of the NCO group.

Example: A new lot of toluene diisocyanate is analyzed at 48.2% NCO. What is the equivalent weight?

$$\text{Equivalent Weight} = \frac{42 \times 100}{48.2} \quad (6.12)$$

$$\text{Equivalent Weight} = 87.1 \quad (6.13)$$

Equivalent Weight of an Isocyanate Blend: For foam systems using a blend of different isocyanates, the net equivalent weight of the blend is given by:

$$\text{Equivalent Weight}_{\text{BLEND}} = \frac{100}{\frac{\text{Wt. \% Iso A}}{\text{Eq. Wt. Iso A}} + \frac{\text{Wt. \% Iso B}}{\text{Eq. Wt. Iso B}}} + \dots \quad (6.14)$$

Equivalent Weight of Water: Water reacts with 2 isocyanate groups and thus the equivalent weight is given by:

$$\text{Eq. Wt. of Water} = \frac{\text{Molecular Weight}}{\text{Functionality}} = \frac{18}{2} = 9 \quad (6.15)$$

Isocyanate Index: The ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100. Theoretical equivalent amount is equal to one equivalent isocyanate per one equivalent B-side compounds; this is an index of 100.

$$\text{Isocyanate Index} = \frac{\text{Actual Amount of Iso}}{\text{Theoretical Amount of Iso}} \times 100 \quad (6.16)$$

FOAM-MAKING CALCULATIONS

The recipe for a desired foam formulation may come from previous work or may be unique. In any case, proper foaming technique requires that each intended ingredient and its concentration be listed. This listing may be handwritten in a databook, handwritten on a foam machine run sheet or generated on a computer. Detailed examples of computerized calculations are given in References 6.1-6.3. Table 6.1 shows a typical output from a computer spreadsheet calculation.

The amount of isocyanate required to react with the polyol, water and other reactive additives is calculated to give the desired stoichiometry. Many foams are prepared at a slight excess of isocyanate; e.g., 105% of theoretical equivalence. In actual practice, the amount of isocyanate is adjusted up or down depending on the particular foam system, the properties desired from that system or knowledge of other effects such as ambient conditions and scale of manufacture.

Table 6.1 Sample Foam-Making Calculations

| FORMULATION | LOT | PARTS | EQ. WT. | EQUIVALENTS |
|--|-----------|-----------|---------|-------------|
| SPECFLEX NC 630, Polyol | | 70.0000 | 1825.0 | 0.0383 |
| SPECFLEX NC 710, Copolymer Polyol | | 30.0000 | 2400.0 | 0.0125 |
| TEGOSTAB B-8708, Surfactant | | 1.0000 | 0.0 | |
| DIETHANOL AMINE, Pure | | 1.7000 | 35.0 | 0.0485 |
| DABCO 33-LV, Catalyst | | 0.1500 | 105.0 | 0.0014 |
| NIAX A-1, Catalyst | | 0.0800 | 233.7 | 0.0003 |
| POLYCATE 77, Catalyst | | 0.2400 | 0.0 | |
| WATER | | 4.2000 | 9.0 | 0.4666 |
| Formula Weight 107.3700 | | | | 0.5678 |
| VORANATE T-80 TDI Equivalent Weight = 87.1 | | | | |
| INDEX | ISO. REQ. | B/A RATIO | | |
| 90.0 | 44.51 | 2.4123 | | |
| 95.0 | 46.99 | 2.2850 | | |
| 98.0 | 48.47 | 2.2152 | | |
| 100.0 | 49.46 | 2.1708 | | |
| 103.0 | 50.94 | 2.1078 | | |
| 105.0 | 51.93 | 2.0676 | | |
| 108.0 | 53.42 | 2.0099 | | |
| 110.0 | 54.41 | 1.9734 | | |

As the table indicates, all recipes and calculations are based on 100 total parts by weight of polyol. There may be more than one polyol in a recipe, but convention dictates that the sum of all polyols add up to 100 parts. The amount of other ingredients is normally listed as some desired parts by weight per hundred parts of polyol.

The calculation procedure for a foam formulation is straightforward:

1. Determine the parts of each polyol. Total parts polyol should equal 100.
2. Determine the parts of other B-side components per 100 parts polyol.

NOTE: If desired, the amount of water coming into the formulation as residual in the polyol can be calculated and used to adjust the amount of water to be purposely added. With most polyols, the amount of residual water present is so low that it can be neglected in most foam calculations. Some copolymer polyols have an appreciable water content. If you are preparing a very high density foam, the water in the polyol may represent a significant percentage of the total.

3. Sum the parts of all B-side materials to get the total formula weight.
4. Record the equivalent weight of each B-side component from the above calculations or from a listing of typical equivalent weights as shown in Table 6.2.
5. Calculate the equivalents of each B-side component.

$$\text{Equivalents} = \frac{\text{Parts}}{\text{Equivalent Weight}} \quad (6.17)$$

Example: VORANOL 4703 polyol used above has an equivalent weight of 1621. How many equivalents are contributed by 50 parts of this material?

$$\text{Equivalents} = \frac{50}{1621} \quad (6.18)$$

$$\text{Equivalents} = 0.030845 \quad (6.19)$$

Example: How many equivalents are contained in 4.2 parts of water?

$$\text{Equivalents} = \frac{4.2}{9} \quad (6.20)$$

$$\text{Equivalents} = 0.466666 \quad (6.21)$$

6. Sum the reactive equivalents of each B-side component to get the total B-side equivalents.
7. Record the isocyanate equivalent weight.
8. Select the desired isocyanate index.

9. Calculate the isocyanate parts required.

$$Eq. Iso = \frac{(Equivalents\ B-Side) \times (Isocyanate\ Index)}{100} \quad (6.22)$$

$$Parts\ Isocyanate = (Eq. Iso) \times (Iso\ Eq.\ Wt.) \quad (6.23)$$

Example: For the formulation in Table 6.1 at a desired index of 105:

$$Eq. Iso = \frac{(0.571080) \times (105)}{100} \quad (6.24)$$

$$Eq. Iso = 0.599634 \quad (6.25)$$

$$Parts\ Iso = (0.599634) \times (87.1) \quad (6.26)$$

$$Parts\ Iso = 52.22812 \quad (6.27)$$

or, 52.2281 parts of isocyanate combine with 107.9842 parts of total B-side to give a 105 index foam.

10. Calculate the B/A ratio.

$$\frac{B}{A} Ratio = \frac{Parts\ B-Side}{Parts\ A-Side} \quad (6.28)$$

For the above example,

$$\frac{B}{A} Ratio = \frac{107.9842}{52.22812} \quad (6.29)$$

$$\frac{B}{A} Ratio = 2.06755 \quad (6.30)$$

Numerous other calculation scenarios exist for special circumstances in flexible foam production. See the additional calculation schemes in References 6.1-6.14.

Table 6.2 Typical Equivalent Weights

| Material | f | OH No. | Eq. Weight |
|-------------------------|------|--------|------------|
| CHAIN EXTENDERS: | | | |
| ethylene glycol | 2 | 1807.9 | 31.0 |
| diethylene glycol | 2 | 1057.4 | 53.0 |
| triethylene glycol | 2 | 747.0 | 75.1 |
| tetraethylene glycol | 2 | 577.7 | 97.1 |
| propylene glycol | 2 | 1474.6 | 38.0 |
| dipropylene glycol | 2 | 836.3 | 67.1 |
| tripropylene glycol | 2 | 583.5 | 96.1 |
| 1,4 butane diol | 2 | 1244 | 45.1 |
| diethyl toluene diamine | 2 | 629 | 89.1 |
| CROSS-LINKERS: | | | |
| glycerine | 3 | 1827.6 | 30.7 |
| diethanol amine | 3 | 1601.0 | 35.0 |
| triethanol amine | 3 | 1128.2 | 49.7 |
| QUADROL | 4 | 768.5 | 73.0 |
| VORANOL 800 | 4 | 800.0 | 70.1 |
| VORANOL 360 | 4.5 | 360.0 | 155.8 |
| VORANOL 446 | 4.5 | 449.0 | 125.0 |
| CATALYSTS: | | | |
| DABCO 33-LV | — | 560.3 | 100.1 |
| ISOCYANATES: | | | |
| toluene diisocyanate | 2 | — | 87.1 |
| ISONATE 181 | 2* | — | 181 |
| ISONATE 191 | 2.2* | — | 139 |
| PAPI 4094 | 2.3 | — | 131 |
| PAPI 4901 | 2.3 | — | 132 |
| PAPI 4027 | 2.7 | — | 134 |
| PAPI 4135 | 2.7 | — | 134 |

* nominal functionality

FOAM-COST CALCULATIONS

To be commercially successful, a candidate foam system must be economically competitive. Many factors go into determining the real cost. Besides raw material costs, there are costs associated with labor, start-up and shutdown losses, flush losses and trim and fabrication losses. If in a simple case all these factors can be taken as equivalent, then foam costs can be compared on the basis of raw materials alone. Table 6.3 gives a sample foam-cost-calculation format.

Table 6.3 Sample Foam-Cost Calculation

| FOAM DENSITY = 1.80 POUNDS PER CUBIC FOOT | | | | |
|---|----------|---------|-----------|-----------------|
| COMPONENTS | AMOUNT | \$/LB* | EXTENSION | % OF TOTAL COST |
| SPECFLEX NC 630, Polyol | 70.0000 | 0.8000 | 56.0000 | 37.10 |
| SPECFLEX NC 710, Copolymer Polyol | 30.0000 | 0.9400 | 28.2000 | 18.68 |
| TEGOSTAB B-8708 | 1.0000 | 3.5000 | 3.5000 | 2.32 |
| DIETHANOL AMINE, PURE | 1.7000 | 0.4800 | 0.8160 | 0.54 |
| DABCO 33-LV, CATALYST | 0.1500 | 4.9000 | 0.7350 | 0.49 |
| NIAX A-1, CATALYST | 0.0800 | 14.3000 | 1.1440 | 0.76 |
| POLYCAT 77, CATALYST | 0.2400 | 9.9500 | 2.3880 | 1.58 |
| WATER | 4.2000 | 0.0000 | 0.0000 | — |
| VORANATE T-80 TDI 105.0 Index | 51.93 | 1.1200 | 58.1616 | 38.53 |
| TOTALS | 159.3000 | | 150.9446 | 100.00% |
| GAS LOSS (at 0% retained) | 10.2667 | | | |
| CALCULATED COSTS | | | | |
| \$/WET LB. = 0.9475 | | | | |
| \$/DRY LB. = 1.0128 | | | | |
| \$/BD. FT. = 0.1519 | | | | |
| \$ PER 3 CUBIC FOOT PART = 5.4693 | | | | |

*These are random prices chosen for use in these examples only. Consult the raw material suppliers for actual prices in your area.

The cost calculation begins by listing all formulation ingredients and their prices. Extension values are obtained by multiplying the weight of each component by its price. The figure for cost per wet pound is a computation for the cost of wet chemicals leaving the mix head. It is the total dollars divided by the total formulation weight.

In normal calculations it is assumed that all of the water totally reacts to yield carbon dioxide gas. This gas causes the foam to rise to the analyzed density and is then totally lost.

The calculation of weight loss due to water is straightforward:

$$\text{gas loss} = \frac{\text{wt. of water} \times \text{MW of CO}_2}{\text{MW water}} = \text{wt. of water} \times \frac{44}{18} \quad (6.31)$$

If the formulation also contained a nonreactive blowing agent, all of that mass would also be lost. It is further assumed that there is no loss of excess isocyanate.

Factoring in the loss of water and other volatile blowing agents leads to the cost per dry pound of foam. This quantity is the total dollars divided by the total formulation weight remaining after loss of the water and other volatile agents.

The price of the foam expressed in dollars per board foot (\$/bd ft) is a common yardstick used in the flexible slabstock foam industry. In order to understand and reduce the cost of a foam, it is often helpful to see where the money is going. Figure 6.1 illustrates where the most economic impact to a foam formulation can be made.

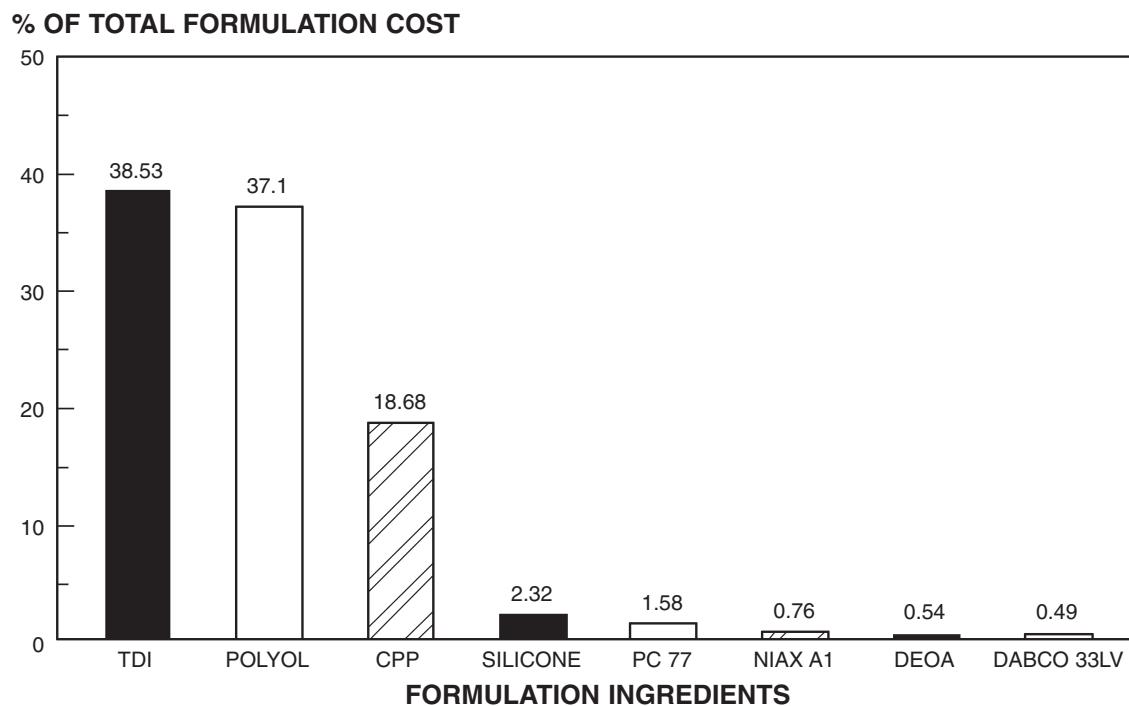
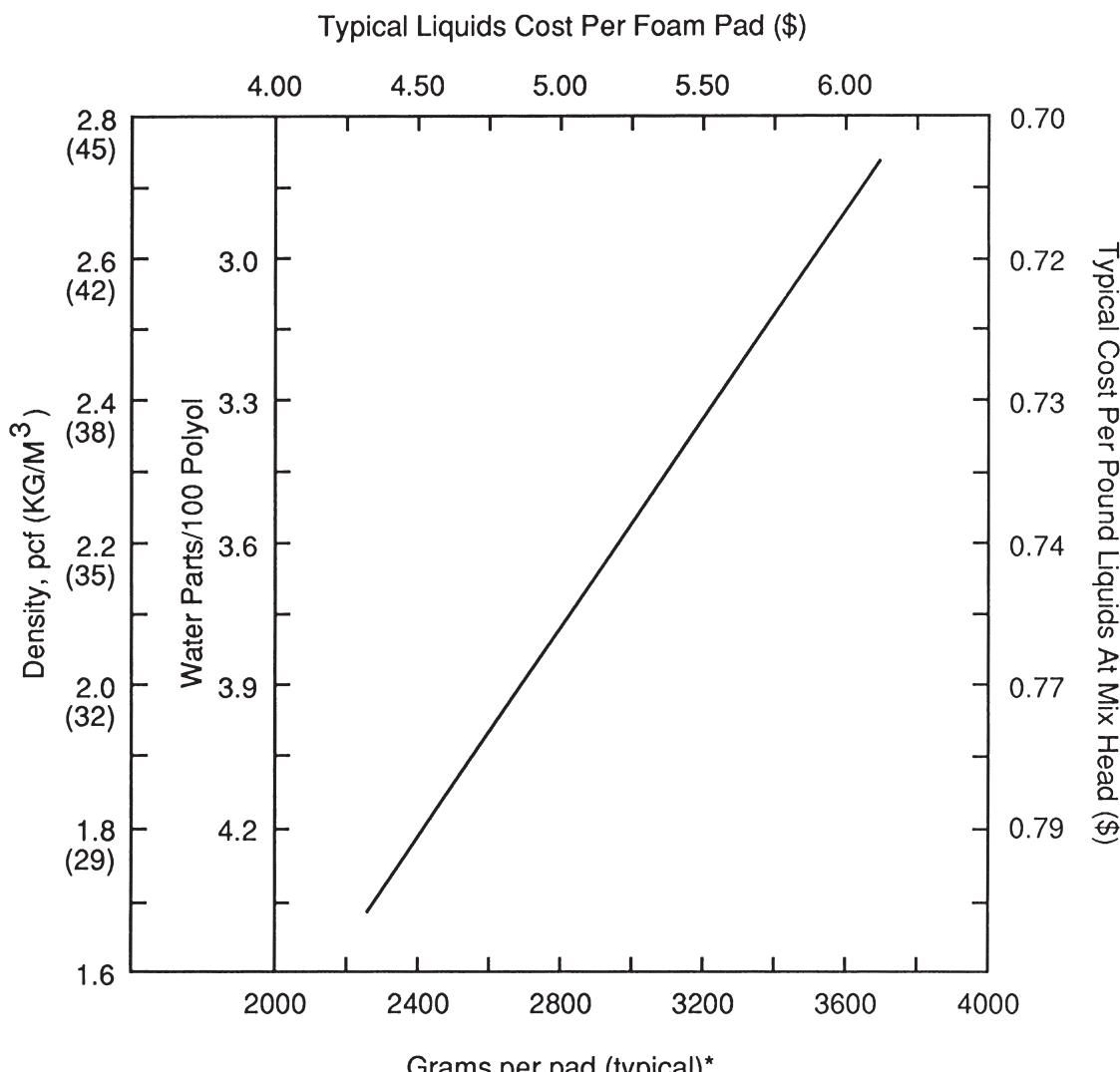


Figure 6.1 Typical Breakdown of Cost Contribution from Each Formulation Ingredient

Molded foam producers often manipulate foam cost figures into a final raw materials cost per molded foam part. When plotted as in Figure 6.2, this information clearly demonstrates the economic advantage of lowering molded foam density.



* Assuming same size Pad

Figure 6.2 Variation In Molded Foam Pad Cost

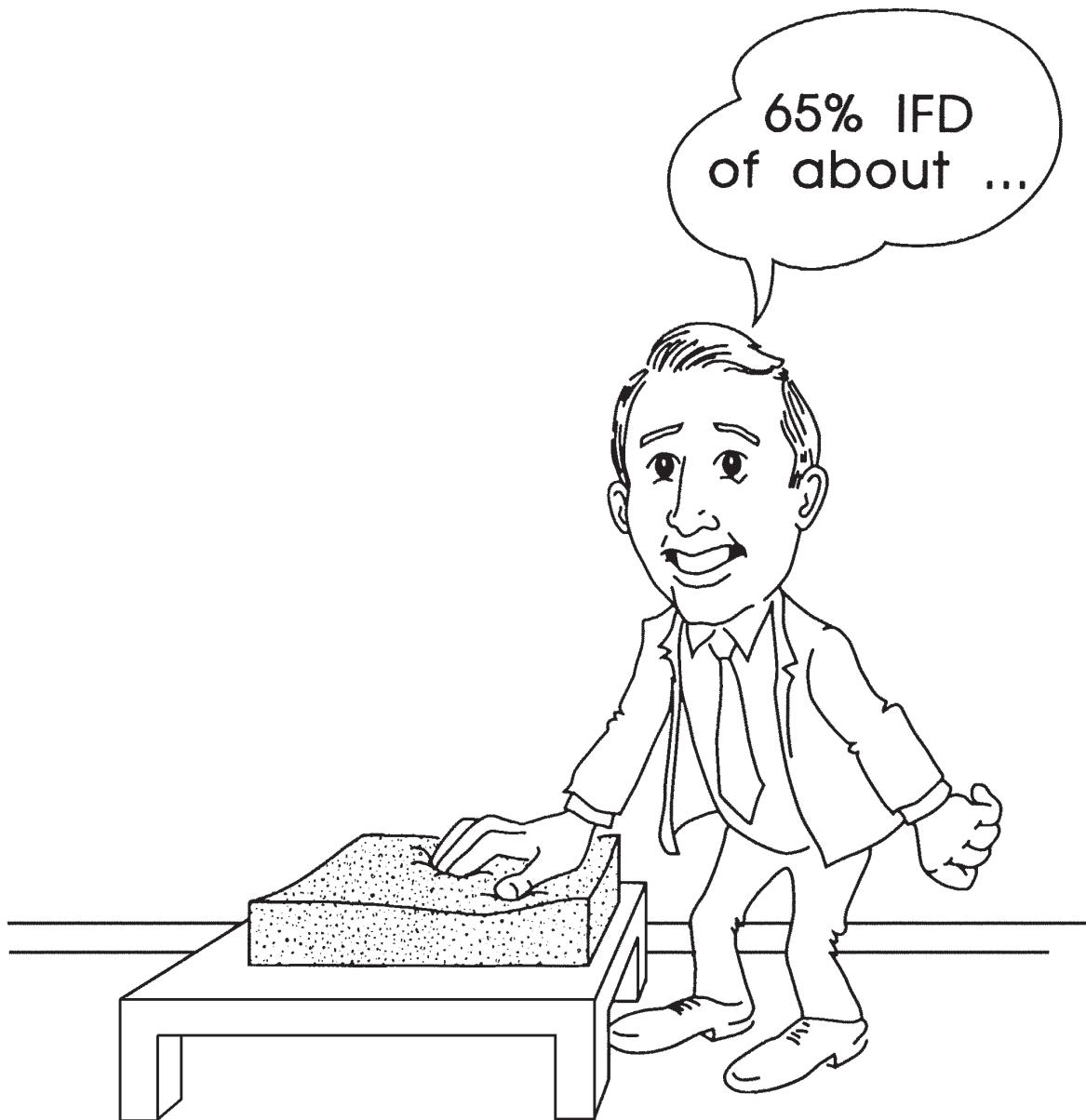
Other examples of foam-cost calculations can be found in References 6.2-6.3, 6.15-6.20.

References

- 6.1 Moss, E.K. "Computer Calculation of Urethane Foam Formulations"; *J. Cell. Plast.* **1969**, 5/5, 282-288.
- 6.2 Consoli, D.S. "Software to manage a Continuous Production of Flexible Polyurethane Foams"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 29.
- 6.3 *Foam Calculations*; The Dow Chemical Company; Form No. CH 383-065-E-894.
- 6.4 *VORANOL® Polyether Polyols, General Urethane Chemistry*; The Dow Chemical Company; Form No. 109-782-86.
- 6.5 Woods, George. *The ICI Polyurethanes Book*; John Wiley and Sons: New York, 1987, 291-294.
- 6.6 Doyle, E.N. *The Development and Use of Polyurethane Products*; McGraw-Hill: New York, 1971, 7-10.
- 6.7 McBrayer, R.L. "Formulating Flexible Urethane Foams"; presented at a seminar sponsored by Technomic Publishing Company, Lancaster, Pennsylvania, 1988.
- 6.8 David, D.J.; Staley, H.B. *Analytical Chemistry of the Polyurethanes*; Robert Krieger Publishing: New York, 1979, 321-323.
- 6.9 *Terms And Formulas Used In Urethane Polymer Preparations*; Olin Corporation; Form No. 751-016RZ.
- 6.10 Bender, R.J. *Handbook Of Foamed Plastics*; Lake Publishing Corporation: Libertyville, Illinois, 1965, 167-172.
- 6.11 Stewart, S.A. *A Glossary of Urethane Industry Terms*; The Martin Sweets Company: Louisville, Kentucky, 1971, 110-115.
- 6.12 Hepburn, C. *Polyurethane Elastomers*; Applied Science Publishers: New York, 1982, 34-48.
- 6.13 Dixon, R.R. "Nomograph for Formulating Polyurethane Foams"; *SPE J.* **1963**, 475-480.
- 6.14 Crammer, M.J. "Polyurethane Reaction"; In *Chemical Processing Nomographs*; Davis, D.S.; Kulwieg, R.A.; Eds., Chemical Publishing: New York, 1969, 244-245.
- 6.15 Riley, M.W. "What's New in Foam Plastics"; *Mat. Des. Eng.* **1961**, March, 119-137.
- 6.16 Baker, P.B. "Economics of Flexible Urethane and Latex Rubber Foams"; *Rub. World* **1958**, 138/5, 733-737.
- 6.17 Baker, P.B. "Economics of Flexible Foams - A Second Look"; *Rub. World* **1959**, 141/1, 81-85.
- 6.18 Tenhoor, R.E. "The World Market for Urethane Chemicals"; *Chem. Eng. News* **1963**, 41, Feb. 4, 94-106.
- 6.19 Kohudic, M.A. "Economics of Urethane Foams - A Summary"; *SPE Journal* **1965**, July, 660-661.
- 6.20 Sayad, R.S.; Williams, K.W. "There Is An Alternative To Fluorocarbon Blowing Agents"; *Plast. Tech.* **1979**, June, 71-74.

Chapter 7

Evaluation and Testing



The physical properties of flexible polyurethane foams are characterized using a number of industry standardized tests. Though extremely time consuming, these data are a necessary part of product development and quality assurance programs.

Chapter 7

Evaluation and Testing

K. Hock, R. Priester, R. Herrington, G. Wiltz, Jr., L. Jeng

In developmental stages, foam physical properties are tested to characterize the material and determine its suitability for chosen applications. In production foams, determination of key physical properties aids in quality control of the product. This chapter describes tests characterizing basic physical properties, durability, and flammability. The historical development of the basic test methods for flexible polyurethane foams is recorded in References 7.1- 7.5.

BASIC PHYSICAL PROPERTIES

ASTM D 3574-95 presents a standard method for conditioning of foam samples and methods for basic physical property tests.^{7.6} Eight tests are discussed here: density, indentation force deflection, compression force deflection, constant deflection compression set, tensile strength, tear resistance, airflow and resilience. Some of these tests have successfully been automated.^{7.7} Most of these basic foam properties have been the subject of math modelling exercises.^{7.8-7.19}

SAMPLE CONDITIONING

ASTM D 3574-95 calls for conditioning of a foam sample by waiting one week or more after the foam has been manufactured before testing and by conditioning the undistorted foam at a specified temperature (generally $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and humidity (generally $50\% \pm 5\%$ relative humidity) for 12 hours prior to testing.

In some tests, mechanical conditioning is used in an attempt to obtain data under conditions close to the actual performance of the product in service.

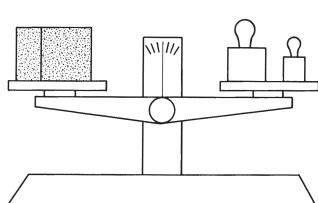


Figure 7.1 Density Measurement

DENSITY TEST

The density measurement as conceptualized in Figure 7.1 is an apparent or bulk density, not the true polymer density. This physical property is important because of its parallel relationship with both cost and load bearing. High densities generally result in higher costs and improved load-bearing properties.

In the test, a representative sample is carefully measured and accurately weighed. The density, normally reported in pounds per cubic foot or kilograms per cubic meter is simply the sample weight divided by its volume. A typical example of how foam properties vary with density is given in reference 7.20.

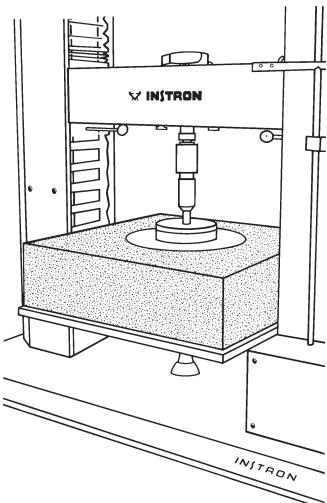


Figure 7.2 IFD Test

INDENTATION FORCE DEFLECTION TEST

The indentation force deflection test (IFD) is a measurement of the load-bearing properties of a foam. In this test (Figure 7.2) the force required to depress a circular plate into the foam is measured. Two types of measurements are important: the indentation resulting from a specified force and the force required to reach a specified indentation.

Experience has shown that these measurements can vary depending on the temperature and relative humidity conditions under which the foam was made, cured and tested. Detailed discussions of this phenomenon are available in Reference 7.21-7.26.

Specified Deflection Tests

ASTM D 3574-95, Test B₁ requires that the sample be placed on a support plate which has been perforated to allow airflow. A circular indentation foot with an area of 323 cm² is placed on top of the foam. Next, the foam is preconditioned to the test by compressing it twice to 75% deflection. After the foam relaxes for six minutes, the desired test deflections are performed. Force and indentation distance data are collected.

Results from this test can be plotted as shown in Figure 7.3. Notice that when the force is decreased (unload), the measured force for an indentation is less than while the force was increased (load). This difference is reported as hysteresis, the force during unload as a percent of the load force. Hysteresis is a measurement of the energy absorbed by a foam when subjected to a deformation. Foams with a high hysteresis show poor resilience and can be slow in regaining their original shape.

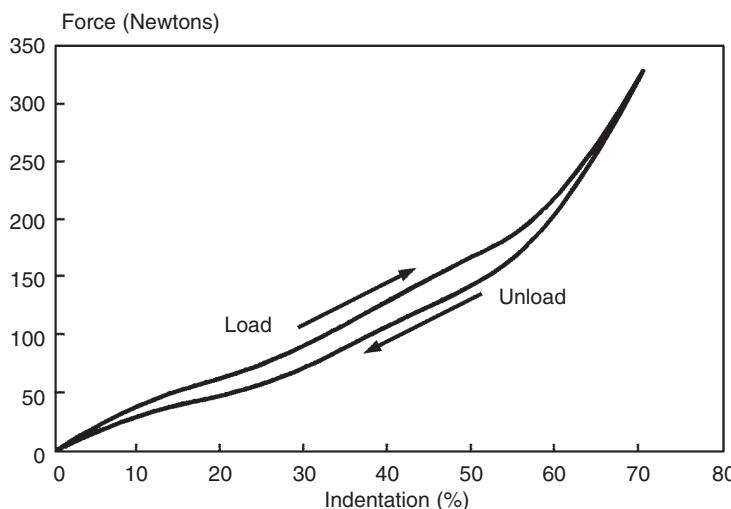


Figure 7.3 IFD Plot

In tabulated form, results are typically given as 25% IFD, 50% IFD, 65% IFD, 25% Return IFD and % Hysteresis Return. The values of 25% and 65% IFD are the forces required during the load cycle for deflections of 25, 50 and 65% of the original foam height. IFD Return to 25% is the force measured during the unload cycle at the 25% deflection point. Percent Hysteresis Return, also called Recovery, is IFD Return to 25% expressed as a percent of 25% IFD.

$$\% \text{ Hysteresis} = \frac{\text{Return } 25\% \text{ IFD}}{\text{Original } 25\% \text{ IFD}} \times 100 \quad (7.1)$$

Two other terms related to IFD are the Guide Factor and the Support Factor. The Guide Factor is the ratio of IFD to density. Foams with higher Guide Factors have cost advantages, but not necessarily performance advantages.

$$25\% \text{ IFD Guide Factor} = \frac{25\% \text{ IFD}}{\text{Density}} \quad (7.2)$$

or,

$$65\% \text{ IFD Guide Factor} = \frac{65\% \text{ IFD}}{\text{Density}} \quad (7.3)$$

The Support Factor is the ratio of 65% IFD to 25% IFD. This number gives an indication of cushioning quality. Higher support factors indicate better cushioning quality. This quantity is also known as the sag factor or as the modulus.

$$\text{Support Factor} = \frac{65\% \text{ IFD}}{25\% \text{ IFD}} \quad (7.4)$$

Specified Force Tests

In some seating applications, it is desired to know how much a given section of foam will compress under the weight of an average person. The test developed to simulate this measure is the Indentation Residual Deflection Force (IRDF) test. An earlier name for this test was Indentation Residual Gauge Load (IRGL).

ASTM D 3574-95, Test B₂ is performed with the same apparatus and general concerns described for the IFD test. Preflexing is to a prescribed load for two cycles. After a six minute relaxation period, the sample is loaded with, for example, a 110 Newton force and the thickness of the pad after one minute is reported as the 110 N. IRDF value. IRDF values at other loads may also be obtained. IRDF values are in centimeters and the original thickness of the foam must be known to make the values meaningful. A higher IRDF value indicates a stiffer foam.

COMPRESSION FORCE DEFLECTION (CFD)

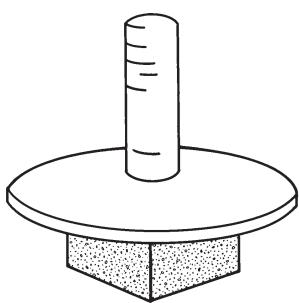


Figure 7.4 CFD Test

The CFD test is similar to the IFD test in that the force required to compress the foam to a specified level is measured and reported. The CFD test uses a plate large enough to apply force across the entire top surface of a 50 x 50 x 20 mm foam sample as shown in Figure 7.4.

The sample is placed on a support plate which has been perforated to allow airflow. The compression foot is brought into contact with the foam and the sample thickness is measured at a 140 Pascals contact force. The sample is conditioned by compressing it twice to 25% of its original thickness. After the sample relaxes for 6 minutes, force is applied to the compression foot so that the sample is compressed at a constant rate. When the sample is compressed to 50% of its original height, this thickness is held for 60 seconds, and the final load is recorded. The test is repeated for three samples and the median is reported as 50% CFD.

Variations on these basic load-bearing tests include changes in sample dimensions and indentor foot area. These changes affect the test results as described in References 7.27-7.29.

CONSTANT DEFLECTION COMPRESSION SET

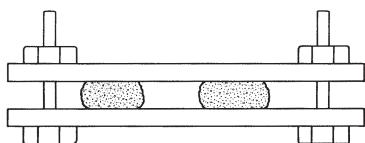


Figure 7.5 Compression Set

In the constant deflection compression set test (commonly called compression set), three carefully measured samples of the foam are placed between metal plates and compressed to 50, 75 or 90% of the sample's original thickness (see Figure 7.5). The samples are held at 158°F (70°C) for 22 hours, removed from the apparatus, allowed to recover for 30 minutes, and remeasured. For slabstock foam, results are reported as a percentage of the original thickness:

$$C_t = \frac{t_o - t_f}{t_o} \times 100\% \quad (7.5)$$

For molded foam, results are given as a percentage of original deflection:

$$C_d = \frac{t_o - t_s}{t_o - t_s} \times 100\% \quad (7.6)$$

where:

C_t = compression set as a percent of original thickness,

C_d = compression set as a percent of original deflection,

t_o = thickness of the original, uncompressed sample,

t_s = thickness of the spacer bar used, and

t_f = thickness of the test specimen following a 30-minute recovery after removal from the apparatus.

As long as the original sample thickness is less than the sample length or width, compression set is independent of sample thickness. When the sample thickness exceeds the width or length, buckling may occur and results will not be reproducible. Samples for this test are normally oriented so that

compression set is measured in the direction of blow (vertically during foaming). Compression set values for samples perpendicular to the direction of blow (horizontal during foaming) are lower.

A wet compression set test is also required by some automobile manufacturers. In a typical procedure, a cut sample (with the molded skin in the case of Renault) is tested at 50% compression for 22 hours at 50°C and 95% relative humidity.

TENSION TEST (TENSILE STRENGTH)

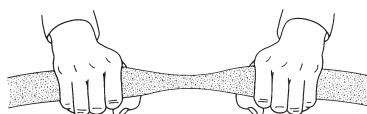


Figure 7.6 Tensile Test

The tension test measures the strength of a foam under tension and gives information about the foam's elasticity. Samples for the test are generally die-cut and are "dogbone" or "dumbbell" shaped. The sample is pulled at a constant rate until it breaks, as conceptualized in Figure 7.6. The force recorded at the breaking point is the tensile strength of the foam, generally reported in kilopascals. The maximum extension of the sample as a percentage of its original length is the elongation at break. Sample extension is typically measured manually by the operator or with the use of automatic extensiometers. Errors have been noted with the use of extensiometers that actually contact and deform the foam sample. Noncontact extensiometers based on laser technology are now available.

The modulus of elasticity is obtained by plotting the stress force against strain in a tension test. This modulus is simply the initial slope of the stress/strain straight line in the region of elastic ideality where Hooke's law holds. Most polyurethane foams have a yield point, the point where deformation is no longer reversible and nonelastic deformation starts. This irreversibility may be due to the tearing of struts in the foam, breaking of cell-windows and the slipping of polymer chains. The stress at the yield point is called the yield strength.

TEAR RESISTANCE

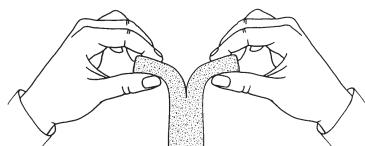
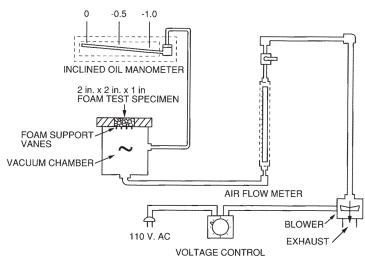


Figure 7.7 Tear Resistance

Another measure of the strength of a foam is its tear resistance. In this test, conceptualized in Figure 7.7, a sample is slit at one end and the force required to continue this tear at a constant rate is measured. Results from this test are highly rate dependent. Tear strengths are not necessarily related to tensile strengths in foams. Results have also been found to vary with sharpness of the sample cutting die.

AIRFLOW



Airflow is a measurement of the openness or porosity of a foam. Figure 7.8 illustrates how air is pulled through a standard thickness sample and the rate observed. Airflow values are very sensitive to the orientation of the sample in the foam, and two values are typically reported: airflow parallel to foam rise and airflow perpendicular to foam rise. In molded foams, airflow through the surface skin is also of interest and can be measured in a procedure using the Gurley Densometer.^{7.30-7.32}

Figure 7.8 Airflow Test

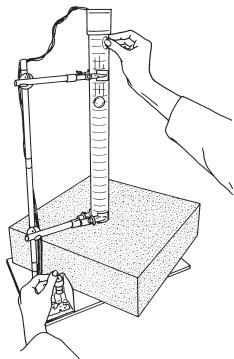


Figure 7.9
Resilience Measurement

RESILIENCE

The resilience of a foam is measured in a ball rebound test as shown in Figure 7.9. The test consists of dropping a steel ball on a foam sample and visually measuring the height of rebound.^{7.33} A typical test procedure and details of equipment construction are given in Reference 7.34. Automated equipment is available.^{7.35-7.36} Results from this test have been correlated to overall cushion comfort.^{7.30,7.37}

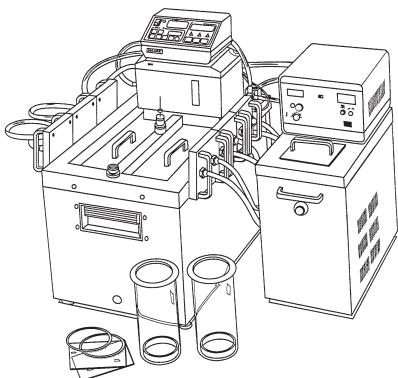


Figure 7.10
Typical Fogging Test
Apparatus

FOGGING

Fogging is an important criterion for foam used in the automobile industry. The term refers to the problem of a light scattering film which forms on interior glass surfaces. Volatile ingredients in any of the interior trim parts have the potential to contribute to the film.

In a typical testing procedure, a sample of material is placed in an apparatus similar to that in Figure 7.10 and heated at a desired temperature to promote release of volatile components. Those components are then condensed on a cooled glass plate and subjected to either a gravimetric or light reflectance loss scenario of quantification.

The evolution of fogging test methods has been traced by McCallum^{7.38} and typical procedures can be found in References 7.39-7.43. Important variables that influence test results are discussed in References 7.38, 7.44-7.47.

DURABILITY TESTING

There are a number of techniques for measuring fatigue in flexible foams at the laboratory-scale.^{7.48-7.50} For the most part, however, they all fall in two categories: static fatigue tests and dynamic fatigue tests.

Within a category, the individual tests vary in the degree of loading or deflection, use of indentation or full size deflection, addition or absence of shear, sample thickness, number of cycles, rate of application of flex and recovery or rest period after flexing. The sample type also varies. Measurements from the testing vary considerably; they include height loss, load loss, physical appearance or loss in other properties.

Descriptions of some standard test methods for commonly used laboratory tests are given below. Improvements in fatigue testing are being reported with an ever-increasing frequency. Many of these new laboratory-scale tests yield improved performance correlations.

More discussion of flexible foam durability issues can be found in Chapter 8.

STATIC FATIGUE TESTS

Two types of static fatigue tests are commonly used: the constant deflection compression-set test and the constant-load creep test.

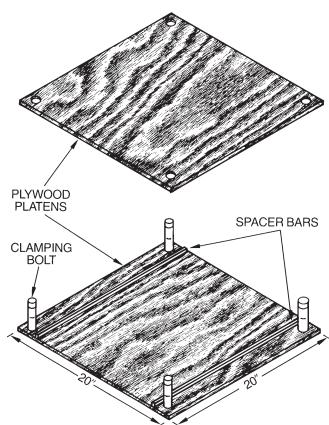


Figure 7.11
Static-Fatigue Test

Constant Deflection Compression Set

The most common static fatigue test used is similar to the simple constant deflection compression-set test described in the previous section. This test is described in ASTM D 3574-95, Test I.^{7.51} A larger foam sample, typically 380 x 380 mm, is used. The foam sample is compressed in a simple apparatus as shown in Figure 7.11. When the compression time is complete, the sample is removed and allowed to recover. The sample height is measured, and the results are given as a percent of original height.

Compression set values correlate with the in-service loss of cushion thickness and changes in foam hardness. However, a low static-fatigue loss as measured by compression set does not always guarantee a satisfactory in-use performance. For product development purposes, the compression-set tests are generally used only as a rough indicator of in-use recovery performance. Compression-set tests are successfully used as quality control tests.

Constant-Load Creep Test

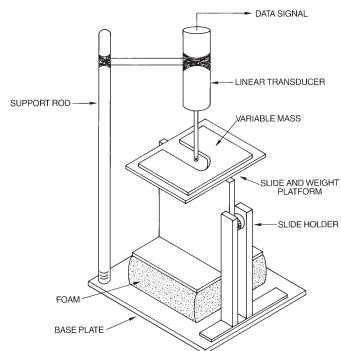


Figure 7.12
Creep Apparatus

Creep is the reversible change in shape with time of a sample under a sustained load. A typical creep apparatus is shown in Figure 7.12. In the test, a foam block (3 x 3 x 2 inches) is placed under a weight platform. The platform is loaded to the desired mass and lowered onto the foam. The percent vertical deflection (creep) is measured over a ten-minute period. Data are plotted as percent deflection versus time, and a creep rate, the slope of the data, is calculated. The creep rate varies with percent penetration into the foam. A high creep rate corresponds to cushion comfort loss.^{7.52-7.53}

As with other static tests, the creep test is generally not a severe enough test to predict performance in service accurately.

DYNAMIC FATIGUE TESTS

Dynamic fatigue tests were developed to simulate the alternating loads experienced by seating cushions under actual service conditions. Two general types of tests have been used: those in which the foam cushion is indented to a fixed percentage of its thickness by an oscillating indentor, and those in which the sample is repeatedly loaded and unloaded with an indentor exerting a fixed load. Dynamic fatigue tests, such as the constant load pounder, in which the degree of indentation increases during the test as the foam softens, have reportedly shown a high correlation with height loss and, to a lesser extent, with hardness loss in the in-service performance of foams.

Two laboratory-scale dynamic testing protocols are commonly used by furniture and automotive foam suppliers:

- Constant-Load Pounding;
- Roller-Shear.

A standardized constant-load-pounding fatigue test, ISO 3385-1975(E), is a common choice for many furniture and automotive foam application areas.^{7,54} Another frequently used test protocol is the ASTM D 3574-95, Test I₃. A modified roller-shear test, the Caster Fatigue Test, which is used in carpet backing applications, gives the best correlation with actual use performance.^{7,55}

Constant-Load Fatigue Tests

ISO 3385-1975 (E)

International Standard 3385-1975 (E) is the standard constant-load-pounding-fatigue test. In the test, a 380mm x 380mm x 50mm foam sample is repeatedly loaded with a force of 750 Newtons at a rate of 70 cycles per minute for 80,000 cycles.^{7,56} The thickness and hardness (IFD) measurements obtained before the test are compared to measurements after fatigue. The percentage loss is used to describe the fatigue durability performance. A typical pounding-fatigue test apparatus is shown in Figure 7.13.

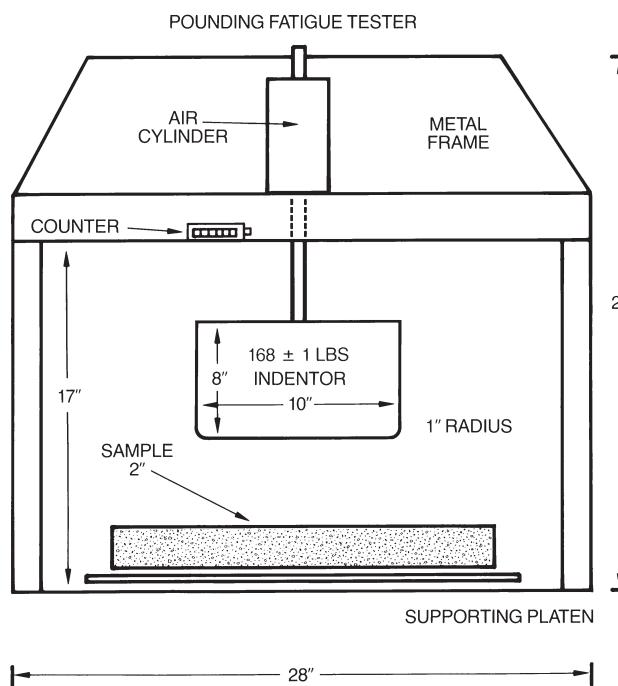


Figure 7.13 Pounding-Fatigue Test Apparatus

Different applications require different fatigue performance grade foams. The five British Standard Institution (BSI) Pounding-Fatigue Performance grades are listed in Table 7.1. Figure 7.14 shows IFD loss versus the initial IFD for each of the BSI grades. This test is also described in ASTM D 3574-95, Test I₃.

Table 7.1 BSI Pounding-Fatigue Performance Grades

| Class | Type of Service | Recommended Applications |
|-------|------------------|--|
| X | Extremely Severe | Heavy-Duty Contract Seats Heavy-Duty Public Transport Seats |
| V | Very Severe | Public Transport Seats Cinema and Theater Seats Contract Furniture Seats |
| S | Severe | Private and Commercial Vehicle Seats Domestic Furniture Seats Public Transport Backs and Armrest |
| A | Average | Private Vehicle Backs and Armrest Domestic Furniture Backs and Armrest |
| L | Light | Padding Scatter Cushions Pillows |

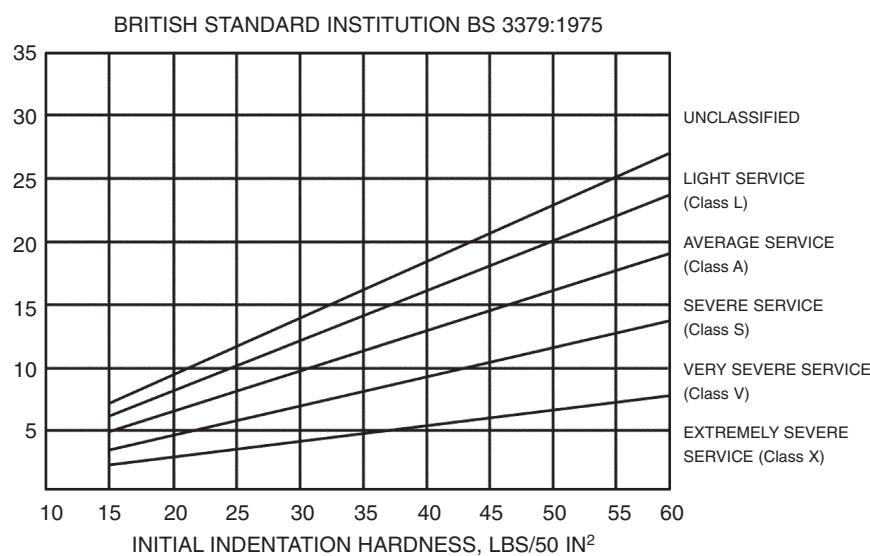


Figure 7.14 Pounding-Fatigue Test Specifications

Jounce Test

The Jounce Test is used to assess fatigue performance for seating cushions.^{7.57} The Jounce Test Equipment is shown in Figure 7.15. A fully trimmed seat assembly is mounted on a frame and subjected to 100,000 vertical cycles (16 hours) under a 122 pound saddle load. The indentor saddle is buttocks shaped. After the test, the seat assembly is tested for load bearing and thickness loss under loads of 1, 25 and 50 pounds. The measured thicknesses are termed the indentation residual deflection force, IRDF. A total loss number, the sum of the percent losses at 1, 25 and 50 pounds, is used to summarize the results. Loss in hardness measured in this test correlates well with in-service performance.

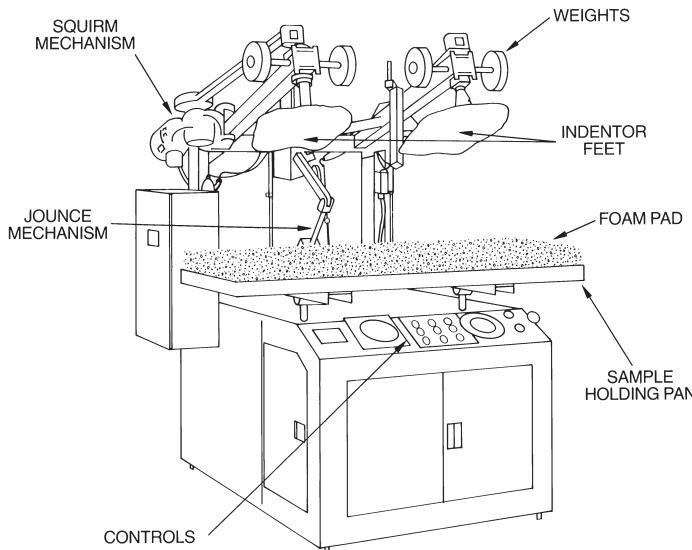


Figure 7.15 Jounce Test Equipment

Roller-Shear Test

The standard Roller-Shear Test and a suggested method of equipment construction are described in ASTM D 3574-95.^{7.58} The apparatus for this test is shown in Figure 7.16. In the test, a reciprocating cylindrical roller rolls back and forth across a foam sample. This action produces both compression and shear strains in the sample. The total applied load is 130 Newtons. The roller

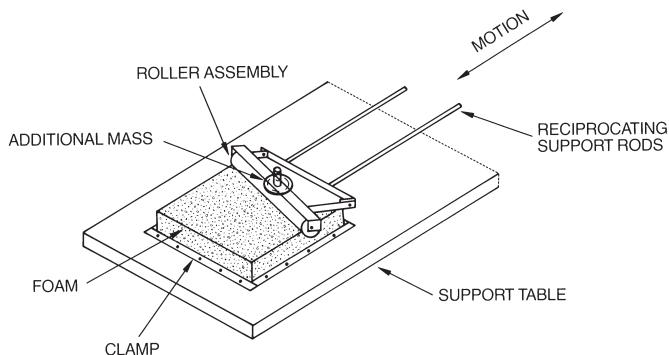


Figure 7.16 Roller-Shear Test Apparatus

passes back and forth at a rate of 1 cycle per second; the test continues for 8000 cycles (5 hours, Procedure A) or 20,000 cycles(12 hours, Procedure B). At the end of the test, the foam is allowed to recover for 1 hour. Next, the sample thickness is measured under loads of 4.5, 110 and 220N (1, 25 and 50 pounds). The measured thicknesses are referred to as the indentation residual deflection force, IRDF. A total loss number, the sum of the percent losses at each load is used to summarize the results.

A Society of the Plastics Industry study reports excellent correlation between the laboratory roller-shear procedure and field evaluations for fatigue.^{7.59} However, the absolute accuracy of the laboratory procedure was not satisfactory.

FLAMMABILITY TESTING

Numerous tests exist for the evaluation of flammability performance of materials and composites. The basic objective of these tests is to screen the performance of new materials and formulations. The tests are carried out on a variety of scales, ranging from bench or laboratory-scale to full-scale tests involving entire rooms or buildings. However, laboratory-scale tests cannot be used to predict the performance of the materials under actual fire conditions.

In recent years, many national standard and insurance organizations have been involved in developing a unified set of tests.^{7.60-7.61} Some of the more widely used are listed in Table 7.2. Several of the tests more commonly used within Dow are described in greater detail below. New tests are continually evolving.

LABORATORY-SCALE TESTS

Laboratory-scale tests are generally used to compare the ignitability and the burn rate of small specimens.* The results can vary widely, depending on the orientation of the specimen, the size of the flame source and the degree of radiant energy.

Limiting Oxygen-Index Test (ASTM D 2683)

The oxygen-index test is used for a wide variety of polymer types, ranging from high-density RIM materials to cellular, low-density polyurethane cushioning materials.^{7.62-7.67} A square-sectioned test bar is vertically mounted in a glass chimney of standard size. A known mixture of nitrogen and oxygen is metered into the bottom of the chimney and the sample is ignited at the top. The ratio of nitrogen to oxygen is varied to find the minimum oxygen concentration required for the sample to show a measurable burn rate. A variation of this test, the Downward Vertical Burn Test, has recently been described by Parrish and co-workers.^{7.68-7.69}

*The results of these tests are not intended to reflect the hazards presented by these materials under actual fire conditions.

Table 7.2 Some Standard Fire Tests^{7.50}

| Test | Test Reference Number |
|--|--|
| Small-Scale, Laboratory Tests Laboratory assessment of horizontal burning of small specimens subjected to a small flame. | ISO 3582(cellular materials); ISO 1210 (plastics); ASTM D 635; MVSS 302 (vehicle interiors) = ISO 3795 |
| Oxygen-index test | ASTM D 2813; ISO 3216 |
| Laboratory assessment of vertical burning of small strips of material | ASTM D 3014 (Butler chimney) |
| Smoke generation from small specimens of material | ASTM E 662 (NBS cabinet) = ISO Dev. Test 5659; ASTM D 2843 (XP-2 chamber) |
| Fire Tests for Building Materials and Building Structures Combustibility tests for building materials | ISO 1182; ASTM E 136 |
| Ignitability of building materials | ISO/DP 5657 (ISO cone) |
| Surface flammability or spread of flame using a radiant heat source | ISO/DP 5658; ASTM E 162 |
| Flame-spread-tunnel tests | ASTM E 84 (Steiner tunnel) = UL Test 723 |
| Fire-resistance test on composite structures | ISO 834; ISO 3008/2009; ASTM E 119 and E108; UL Corner tests; FMC corner test |
| Calorific value or potential heat emission | ISO 1716 |
| Fire Tests for Furniture Upholstery Ignitability, cigarette/match and smouldering tests | ASTM D 3453 (definition only); State of California Bulletins 116-117 |
| Mattress and cushion flammability | US Federal Reg 137; DOC FF 4-72 |

Key to Abbreviations

| | |
|------|--|
| MVSS | Federal Motor Vehicle Safety Standard, (USA) |
| ISO | International Organization for Standardization |
| ASTM | American Society for Testing and Materials |
| UL | Underwriter's Laboratories Inc, USA |
| FMC | Factory Mutual Corporation |
| DOC | USA, Department of Commerce |

U. S. Safety Standard MVSS 302

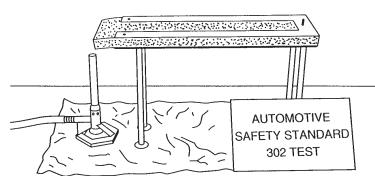


Figure 7.17 MVSS 302 Test

This test (shown in Figure 7.17), generally used in the evaluation of automobile seating foams, uses specimens having dimensions of 355 x 102 x 13 mm thick and cut so as to include the molded skin. A bunsen-burner flame is applied to one end of the skin-side down sample for 15 seconds. The rate of flame spread over measured lengths on the sample is recorded for 5 replicate samples. A flame-spread rate of less than 10.2 cm/min must be obtained for each sample in order to pass the test.^{7.70-7.72} Five ratings categories are used to further define a materials performance.^{7.73-7.74}

Some of the key variables affecting test ratings include:

- Sample thickness.
- Sample location on original molded pad.
- Type of mold release used.
- Temperature of burner flame.
- Sample positioning within the chamber.
- Use of nonstandard test chambers.
- Problems with airflow in and around the test chamber.

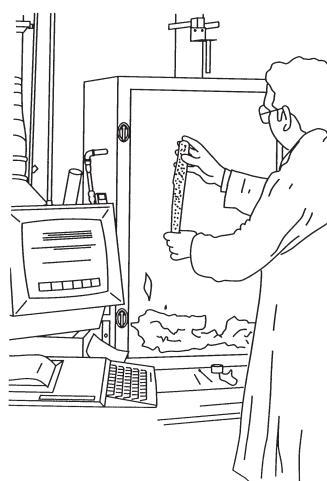


Figure 7.18
Typical Vertical Burn Test

Federal Specification CC-T-191b Method 5903

The State of California requires that all cushioning material used in upholstered furniture pass the type of test illustrated in Figure 7.18.^{7.75-7.76} The test involves suspending a 304.8 x 50.8 x 25 mm sample vertically above a wingtipped bunsen-burner flame. The flame is applied to the lower edge of the foam for 12 seconds. The average burn distance, the average char length and the average flame time are reported using a set of five samples.

British Standard 5852 Part 2

This standard was developed under the direction of the British Furniture Standards Committee for the assessment of the ignitability of upholstered assemblies subjected to either a smouldering cigarette or a lighted match.^{7.77} The desired test apparatus consists of two rectangular steel frames which are hinged together and capable of being locked at right angles to each other. Two representative foam samples are mounted in the right-angle assembly. A wooden crib constructed of the softwood *Pinus silvestris* is constructed on the foam surface and in contact with the upright sample. The crib is ignited, using alcohol saturated batting, and the burn performance of the assembly is monitored. Key performance criteria include flaming drips, charring, smouldering after flame and total weight loss.

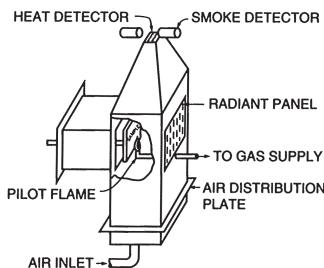


Figure 7.19
Ohio State University
Release Rate Apparatus

Ohio State Heat Release Rate Test (ASTM E 906)

The OSU test (Figure 7.19) is capable of estimating the ignition resistance of a wide variety of materials under varying levels of fire development. The samples are burned under controlled levels of incident radiation to approximate the environment at various stages of a fire. Several representative samples are burned in either a vertical or horizontal position. The heat and smoke evolution are monitored with time. The total burn time and total weight loss for each sample are also monitored. Relative performance is used to evaluate the flammability of the materials.^{7.68-7.69, 7.78-7.81}

FULL-SCALE FLAMMABILITY TESTS

The performance of materials in a real fire situation can vary markedly from that observed in the small-scale tests. In the case of fires involving building materials, there are many parameters that affect the course of a real fire and many hazards can arise. One of these is smoke. Most deaths in fires result from asphyxiation from lack of oxygen or from inhalation of smoke or toxic vapors.^{7.82} For this reason, the full-scale tests generally measure both flame spread and smoke density.

One of the best-known large-scale tests for building materials is the Steiner Tunnel test (ASTM E 84-81a). The test requires representative test specimens 7.3 m long by 514 mm wide. The thickness is defined by the application. Twin gas burners are ignited and the rate of flame-spread, the temperature rise and the amount of smoke produced are monitored. These values are used to classify the materials.

Similarly, in the case of upholstery and furnishings, most fatalities are due to smoke or smouldering materials. The main large-scale test applicable to this application area, and in principal to low-density foam in general, is the U. S. Department of Commerce, DOC FF 4-72, "Flammability Standard for Mattresses." This test, much like the British Standard 5852 Part 1 and 2, determines the resistance of a mattress ignition by glowing cigarettes placed in defined positions. The test protocol requires that charring not extend more than 5.2 cm in any direction from the ignition point. Adaptations of this test have been specified in California and Maryland.^{7.75-7.76}

References

- 7.1 Anon. "Proposed Tentative Specifications and Methods of Test for Flexible Urethane Foam"; *Rub. Age* **1956**, August, 804-810.
- 7.2 Editorial, "New Specifications for polyurethane foam in upholstery"; *Brit. Plast.* **1961**, 34/2, 73-74.
- 7.3 Jones, R. E.; Patten, G; Steingisen, S. "Section IV - Testing Of Foam Plastics"; In *Handbook of Foamed Plastics*; Bender, R. J., Ed.; Lake Publishing Corporation: Libertyville, Illinois, 1965, 52-68.

- 7.4 Rogers, T. H. "Development of Test Methods for Flexible Cellular Materials in ASTM D-11"; *J. Cell. Plast.* **1968**, 4/10, 392-394.
- 7.5 Touhey, W. J. "Development of Test Methods for Cellular Plastics in SPI"; *J. Cell. Plast.* **1968**, 4/10, 395-397.
- 7.6 "Standard Methods of Testing, Flexible Cellular Materials-Slab, Bonded, and Molded Urethane Foams"; Annual Book of American Society for Testing and Materials Standards, Volume 09.02, D 3574-86; ASTM: Philadelphia, 1990, 320-335.
- 7.7 Graf, W. C.; Schondlowski, H. "Automation Of Compression and Tensile Testing Of Urethane Foams"; *Proceedings Of The SPI-3rd International Cellular Plastics Conference*; The Society of the Plastics Industry: New York, 1972, 225-236.
- 7.8 Lambert, A. "Theoretical Relationships Between Density, Hardness, Temperature and Gas Evolved in Conventional, Flexible Polyether Urethane Slabstock Foam"; *Eur. J. Cell. Plast.* **1980**, January, 25-35.
- 7.9 Wang, S.L.; Frisch, K.C.; Malwitz, N. "A Study Of The Mass and Energy Balance In Foaming Polyurethane Foams"; *Proceedings of the SPI-30th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 363-368.
- 7.10 Lawler, L.F.; Schiffauer, R. "Advanced Property Prediction Models for Flexible Slabstock Foam"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 288-296.
- 7.11 Ramesh, N.S.; Malwitz, N. "Computer Simulation Of Polyurethane Foam Reactions Using Material And Energy Balance Calculations"; Proceedings Annual Technical Conference - *Soc. Plast. Eng.* **1994**, 52/2, 1941-1945.
- 7.12 Fabishak, D.M. "Derivation And Use Of Equations For Loading Indentation Curves"; *J. Cell. Plast.* **1972**, 8/2, 82-84.
- 7.13 Schiffauer, R. "Mathematical Property Prediction Models for Flexible Polyurethane Foams - A Comparison between Conventional Slabstock, High Resilience Slabstock and High Resilience Molded Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 225-238.
- 7.14 Cavender, K.D.; Kinkelaar, M.R. "Load Bearing Response of HR Molded Foam as a Function of Processing and Testing Parameters"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 248-251.
- 7.15 Lederman, J.M. "The Prediction of the Tensile Properties of Flexible Foams"; *J. Appl. Polym. Sci.* **1971**, 15, 693-703.
- 7.16 Hilyard, N.C.; Collier, P. "A Structural Model for Air Flow in Flexible PUR Foams"; *Cell. Polym.* **1987**, 6/6, 9-26.
- 7.17 Jones, R.E.; Fesman, G. "Air Flow Measurement and Its Relations to Cell Structure, Physical Properties, and Processability for Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 200-216.
- 7.18 Gent, A.N.; Rusch, K.C. "Permeability of Open-cell Foamed Materials"; *J. Cell. Plast.* **1966**, 2/1, 46-51.
- 7.19 Hilyard, N.C. "Hysteresis and energy loss in flexible polyurethane foams"; In *Low density cellular plastics, Physical basis of behaviour*; Hilyard, N.C.; Cunningham, A., Eds., Chapman & Hall: London, 1994; 235-269.

- 7.20 Kreter, P.E. "Polyurethane Foam Physical Properties As A Function Of Foam Density"; *J. Cell. Plast.* **1985**, 21/5, 306-310.
- 7.21 Hogan, J.M.; Pearson, C.J.; Rogers, T.H.; White, J.R. "Humidity Characteristics of HR and Hot Urethane Foams"; *J. Cell. Plast.* **1973**, 9/5, 219-225.
- 7.22 Saotome, K.; Matsurbara, K.; Yatomi, T. "The Improvement of Humidity Resistance in HR Polyurethane Foam"; *J. Cell. Plast.* **1977**, 13/3, 203-209.
- 7.23 Woods, G. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science Publishers: London, 1982, 119-120.
- 7.24 Moreland, J.C.; Wilkes, G.L.; Turner, R.B. "Viscoelastic Behavior of Flexible Slabstock Polyurethane Foams as a Function of Temperature and Relative Humidity"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 500-508.
- 7.25 Dounis, D.; Wilkes, G.L.; Turner, R.B. "The Effects of Temperature and Relative Humidity on the Load Relaxation Behavior of Molded Polyurethane Foams"; *Polymer Preprints, Vol. 35, No. 2, 1994*; American Chemical Society: Washington, 1994, 781-782.
- 7.26 Brasington, R.; Kinkelaar, M.R.; Cavender, K.D. "New Polyols for Improved Automotive Seating Durability Performance"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 9.
- 7.27 Anon. "Load-Bearing Properties of Flexible Urethane Foam"; *Plast. Tech.* **1962**, 8/4, 26-32.
- 7.28 Lambert, A. "Correlation Between Hardness Tests on Flexible Polyurethane Foam"; *J. Cell. Plast.* **1974**, 10/1, 35-42.
- 7.29 Ashe, W.A.; Grace, O.M. "Polyurethanes Tomorrow - Testing of Slab Foams"; *J. Cell. Plast.* **1989**, 25/4, 371-390.
- 7.30 Hartings, J.W.; Hagan, J.H. "Fatigue Investigations of Urethane Seat Pads"; *J. Cell. Plast.* **1978**, 14/2, 81-86.
- 7.31 Rosemund, W.R.; Sander, M.R. "The Use of Silicone Surfactants and Amine Catalysts To Vary Processing and Properties of Various Urethane Foam Systems"; *J. Cell. Plast.* **1977**, 13/3, 182-193.
- 7.32 Blair, G.R.; Wilson, A.R. "Polyurethane Automotive Cushioning: Material Properties After In Car and Simulated Durability Testing"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 413-417.
- 7.33 Jones, R.E.; Hersch, P.; Stier, G.G.; Dombrow, B.A. "Measuring Resilience of Flexible Urethane Foams"; *Plast. Tech.* **1959**, 5/9, 55-59.
- 7.34 Polis, S. "Status of Comprehensive Test Results Of Commercial Flexible Foam Slab Formulations"; *Proceedings of the SPI-24th Annual Urethane Division Technical Conference*; Technomic: Lancaster, Pa., 1978, 59-69.
- 7.35 *Time Tech TT502 Ball Rebound Foam Resilience Tester*; Time Tech, Inc. Wilmington , De., 1996.
- 7.36 Herrington, R.M., personal communication with Air Products and Chemicals Company, 1996.
- 7.37 Wolfe, H.W. "Cushioning And Fatigue"; In *Mechanics Of Cellular Plastics*; Hilyard, N.C., Ed., MacMillan: New York, 1979, 105.

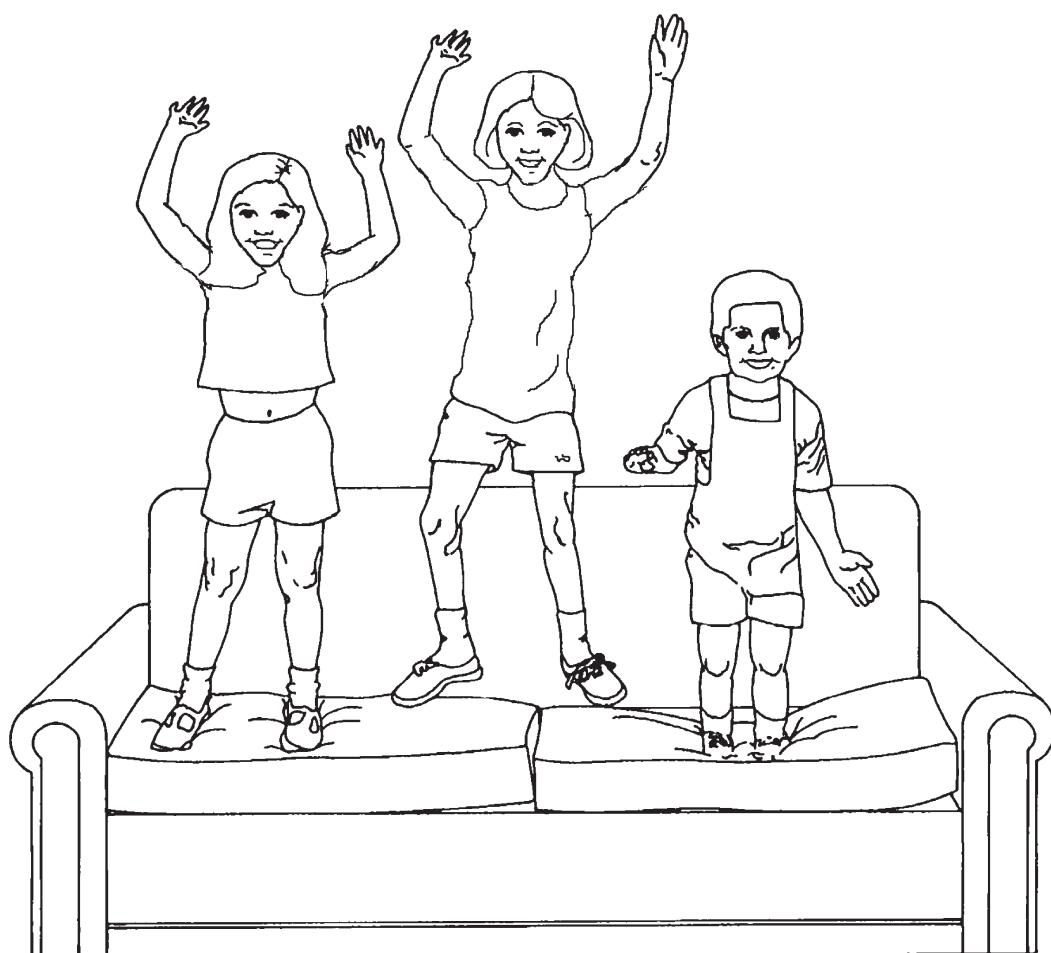
- 7.38 McCallum, J.B. "Ford Motor Co. Develops Its Own Test Method For Predicting Light-Scattering Window Film"; *Textile Chemist and Colorist* **1989**, 21/12, 13-15.
- 7.39 "Standard Test Method for Determination of Fogging Characteristics of Vehicle Interior Trim Materials"; American Society for Testing and Materials, D 5393-93; ASTM: Philadelphia, 1993.
- 7.40 "Determination Of Fogging Characteristics Of Automotive Interior Trim Materials"; General Motors Engineering Standard GM9305P, January, 1992.
- 7.41 "Interior Trim - Fogging Characteristics"; Ford Laboratory Test Method BO-116-03, 1990.
- 7.42 "Determination of the Windscreen Fogging Characteristics of Trim Materials in Motor Vehicles", Deutsches Institut fur Normung (DIN) test method DIN 75201R and DIN 75201G.
- 7.43 "Test Procedure To Determine The Fogging Characteristics Of Interior Automotive Materials"; SAE Test Method J1756, 1994.
- 7.44 Coupland, F.E. "Understanding the Oil Immersion Fog Test"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1988; Paper No. 880504; SAE: Warrendale, Pa.
- 7.45 Baatz, G.; Franyutti, S. "Low-Fogging Polyester-Based Flexible Foams"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994; Paper 9.
- 7.46 Bradford, L.; Pinzoni, E.; Wuestenek, J. "Clearing the Fog About the Effects on Fogging of Common Liquid Fire Retardents in Flexible Foam"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 358-361.
- 7.47 Loock, F.; Lampe, Th.; Bahadir, A.M. "Temperature Dependence of the Fogging Phenomenon"; *Kunststoffe* **1993**, 83/3, 201-205.
- 7.48 Rothermel, H.M. "Determination of Material Properties", In *Polyurethane Handbook*; Oertel, G., Ed., Hanser: New York, 1985; 455-507.
- 7.49 Wolfe, H.W. "Cushioning and Fatigue"; In *Mechanics of Cellular Plastics*; Hilyard, N. C., Ed., MacMillan, New York: 1979; 99-145.
- 7.50 Woods, G. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science Publishers: London, 1982, 126-128, 296.
- 7.51 "Standard Methods of Testing, Flexible Cellular Materials-Slab, Bonded, and Molded Urethane Foams"; Annual Book of American Society for Testing and Materials Standards, Volume 09.02, D 3574-95; ASTM: Philadelphia, 1990, 320-335.
- 7.52 Saunders, J.H.; Frisch, K.C. *Polyurethanes: Chemistry and Technology, Part I. Chemistry*; Interscience: New York, 1962.
- 7.53 Campbell, G.A. "Compressive Creep of Polyurethane Foam"; Report GMR-2662, General Motors Research Laboratories, April, 1978.
- 7.54 Ashe, W.A.; Grace, O.M.; Otten, J.G. "BASF Wyandotte Pounding Fatigue Apparatus"; *Proceedings of the SPI-25th Annual Urethane Division Technical Conference*; Technomic: Lancaster, Pa., 1979, 107-112.
- 7.55 Ashe, W.A. "Fatigue Test for Carpet Cushion"; *Proceedings of the SPI-30th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 320-325.
- 7.56 "Flexible Cellular Materials-Test for Dynamic Fatigue by Constant Load Pounding"; International Standard 3385.

- 7.57 Hartings, J.W.; Hagan, J.H. "Fatigue Investigation of Urethane Seat Pads"; *J. Cell. Plast.* **1978**, 14/2, 81-86.
- 7.58 "Dynamic Fatigue Test by the Roller Shear at Constant Forces"; American Society for Testing and Materials, D3574-86; ASTM: Philadelphia, 1990.
- 7.59 Knight, J.E. "SPI Study-Flexible Foam In-Use Fatigue Testing for Chairs," *Proceedings of the SPI-30th Annual Technology/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 48-57.
- 7.60 Babrauska, V.; Krasny J.F. "Fire Behavior of Upholstered Furniture" (NBS Monograph 173), (U. S.) Natl. Bureau Standard, 1985.
- 7.61 Strength, R.S.; Sherman, M. "Fire Safety of Plastics Displays and Decorative Items: A Status Report on an SPI Test Program," *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 268-272.
- 7.62 Fenimore, C.P.; Martin, F.J. "Candle-type test for flammability of polymers"; *Mod. Plast.* **1966**, 4/3, 141-192.
- 7.63 Goldblum, K.B. "Oxygen Index: Key to Precise Flammability Ratings"; *SPE J.* **1969**, 25/2, 50-52.
- 7.64 Isaacs, J.L. "The Oxygen Index Flammability Test-Its Development and Application"; *SPE Technical Papers, Vol. 15* **1969**, 143-147.
- 7.65 Isaacs, J.L. "The Oxygen Index Flammability Test" *J. Fire & Flamm.* **1970**, 1/1, 36-47.
- 7.66 Isaacs, J.L. "The Oxygen Index flammability test"; *Mod. Plast.* **1970**, 47/3, 124-128.
- 7.67 Batorewicz, W.; Hughes, K.A. "The Application of the Oxygen Index to Urethane Foam"; *J. Fire & Flamm.* **1971**, 2/10, 260-270.
- 7.68 Parrish, D.B.; Petrella, R.V.; Beal, G.E. "Use of a Downward Vertical Burn Test and the OSU Heat of Release Calorimeter for Evaluation of Fire Resistance of High Performance Flexible Foam," *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 201-208.
- 7.69 Szabat, J.F.; Zirk, W.E.; Parrish, D.B. "Development of a Classification System for Combustion Modified Polyurethane Based on the OSU Calorimeter; Part 1," *Proceedings of the SPI-31st Annual Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1988, 190-200.
- 7.61 Federal Motor Vehicle Safety Standard (FMVSS) 302- Test Procedure and Specimen Preparation, Docket 3-3, Notice 6: *Fed. Reg.* 38, No. 95, May 17, 1973.
- 7.62 "Laboratory Procedures For Flammability Compliance Tests, Federal Motor Vehicle Safety Standard No. 302"; *Technical Publication TP-302-02*, June 1973; U.S. Department of Transportation; Washington, D.C.
- 7.63 Storrs, C.D.; Lindemann, O.H. "A General Discussion of Flammability as Related to the Automotive Industry and MVSS 302"; Proceedings of the SAE Automotive Engineering Congress, Detroit, Michigan, 1972; Paper No. 720263; SAE: Warrendale, Pa.
- 7.64 "Procedure For Testing Flammability Of Materials"; General Motors Engineering Standard GM9070P, July, 1993.
- 7.65 "Flammability of Interior Trim"; Ford Motor Company, Engineering Specification ES-E97B-1011014-AA.

- 7.66 Flammability Information Package, Bureau of Home Furnishings, Dept. of Consumer Affairs, State of California, N. Highlands, 1981.
- 7.67 Babrauskas, V. "Flammability of Upholstered Furniture with Flaming Sources"; *Cell. Polym.* **1989**, 8, 198-224.
- 7.68 BS 5852 Fire Tests for Furniture - Part 2. Methods of Test for the Ignitability of Upholstery Composites for Seating by Flaming Sources (BS 5852:Part 2:1982) British Standard Institute, London, 1982.
- 7.69 Herrington, R.M. "The Rate of Heat, Smoke, and Toxic Gases Release from Polyurethane Foams," *J. Fire Flam.* **1979**, 10, 308 -325.
- 7.70 Herrington, R.M.; Story, B.A. "The Release Rate of Heat, Smoke, and Primary Toxicants from Burning Materials," *J. Fire Flam.* **1978**, 9, 284-307.
- 7.71 Stone, H.; Pcolinsky, M.; Parrish, D.B.; Beal, G.E. "The Effect of Foam Density on Combustion Characteristics of Flexible Polyurethane Foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 603-614.
- 7.72 Gallagher, J.A.; Smiecinski, T.M; Grace, O.M. "The OSU Heat Release Unit as a Screening Tool for California TB 133"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 620-627.
- 7.73 Balkon, J. "An Investigation of the Role of Forensic Toxicology/Pathology and the Forensic Toxicologist in Fire and Fire/Arson Fatalities - Final Report on Phase 1/Final Report on Phase 2," *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 218-239.
- 7.74 "Flammability of Interior Trim"; Ford Motor Company, Engineering Specification ES-E97B-1011014-AA.
- 7.75 Flammability Information Package, Bureau of Home Furnishings, Dept. of Consumer Affairs, State of California, N. Highlands, 1981.
- 7.76 Babrauskas, V. "Flammability of Upholstered Furniture with Flaming Sources"; *Cell. Polym.* **1989**, 8, 198-224.
- 7.77 BS 5852 Fire Tests for Furniture-Part 2. Methods of Test for the Ignitability of Upholstery Composites for Seating by Flaming Sources (BS 5852:Part 2:1982) British Standard Institute, London, 1982.
- 7.78 Herrington, R.M. "The Rate of Heat, Smoke and Toxic Gases Release from Polyurethane Foams", *J. Fire Flam.* **1979**, 10, 308-325.
- 7.79 Herrington, R.M.; Story, B.A. "The Release Rate of Heat, Smoke and Primary Toxicants from Burning Materials", *J. Fire Flam.* **1978**, 9, 284-307.
- 7.80 Stone, H.; Pcolinsky, M.; Parrish, D.B.; Beal, G.E. "The Effect of Foam Density on Combustion Characteristics of Flexible Polyurethane Foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 603-614.
- 7.81 Gallagher, J.A.; Smiecinski, T.M.; Grace, O.M. "The OSU Heat Release Unit as a Screening Tool for California TB 133"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 620-627.
- 7.82 Balkon, J. "An Investigation of the Role of Forensic Toxicology/Pathology and the Forensic Toxicologist in Fire and Fire/Arson Fatalities-Final Report on Phase 1/Final Report on Phase 2," *Proceedings of the SPI-31st Annual Technical /Marketing Conference*; Technomic: Lancaster, Pa., 1988, 218-239.

Chapter 8

Durability



A real world durability test in progress.

Chapter 8

Durability

R. Moore, G. Wiltz, Jr., R. Priester, D. Hunter, D. Laycock

In many end uses, flexible polyurethane foam is subjected to cyclic stress situations in which the foam is loaded and unloaded many times during its working life. In most cases, a foam subjected to cyclic stress will gradually lose much of its ability to bear loads and will be unable to provide the comfort level originally intended. Cyclic stress may also impair the foam's dimensional stability and degrade its appearance qualities. Such harmful effects, which are generally classified as durability or fatigue failures, occur most commonly in carpet underlayment, seating and bedding applications.

FATIGUE IN POLYMERS

Fatigue in polymers is a well-known and much-studied phenomenon.^{8,1} In the general case involving fatigue failures, a polymeric material will be rated as failed when rupture or breakage of the sample occurs. In the case of flexible foams, actual rupture failures are rare, and often fatigue is only seen as the decline of load bearing and dimensional stability. This has created problems in interpreting foam fatigue, especially in being able to determine the actual "failure" condition, which often represents a subjective judgment on the part of a consumer.

Results of polymer fatigue studies typically indicate failure at much lower loadings than would be observed in static testing to failure. Fatigue is often expressed in terms of a failure "envelope", with the number of cycles to failure plotted against the applied load. This defines the stress level a specimen can be expected to withstand without failure. In these tests, when the stress level is increased, the fatigue life of the specimen is invariably decreased. At certain low levels of stress, however, polymers are frequently observed to have an "infinite" life; that is, failure does not occur even after large numbers of cycles. Figure 8.1 shows examples of these plots for a variety of polymers.^{8,1}

Other fatigue test methods study the propagation of well-defined flaws or cracks created in specimens as a function of fatigue cycling, and fatigue failure mechanisms are often successfully modeled using crack propagation theories and damage process accumulation models. In studies of foam fatigue, such ideas and mechanistic modeling have not generally been used, partly because it is difficult to detect actual failure in a foam structure and to propagate a stable crack in a foam. Most foam fatigue testing involves subjecting a foam to some type of controlled stress fatigue test under a certain type of controlled shear. The loss in specific properties is then measured as a function of the number of cycles and the foam is rated as suitable for use in either mild or extreme service conditions.^{8.2}

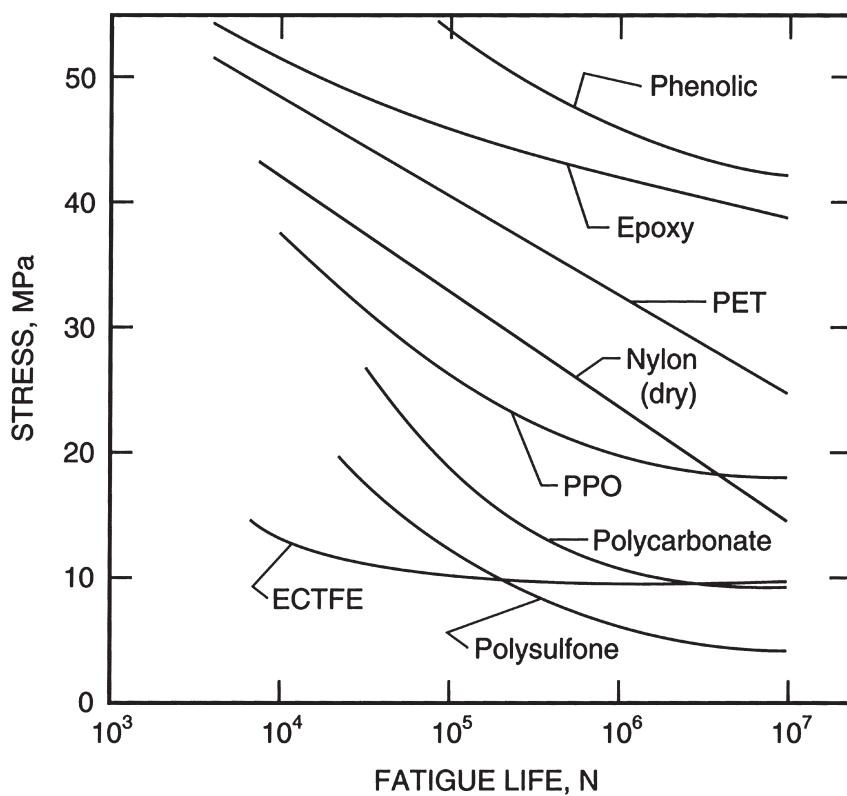


Figure 8.1 Failure Envelopes For Various Polymers

PRINCIPLES OF FOAM FATIGUE

Understanding foam fatigue depends to a large extent on a knowledge of the loadbearing behavior of a foamed polymer. Figure 8.2 shows a typical stress-strain curve for a polyurethane foam under compression.^{8.3}

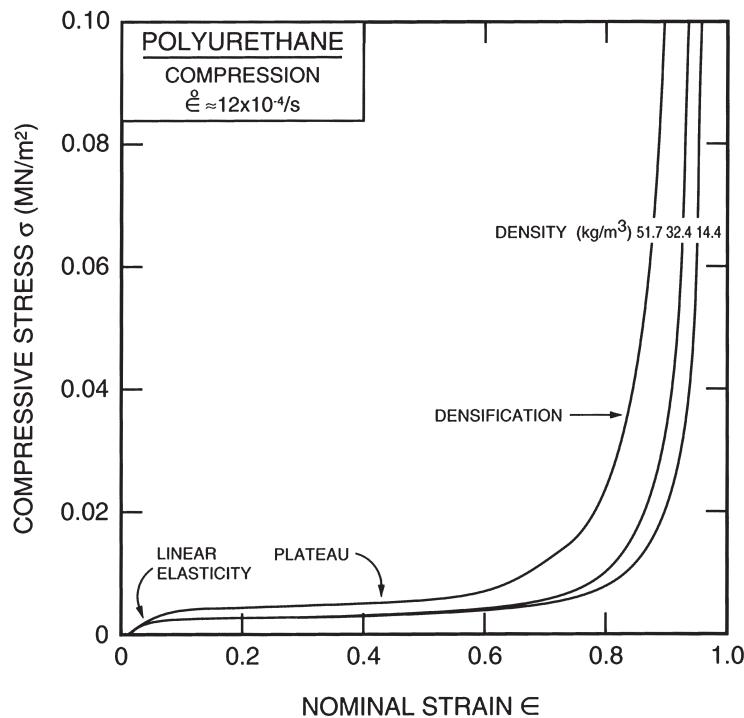


Figure 8.2 Compressive Stress-Strain For A Flexible Polyurethane Foam

During the compression cycle, the foam exhibits three regimes. In the first regime, at the beginning of the cycle, the stress response to strain is linear where the struts bend in response to the stress. In the second regime, as the struts are in the process of buckling, the stress response to strain becomes flat. Eventually, with continuing compression, the struts buckle completely. At that point, the stress response increases dramatically. When the compression is released, the struts unbuckle and return to their original dimensions. The unload curve always shows lower stress than the load curve and the area between the two curves is known as the hysteresis.

The hysteresis is a measure of the amount of work lost during a compressive cycle either as a result of heat or of some type of damage process. The foam's stress-strain behavior is a function of both its cellular and its polymeric nature. Various theoretical models have been proposed to explain the stress-strain behavior of foams, including the work of Gent and Thomas^{8,4}, Hilyard^{8,5}, Rusch^{8,6}, Nagy^{8,7}, Rhodes^{8,8} and Gibson and Ashby.^{8,3} Gibson and Ashby developed a model for foam mechanical behavior in which the cellular effects could be accounted for by using the square of the density as a scaling factor. By this means they were able to develop the following relationships to relate the behavior of the foam in the three regimes of the stress-strain curve to the modulus of the polymer:

$$\text{Foam Modulus/Polymer Modulus} = (\text{Foam Density/Polymer Density})^2 \quad (8.1)$$

$$\text{Buckling Stress/Polymer Modulus} = 0.05 (\text{Foam Density/Polymer Density})^2 \quad (8.2)$$

$$\text{Limiting Strain} = 1 - 1.4 (\text{Foam Density/Polymer Density}) \text{ at Densification} \quad (8.3)$$

Using these expressions and further refinements, Gibson and Ashby have been able to predict foam mechanical properties based on knowing only the polymer density, modulus and the foam density. The impact of foam density in determining the mechanical and durability properties of foam is thus expected to be of paramount importance and will be discussed in a later section.

For evaluating the durability of foam, the typical measurement employed is that of ILD (or IFD) or CLD (or CFD) retention. The ILD measurement is actually a stress relaxation experiment, in which a foam is compressed to a constant percentage of its original height and allowed to relax over a period of time.^{8,2} Figure 8.3 shows the CLD behavior of a flexible polyurethane foam plotted as applied load versus time before and after a fatigue test.

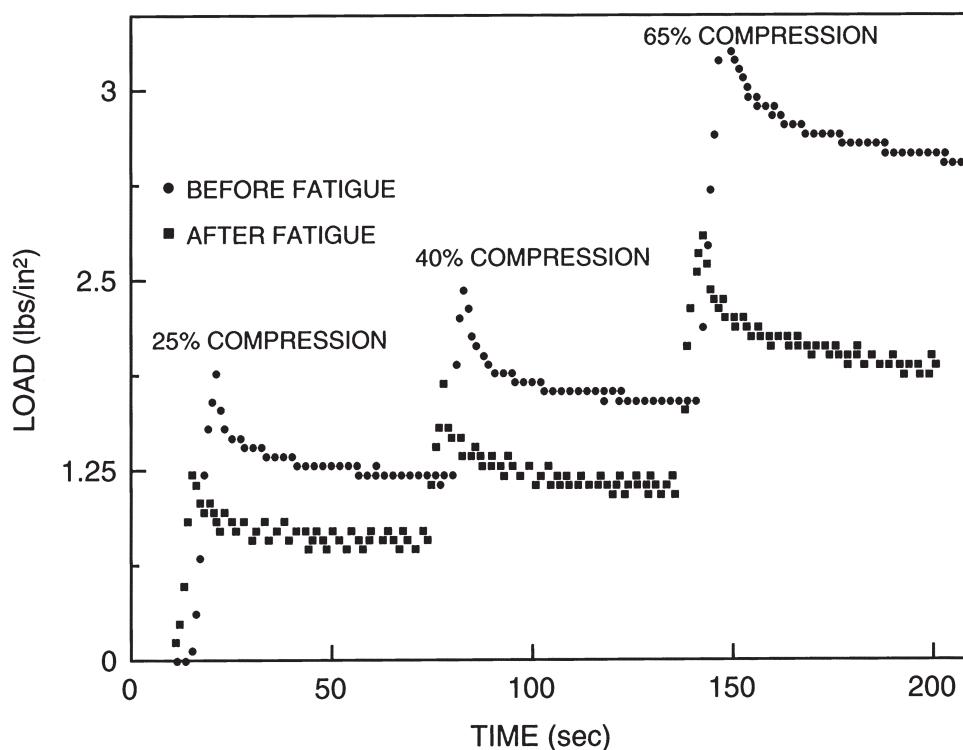


Figure 8.3 Foam Stress Relaxation Before And After Fatigue

It can be seen that the actual maximum load bearing of the foam occurs at the initial point when the foam is compressed to the 25% indentation point, and is followed by a period of stress relaxation. The extent to which the foam stress relaxes is found to be constant for the two samples; the main difference is that the fatigued foam had significantly lower stress at the initial 25% compression. This behavior would tend to indicate that no actual breakdown in the polymer structure itself has occurred, but that the primary mechanism of fatigue is the breaking of struts and/or windows in the foam. Electron micrographs of foams taken after fatigue testing support this view as the structural changes are consistent with strut fracture.^{8,9} The mechanism by which the struts fracture is a matter of debate. Some studies have

indicated that the primary fatigue mechanism is a crazing event in which the buckled struts form small fissures or crazes during the bending process. These fissures continue to grow as the foam is flexed repeatedly until the strut fails. Proposal of this mechanism is based on evidence gathered from acoustic emission, electron microscopy, and penetrant liquid stress-depression experiments.^{8,10} Other possible mechanisms include a cavitation or voiding mechanism which involve dewetting of the rubber-phase around the particulate hard-phase, followed by a failure of the rubber-phase^{8,11}. Another proposed mechanism involves breakdown of the polyurea hard-phase hydrogen-bonding which is followed by softening of the hard-segments or phase mixing of the hard and soft-segments and eventual stress overload of the softer rubber-phase.^{8,12-8,13} The type of mechanism will also depend on the foam itself, since foams containing high-loadings of fillers or hard-phases would be expected to be more prone to a crazing or cavitation failure than foams containing more soft-phase, which would be more prone to failure of the hydrogen-bonded polyurea structure.

FATIGUE TEST METHODOLOGIES

One of the most critical aspects of assessing fatigue behavior is the development of a testing procedure. The literature contains references to a wide variety of fatigue test methods, some of which were reviewed in Chapter 7.^{8,2,8,13-8,17} Most common fatigue tests use a constant compression or stroke control apparatus where the foam is compressed to a constant percentage of its original height.

In actual end-use situations, foam is almost always subjected to load control compression. The load applied will depend on the weight of the object compressing the foam and the geometry of the compressing object. In carpet underlay applications, a typical load applied by an average man wearing flat-sole shoes will be approximately 100-150 lb/in². This loading typically would compress a prime underlay carpet pad to 90-95% of its original height. Another aspect of fatigue testing is introducing the proper shear effects. Some tests have been developed using a roller mechanism that can be set at an angle to the foam to apply the load. For carpet underlay applications, several references have reported on the correlation of this type of test to infield performance.^{8,15-8,16} In general, the correlation of fatigue tests to infield service measurements are found to be poor. This has led to a variety of problems, especially in being able to develop test conditions that will duplicate field failures.^{8,15} This type of problem can be magnified to an even greater extent if an extremely severe test is developed to duplicate failures that occur only on a limited basis. This can lead to a situation where foams are over designed to meet a criterion that may be unrealistic.

Cavender^{8,17} discussed a dynamic flex durability test utilizing an environmental control factor and a preprogrammed hydraulic actuator driven IFD foot to load a cushioning specimen at two preset deflections above and below the design deflection. The loads were applied at a frequency of 5 Hz (considered the typical frequency found in automobiles). Creep and load and height loss data are then collected. Later, Cavender in related work,

described a computerized method for real time testing of foam performance in connection with novel polyol technology.^{8,18} The ACDF test was later described for measurement of dynamic flex fatigue properties of molded foam. This test method utilizes similar computerized dynamic measurements coupled with a quantitative measurement of vibrational transmissivity (via accelerometer placements on the foam pad specimen during testing).^{8,19}

CHEMICAL AND PHYSICAL EFFECTS IN FOAM FATIGUE

A significant amount of work has been performed to relate various aspects of foam chemistry and processing to fatigue. Overviews have been given by Dwyer, Wolfe, Hoffmann and others.^{8,20-8,28} Table 8.1 shows a summary of these effects. Important correlations are further discussed below.

WATER

Water in the formulation plays an important role in determining the durability characteristics of a foam. The effect seems to be greater at elevated temperature and humidity and has been suggested to be of greater importance than density changes in the foam.^{8,29} Patten and Priest reported that % ILD loss values tend to increase with increasing water levels after fatiguing with 60 pound roller shear.^{8,30} This loss in properties was attributed to the higher urea content and more hydrogen bonding in HR foams. A further load-relaxation study concluded that foams with higher hard-segment content (higher water) displayed higher stress levels;^{8,31} all of which might be seen to be similar to compression set behavior.

POLYOL

Several conflicting reports have been published on the effect of polyol molecular weight on durability. Early studies showed that minor changes in the molecular weight or primary hydroxyl content in polyoxypropylene-based triols had little effect on fatigue.^{8,25} In carpet underlay applications, HR slabstock foams (higher-molecular weight, ethylene-oxide-capped polyols) have been reported to have better durability than conventional slabstock foams.^{8,14 -8,32}

HR molded foams have been shown to display better fatigue results as molecular weight and functionality are increased.^{8,23} Addition of diols and low molecular weight triols have led to reduced fatigue resistance. Decreased monol (unsats) content leads to formation of better networks, improved tensile and tear resistance and was reported to be beneficial to fatigue performance.^{8,23} Better damping characteristics were reported as lower resonance frequency with over packing, increased amounts of fillers and higher index as contributing factors.

Table 8.1 Chemical and Physical Factors Affecting Foam Durability

| Fatigue Test Method | Variable | Fatigue Trend | Reference |
|--|---|--|--|
| | ↑ Higher ↓ Lower | ↑ Worse Fatigue ↓ Better Fatigue – No Change | |
| Dynamic Flexing, Roller Shear | Isocyanate Level ↑ Compression Set Density | ↓ – – | 8.26 8.26 8.26 |
| Dynamic Fatigue, Constant Load, 20,000 Cycles | Minor Changes in MW/1°OH Content Higher MW Polyols ↑ SAN Copolymer ↑ Isocyanate Index ↑ Water Amount ↑ Inert Blowing Agent ↑ Cell Structure: Fineness, Porosity ↑ Blowing/Gelling Catalyst ↑ Density ↓ Hysteresis ↑ Compression Set | – ↑ ↑ ↓ ↑ ↓ (Slight) ↑ (Slight) ↑ (Slight) ↑ ↑ Not Established | 8.25 8.20 8.20 8.20 8.35 8.35 8.27 8.27 8.20 8.20 |
| Jounce Test | Resiliency (Ball Rebound) ↑ | ↓ | 8.26 |
| Field Trial, Human Chair Occupancy | Compression ↓ Density ↓ Tensile, elongation ↑ | ↓ ↑ ↓ | 8.26 8.26 8.26 |
| Roller Shear | Density ↑ Filler ↑ Firmness (IFD) ↑ HR Polyol ↑ Flame Retardant | ↓ (Fatigue losses greater around 1.2 lb/ft ³) ↑ (Compared to softer foams at same density) – (Relative to conventional polyol) – | 8.28 8.28 8.28 8.28 8.28 |
| Static Fatigue, Constant Deflection | Polyol MW ↓ Functionality ↑ Tin Catalyst (DBTDL) ↑ Blowing Cat: NIAX A-1 ↓ Blowing Cat: NIAX A-4 ↑ Gel Cat: DABCO 33 LV ↑ Water level Index Surfactant | ↑ ↓ ↑ ↓ ↓ ↓ – (Slight) – (Slight) – (Slight) | 8.21 8.21 8.21 8.21 8.21 8.21 8.21 8.21 8.21 |

ISOCYANATE

Isocyanate type has recently become an area of interest. In some carpet underlay areas, the use of HR slabstock polyols and diphenylmethylenediisocyanate (MDI) type isocyanates have been reported to give foams that exhibit better durability than conventional slabstock copolymer polyols and toluene diisocyanate (TDI).^{8,32}

The use of TDI with increased 2,6 isomer content has been found to give poorer durability in static fatigue testing as a result of increased hydrogen-bonding for this isomer.^{8,33}

The effect of isocyanate index on durability has received a great deal of attention. Most reports agree that indexes significantly greater than 100 result in a deterioration of fatigue performance.^{8,20, 8,26} In carpet underlay testing, it has been reported that increasing foam hardness by the incorporation of copolymer polyol gives significantly better foam durability than increasing hardness by increasing the isocyanate index.^{8,24} This effect has been attributed to less efficient growth of the polymer molecular weight at high index, partially as a result of the excess stoichiometry and partially because of the increase in crosslinking.

BLOWING AGENT

The most recent report on the effect of water level was made by Cavender, who studied the durability of HR molded foams of varying foam density.^{8,17} In preparing these foams, the water level was changed, while constant foam hardness was maintained by varying the level of copolymer polyol. This report showed that density and hysteresis were the main factors affecting fatigue and that lower density gave worse fatigue performance. This study also showed that hysteresis is related to density, since higher-density foams gave better hysteresis behavior; that is, improved ability to recover from compression. The report indicated, however, that with a constant-density formulation, durability improvements could be achieved by changing the polyols to give a polymer with better hysteresis behavior. Cavender's work also showed the important effect of humidity on the results of durability testing; that is, lower-density foams showed poorer durability under humid conditions than higher-density foams. It should be kept in mind, however, that the composition of the foams was varied during preparation to maintain a constant hardness; thus, the lower-density foams presumably contained higher hard-segment levels. This may also account for their poorer durability behavior.

Recently developed liquid carbon dioxide technology in molded foam may provide benefits with respect to compression set and fatigue performance.

SURFACTANTS AND CATALYSTS

Surfactants which promote fine cell-structure with a high degree of porosity improve fatigue performance.

The use of blowing and gelling catalysts combinations is standard practice in the manufacture of polyurethane foam. Durability is generally found to be poorer for foams in which the catalyst balance is tilted in favor of one reaction over another.

Studies have shown that fatigue is improved in the absence of tin catalysts while optimization of performance can be achieved with moderately high levels of gelling catalysts; a predominant blowing reaction early in the formation seems to provide better hard-segment order and, better fatigue performance.^{8,23}

RECENT TRENDS IN DURABILITY RESEARCH

Recent research into foam durability has attempted to separate fatigue effects that are due to the cellular nature of the foam from those which are due to the polymer. Figure 8.4 shows durability performance data for prime carpet underlay foams which were submitted to controlled walk testing as part of a cooperative study involving foam chemical suppliers, foam manufacturers and a major university.^{8,34}

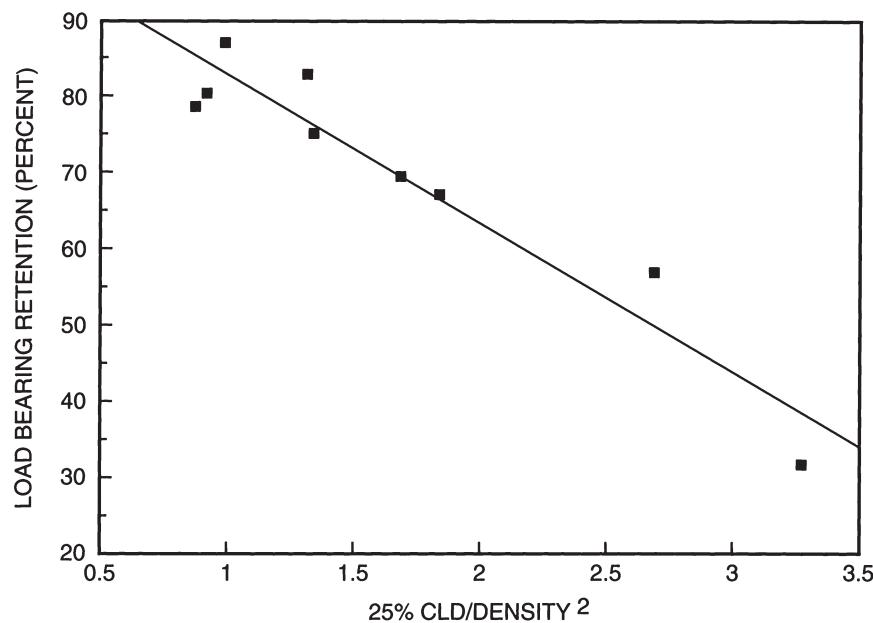


Figure 8.4 Durability Data for Prime Carpet Underlay

The data are plotted as 25% CLD retention after 160,000 walks versus 25% CLD divided by the square of density. The square density function is derived from the theory of Gibson and Ashby, which shows that the actual stress on a foam is a function of density squared.^{8,3} The linear relationship shows the interaction of hardness and density in determining fatigue. Figure 8.5 shows data from Reference 8.13 plotted in the same manner, indicating that this relationship has validity for data from several sources.

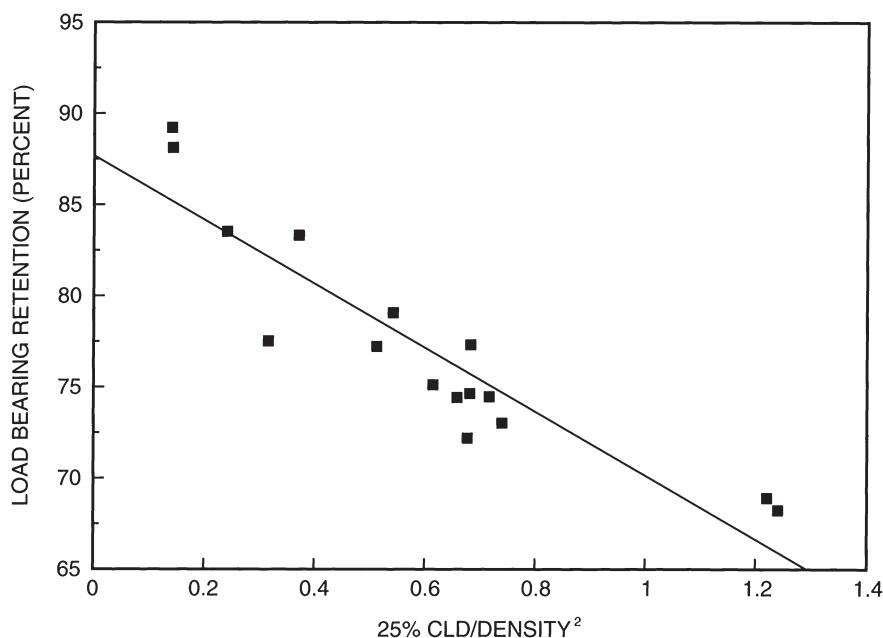


Figure 8.5 Load-Bearing Retention Data For Prime Carpet Underlay Foams

The main idea to be learned from this type of analysis is that the most important cellular factor influencing carpet cushion fatigue is density. These data show that foams with density less than $2 \text{ lb}/\text{ft}^3$ would be more likely to suffer catastrophic loadbearing failures after only limited in-service use. Another important finding is that increased foam hardness is also detrimental to fatigue performance, and that if high-hardness is desirable in a certain grade of foam, then foam density should also be raised.

In order to decouple the cellular effects from the polymer effects, the data from this study were further analyzed by normalizing the loadbearing retention by dividing by the 25% CLD over density squared factor. This normalization removes the cellular effects from the data and allows a correlation to be made of durability behavior to polymer properties. Figures 8.6 and 8.7 show the normalized loadbearing retention plotted as a function of foam hysteresis (via ASTM D 3574) and foam storage modulus determined from dynamic mechanical spectroscopy.

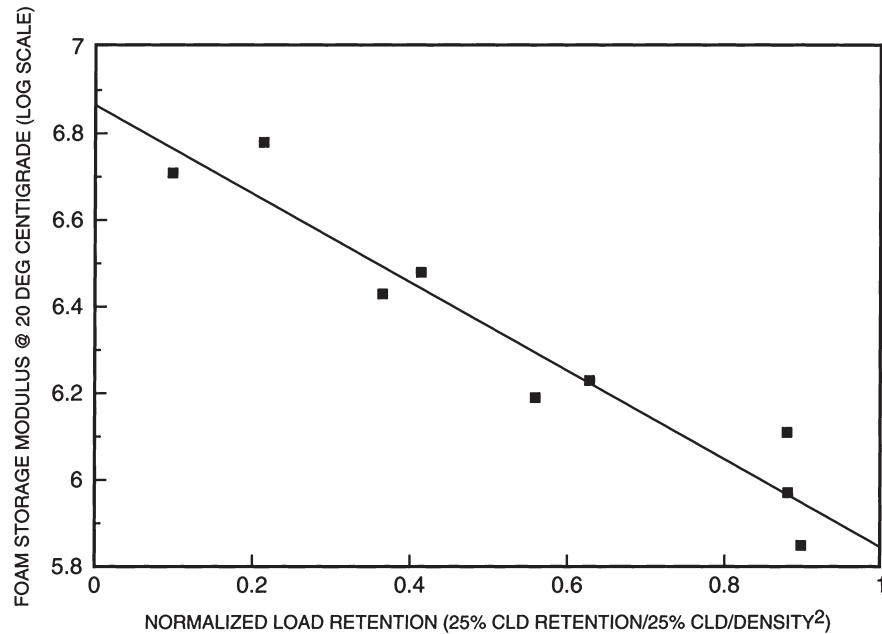


Figure 8.6 Foam Storage Modulus Related To Load-Bearing Retention In Prime Carpet Underlay Foams

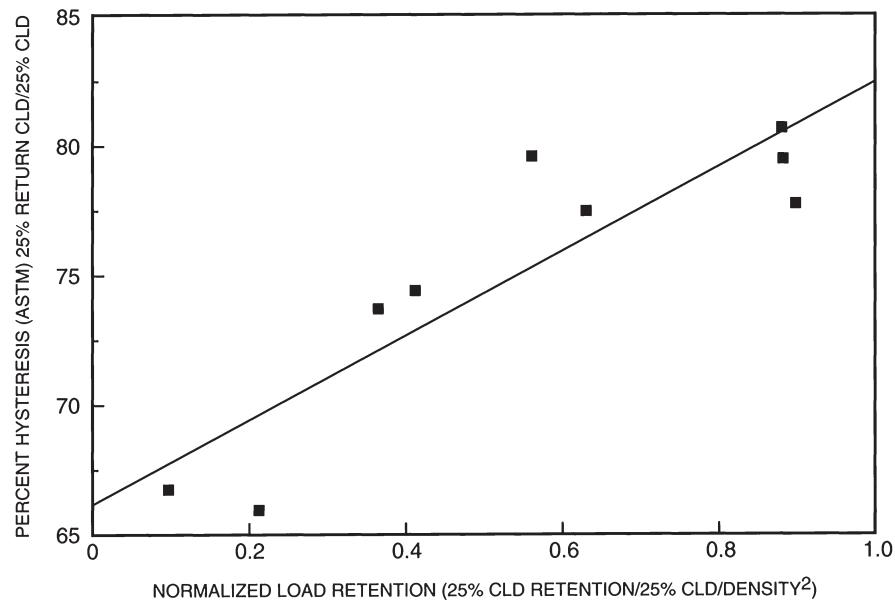


Figure 8.7 Foam Hysteresis Related To Load-Bearing Retention In Prime Carpet Underlay Foams

These parameters which are more directly related to the molecular properties of the polymer in the foam, show some interesting effects. The hysteresis data show that foams with lower hysteresis (worse ability to recover from compression) have worse durability than high-hysteresis foams, and that foams with higher storage modulus (stiffer polymer in the struts) have worse durability than softer polymers. High storage modulus and low hysteresis are characteristics associated with foams that contain high levels of hard-segments (either polyureas or SAN copolymer particles). Lower-density foams which are all water-blown will contain higher levels of polyurea than higher-density foams. This gives a negative durability effect both in lowering density and in raising hard-segment content. Adding SAN copolymer polyol to low-density foams will lead to higher hard-segment content and therefore cause the durability to worsen.

SUMMARY

In summary, several issues are found to be important in foam durability. The most important issue is that the development of laboratory-scale tests is one of the critical factors that help researchers assess the in-field performance of foams in environments where cyclic fatigue is expected to be a problem. The fact that few well-correlated tests exist is an indication that this remains a major unresolved issue in the study of foam durability. The second issue is that a good understanding of foam durability requires that the effects due to the cellular nature of the foam and the effects due to the polymer must each be accounted for collectively to develop a better understanding of their roles, both individually and together in assessing foam durability. It is only through such studies that a firm theoretical foundation can be built so that further foam durability improvements can be made.

References

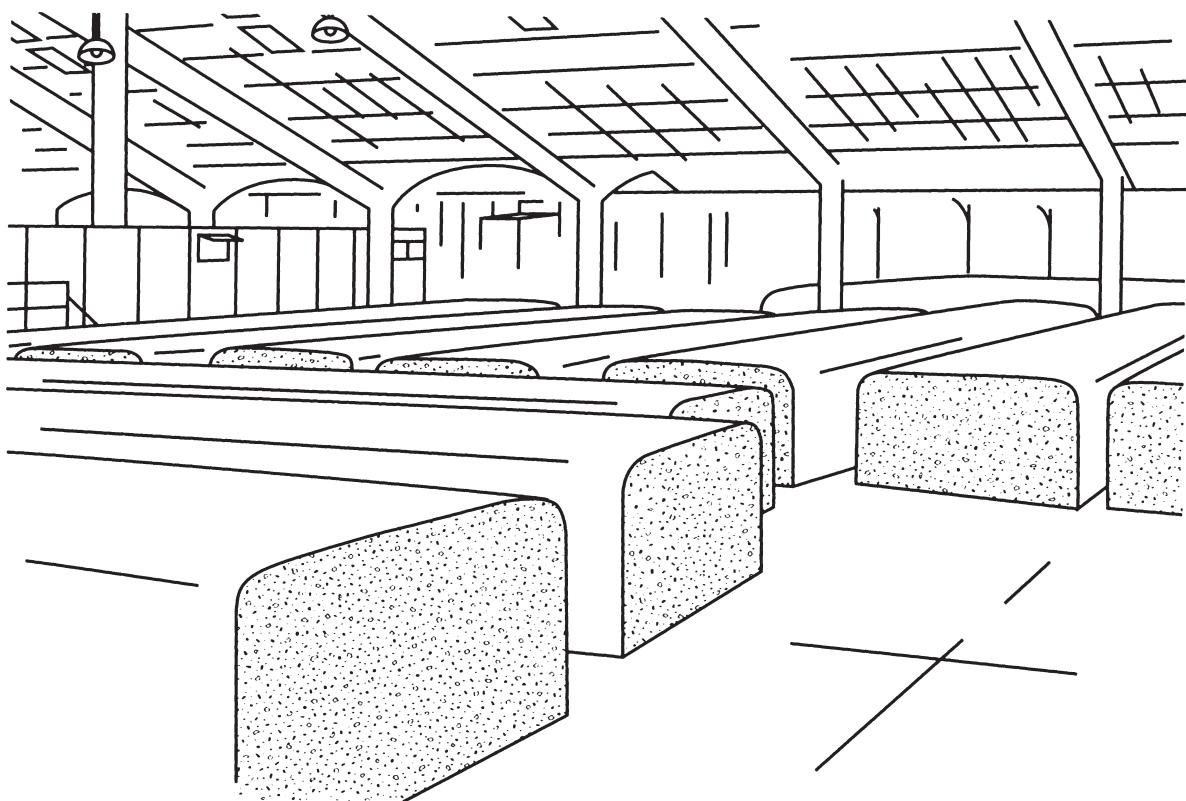
- 8.1 Hertzberg, R.W.; Manson, J.A. *Fatigue of Engineering Plastics*; Academic Press: New York, 1980.
- 8.2 ASTM Standard D 357486, Standard Methods of Testing Flexible Cellular Materials Slab, Bonded, and Molded Urethane Foams.
- 8.3 Gibson, L.J.; Ashby, M.F. *Cellular Solids, Structure and Properties*; Pergamon Press: Oxford, 1988.
- 8.4 Gent, A.N.; Thomas, A.G. "The Deformation of Foamed Elastic Materials"; *J. Appl. Polym. Sci.* **1959**, 1/1, 107-113.
- 8.5 Hilyard, N.C. *Mechanics of Cellular Plastics*; MacMillian: New York, 1979.
- 8.6 Rusch, K.C. "Load Compression Behavior of Flexible Foams"; *J. Appl. Polym. Sci.* **1969**, 13, 2297-2311.
- 8.7 Nagy, A.; Ko, W.L.; Lindholm, U.S. "Mechanical Properties of Foamed Materials Under Dynamic Compression"; *J. Cell. Plast.* **1974**, 10/3, 127-134.
- 8.8 Parma, P.; Rhodes, M.B.; Salovey, R. "Mechanical Properties of Particulate Filled Polyurethane"; *J. Appl. Phys.* **1978**, 49/10, 4985-4991.
- 8.9 Lee, W.M. "Cell Structure Deformation Of High Resilient Polyurethane Foam By Scanning Electron Microscopy"; *Proceedings of the SPI-6th International Conference of the Polyurethane Division*; Technomic: Lancaster, Pa., 1983, 422-427.
- 8.10 Kau, C.; Huber, L.; Hiltner, A.; Baer, E. "Damage Evolution In Flexible Polyurethane Foams"; *J. Appl. Polym. Sci.* **1992**, 44/12, 2069-2080.
- 8.11 Yilmazer, U.; Farris, R.J. "Mechanical Behavior and Dilatation of Particulate Filled Thermosets in the Rubbery State"; *J. Appl. Polym. Sci.* **1983**, 28, 3369-3386.
- 8.12 Yamamoto, T.; Shibayama, M.; Nomura, S. "Structure and Properties of Fatigued Segmented Poly(urethaneureas) III. Quantitative Analyses of Hydrogen Bond"; *Polym. J.* **1989**, 11, 895-903.
- 8.13 Wolfe, H.W. "Cushioning and Fatigue"; In *Mechanics of Cellular Plastics*; Hilyard, N.C., Ed., MacMillan: New York, 1979, 99-145.
- 8.14 Stevens, B.N.; Scott, J.F. Burchell, D.J.; Baskent, F.O. "A Comparison of the Dynamic Fatigue Performance of Typical Carpet Underlayment Foams"; *J. Cell. Plast.* **1990**, 26/1, 19-38.
- 8.15 Stevens, B.N.; Sepulveda, C. "Duplication of Catastrophic Fatigue of Carpet Underlayment Foams"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 255-259.
- 8.16 Ashe, W.A. "Fatigue Test For Carpet Cushion"; *Proceedings of the SPI-30th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 320-325.

- 8.17 Cavender, K.D. "New Dynamic Flex Durability Test"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 282-288.
- 8.18 Cavender, K.D., "Real Time Foam Performance Testing"; *Proceedings of the SPI-34th Annual Polyurethane Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1992, 260-265.
- 8.19 Cavender, K.D.; Kinkelaar, M.R. "Real Time Dynamic Comfort and Performance Factors of Polyurethane Foam in Automotive Seating", SAE Intl. Congress and Exhibition, Detroit, 1996, Paper 960509.
- 8.20 Dwyer, F.J. "A Review of the Factors Affecting Durability Characteristics of Flexible Urethane Foams"; *J. Cell Plast.* **1976**, 12/2, 104-113.
- 8.21 Wolfe, H.W.; Brizzolara, D.F.; Bryam, J.D. "Factors Affecting Fatigue in HR Adduct Foam Statistically Oriented Preparation and Evaluation"; *J. Cell. Plast.* **1977**, 13/1, 48-56.
- 8.22 Hoffmann, J.; Ostromow, H.; Prager, F.; Rothermel, H.M.; Vogel, J. "Determination of the Composition and Properties of Polyurethanes"; In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: New York, 1985, 450-494.
- 8.23 Woods, G. *Flexible Polyurethane Foams, Chemistry and Technology*, Applied Science Publishers: London, 1982, 126-128.
- 8.24 "Fatigue of Virgin Urethane Carpet Cushion"; Product Bulletin SC788, Union Carbide Urethane Intermediates Division, 1988.
- 8.25 Beals, B.; Dwyer, F.J.; Kaplan, M. "Physical Property Relationships and Chemical Factors Affecting Flex Fatigue Characteristics of Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 32-41.
- 8.26 Ball, G.W.; Doherty, D.J. "Fatigue in Flexible Urethane Foams. Part I: Results of an Extensive Field Trial"; *J. Cell. Plast.* **1967**, 3/5, 223-232.
- 8.27 Jones, R.E.; Fesman, G. "Air Flow Measurement and its Relations to Cell Structure, Physical Properties, and Processability for Flexible Urethane Foam"; *J. Cell. Plast.* **1965**, 1/1, 200-216.
- 8.28 Stone, H. "Fatigue Testing of Flexible Foams"; *Proceedings of the SPI-27th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982, 124-137.
- 8.29 Radovich, D.A.; Brock, M. "Factors Influencing the Durability of Automotive seating Foams"; *Proceedings of the SPI-32nd Annual Polyurethanes Technical / Marketing Conference*, Technomic, Lancaster Pa., 1989, 38-43.
- 8.30 Patten, W.; Priest, D.C. "Highly Resilient, Cold Molded Urethane Flexible Foam"; *J. Cell. Plast.* **1972**, 8/3, 134-143.
- 8.31 Dounis, D.V.; Wilkes, G.L.; Turner, R.B. "The Effects of Temperature and Relative Humidity on the Load Relaxation Behavior of Molded Polyurethane Foams", *Polymer Preprints*, Vol 35, No. 2, 1994; American Chemical Society: Washington, 1994, 781-782.

- 8.32 McKenna, E.H.; Wujcik, S.E.; Pask, R.F. "Improved Fatigue Resistance of Polyurethane Carpet Underlay"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 473-479.
- 8.33 Kane, R.P. "The Fatigue of Flexible Urethane Foams"; *J. Cell. Plast.* **1965**, 1/1, 217-222.
- 8.34 Moore, D.R.; Ridgway, D.; Hicks, J.; Neill, P.L.; Sepulveda, C. "Evaluation and Characterization of polyurethane Carpet Pads by In-Use Traffic Testing"; *Proceedings of the SPI-34th Annual Polyurethanes Technical/Marketing Conference*, Technomic: Lancaster, PA, 1992, 502-511.
- 8.35 Saunders, J.H.; Frisch, K.C. *Polyurethanes, Chemistry and Technology; Part 1, Chemistry*; Robert Krieger: New York, 1962, 327-345.

Chapter 9

Slabstock Foam



In the manufacture of flexible slabstock foam large slabs or “buns” of foam are made in a semicontinuous process, cut and placed in a large storage area for a minimum of several hours. This allows the foam to cure before further cutting and fabricating. This diagram illustrates a typical slabstock foam storage area.

Chapter 9

Slabstock Foam

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Flexible slabstock polyurethane foams are produced as large buns using a semi-continuous process. The equipment used in the production of slabstock foam is discussed in detail in Chapter 5. After curing, the buns can be cut into a variety of desired shapes. The foam pieces cut from the bun can then be used as is or cut, sewn, glued or stapled to each other or to other objects or materials. The relative ease of fabrication helps ensure complete cushioning of delicate objects, allows manufacturers to produce complex sizes and shapes, and makes flexible slabstock foam one of the most adaptable cushioning and comfort products.

Cushioning and comfort properties can be tailored to meet the requirements of a variety of applications by simply modifying the formulation used to produce the slabstock foam. Formulation changes, the effects of which are well understood, can be made easily and can increase or decrease the density and load-bearing characteristics of the foam, resulting in a softer or harder foam. Additives are available that can modify the polymer chemistry or the cell-structure and allow manufacturers to “fine tune” properties. Other additives can modify foam flammability, dissipation of static electricity and many other important properties.

Mechanical processes such as partially crushing the foam to open cells or cause foam densification can modify the foam characteristics after the foam has been produced to meet the needs of specialized applications.

Simple and adaptable manufacturing processes coupled with the wide array of products that can be produced have traditionally made flexible polyurethane slabstock foams economical and versatile choices for many markets. Process and formulation changes that slabstock manufacturers are making during the 1990s will allow the industry to continue to produce these high-quality and economical products while also addressing the environmental concerns of customers and the public.

This chapter will describe slabstock markets, the various types of flexible slabstock foam, the role of each major formulation component and trends facing the industry over the next few years – particularly approaches to environmental issues, fatigue and flammability. Typical formulations and physical properties are provided for several foam types.

SLABSTOCK FOAM MARKETS

Although the markets for flexible slabstock foams are relatively mature, they are very large. For instance, approximately 1.5 billion pounds (680M MT) of flexible slabstock foam were produced in North America during 1994.^{9,1} In fact, globally flexible slabstock accounts for more than 50% of the overall polyurethane market. The U.S. market breaks down into furniture (40%), bedding (15%), transportation cushioning (12%), carpet underlayment (25%) and packaging (5%). The balance is used in textiles, household goods and several miscellaneous applications.

TYPES OF SLABSTOCK FOAM

There are four main types of flexible slabstock foam; conventional foam, high-resilience foam, filled foam and high-loadbearing foam. Each type is formulated differently to provide different cushioning characteristics depending on the intended market.

Conventional Foam - Conventional formulations can be modified to produce a wide range of foam properties quickly and easily. They can be classified in four general hardness (or softness) grades as shown in Table 9.1. The hardness is defined by the indentation force deflection (IFD) of the foam, which can be manipulated by changing certain foam formulation components. Because conventional foam constitutes the majority of the flexible slabstock foam produced, most of the information discussed in this chapter refers to this type of foam.

Table 9.1 Hardness Grades For Conventional Flexible Slabstock Foams (N.A.)

| Foam Grade | Density Range lb/ft ³ | Indentation Force Deflection lb/50in ² |
|--------------|-------------------------------------|---|
| Supersoft | 1.0-1.8 | 10-20 |
| Soft | 1.0-1.5 | 20-30 |
| Intermediate | 1.2-1.4 | 30-40 |
| Hard | 1.2-3.0 | >40 |

High-Resilience Foam - High-Resilience slabstock foams are discussed in greater detail later in this chapter. These products are available in a wide range of densities and hardness levels and are primarily designed to offer enhanced support characteristics. Since these products are more expensive than other slabstock foams, their use is usually limited to high-performance products.

Filled Foams - Filled slabstock foams use inorganic fillers to increase the foam density and improve the load-bearing characteristics – especially the modulus or support factor.^{9.2-9.4} The characteristics of filled foam often lead to the perception that they are higher-quality products. However, this perceived quality improvement is usually accompanied by a reduction in tensile strength, elongation, tear strength and perhaps a long-term decrease in the fatigue resistance of the foam. Fillers like melamine can also be used for improved flammability resistance in countries with stringent flammability standards like the UK or for foams to be used in public occupancy applications. These products are discussed in greater detail in the section on foam flammability later in this chapter.

High Load-Bearing Foams - High Load-Bearing foams incorporate a graft polyol in the formulation to increase the hardness of the foam.^{9.5-9.8} However, manufacturers must carefully balance the improvement in hardness against density increases to avoid sacrificing other foam physical properties. Otherwise, high load-bearing foams may suffer from decreased fatigue resistance. High Load-Bearing foams are most commonly used for the production of carpet underlayment in North America. Grafted polyol filled foams are also useful in reduced pressure conditions (high-altitude, low-pressure foaming) and for specialty applications like packaging.

FORMULATION COMPONENTS

Polyols - Most flexible slabstock foams are made with polyether polyols. Polyether polyols are long-chain alcohols that are made by polymerizing common hydrocarbon oxides. This results in ether linkages(-[R-O-R]_n-) that connect the hydrocarbon portions of the chain and hydroxyl functional groups (-OH) at the ends of the chain.^{9.9}

Triols with a molecular weight from 3000 to 4000, made by copolymerizing a mixture of propylene oxide and ethylene oxide with glycerine as the initiator, are often used to produce conventional flexible slabstock foam. Because water and traces of allyl alcohol act as co-initiators to produce some diol and monol, the overall functionality of the polyol is between 2 and 3. Polyols with slightly higher functionalities are also commercially available.

Several properties of the foam can be controlled by varying the functionality of the polyol. For example, increasing the polyol functionality without changing the molecular weight will produce a slight increase in foam hardness and a small reduction in tensile strength, tear strength and elongation. In addition, as functionality increases the time at which gel point occurs decreases. This is illustrated in Chapter 3, Figure 3.30.

Increasing the equivalent weight of the polyol (the molecular weight divided by the functionality) while maintaining the functionality of the polyol will produce a foam with increased tensile strength, tear strength and elongation. However, the increased equivalent weight will also reduce polyol reactivity.

Altering the level and distribution of ethylene oxide in the molecular chain can have a dramatic effect on the reactivity, emulsifying capacity and hydrophilicity (i.e., affinity for water) of the polyether. For example, a higher level of ethylene oxide in the recipe will increase the reactivity of the polyol. If the ethylene oxide is added stepwise rather than as a mixture of oxides, a block polyol will be formed rather than a random polyol. If the resulting ethylene oxide block is at the end of the polyol chain, reactivity will be increased even further because the terminal hydroxyl groups now form a more-reactive primary alcohol. As the ethylene oxide level within the polyol increases, the hydrophilicity and emulsifying capacity increase as well.^{9,10}

Isocyanates - The most common isocyanates used in the manufacture of polyurethane foams are covered in detail in Chapter 2. Although MDI and its polymeric forms can be used, mixtures of 2,4- and 2,6-toluene diisocyanate (TDI) are the isocyanates of choice for the production of most flexible slabstock foam. TDI is a low-cost, high-quality product that allows manufacturers to produce many types of flexible slabstock foam with a wide range of physical properties. Although TDI is available in 2,4-TDI:2,6-TDI isomer mixtures of 80:20 or 65:35 as well as the pure 2,4-TDI isomer, the 80:20 product is more commonly used. However, when necessary, the reactivity of the system and the resulting foam properties can be modified by using blends of the various isomer-ratio mixtures.

Catalysts - Slabstock foam production requires the use of catalysts. As discussed in Chapter 2, two major reactions take place during foam formation. In the polymerization (or gelling) reaction, polyfunctional isocyanates react with polyols to form polyurethane. In the gas-producing (or blowing) reaction, the isocyanate reacts with water to form polyurea and carbon dioxide. These reactions take place at different rates; both reaction rates are dependent on temperature, catalyst level, catalyst type and a variety of other factors. However, to produce high-quality foam, the rates of the competing reactions must be properly balanced.

If the gas-producing reaction (blowing) occurs faster than the polymerization reaction (gelling), the gas generated by the reaction may expand before the polymer is strong enough to contain it and internal splits or foam collapse can occur. In contrast, if the polymerization occurs faster than the gas-producing reaction, the foam cells will remain closed, causing the foam to shrink as it cools. When the two reactions are properly balanced, open cells dominate in the foam structure. Open cells offer little resistance to diffusion and cell-pressure quickly equilibrate without significant foam shrinkage.

Tin(II) compounds, especially stannous octoate, are usually chosen as one of the catalysts in flexible slabstock production. Tin(II) catalysts strongly catalyze the polymerization reaction. Polyols and formulations that permit a

range of tin(II) levels to be used without causing processing problems are desirable. This range is usually referred to as the processing or tin latitude. To put this in perspective, insufficient catalyst will lead to foam splits or possibly collapse if the polymer fails to gel sufficiently. Excessive catalyst will result in closed cells and shrinkage as described above. The larger the processing latitude, the better the chance foam manufacturers have of successfully producing flexible slabstock foam with desirable physical properties and without processing problems (see also Figure 2.13 in Chapter 2).

Table 9.2 shows how stannous octoate requirements change in response to other changes in the foam formulation.

Table 9.2 Variables Affecting Stannous Octoate Requirements

| Formulation Change | Stannous Octoate Requirement |
|------------------------------------|------------------------------|
| Increased water content | Increased |
| Increased methylene chloride level | Increased significantly |
| Increased acetone | Increased significantly |
| Increased liquid CO ₂ | Increased |
| Increased isocyanate index | Decreased |

In contrast to tin(II) compounds, tertiary amines catalyze the gas-producing reaction. The residual catalyst either escapes from the finished foam after production or are incorporated into the polymer structure. Since the various tertiary amines in use differ greatly in catalytic activity and efficiency, overall reaction rates can be optimized by mixed catalyst systems.

Although the amine and tin(II) compounds catalyze different reactions within the foaming sequence, they do not act entirely independently. Typically, each catalyst influences both reactions in the foaming sequence, and the ability of foam manufacturers to maintain the proper balance between the two foaming reactions can be greatly influenced by the composition and selection of specific catalysts.

Water and Alternative Blowing Agents -Water, trichlorofluoromethane (CFC-11), methyl chloroform and methylene chloride have historically been used as blowing agents for flexible slabstock foams.^{9.11-9.12} Acetone and isopentane are relatively new blowing agents and their acceptance and use is increasing. Methylene chloride is still the predominant auxiliary blowing agent used at the time of writing this book. Water is present in every foam formulation. The water reacts with isocyanate, forming polyurea compounds which remain in the foam, and carbon dioxide, which acts as a blowing agent. Auxiliary CO₂ can also be added as a liquid to augment the blowing portion of the reaction. The characteristics of some of these auxiliary blowing agents are listed in Figure 9.1. The volatile, nonreactive materials

supplement the blowing capacity of the carbon dioxide. As the temperature of the reacting polyurethane increases, these materials vaporize and the gas formed by vaporization provides the additional blowing action.

| | <u>ACETONE</u> | <u>METHYLENE CHLORIDE</u> | <u>CFC-11</u> |
|----------------------|---|---|--|
| FORMULA | $\text{H}_3\text{C} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$ | $\text{Cl} - \overset{\text{Cl}}{\underset{\text{H}}{\text{C}}} - \text{H}$ | $\text{Cl} - \overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}} - \text{F}$ |
| MOLECULAR WEIGHT | 58.1 | 84.9 | 137.4 |
| BOILING POINT, °C | 56.5 | 40 | 24 |
| HEAT OF VAPORIZATION | | | |
| BTU/LB | 224 | 142 | 78 |
| CAL/G | 125 | 79 | 43 |

Figure 9.1 Blowing Agent Properties

Without auxiliary blowing agent, the amount of water added in the formulation determines the density of the foam. A formulation containing 2.0 parts of water per hundred parts polyol (pphp) will yield a density of about 2.8 lb/ft³ (45 kg/m³), 3.0 pphp water a density of 2.0 lb/ft³ (32 kg/m³) and 4.0 pphp water a density of 1.6 lb/ft³ (25 kg/m³). The relationship between the amount of water in the formulation and the resulting foam density is shown in Figure 9.2.

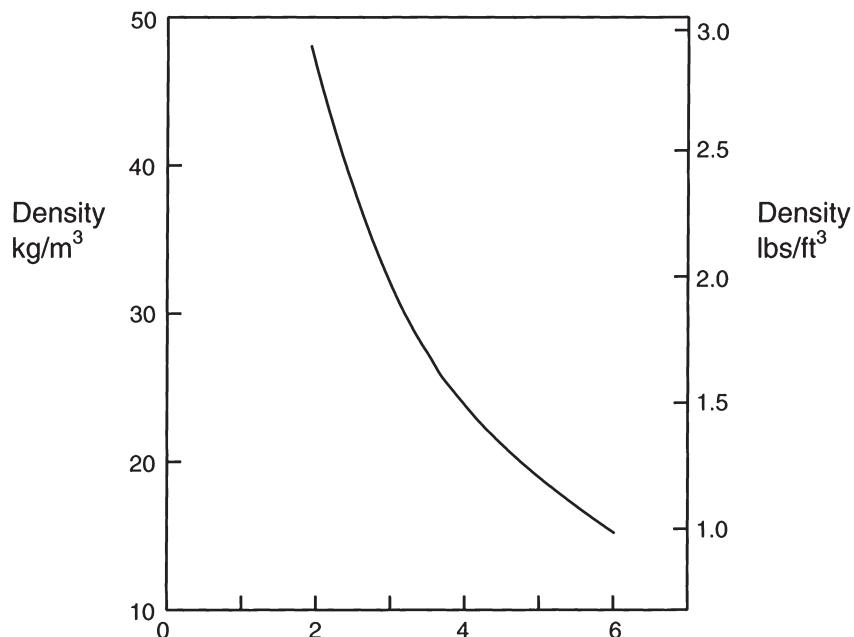


Figure 9.2 Relationship Between Water Level And Foam Density

Historically, slabstock-foam formulations have used an isocyanate index above 100. This, coupled with the exothermic character of the gas-producing reaction, has made formulations with more than 5.0 pphp of water impractical. Excessive heat build-up from such a formulation could lead to degradation and possible self-ignition of the foam buns. Instead, auxiliary blowing agents, which do not participate in foam chemistry, are used when foam densities must reach 1.2 lb/ft³ (19 kg/m³) or below. As a rule, 10 pphp of CFC-11, 8.5 pphp of methylene chloride, 6 pphp of acetone or 13 pphp of methyl chloroform is equivalent to 1 pphp of water.

Hardness, as measured by IFD, is controlled by changing the isocyanate index and the level and type of polyol in the formulation. The use of auxiliary blowing agents also produces softer foams over the entire density range. Figure 9.3 is a contour plot that shows how the density and hardness of slabstock foam changes as the level of water and auxiliary blowing agent increase. Increased water creates more polyurea in the polymer, leading to an increase in hardness. In contrast, for auxiliary blowing agents the hardness decreases with increasing blowing agent level.

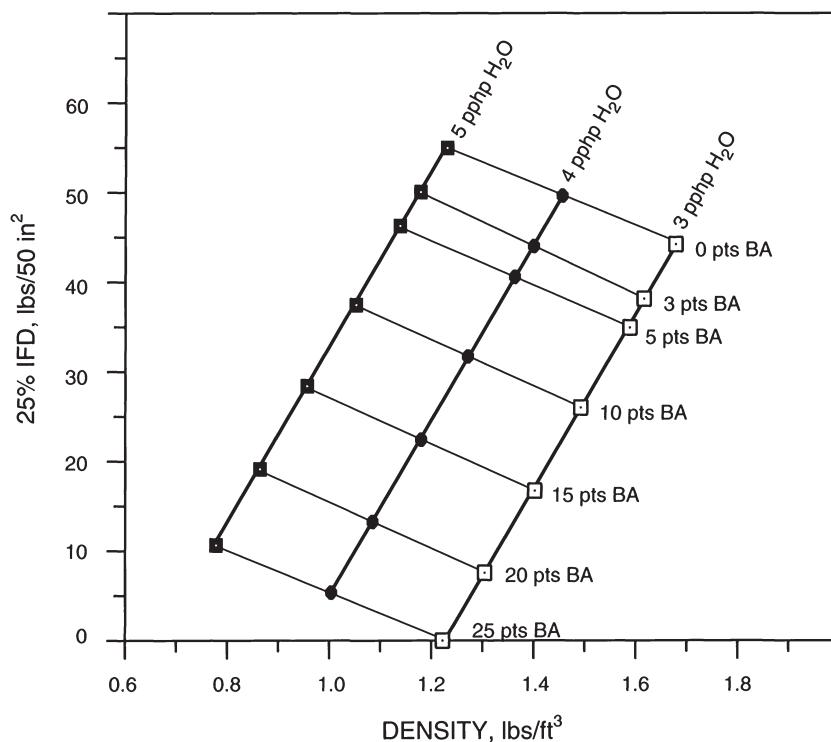


Figure 9.3 Foam IFD and Density Response for Methylene Chloride

Surfactants - Silicone surfactants act as emulsifiers and foam stabilizers in the foam manufacturing process. They are discussed in more detail in Chapter 2. Most silicone surfactants in use are composed of polyetherpolysiloxane copolymers. These materials contain both hydrophobic and hydrophilic groups, enabling them to retain an affinity for both water and organic phases and thereby remain near the interface. In flexible slabstock foams, surfactants help solubilize formulation components and stabilize the rapidly expanding froth. Surfactant manufacturers can vary the polysiloxane and polyether segments, producing a range of products for the wide variety of foam formulations and systems.

If the level of silicone surfactant is incorrect, foam stability problems may lead to excessive “sigh back” (foam settling from its maximum height), shrinkage or closed-cells. In addition, the processing window for the tin(II) catalyst may be narrowed considerably.

Summary

The properties of flexible foams can be tailored to the requirements of various applications by properly selecting the level and type of polyol and other formulation components. The most important properties of the foam are density, hardness and porosity. The measurement of these properties is described in Chapter 7. The formulation variables that most affect these key properties are the isocyanate index, the amount of water, the amount of auxiliary blowing agent and the catalyst level and type.

FATIGUE

Fatigue is usually described as the loss in load-bearing characteristics as a function of time or use. The loss in load-bearing characteristics may be measured by hardness (IFD) changes, compressive force deflection (CFD) changes or other physical property changes. In some cases dimensional changes, such as loss in thickness, may also reflect fatigue. The basic principles of fatigue and possible mechanisms are described in detail in Chapter 8.

Fatigue, particularly as it relates to carpet padding, has been an area of growing concern to U. S. slabstock producers. The use of prime carpet pad, which is made by cutting slabstock into thin sheets, has been declining because some carpet manufacturers believe these products are lower in quality and have poorer fatigue resistance than padding made from bonded foam. Studies conducted by researchers at The Dow Chemical Company suggest that this is not the case and that the fatigue resistance of high-quality prime carpet pad is at least equivalent to rebond pad.^{9,13} In addition, these studies reveal that, as expected, carpet appearance deteriorates with traffic. However, within experimental error, appearance retention was unaffected by the type or density of carpet pad used. These findings are in conflict with the perception that density is the most influential factor in determining carpet pad fatigue performance and carpet appearance retention. Instead, The Dow Chemical Company study suggests that the relationship between IFD and density is more important in determining fatigue characteristics and choice of carpet pad is not as important in determining carpet wear characteristics.

Recent formulation changes, dictated by environmental considerations, have resulted in formulations that use a higher water level and a lower isocyanate index. There is growing speculation that these changes may be detrimental to the long-term fatigue resistance of the foam.

Research is underway to further identify the causes of fatigue. An improved understanding of the fundamental nature of fatigue will enable scientists to begin designing foam structures and polymer morphologies that result in improved fatigue resistance.^{9,14-9,15}

ENVIRONMENTAL ISSUES OF THE 1990s

During the 1990s, slabstock foam producers have faced increasing pressure from environmental interests to reduce and eventually eliminate the use of chlorofluorocarbons (CFCs) and other common auxiliary blowing agents. The use of CFCs in flexible slabstock has already been eliminated in most industrialized countries.^{9,16-9,17}

A secondary, and perhaps longer-term, environmental issue is the impact of polyurethane foam products on municipal waste streams. Once a foam product outlives its usefulness, it is discarded. Since municipal waste is still largely sent to landfills in the United States and other industrialized countries and the nature of foams is such that they take up a large volume in relation to

their weight, manufacturers are beginning to identify and develop waste-reduction alternatives. Both of these environmental issues are addressed in the following sections.

Blowing Agent Reduction/Elimination

In the United States, proactive moves by the government led to amendments being incorporated into the Clean Air Act which accelerate the terms of the Montreal Protocol.^{9,18} Under these amendments manufacturers are prohibited from using CFCs and other ozone depleting compounds as auxiliary blowing agents for flexible slabstock foam. Many of the options for alternative technologies for foam producers have been compiled by the United States Environmental Protection Agency (EPA) in a handbook.^{9,19} The elimination of volatile organic compounds (VOC's) has also been implemented in Europe. The TA luft regulation in Germany and similar regulations in Scandinavia and Italy have in practice eliminated the use of blowing agents other than liquid CO₂.

Until the late 1980s, CFC-11 was the auxiliary blowing agent of choice for flexible slabstock foam. By 1990 the volume of CFC-11 was very small in the U.S. as a result of a use tax. The focus of the replacement efforts has been on the soft and super-soft foam grades since, as Table 9.3 shows, that is where almost 90% of the auxiliary blowing agent volume is being used.

Table 9.3 Estimated CFC-11 And Foam Grade Production Levels (1989 Estimates)

| Foam Grade | Proportion of United States Production | Average Use Level of CFC-11 (pphp) |
|--------------|--|------------------------------------|
| Supersoft | 10% | 22 |
| Soft | 35% | 10 |
| Intermediate | 20% | 4 |
| Hard | 35% | 0 |
| Total | 100% | — |

Methylene chloride has replaced CFC-11 for most foam producers. The use of methylene chloride was introduced to the industry around 1975.^{9,11,9,20-9,21} This blowing agent has a negligible potential toward ozone depletion and is not considered to be a contributor to smog, acid rain or global warming. However, the 1990 Clean Air Act has listed methylene chloride as one of the 189 chemicals to be regulated as a hazardous air pollutant. This has lead to a proposed NESHAP (National Emissions Standard for Hazardous Air Pollutants) regulation that would require compliance in the U.S. late in the year 2000, leading to a significant reduction in the use of methylene chloride.

Methyl chloroform (1,1,1-trichloroethane) was an addition to the list of alternative blowing agents for slabstock foam production. It was introduced

to the polyurethane industry by The Dow Chemical Company in 1989.^{9,12,9,22} However, the production of methyl chloroform has been phased out as of January 1st, 1996 in the U.S. and is no longer available as an auxiliary blowing agent.

Acetone is being licensed as an alternative blowing agent by a foam manufacturer.^{9,19} It is not viewed as a contributor to ozone depletion or to global warming and has recently been delisted as a volatile organic compound (VOC) in the U.S. In contrast to the chlorine-containing blowing agents, acetone is flammable. Its use requires significant changes to foam processes, particularly revisions to bring foam lines and curing areas into compliance with the explosion-proof electrical classifications of the National Electric Code.

The 1990's have seen additive systems developed that do allow foam producers to partially remove auxiliary blowing agents from flexible slabstock formulations while still obtaining soft foams. These products appear to achieve this softening effect by altering the orientation of hard-segments within the polyurethane polymer matrix.

A number of the additives now available allow foam to be processed at low TDI index (below 100) while maintaining foam integrity.^{9,23-9,29} This lower TDI index again reduces hard segment formation and produces softer foam without as much auxiliary blowing agent being needed. The latest technology is said to enable an average foam plant to reduce methylene chloride usage by up to 90%.^{9,27} This change in morphology has been especially valuable in helping foam producers who face severe regulatory restrictions to reduce their use of auxiliary blowing agents. These additives or modifiers facilitate softening of foams with reduced auxiliary blowing agent levels but do not address the density reduction provided by these blowing agents.

Along with low TDI indices being used to promote soft foams, a current trend is to significantly increase water levels in formulations to reduce foam density. The increased water allows the reduction of auxiliary blowing agent to maintain a certain density. The inherent problem is that the high water levels, greater than 5.0 pphp, increases the potential of scorch from high foam exotherms. Forced Cooling is a technology which has successfully been used by several slabstock producers in the U.S. to overcome this problem.^{9,28-9,29} The concept is simple. After production, foam blocks are cooled by having ambient air pulled through them. This essentially eliminates scorch or discoloration and allows the production of low-density foams without the use of auxiliary blowing agents. Cannon-Viking makes the Enviro-Cure system and General Foam Corporation supplies Rapid Cure as examples of commercially available forced cooling equipment.

Additional benefits from forced cooled foam blocks are:

- 1) less IFD variation within a foam block and,
- 2) considerably less time for curing thus reducing storage and inventory requirements.

Disadvantages may include an overall reduction in IFD, increased compression set values and visible emissions from the exhaust exit stacks.

The early 1990's also saw mechanical solutions to eliminating auxiliary blowing agents become commercially available. Liquid CO₂ can now be incorporated into the slabstock foaming system to provide density reduction as well as softening.^{9,30} Mechanical equipment to provide pressures to keep the liquid CO₂ in solution and special dispensing equipment to allow the CO₂ to expand properly at the right time are necessary. These systems can completely replace volatile auxiliary blowing agents with liquid CO₂ and produce the complete line of flexible slabstock foam grades. Cannon-Viking Limited manufactures the CarDio and Henneke Machine Company the Novaflex liquid CO₂ systems. Beamech Group Limited of Europe also have similar systems available.

Another mechanical alternative to eliminating auxiliary blowing agents is "Variable Pressure Foaming".^{9,31} This system encapsulates the entire foaming operation in a vacuum/pressure chamber where the pressure can be controlled. For soft, low-density foams, a vacuum pressure of 0.5 atmosphere can be achieved. This system produces excellent foam properties and is economical to use due to lower water levels needed to make the low density foam types. The elimination of auxiliary blowing agents also contribute to its economic efficiency. This technology successfully produces all foam grades without the use of auxiliary blowing agents. However, a sophisticated computer system to control the process and chamber pressures along with a strict operating discipline is needed to successfully operate this equipment. Also very high capital cost for purchase and installation prohibit many foamers from seriously considering this approach. Beamech Group Limited has equipment of this type available. The mechanical aspects of these three technologies are also described in Chapter 5.

Recycle/Recovery

Flexible polyurethane slabstock foams are recyclable. Virtually all scrap from foam production and fabrication operations is collected, ground and bonded together with a polyurethane binder to produce carpet underlayment pad.^{9,32} The process not only includes scrap from domestic slabstock foams but flexible molded and scrap foams from foreign sources as well. Other uses for rebond foams include specific seating and cushioning applications such as gym mats, seat inserts, headrests and school bus and golf cart seats. Additional rebond uses are being developed including sound absorption firewall, door and automotive carpet pads.

Post-consumer foam scrap is not widely recycled because of the diversity of location and the lack of a collection infrastructure. Several companies in the United States have found it profitable to collect scrap foam from furniture, bedding, and carpet underlayment and process it into rebond foam. The volume of scrap collected has steadily increased as the value of the scrap is being recognized.

Incineration of scrap foam to recover its energy value has proved to be safe and economical. In addition, chemical processes to partially recover basic urethane chemicals are being practiced and other options are being studied. Additional uses for flexible foam scrap are being sought to increase the amount of flexible polyurethane slabstock foam that is recovered and recycled.

Refer to Chapter 14 for more information on recovery and recycling.

FLAMMABILITY ISSUES

The flammability of flexible polyurethane foam is important because its growing use in upholstered furniture and bedding presents the possibility that foam could contribute to a life-safety hazard for humans. Because it provides unsurpassed comfort and durability at relatively low cost, flexible polyurethane foam has replaced most other comfort cushioning materials in upholstered furniture worldwide. It is used in a substantial number of residential mattresses for the same reasons. Since flammability of flexible foam is related primarily to upholstered furniture and bedding, the issue becomes one of composite upholstered furniture and bedding flammability.

Why Foam Burns

Polyurethane foam used for cushioning is normally prepared from polyoxypropylene-polyoxyethylene copolymers reacted with toluene diisocyanate and water to form a low-density foam. The components of the foam contain carbon, nitrogen, hydrogen and oxygen atoms. The presence of these atoms ensures that the foam can never be made entirely noncombustible. The very properties that make polyurethane foam so desirable from a comfort standpoint can contribute to the hazard if furniture or bedding is ignited.

Furniture-cushion foam normally is very low in density. This results in a large surface area, which allows a free oxygen pathway into the foam. The low-density also means that the thread-like size of the individual foam struts allows the foam to be easily heated by adjacent sources. This low thermal inertia is what makes a piece of polyurethane foam feel warm to the touch. Body heat can quickly warm the area of the foam being touched. From a flammability standpoint this means that even small ignition sources, such as a match or cigarette, can warm the small polymer fibrils in certain types of uncovered polyurethane foam to their ignition point.^{9.33-9.34}

Role of Smoking Materials in Furniture Fires

Unfortunately, people using smoking materials in or near furniture and bedding result in a number of fatalities each year. Careless use of cigarettes near upholstered seating and bedding resulted in the death of 810 persons in the United States during 1988.^{9.35} A typical scenario for residential fatalities is that a lighted cigarette is dropped, lodges in the crevice between furniture

cushions and is not retrieved. During the night, after the family has retired, the smoldering cigarette ignites the furniture cushions and the fire spreads throughout the house before the sleeping family is aware of the danger. At this point the escape route may be impaired, the oxygen level in the house may be reduced and/or a high level of carbon monoxide may have developed. Any of these factors can incapacitate the occupants and result in their deaths. Very few occupants are killed by heat or flames alone. The foam inside the furniture is perceived by some as the major hazard because of the rapid burning rate of certain types of foam in a developing fire.

There have been, however, no known fire fatalities resulting from spontaneous combustion of polyurethane foam in upholstered furniture. Since foam is always used as a filler inside an upholstered cushion there is essentially no way that smoldering cigarettes or flaming ignition sources can reach the foam without first penetrating the upholstered cover. The foam involvement is therefore related to the lack of resistance of the cover to ignition.

Role of Upholstery Fabric in Furniture Flammability

There are many publications that suggest that flammability assessment must be done on the specific construction used to make the article rather than in any single component of the upholstered furniture.^{9.36-9.38} To illustrate this point, a series of full-scale burns showed that chairs exposed to smoldering cigarettes did not develop flaming combustion if the fabric was made from a thermoplastic fiber (polyolefin, nylon etc.), even if the foams contained no fire-retardant additives.^{9.36} The same combination of thermoplastic fabric and foam, when exposed to a burning methenamine pill source, ignited quickly. Changing the fabric cover in the chairs to a more fire-resistant cellulosic composition greatly improved the resistance to open-flame ignition but failed to completely eliminate ignition by smoldering cigarettes.

The significance of fabric choice is demonstrated even more convincingly in a series of full-scale burn tests involving couches with various fabrics and cushion fillings. They were burned at the RAPRA fire-test facility in the United Kingdom (UK) for the British Rubber Manufacturers Association (BRMA).^{9.39} In this study, the replacement of standard polyurethane foam with noncombustible mineral fiber had less impact on the rate of growth of the fire than did the choice of fabric.

Improving Flame Resistance

Although a life-safety hazard results from ignition of the entire upholstered cushion, significant efforts have been made by the flexible polyurethane-foam industry to improve the fire resistance of uncovered foam. A number of methods exist for improving foam fire resistance. These include:

- Addition of phosphorus and/or halogen-containing fire retardants during foam preparation. The halogens interrupt the free-radical nature of the combustion and the phosphorus helps form a barrier that restricts the

organic material in the foam from feeding the flame.

- Addition of fillers along with the fire retardants. The most effective fillers are melamine and hydrated alumina. Since these fillers are added to the formulation at concentrations of 15 to 150 pphp of polyol, the percentage of combustible material in the flexible foam is also reduced. Melamine melts away from the flame and forms both a nonflammable gaseous environment and a molten barrier that helps isolate the combustible polyurethane from the flame.^{9.40} Aluminum hydrate releases water of hydration to cool the flame, and along with other additives, forms a noncombustible inorganic protective char at the flame front.^{9.37}
- Protection of the foam by fire-resistant upholstery fabric or liners between the upholstery fabric and the foam cushion.^{9.38}

Standards and Regulations in the United States

The initial target of United States regulations was to improve the resistance of the finished furniture article to ignition by smoking materials. After considerable study and negotiation, the Consumer Product Safety Commission (CPSC) permitted furniture manufacturers, represented by the United Furniture Action Council (UFAC), to devise and regulate a voluntary program that focused on the construction of the complete upholstered-furniture cushion. This, along with the growing use of smoke detectors to provide an early warning of night time fire danger, has resulted in a decrease of upholstered-furniture-related fire fatalities over the years.

In addition to the voluntary national UFAC cigarette-smoldering standard, a California regulation requires smoldering-cigarette ignition resistance and resistance to small-scale flaming ignition sources in upholstered-furniture foam sold in that state. This is explained in Technical Bulletin 117, issued by the California Bureau of Home Furnishings and Thermal Insulation.^{9.41}

California has also issued Technical Bulletin 133,^{9.41} which provides a flammability-rating test for complete upholstered-furniture items that might be used in public-occupancy areas - places such as hospitals, hotel lobbies, theaters and schools where the consequences of an uncontrolled fire might threaten many people. This test involves the entire upholstered item. Beyond Technical Bulletin 117, there are no flammability standards for foam cushioning alone. In practice, the specified ignition source (five crumpled sheets of newspaper or an equivalent gas-fired burner) is quite severe and has normally required the presence of fire retardants and either melamine or hydrated alumina in the foam to pass the test, even when the foam is covered by upholstery fabric. In many cases a combination of melamine foam and a fire-barrier layer is used with certain less-resistant fabrics. This standard has been adopted by various cities in California and by the State of Illinois. Adoption is expected shortly by the State of California and up to ten additional states.

Technical Bulletin 133 is also under review for inclusion as an American Society of Testing Materials (ASTM) standard. It is also being listed as a National Fire Protection Association (NFPA) standard test. In January 1991, the procedure in Technical Bulletin 133 was modified in California to measure the heat released on burning to establish pass or fail criteria. These heat-release data are also useful to include in the fire models discussed below.

European Regulatory Developments

The most significant recent development worldwide on furniture-flammability regulations occurred in the UK where, in 1989, Statutory Instrument 1324 was implemented. This law mandated a significant improvement in the fire performance of foam used in residential furniture. British Standard 5852, Part 2, Source 5 modified test is the specified test procedure and statutory instrument No. 1324 (Sch. 1, Pt. 1, Para. 5) allowing a maximum weight loss of 60 grams.^{9,42} This test involves a small furniture mock-up with a 17-gram wooden-crib ignition source. To pass this test, a High-Resilience foam must contain fire retardants and 15 to 30 parts melamine filler per hundred parts polyol. These foams are referred to as Combustion Modified High Resilience foams (CMHR). In March 1990, this regulation was expanded to include upholstery fabrics, which are now required to pass a less-severe match-equivalency test specified by British Standard 5852, Part 1, Source 1.

More recently Combustion Modified Conventional (CMC) foams also known as CM ethers (CME) were developed as an alternative to CMHR foams. Because these foams, generally based on an all PO polyol, are essentially "Conventional", they have the high toughness and durability factors (as expressed by compression sets) associated with conventional foams.

Attempts are being made to harmonize furniture-flammability regulations throughout the European Community (EC). One proposal supported by some of the involved parties would call for two "essential requirements" (ER) to define the fire safety of furniture:

- The first ER would concern ignitability and involve the use of a cigarette and match test.
- The second ER would deal with post ignition behavior (Rate of Heat Release (RHR), smoke, toxic gases and weight loss).

Future Flammability Issues

The need to test composite items is generally recognized throughout the fire-science community. When materials are evaluated in a composite test the results are recorded, but the impact of the results on fire safety is not always clear. The fire-science community is now developing computer models for fire situations to better predict fire hazards without requiring full-scale testing. Accurate measurements of mass burning rate and rate of heat release from fire-test results are the major experimental data needed for the

computer models. The computer models also contain a large amount of experimental data on heat and toxic-gas transport through various structures.

Ideally, the data from a burn test can be entered into a computer fire model to determine if the fire hazard is increased or reduced by various materials or interior furnishings. In the United States, fire modeling has been spearheaded by the Center for Fire Research of the National Institute of Standards and Technology. They have developed a model called *HAZARD ONE* that runs on a personal computer and permits the user to model the impact of materials and furnishings on fires in multiroom buildings. These models have been developed and improved over a number of years. The major focus now is to extend the predictive ability to large buildings using main-frame computers.

The United States Consumer Product Safety Commission has simplified the *HAZARD ONE* model and calls the simplified version *CPSCHAZ-1*. *CPSCHAZ-1* is designed to model the effect on life safety in various locations within a model six-room ranch house. Data from composite burns of foam and fabric on a cone calorimeter or full-scale burn tests may be entered into the model and used to estimate the impact of changes of interior furnishings on life safety. When these models are perfected and validated they are intended to be used as a basis for flammability regulations.

In Europe, the CBUF research program funded by the EU Commission presented the following conclusions after two years of work:

- Modeling is possible by using the cone calorimeter to predict results of large scale burn tests.
- Rate of Heat Release (RHR) is the most important criteria to determine escape time.

So far, no practical legislation was introduced as a result of this work. The results of the study are still under discussion.

DISCOLORATION OF FLEXIBLE SLABSTOCK FOAM

Discoloration of slabstock polyurethane foam is occasionally observed during the continuous foaming processes that are typically used in commercial production facilities. This phenomenon is seen as a faint to very-dark tan to dark-brown area, usually limited to the center of the foam bun. The presence of this discoloration is not recognized until the foam bun is cut after curing. Color formation in flexible foam is not only an aesthetic concern during conversion but may suggest the beginning of degradation or the precursor to combustion. Both foam producers and raw-material manufacturers take steps to control color development during slabstock-foam production.

Foam discoloration can be separated into two general classes based on the source of the color bodies:

- Additive (most commonly fire retardants) or contaminant-induced
- Thermally induced “scorch” discoloration

The formation of color in foams containing additives such as fire retardants can occur under moderate temperature and environmental conditions, whereas thermal discoloration results from elevated and sustained exotherms within the slabstock bun. Additive-induced discoloration may be observed at any time of the year, while, depending on geographical location, “scorch” is more frequently restricted to the summer.

Additives - As mentioned above, the addition of certain fire retardants (FR) increases the risk of discoloration. FR additives that include aliphatic halogens and/or phosphate esters are most prone to cause discoloration and often contain antioxidants to minimize this possibility. Aryl halide fire retardants - particularly aromatic bromides - have better thermal stability and are less prone to cause discoloration.^{9.44}

Contaminants - A wide variety of contaminants are potential contributors to discoloration during the production of flexible foam. Among this group are metals that may be present in the water used for foam formulations - particularly iron.^{9.43} Because the cellular nature of polyurethane foam results in a high surface area, very small concentrations of highly colored compounds may result in visible discoloration in the final product.

Reaction Exotherm - The most-recognized cause of color formation in foam is an elevated and sustained exotherm in the center of the foam bun that results from the water-isocyanate reaction. In general, the bun temperature will reach a maximum within one hour of being poured. As the bun begins to cool, oxygen-rich air from the surrounding environment is drawn into the hot foam. Temperature profiles obtained by placing thermocouples across the center of a semicommercial foam bun show the effect of increasing the water level in the formulation (Figure 9.4). As the water level is increased from 4 to 6 pphp polyol, the maximum exotherm increases by nearly 86°F (30°C). Because the maximum exotherm is mainly a function of the water isocyanate reaction, these measured temperatures can be extrapolated to production-

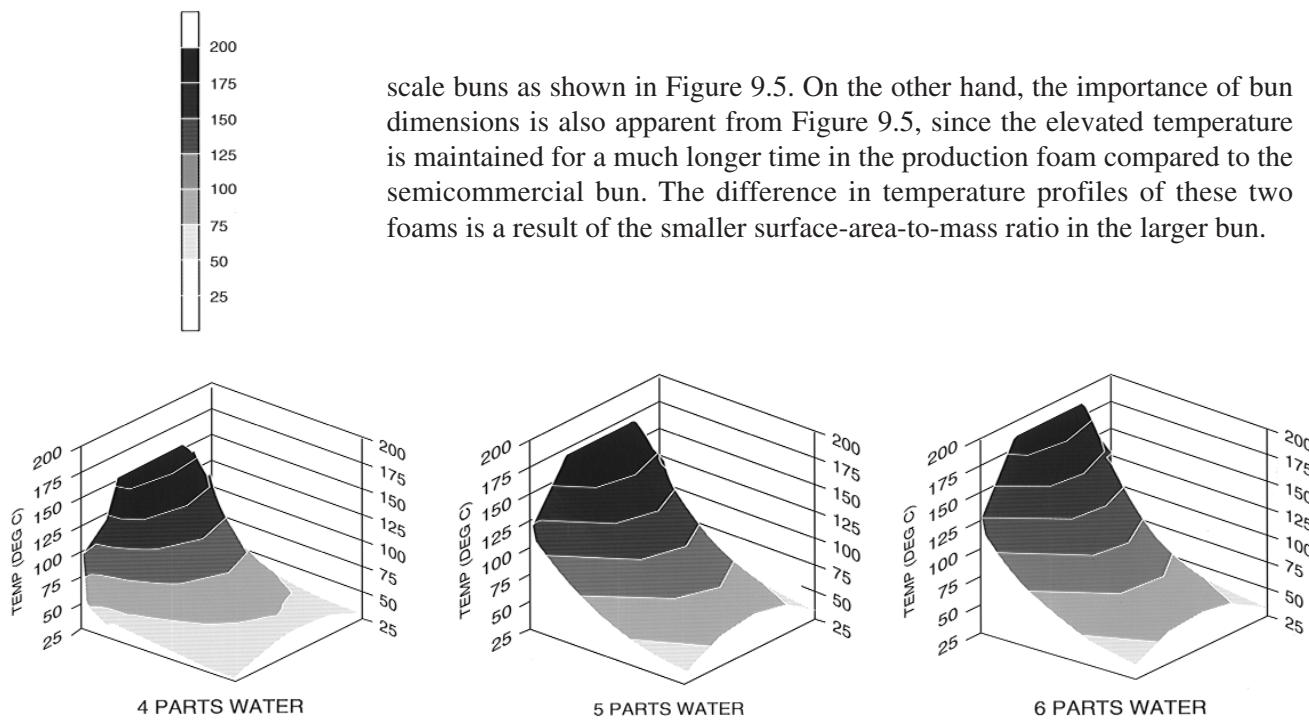


Figure 9.4 Time/Temperature Profiles in Semicommercial Bun

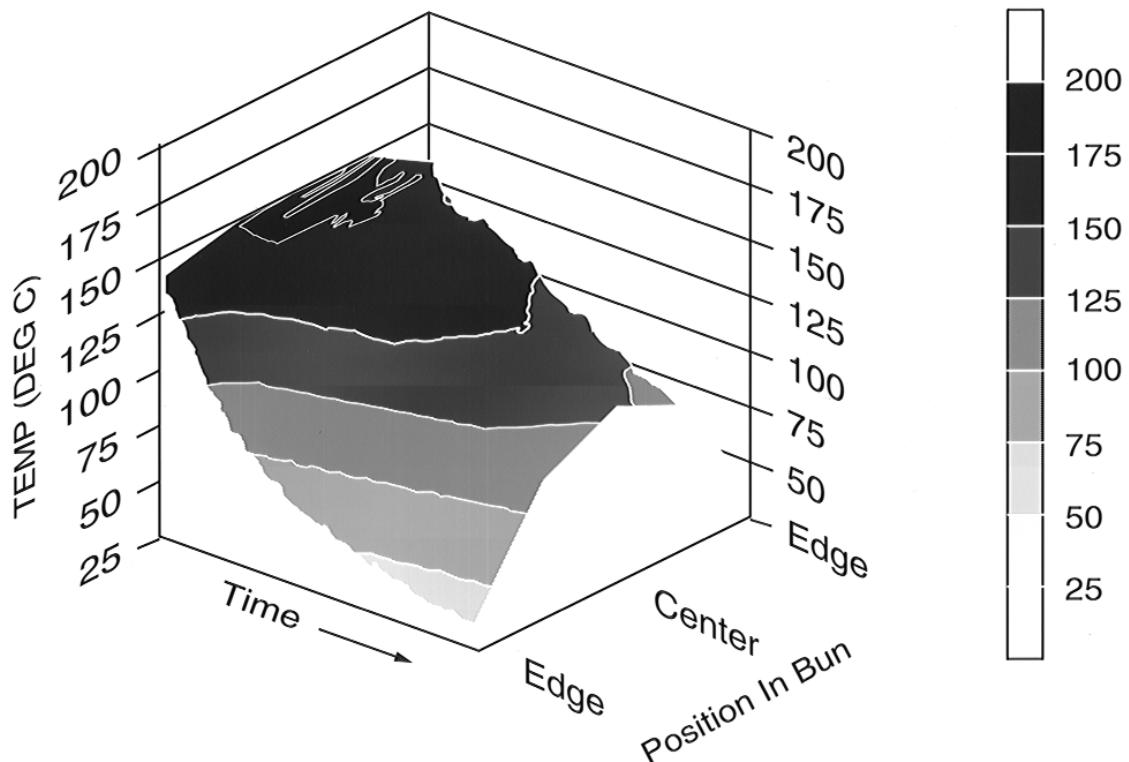


Figure 9.5 Time/Temperature Profile of a Commercial Foam Bun Across the Center

Additional factors which affect the thermal history are bun handling and pump metering errors. Stacking freshly poured foam buns will further slow the rate of heat transfer as buns on the outside of the stack insulate the ones inside the stack. Allowing buns to cool prior to stacking will decrease the likelihood of discoloration. The ratio of the water and polyol to isocyanate is controlled by metering pumps. If calibration errors or mechanical failures occur, these ratios may change and excessive exotherms can occur.

The importance of the thermal histories to which the foam buns have been subjected is two-fold. First, the sustained elevated temperatures provide thermal energy to drive oxidative degradation of the polyurethane polymer as well as other endothermic color-forming reactions.^{9,45} Second, severe temperature gradients will result in volatilization of antioxidants and other additives that may be present in the foam.^{9,46} A formulation containing 4.0 pphp water may lose more than 60% of its initial antioxidant level because of the thermal gradient within the bun. The distribution of these volatile additives within the bun may also become nonhomogeneous; volatile additives “evaporate” from the center of the bun, migrate outward from the center and “condense” closer to the surface of the bun (Figure 9.6).

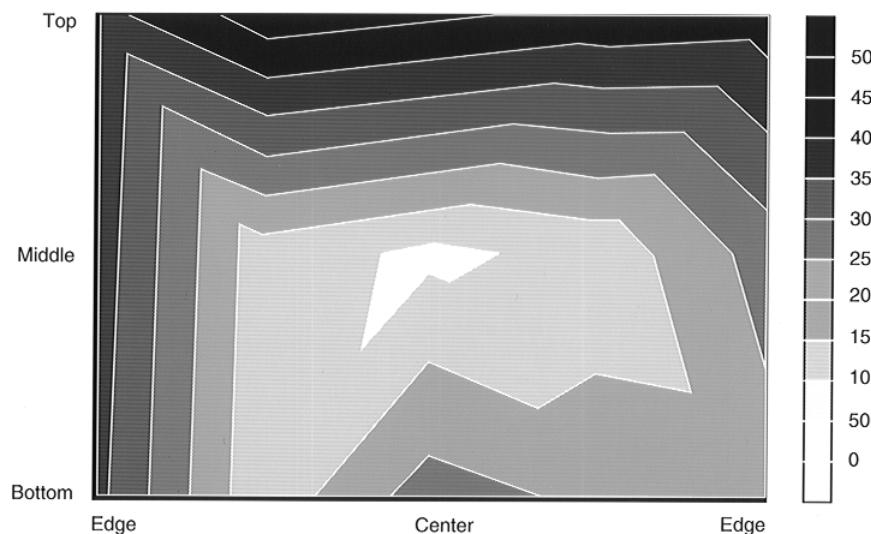


Figure 9.6 Phenolic Antioxidant Profile

Polyol Composition - Polyol quality is also an important variable in the production of color bodies in foam. The presence of peroxides and polyol oxidation products is known to increase the risk of discoloration.^{9,44} Also, the type and concentration of the inhibitor (antioxidant) package will affect the tendency of the polyol to cause color formation. The role of the inhibitor package is discussed in the antioxidants section below.

Environment - Ambient conditions in most commercial production facilities are poorly controlled. As a result, when the weather becomes hot and humid outdoors, freshly made foam buns may be exposed to similar conditions indoors. Foam producers know well that changing weather conditions require formulation changes and can affect the risk of foam discoloration.

Antioxidants

Antioxidants are always added to polyols to reduce the likelihood of discoloration. Antioxidants are effective inhibitors of free-radical thermooxidation reactions - the primary cause of polymer degradation and discoloration (Figure 9.7).^{9,43} Primary antioxidants function by donating hydrogen directly to the free radicals that are produced during the initiation or propagation steps of the degradation process. Commonly used primary antioxidants for polyols include hindered phenolics (e.g., 2,6-di-butyl-4-methylphenol, BHT) and hindered secondary amines (e.g., p,p-dioctyl-diphenylamine). Secondary antioxidants may also be used to prevent discoloration. These inhibitors minimize the formation of alkoxy and hydroxy radicals by degrading the hydroperoxides formed during foam decomposition. Thioesters (e.g., phenothiazine, PTZ) and phosphites (e.g., phenyl-di-dodecyl-phosphite, PDDP) are used as secondary antioxidants.

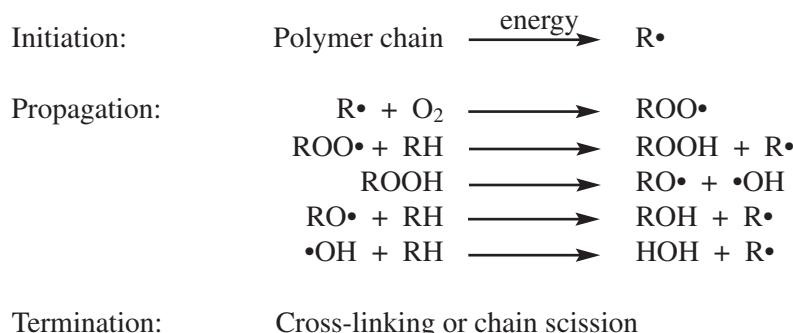


Figure 9.7 Free-Radical Thermo-Oxidation Reaction

The addition of antioxidants to polyols may also result in several undesirable side effects depending on the type of antioxidant used. Phenolic antioxidants - especially BHT - have long been known to migrate into fabric coverings and under certain conditions cause staining.^{9,47-9,48} The “yellowing” occurs when basic fabric finishes or basic cleaners are used. Acid finishes and rinses together with sunlight can reduce or eliminate the color. Secondary-amine antioxidants are thought to be significant contributors to discoloration. Thioesters can react with oxides of nitrogen (exhaust fumes) to form orange to red color bodies. Finally, certain phosphite antioxidants suffer from hydrolytic instability and can decompose to deleterious phosphoric acid during extended storage in polyol solutions.^{9,43} For these reasons, antioxidants are selected for optimum performance in the final intended application.

Foam Discoloration Test Methods

As is apparent from the discussion on the advantages and disadvantages of antioxidants, a judicious evaluation and selection process is necessary to properly optimize an inhibitor package. Many test methods for evaluating antioxidants in polyols have been used in the past. Differential scanning calorimetry of the polyol/antioxidant mixture can determine the effectiveness of a given stabilizer in preventing polyol oxidation.^{9,49} While heating the mixture at a constant temperature and under a controlled oxygen concentration, a reproducible time to reach the degradation exotherm (oxygen induction time, OIT) can be determined. Volatility of stabilizers can be determined by differential scanning calorimetry (DSC) where the weight loss of a given material is measured during a controlled heating of the sample. To include all raw-material sources of discoloration, the inhibitor package should be evaluated during the foaming process. Several ‘infoam’ test procedures have been reported including dry-oven^{9,49} and microwave-oven^{9,50} methods. These tests attempt to mimic the thermal history of production foam within an accelerated time frame. The final evaluation of a newly developed inhibitor package must take place in a production foam in order to include all of the possible contributors to foam discoloration. Even with the above test methods it is difficult to predict actual commercial performance or identify causes of discoloration.

HIGH-RESILIENCE FOAMS

High-Resilience (HR) slabstock foam refers to foams having a “high resilience” as measured by the percent rebound of a steel ball dropped onto a foam sample. HR foams have resilience test values significantly higher than conventional slabstock foams. HR foam is defined by American Society of Testing Materials (ASTM) Standard D 3770 as shown in Table 9.4. ^{9,51} The term “high comfort” is sometimes used to refer to foams having densities 1.5 to 2.5 lb/ft³ (24 to 40 kg/m³)^{9,52} and made with HR polyols. In practice, the bounds of the ASTM standard are relaxed to cover foams with an increased density range and any foams made with “HR polyols” are also generally included.^{9,53}

HR slabstock foams are very similar to those made for cold molded applications. Chapter 11 contains information on HR molded foam.

Properties

In the industry, it is generally accepted that foams with a compression modulus of greater than 2.2, a dropping-ball resilience of greater than 55% and made with “HR chemistry” are referred to as HR foams. In contrast, conventional slabstock foams have a dropping-ball resilience of 40 to 48% and a support factor of 1.7 to 1.9. The higher support factor gives HR foams greater cushioning comfort. HR foams also have superior dynamic-fatigue performance at a given density than conventional foams.^{9,53-9,54}

Table 9.4 Physical Properties Of High-Resiliency Slabstock Foam Per ASTM D 3770-79

| Physical Property | HR-I | HR-II |
|--|-----------|--------|
| 4-inch IFD, 25%, lb | ≤ 15 | > 15 |
| Density, minimum, lb/ft ³ | 1.5 | 2.5 |
| Resilience, miinimum, % ball rebound | 60 | 60 |
| Support factor, 65% IFD/25% IFD, min. | 2.4 | 2.4 |
| Recovery ratio, 25%R/25% IFD, minimum, % | 75 | 80 |
| Tensile strength, minimum, lb/in ² | 7 | 10 |
| Compression set, C _t , maximum, 50% | 15 | |
| Compression set, C _t , maximum, 75% | | 10 |
| Static fatigue | | |
| Loss in thickness, maximum, % | | 2 |
| Loss in force deflection @ 25%. maximum, % | | 20 |
| Moisture resistance | | |
| Compression force deflection loss, maximum, % | 20 | 20 |
| Constant deflection compression set, maximum, % (75% deflection) | 15 | 15 |

Typical Uses

On a worldwide basis high quality bedding and furniture make up the bulk of the end-use applications for HR foam. These represent 15% of the market in France and Benelux and they have significant market share in Scandinavia, as their advantageous FR performance allows them to more easily pass the Cal 117 flammability standard. Similarly in the UK, Combustion Modified High Resilience (CMHR) foams account for more than one third of the slabstock foam market. In the United States they represent approximately 5% of the production.

Formulation Components and Effects Polyols/Chemistry - Polyols for conventional slabstock foams are typically triols with a molecular weight of 3000 to 3500 that incorporate mixed ethylene oxide and propylene oxide polyether segments.^{9.55} In contrast, polyols for high-resilience foams are typically 4500 to 6000 molecular weight block polyether triols. Since the reactivity of conventional polyols decreases with increasing molecular weight, the propylene oxide backbone is capped with end blocks of ethylene oxide. The high ratio of primary hydroxyl groups obtained from capping results in a reactivity that is similar to or greater than the reactivity of conventional polyols.^{9.56-9.57} A side benefit is improved compatibility of HR polyols with toluene diisocyanate and water, allowing the use of low-efficiency surfactants. HR polyols generally contain suspended organic particles to control foam hardness and processability. These particles can be made of styrene-acrylonitrile (SAN) copolymers grafted to a polyol chain. These are referred to as grafted or copolymer polyols. Urea is also used as a

dispersion (PHD polyols) or particles can be made *in situ* by the foamer using the PIPA (Poly Isocyanate Poly Addition) patented process. More recently higher functional reactive polyols were shown to improve processability at low or no solid content.

However, without a stabilizing agent or cross-linker, such as diethanolamine (DEOA),^{9,58} stable foams cannot be produced. DEOA has a marked effect on foam open-cell-content. Increased DEOA level increases the proportion of intact cell-walls and also measurably reduces the foam hardness or indentation force deflection (IFD). It is this complex interaction of components that constitutes “HR foam chemistry.”

Surfactant – The silicone surfactants used to produce HR foams are less efficient than those used for conventional foams. The use of conventional surfactants produces severely shrunken foams. Foams with a higher open-cell-content can be produced with low-efficiency surfactant, but processing latitude will often be compromised. Most silicone surfactant suppliers have a range of HR silicones available to permit the best combination of foam properties and processing for each foam line.

Catalysts – A major difference between HR and conventional slabstock foams is the control of processing with catalysts. The catalyst requirement is altered by the need for DEOA to provide stabilization during the formation of HR foam. Often the catalyst selection is based on operator preference.

Tertiary amine catalysts have little effect except on foam properties, but are needed to adjust the full-rise position on a foam line. Generally, a polymerization (gelling) oriented amine catalyst or catalyst blend is recommended. Amines can affect the open-cell-content of foams – some act synergistically with silicone surfactant.

In typical conventional foams, changes in tin catalyst levels that are as small as 5% can have a significant effect on the open-cell-content of the foam, as measured by air-flow testing. However, tin catalyst has very little effect on the open-cell-content of HR foams. As shown in Figure 9.8, up to a 50% change can be made with no significant change in air flow. But the proper concentration of tin catalyst is generally necessary to prevent foam collapse. Either tin(II) catalyst, stannous octoate, or tin(IV) catalyst, dibutyltin dilaurate (DBTDL), are recommended.^{9,52} DBTDL is often required for foams with densities above 2.0 lb/ft³ (32 kg/m³) to prevent delayed settling of the center of foam blocks and to obtain lower compression-set test values.

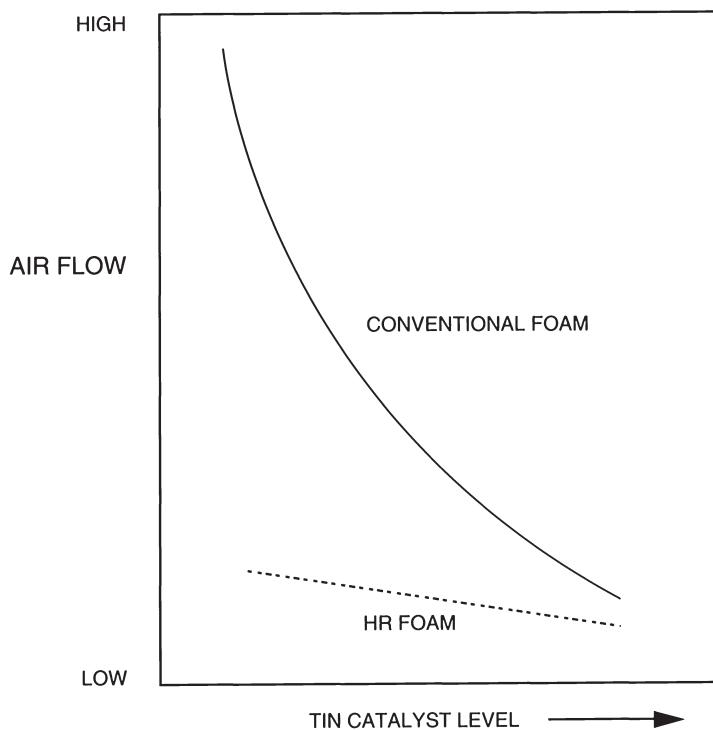


Figure 9.8 Tin Catalyst/Foam Openness Conventional vs. HR Foams

Cell-Opening – The use of DEOA produces foams with a significant portion of the cell-walls intact. Consequently these foams may shrink on cooling. The use of particulate materials such as grafted particles or finely divided inert fillers like melamine or calcium carbonate assist the cell-opening event. High EO containing polyols can also be used. As cell-openers make the reacting foam less stable they have to be used very carefully if foam collapse is to be avoided.

Mechanical opening of cell-walls by crushing can be an effective means to produce “open” HR foams. Slabstock foams may suffer a permanent “set” if crushed too soon, or if the catalysts used are not properly selected.

Ignition Resistance*

HR foams are more resistant to ignition than conventional foams. They melt at lower temperatures, thereby receding from the flame source, decreasing the surface area and reducing ignitability. The amount of additional fire retardant needed to pass performance tests such as California Bureau of Home Furnishings Bulletin 117 is typically one-third that required for conventional foams. Addition of solid agents such as melamine, aluminum hydrate, etc., in the proper proportions can produce foams with improved performance. Such foams are specified in the United States for “public” or “high-risk” occupancies where added ignition resistance is desired.^{9.59}

*FR - The content of this document is not intended to reflect hazards presented by this or any other material under actual fire conditions.

HR Foam Production

HR foam chemistry differs from conventional chemistry, resulting in differences in how the foams are made. However, all standard methods of foam production can be used to produce either HR or conventional foams, including box-foamers, conventional foam machines, or horizontal or vertical-trough machines.^{9,60} Either high or low-pressure mixing systems can be used. HR foams are much more dependent on machine conditions to achieve good-quality foams. Cell-nucleation, air injection, mixing conditions, smoothness and coordination of conveyor operation can have a significant effect on HR foam production. However, once machine conditions have been determined and production experience gained, HR foams can be processed with scrap rates that are similar to conventional foams.

SPECIALTY FOAMS

Beside the more traditional applications for flexible slabstock foams such as furniture and bedding, continuous development has lead to technologies that have the potential to grow the market in niche segments.

MDI-BASED SLABSTOCK FOAMS

High-Resilience Foams

High-Resilience MDI-based slabstock foams are designed to meet the severe requirements of the European luxury bedding market that is traditionally dominated by latex and pocketed spring.^{9,61} The technology is based on high molecular weight reactive polyols and purposely developed isocyanates. The basic chemistry is very similar to TDI-based High Resilience foams described earlier in this chapter. To achieve optimal physical properties, densities above 45 kg/m³ (2.8 lb/ft³) are recommended.

Benefits to the foam manufacturers are:

- fast development of the final physical properties of the foam;
- index response: foam hardness can be varied significantly dependent on the amount of isocyanate used in the formulation;
- limited hardness dispersion within a foam block;
- use of existing equipment.

Additional Benefits for the foamers, transformers and users are:

- Environmental friendliness as the system uses all-water-blown technology. Other positive factors are that low-vapor pressure of MDI compared to TDI reduces exposure risks and volatile organic compounds (VOC) emission in the atmosphere. Also there is no need for halogenated liquid flame retardants to help processability or to pass small scale flammability tests. Furthermore, for demanding tests like BS

5852 part 2 source 5, the use of melamine as sole flame retardant has been shown to be sufficient.^{9,62} The possibility to manufacture halogen-free foams is also a potential advantage for chemical recycling and fogging in automotive applications.

- Excellent physical properties: the main goal is to achieve properties which are as close as possible to the reference materials that are latex and pocketed springs.

The foams typically feature:

- Sag factors typically around 3. Further enhancement by the use of latex. Latex-like compression curves.^{9,62}
- Resilience above 60% is consistently met.
- Good dry and wet-compression sets. Values below 5 and 10% are met.
- Hardness losses below 15% in dynamic fatigue tests.

A typical example is given in Table 9.12.

Packaging Foams

TDI-based flexible slabstock foams have traditionally been used in the packaging field. Recently, a novel combination of specialized MDI and polyols has been developed for the production of foams with highly desirable cushion packaging performance characteristics. This system can be processed on conventional slabstock machines, using additive streams which are normally available. The foams advantageous performance characteristics include: effective protection of heavier items than afforded by conventional polyurethane foams, outstanding creep strain performance, excellent performance after multiple impact and potential reduction in packaging dimensions.^{9,63}

Cushioning Curves

An important measure of packaging performance is given by the cushioning curves as seen in the following example.

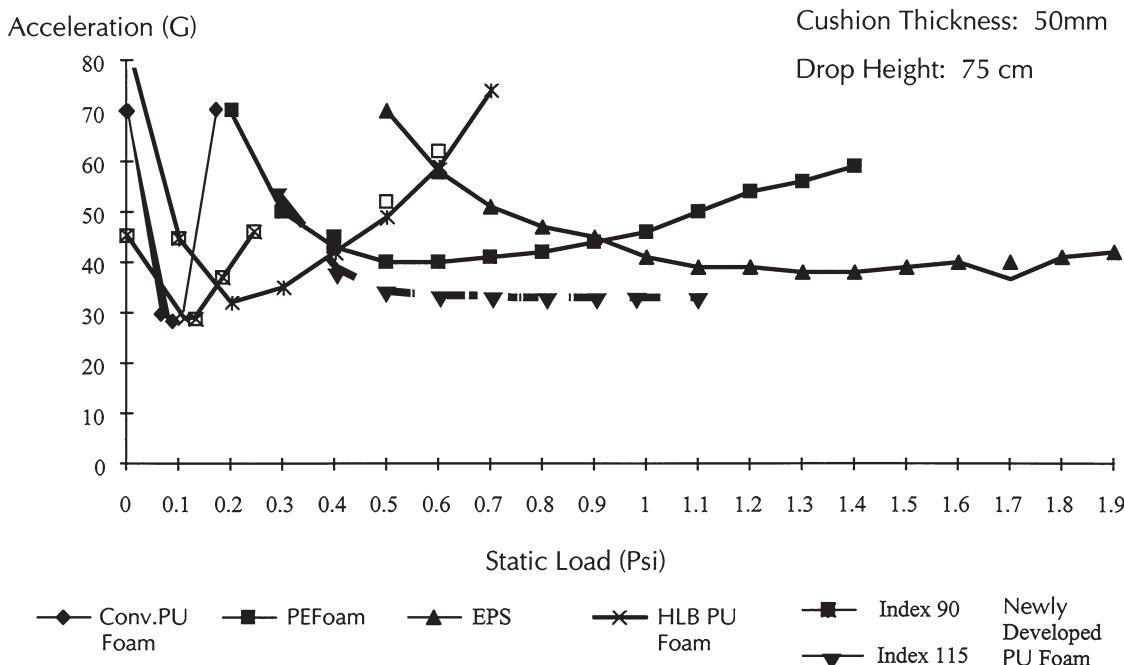


Figure 9.9 Cushioning Curves of Various Packaging Materials

These curves are generated using sophisticated and specialized techniques and equipment. This is done by dropping different weights from different heights onto different thicknesses of the packaging material, while measuring and recording the acceleration (G) of the weight during impact.^{9,64} The plot of G versus weight (converted to static load - psi or Newtons) is known as a cushioning curve. The fragility of an item to be packaged is also measured in terms of G and static load. Hence, any item with a fragility value above the cushioning curve for a given thickness of a packaging material will be effectively protected.

Thus, in the examples shown, the conventional PU foam will effectively protect items with a fragility of 30G and around 0.1 psi static load. HLB PU foam will protect items with the same level of fragility but with a slightly higher static load. Both, polyethylene and expanded polystyrene foams will provide protection for items with static load ranging from about 0.4 psi to 1.9 psi and more, but with a fragility of only 40G. The newly developed PU foam at 90 isocyanate index provides protection for 30G fragility, but most importantly, in the static load range of 0.2 to 0.4 psi, which was not covered by the other materials. Furthermore, this new foam at higher index (Index 115 shown) provides protection at static loads higher than 0.4 psi, and for

fragility levels of approximately 30-40G. This level of fragility protection for these higher weight ranges of packaged items was not previously achievable with the usual packaging materials and represents a distinct advantage, particularly for packaging of valuable electronic goods.

OTHER SPECIALTY FOAMS

Antistatic Foams

It is possible to include inherent static control properties in flexible polyurethane foam making it an excellent choice for electronics packaging applications. For this purpose Dow has developed a patented technology based on STATURE II static control additive. Polyurethane foams containing STATURE II comply with the Electronic Industries Association (EIA) 541 and MIL-B-81705B specifications under all test conditions, including testing after conditioning by water shower and heat aging. In addition to their remarkable static control properties, polyurethane foams containing STATURE II static control additive also exhibit excellent cushioning characteristics and strength, making them suitable for a broad range of applications.

Low-Recovery or Viscoelastic Foams

Low-resilience/slow recovery foam is a type of specialty slabstock foam characterized by a significantly lower rate of recovery from applied stress and low resilience as measured by ball rebound (Refer to Chapter 7 for a description of the Ball Rebound Test). Low resilience foams have a ball rebound value of less than 20% compared with around 40% for conventional foam. These foams have found many specialty applications, for example in the bedding and medical markets, because of their unique soft feel and reduction in stress points when used for load bearing. They also exhibit good sound and vibration damping properties.

In order to slow down the rate of recovery of conventional flexible foam, the restraining forces from a combination of internal viscosity, and “anchors” such as hydrogen-bonding formed in equilibrium with the compressed state, need to be increased. The internal viscosity at ambient temperatures can be increased by reducing the temperature difference between ambient and the glass transition temperature of the foam soft-segment.^{9.65-9.66} The desired glass transition temperature is generally affected by the equivalent weight of the polyols used in the foam. Conventional flexible foam, based on a 3000 molecular weight polyether triol, has a typical glass transition temperature around -50°C. Shifting the foam glass transition temperature to above 0°C by using some lower equivalent weight polyols in combination with the conventional 3000 molecular weight triol will slow down the recovery and lower the foam resilience while maintaining foam flexibility.

The increase in overall soft-segment glass transition temperature will also tend to increase the stiffness of the foam. However, physical properties of low resilience foams are highly index sensitive. A wide range of different foam hardnesses can be achieved between 65 to 85 index. Incorporation of cell opener is also critical to successful processing because of the closed-cell nature of low resilience foam.

Dow has developed a unique technology based on VORANOL polyols which, when used in conjunction with TDI 65/35, leads to low recovery foams featuring densities as low as 40 kg/m³. Very low resilience and a steep temperature response are the key properties of these foams. The main application is in the manufacturing of hospital mattresses and orthopedic (anti-bruise) cushions, but the foam's exceptional dampening properties can offer openings into new markets including for example vibration insulation.

Hypersoft Foams

Extremely soft, low-density hydrophilic foams can be produced without the use of additional blowing agents using a 75/25 combination of high EO and conventional type of polyols. Down to density 21 kg/m³ (1.3 lb/ft³) and 40% ILD below 30N (25% IFD below 10 lbs) can be produced on conventional equipment.

TYPICAL FORMULATIONS FOR SLABSTOCK FOAM

This section includes a number of typical flexible slabstock foam formulations, including several conventional formulations as well as filled, fire-resistant, high-load-bearing formulations and specialty foams formulations.

Table 9.5 Conventional Foam – Firm Grade

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORANOL 3010 or CP 3040 Polyol | 100 |
| Water | 3.9 |
| Niax L-620 | 1.0 |
| Dimethylethanolamine (DMEA) | 0.18 |
| Auxiliary Blowing Agent | – |
| Stannous Octoate | 0.23 |
| Isocyanate Index | 112 |
| VORANATE T-80 TDI | 51.6 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 1.6 (25.6) |
| Tensile strength, lb/in ² (kPa) | 21.9 (151) |
| Tensile elongation, % | 247 |
| Tear strength, lb/in. (N/m) | 3.1(542) |
| Resilience, % | 47 |
| Compression set, 90% | 5.6 |
| 4-inch IFD, 25%, lb/50 in ² | 41 |
| 4-inch IFD, 65%, lb/50 in ² | 69 |
| 40% ILD (N) | 160 |
| Hysteresis return, % | 66 |
| Modulus | 1.7 |
| Air flow, middle, std ft ³ /min | 4.3 |

Table 9.6 Conventional Foam – Supersoft Grade

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORANOL 3010 or CP 3040 Polyol | 100 |
| Water | 3.0 |
| Tegostab BF-2370 | 1.5 |
| Dimethylethanolamine (DMEA) | 0.37 |
| Methylene Chloride (MeCl_2) | 22.5 |
| Stannous Octoate | 0.475 |
| Isocyanate Index | 100 |
| VORANATE T-80 TDI | 37.7 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 1.0 (16) |
| Tensile strength, lb/in ² (kPa) | 7.4 (51) |
| Tensile elongation, % | 287 |
| Tear strength, lb/in. (N/m) | 1.7(298) |
| Resilience, % | 48 |
| Compression set, 90% | 8.1 |
| 4-inch IFD, 25%, lb/50 in ² | 8 |
| 4-inch IFD, 65%, lb/50 in ² | 15 |
| 40% ILD (N) | 20 |
| Hysteresis return, % | 74 |
| Modulus | 1.7 |
| Air flow, middle, std ft ³ /min | 6.6 |

Table 9.7 Filled Foam With Inorganic Filler

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORANOL 3010 Polyol | 100 |
| Water | 2.5 |
| Tegostab BF-2370 | 1.0 |
| Dimethylethanolamine (DMEA) | 0.3 |
| Stannous Octoate | 0.325 |
| Barium Sulfate, (BaSO_4) | 50 |
| Calcium Carbonate, (CaCO_3) | 50 |
| Auxiliary Blowing Agent | — |
| Isocyanate Index | 108 |
| VORANATE T-80 TDI | 35.5 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 3.9(62.5) |
| Tensile strength, lb/in ² (kPa) | 12.6(87) |
| Tensile elongation, % | 164 |
| Tear strength, lb/in. (N/m) | 1.27(222) |
| Resilience, % | 48 |
| Compression set, 90% | 2.8 |
| 4-inch IFD, 25%, lb/50 in ² | 64 |
| 4-inch IFD, 65%, lb/50 in ² | 129 |
| 40% ILD (N) | 250 |
| Hysteresis return, % | 72 |
| Modulus | 2.2 |
| Air flow, middle, std ft ³ /min | 1.1 |

Table 9.8 Fire Resistant Foams Using Melamine Polymer
Passing BS5852 Part 2 Crib 5 Test*

| | Parts per hundred parts polyol | |
|--|--------------------------------|------------------------|
| VORANOL CP 3008 Polyol | 100 | – |
| VORALUX HN 360 Polyol | – | 100 |
| Water | 4.0 | 2.4 |
| Niax L-620/Tegostab B-8681 | 0.6 | 0.3 |
| Dabco 33-LV/Niax A -1 | 0.15 | 0.25 |
| Diethanol Amine (DEOA) | – | 1.2 |
| Melamine | 25 | 15 |
| Fire Retardant | 10 | 2 |
| Stannous Octoate | 0.5 | 0.25 |
| VORANATE T-80 TDI Isocyanate Index | 105 | 110 |
| Physical Properties | | |
| Density, lb/ft ³ (kg/m ³) | 1.81(29) | 2.50(40) |
| Tensile strength, lb/in ² (kPa) | 14.5(100) | 18.9(130) |
| Tensile elongation, % | 150 | 160 |
| Tear strength, lb/in. (N/m) | 1.1(200) | 3.3(580) |
| 4-inch IFD, 25%, lb/50 in ² | 34 | 38 |
| 40% ILD (N) | 135 | 150 |
| Compression Set 75% (%) | 7 | 4 |
| Wet Compression Set 70% (%) | 9 | ND |
| Comment | Combustion Modified Ether | Combustion Modified HR |

*FR -The content of this document is not intended to reflect hazards presented by this or any other material under actual fire conditions.

Table 9.9 Foam Formulation Using Several Additives To Impart Fire Resistance*

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORALUX HN 360 Polyol | 100 |
| Water | 2.6 |
| Tegostab B-8681 | 1.0 |
| Dabco 33-LV/Niax A-1 | 0.85 |
| Diethanol Amine (DEOA) | 1.2 |
| Flame Retardant | 100 |
| Hydrated Alumina | 30 |
| Decabromodiphenyl Oxide | 22 |
| Antimony Trioxide | 8 |
| Poly(ethylene maleic anhydride) | 2.5 |
| Methylene Chloride (MeCl_2) | 0.63 |
| Dibutyltin Dilaurate | 0.15 |
| Isocyanate Index | 105 |
| VORANATE T-80 TDI | 35.5 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 3.8(61) |
| Tensile strength, lb/in ² (kPa) | 11(76) |
| Tensile elongation, % | 120 |
| Tear strength, lb/in. (N/m) | 0.9(158) |
| 4-inch IFD, 25%, lb/50 in ² | 65 |
| 40% ILD (N) | 252 |
| Flammability Properties | |
| Oxygen Index, % O ₂ | 29 |
| California 117 | Pass* |
| Radiant panel, flame-spread index | 25 |
| Smoke density, flame mode | 200 |

*FR -The content of this document is not intended to reflect hazards presented by this or any other material under actual fire conditions.

Table 9.10 High-Load-Bearing Foam Formulation

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORANOL 3943 Polyol / VORALUX HL 400 Polyol | 85 |
| VORANOL 3512 Polyol / VORANOL 3322 Polyol | 15 |
| Water | 2.25 |
| Niax L-620 | 1.0 |
| Dimethylethanolamine (DMEA) | 0.09 |
| Methylene Chloride (MeCl_2) | — |
| Stannous Octoate | 0.10 |
| Isocyanate Index | 112 |
| VORANATE T-80 TDI | 51.6 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 2.7 (43) |
| Tensile strength, lb/in ² (kPa) | 12.6 (87) |
| Tensile elongation, % | 210 |
| Tear strength, lb/in. (N/m) | 2.4 (420) |
| Resilience, % | 38 |
| Compression set, 90% | 6.2 |
| 4-inch IFD, 25%, lb/50 in ² | 119 |
| 4-inch IFD, 65%, lb/50 in ² | 249 |
| Hysteresis return, % | 68 |
| Modulus | 2.1 |
| Air flow, middle, std ft ³ /min | 1.1 |
| 40% ILD (N) | 400 |

Table 9.11 Formulation For A Medium-Density, High-Resilience Foam

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORALUX HN 360 Polyol | 100 |
| Water | 2.2 |
| Tegostab B-8681 | 0.9 |
| Dabco 33-LV/Niax A-1 | 0.36 |
| Diethanol Amine (DEOA) | 0.7 |
| Flame Retardant | 5 |
| Dibutyltin Dilaurate | 0.25 |
| Isocyanate Index | 115 |
| VORANATE T-80 TDI | 31.8 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 2.6(42) |
| Tensile strength, lb/in ² (kPa) | 17.3(120) |
| Elongation, % | 150 |
| Tear, lb/in. (N/m) | 1.4(245) |
| Resilience, % | 60 |
| 75% Compression set, (%) | 4.4 |
| 90% Compression set, (%) | 5.1 |
| 4-inch IFD, 25%, lb/50 in ² | 36 |
| 4-inch IFD, 65%, lb/50 in ² | 89 |
| Hysteresis return, % | 80 |
| Support factor (modulus) | 2.5 |
| California 117 Vertical burn | Pass* |
| California 117 Smolder | Pass* |
| 40% ILD (N) | 140 |

*FR -The content of this document is not intended to reflect hazards presented by this or any other material under actual fire conditions.

Table 9.12 Formulation For An MDI-based, High-Resilience Foam

| | Parts per hundred parts polyol |
|--|--------------------------------|
| VORANOL CP 6008 Polyol | 100 |
| Water | 2.0 |
| Tegostab B-8681 | 0.3 |
| Dabco 33-LV / Niax A-1 | 0.2 |
| Diethanol Amine (DEOA) | 1.4 |
| VORANOL 4053 | 2.0 |
| Dibutyltin Dilaurate | 0.05 |
| ISONATE M450 Isocyanate Index | 105 |
| Physical Properties | |
| Density, lb/ft ³ (kg/m ³) | 3.18 (51) |
| Tensile strength, lb/in ² (kPa) | 12.8 (88) |
| Elongation, % | 110 |
| Tear, lb/inch (N/m) | 0.8 (140) |
| Resilience, % | 62 |
| Wet Compression set, 70% (%) | 2.5 |
| Compression set, 75% (%) | 3.5 |
| 4-inch IFD, 25%, lb/50 in ² | 36 |
| 40% ILD (N) | 137 |
| Support factor (modulus) | 3.0 |
| California 117 Vertical burn | Pass* |
| California 117 Smolder | Pass* |

*FR -The content of this document is not intended to reflect hazards presented by this or any other material under actual fire conditions.

References

- 9.1 "End Use Market Survey of the Polyurethane Industry in the United States"; Allegheny Marketing, Sept. 1995.
- 9.2 Currier, V. "How to Compound High-Density Urethane Foams"; *Plast. Tech.* **1996**, 12/8, 35-37.
- 9.3 Doyle, E.N. *The Development and Use of Polyurethane Products*; McGraw-Hill: New York, 1971; 238.
- 9.4 Ferrigno, T.H. "The Use of Extenders in Flexible Urethane Foams"; *SPE Journal* **1960**, June, 638-640.
- 9.5 Ramlow, G.G.; Hwyman, D.A. Grace, O.M. "New Graft Polyols for High Load-Bearing Foams"; *J. Cell Plast.* **1983**, 19/4, 237-242.
- 9.6 Spitler, K.G.; Lindsey, J.J. "PHD Polyols, A New Class of PUR Raw Materials"; *J. Cell. Plast.* **1981**, 17/1, 43-50.
- 9.7 Kuryla, W.C.; Critchfield, F.E.; Platt, L.W.; Stamberger, P. "Polymer Polyols, A New Class of Polyurethane Intermediates"; *J. Cell. Plast.* **1966**, 2/2, 84-96.
- 9.8 Heyman, D.A.; Grace, O.M. "High Polymer Content Graft Polyols" *Proceedings of the SPI-28th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1984, 257-260.
- 9.9 Woods, G. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science Publishers, London, 1982.
- 9.10 Sparrow, D.J.; Thorpe, D. "Polyols for Polyurethane Production"; In *Telechelic Polymers, Vol.2, "Synthesis and Applications"*; Goethals, E.J., Ed., CRC Press: Boca Raton, Florida, 1989, 181-228.
- 9.11 Burt, J.G.; Brizzolara, D.F. "Auxiliary Blowing Agents for Flexible Polyurethane Foams" *18th Annual Technical Conference; Cellular Plastics Division*, The Society of the Plastics Industry, Inc., Detroit, MI, Oct; 1975, 35-39.
- 9.12 Hicks, J.S.; Schrock, A.K. "Polyol Technologies to Reduce or Eliminate Use of CFC's in Flexible Slabstock Foams"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 348-355.
- 9.13 Ridgway, D. "Evaluation of Polyurethane Carpet Pads By In-Use Traffic Testing"; The Dow Chemical Company, Form No. 109-01063-491; May 1991.
- 9.14 Wolfe, H.W. "Cushioning and Fatigue"; In *Mechanics of Cellular Plastics*; Hilyard, N.C., Ed., MacMillan: New York, 1979, 99-145.
- 9.15 Gibson, L.J.; Ashby, M.F. *Cellular Solids - Structure and Properties*; Pergamon Press, Oxford, England, 1988.
- 9.16 Cogan, D.G. *Stones in a Glass House - CFC's and Ozone Depletion*; Investor Responsibility Research Center, Washington, D.C., 1988.

- 9.17 Schneider, S. "Cooling It"; *World Monitor*, July 1990, 30-38.
- 9.18 Makijani, A.; Bikel, A.; Makhijani, A. "Beyond the Montreal Protocol; Still Working on the Ozone Hole" *Technology Review* May/June, 1990.
- 9.19 "Handbook for Reducing and Eliminating Chlorofluorocarbons in Flexible Polyurethane Foams"; United States Environmental Protection Agency, 21A-4002, April 1991.
- 9.20 Sayad, R.S.; Williams, K.W. "Methylene Chloride Urethane Grade As a Viable Auxiliary Blowing Agent in Flexible Slabstock Foam"; *J. Cell. Plast.* **1979**, 15, 32-38.
- 9.21 Moore, T.L. "Update on Methylene Chloride: now You Can Use Higher Levels"; *Plast Tech.* **1982**, November, 57-59.
- 9.22 Patent U.S. 5,073,860, D.B. Parrish et al to The Dow Chemical Company, August 6, 1991.
- 9.23 Hennington, R.M. Zellmer, V.; Klincke, M. "Soft Flexible Foam Without Auxiliary Blowing Agents"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 492-499.
- 9.24 Vandichel, J.C. N.E.; Appleyard, P. "Reduction of CFC-11 Usage in Flexible Polyurethane Foams through Modification to Polymer Morphology"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 486-499.
- 9.25 Walker, M.K.; Parrish, D.B.; Thomas, R.E. "Extended IFD Range Polyols for Low Density, Soft and Supersoft Flexible Foams Requiring Reduced Auxiliary Blowing Agent"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 251-254.
- 9.26 Post, D. "CFC Free Soft Slabstock Foams by Low TDI Index"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990, 356-360.
- 9.27 Lawler, L.F.; Boo, K.H. "Additives to Produce Soft Foams with Conventional Polyols and Lower Blowing Agent Levels"; *Conference Papers, UTECH Asia 97*, Crain Communications: London, 1997.
- 9.28 Stone, H.; Reinink, E.; Lichvar, S.; Carlson, W.; Sikorsky, C. "The Rapid Cure Process - Industrial Experience, Engineering and Formulation Principles"; *Proceedings of the Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1993, 270-278.
- 9.29 McAfee, C.D.; Wiltz, E.P.; Skorpenske, R.G.; Ridgway, D.H.; McClusky, J.V. "Understanding the Fundamentals of Forced Cooling in the Production of Blowing Agent Free Flexible Slabstock Polyurethane Foams"; *Proceedings of the Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 1993, 279-287.
- 9.30 Taverna, M.; Meloth, H.; Griffiths, T. "Two years of industrial experience with liquid CO₂ - Blowing Slabstock Foams"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996, Paper 30.

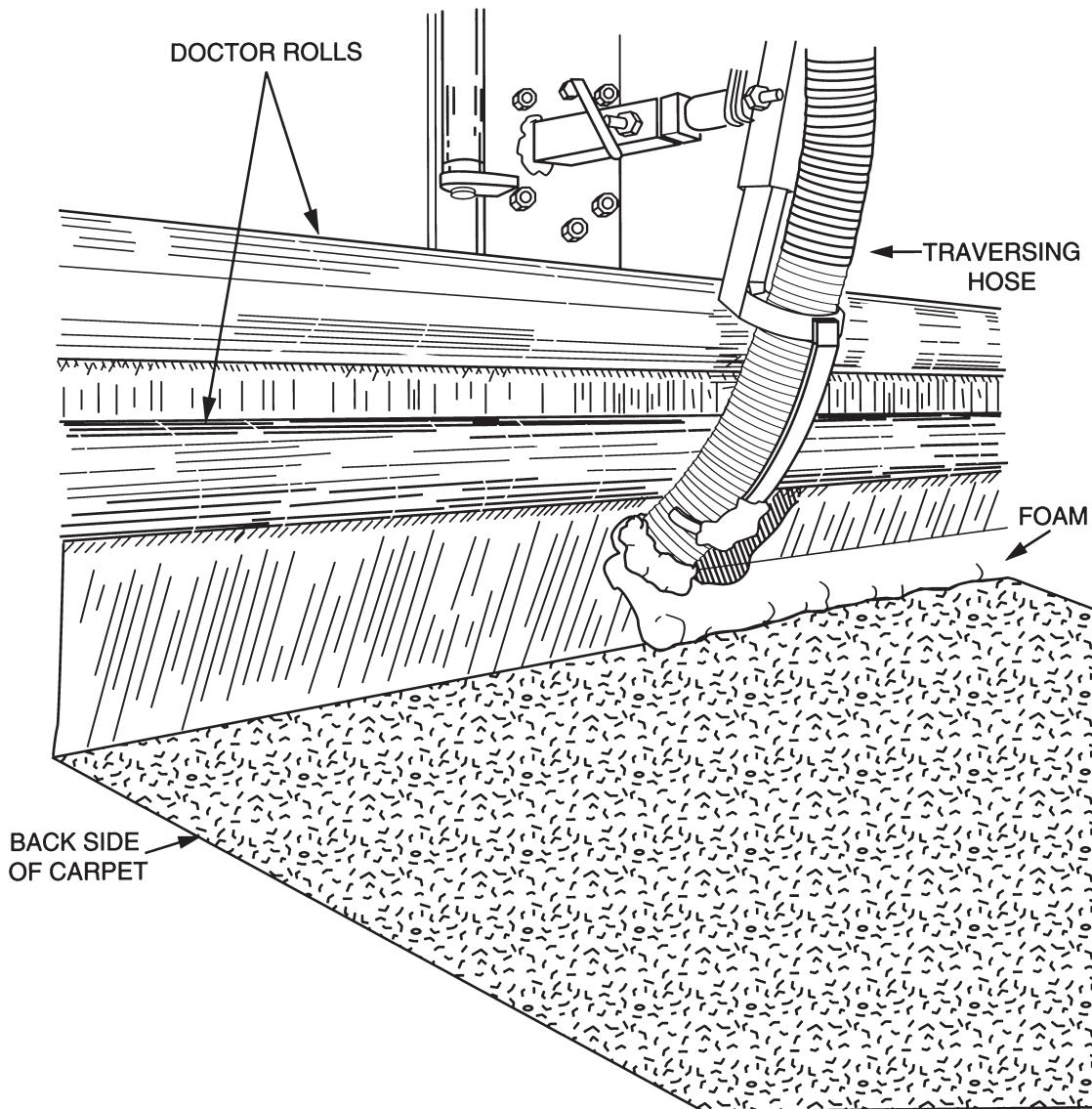
- 9.31 Clockaerts, M.; Mortelmans, R. "Variable Pressure Foaming in Continuous Slabstock Production"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994, Paper 34.
- 9.32 "Basics of Bonded Foam - 1991"; The Dow Chemical Company; Form No. 109-01056-591.
- 9.33 Wooley, W.D. "Are Foams a Fire Hazard?"; *Proceedings of Fire and Cellular Polymers*; Elsevier: London, 1984; 37-39.
- 9.34 Drysdale, D.D.; Thomson, H.E. "Ignition of PUFs: A Comparison of Modified and Unmodified Foams"; *Proceedings of Flame Retardants 90*; Elsevier: London, 1990; 191-205.
- 9.35 Data from United States Consumer Product Safety Commission and National Fire Protection Association.
- 9.36 Rua, L.; Condit, D.; Nakos, S.; Orsi, J. "Evaluations of the Fire Performance of Flame Retarded Flexible Polyurethane Foam in an Upholstered Furniture Application"; *Journal of Consumer Product Flammability* **1980**, 7, 99-126.
- 9.37 Szabat, J., "Flexible Polyurethane Foam for High Risk Occupancies"; *J. Consumer Product Flammability*, **1981**, 8, 189.
- 9.38 Schuhmann, J.; Hartzell, G. "Flaming Combustion Characteristics of Upholstered Furniture"; *J. Fire Sci.* **1989**, 7, 386-402.
- 9.39 Powell, D. "Role of combustion Modified Foams in Furniture: A Closer Look"; *Fire Prevention* **1989**, 27-30.
- 9.40 Van der Plaats, G.; Soons, H.; Snellings, R. "The Thermal Behavior of Melamine"; DSM Corporate Research and Patents Department; Letter report WdB/GLB/860, February 20, 1990.
- 9.41 Flammability Information Package - Contains Technical Bulletins 116, 117, 131, 133, 106 and 26. State of California, Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation, 3485 Orange Grove Avenue, North Highlands, CA., 95660-5595; December 1987.
- 9.42 BS 5852 Fire Tests for Furniture-Part 2. Methods of Test for the Ignitability of Upholstery Composites for Seating by Flaming Sources (BS 5852; Part2; 1982) British Standard Institute, London, 1982.
- 9.43 Lutz, Jr., John T.; Ed. *Thermoplastic Polymer Additives: Theory and Practice*, Marcel Dekker: New York, 1989, 93-204.
- 9.44 Buist, J.M.; Ed. *Developments in Polyurethanes-1*, Chapter 4 (G. Woods), Applied Science: London, 1978, 77-117.
- 9.45 Pospisil, J.; Klemchuk, P.P. *Oxidation Inhibition in Organic Materials*, Volume I, Chapter 4 (François Gugumus), CRC Press: Boca Raton, Florida, 1990, 61-172.
- 9.46 Skorpenske, R.G.; Schrock, A.K.; Beal, G.E. "Antioxidant Behavior in Flexible Polyurethane Foam, "Proceedings of the SPI – 33rd Annual Technical/Marketing Conference"; Technomic: Lancaster, Pa., 1990, 339-347.

- 9.47 Schmid, H.R.; Krucker, W. "Why Do Textiles Yellow and What Can Be Done To Prevent It"; *Textile. Veredlung.* **1985**, 20/9, 272-275.
- 9.48 Williams, D.J. "Case Studies Of Storage Yellowing Of White Polyester Sewing Threads And The Development Of A Laboratory Test to Simulate Such Yellowing"; *J. Soc. Dyers. Colour.* **1984**, 100/9, 268-274.
- 9.49 Pernice, R.; Pizzoli, P. "Scorching of PUR Flexible Foams - A New Lab Test to Evaluate the Performance of Stabilizing Additive"; *J. Cell. Plast.* **1988**, 24/6, 589-600.
- 9.50 Stratton, G.L.; Gaul, J.M. "Evaluation of Hindered Phenols for Minimization of Foam Discoloration Using the Microwave Scorch Test"; *J. Cell. Plast.* **1984**, 20/5, 346-350.
- 9.51 "Flexible Cellular Materials - High-Resilience Polyurethane Foam (HR)"; American Society for Testing and Materials, D 3770-79; ASTM: Philadelphia, 1990, Vol. 09.02, 529-530.
- 9.52 Pavanyi, J.; Baskent, F.O. "High Comfort Foams: A New Approach to Performance Cushioning"; *Proceedings of the 27th Annual SPI Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982, 290-296.
- 9.53 Bargiband, R.F.; Illger, H.W.; Hettel, H. "Quality HR Slabstock Foam– Back to Basics"; *Proceedings of the 30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 40-46.
- 9.54 Stone, H. "Fatigue Testing of Flexible Foams"; *J. Cell. Plast.*, **1983**, 19/1, 47-60.
- 9.55 Robson, J.H.; Priest, D.C. "Slab High Resilience Foam"; *J. Cell. Plast.* **1973**, 9/1, 19-24.
- 9.56 Ammann, R. "High Resilient Slabstock Foam Made With Crosslinker Compounds"; *J. Cell. Plast.* **1977**, 13/3, 194-197, 209.
- 9.57 Chandalia, K.B.; Preston, F.J. "A Novel Approach to High Resilience Foam"; *J. Cell. Plast.* **1979**, 15/2, 114-118.
- 9.58 Kollmeier, H.J.; Burkhart, G.; Klietsch, J.; Lammerting, H. "Reaction Sequences in High-Resilience Foam"; *Plast. Compd.* **1985**, July/August, 64-74.
- 9.59 Szabat, J.F.; Zirk, W.E.; Parrish, D.B. "Development of a Classification System for Combustion Modified Flexible Polyurethane Foam Based on the OSU Calorimeter; Part 1 (An SPI Project)"; *J. Cell. Plast.* **1989**, 25/3, 189-216
- 9.60 Hull, G.K."Technology and Application of "Polymer Polyol" Based, Low Density, High Resilience (HR) Slabstock Foam in Europe"; *J. Cell. Plast.*, **1977**, 13/3, 198-202.
- 9.61 Mispreuve, H.A.; Knaub, P.M.A. "MDI Slabstock in Luxury Bedding: A Perfect Match"; *Conference Papers, UTECH 94*; Crain Communications, 1994, Paper 37.
- 9.62 Mispreuve, H.A.; Stahler, L. "Latest Development in MDI-based Slabstock Technology"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996, Paper 36.

- 9.63 Mispreuve, H.A.; Woods, T.; McIntyre A. "Developments in MDI-based Polyurethane Packaging Foams"; *Proceeding of SPI Polyurethanes 1995 Conference*; Technomic: Lancaster, Pa., 1995, 334-338.
- 9.64 Designing Cushion Packaging with Flexible Polyurethane Foams, Dow USA Brochure 109-920-88.
- 9.65 Buist, J.M.; Gudgeon, H. *Advances In Polyurethane Technology*; MacClaren And Sons Ltd., London, 1968, 99-102.
- 9.66 Saunders, J.H.; Frisch, K.C. *Polyurethanes: Chemistry And Technology*; Robert E. Krieger Publishing Company: Malabar, Florida, 1962, 331-335.

Chapter 10

Carpet Backing



Several processes have been developed for the continuous application of polyurethane foams directly to the back of carpets. This chapter discusses this application in more detail.

Chapter 10

Carpet Backing

K. Skaggs, R. Herrington, M. Norton

The concept of forming a flexible polyurethane foam directly on the back of a carpet was described as early as 1959.^{10.1} Advantages in the areas of improved tuft-lock, energy absorption, heat and sound absorbance, the non-slip character and longer appearance retention of the carpet face were recognized early on. Commercial success for polyurethanes in this area came at the expense of the traditional backing materials; foamed rubber latex and foamed polyvinyl chloride (PVC).^{10.2} In addition to physical property and plant-capital advantages, frothed polyurethanes were found to be more energy efficient than alternative backings.^{10.3} Detailed reviews of the processes and applications for mechanically frothed polyurethane foams are given in References 10.4-10.11.

The carpet industry serves five major market segments, as shown in Figure 10.1. For the contract marketplace, Dow offers a line of technology for making THE ENHANCER carpet backing. Other aspects of the foam-backed carpet market are discussed in References 10.12-10.14.

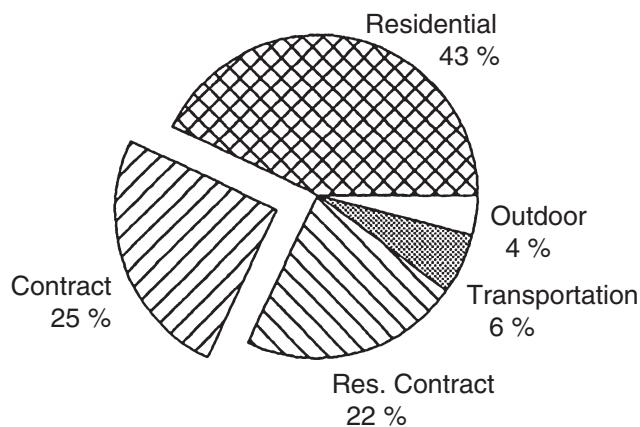


Figure 10.1 Market Segments in the Carpet Industry

MECHANICALLY FROTHED SYSTEMS:

The process for producing Dow's trademark brand of frothed polyurethane is described in Chapter 5 and the above references. Due to the demands placed on carpets in high-traffic areas, the merits of technically advanced products are important. Dow licenses production of multiple classes of THE ENHANCER for use in different traffic areas. The precoat and foam density and coating weight applied depend on the predicted traffic and use. The polyurethane chemistry used in the mechanically frothed technology is similar to that used in elastomers.^{10,15} The polymers produced are extended with inorganic fillers, alumina trihydrate and calcium carbonate to reduce cost. Typical formulation listings for the precoat and foam systems are given in Table 10.1.

Table 10.1 Precoat and Foam Formulations

| Precoat Formulation | | Foam Formulation | |
|---------------------|-----------|---------------------|-----------|
| | pphp | pphp | |
| VORANOL 9690 Polyol | 100 | VORANOL 9000 Polyol | 100 |
| Alumina Trihydrate | 100 | Alumina Trihydrate | 50 |
| CaCO ₃ | 105 | CaCO ₃ | 60 |
| Tin catalyst | 0.1 | Surfactant | 0.125 |
| | | Tin catalyst | 0.1 |
| ISONATE 7045 | 110 Index | ISONATE 7045 | 105 Index |
| Isocyanate | | Isocyanate | |

Formulations for THE ENHANCER have been optimized to produce the best physical properties. Through experimentation, it was learned that a polyol with about 15% ethylene-oxide capping level is required to provide a stable froth; thus, the foam formulation uses VORANOL 9000 polyol to fulfill this need. Other mechanically frothed systems rely on special surfactants to provide stable froths.^{10,9-10,11} The polyol used in the precoat system is a propylene oxide based polymer so that water absorption is minimized. The precoat layer acts as a barrier between the carpet and the foam and gives better tuft-lock properties than foam alone.

THE ENHANCER carpet backing is produced in multiple classes: Class I, II, III, IV, Laminate and TacFast versions of the aforementioned classes. Class I is for moderate-use carpet: 500 or less traffic contacts per day. Class II is for heavy-use carpet: 500 to 1000 traffic contacts per day subject to frequent random traffic and regular traffic consistently following the same directional pattern with heavy trackage of dirt, grit, considerable twisting, turning and moderate spillage. Class III is for heavy duty use carpet: 1000 or more concentrated traffic contacts per day following the same directional

Table 10.2 Specification Guidelines for The ENHANCER Carpet Backing

| BACKING CLASSIFICATION | II <u>Heavy Use</u> Under 1,000 traffics/day | III <u>Heavy Duty Use</u> 1,000 or more traffics/day | IV <u>Extra Heavy Duty Use</u> 1,000 or more traffics/day | Laminate <u>Extra Heavy Duty Use</u> 1,000 or more traffics/day | Residential <u>Single Family</u> Owner-occupied residential |
|---|--|---|--|--|---|
| BACKING DENSITY¹ (lbs./ft. ³) ASTM D3676-78 | 14 | 18 | 20 | N/A | 12 |
| LAMINATE DENSITY Min. (oz./yd ²) ASTM D3676-78 | N/A | N/A | N/A | 44 oz./yd ² Single Stitch 54 oz./yd ² Graphics Stitch | N/A |
| COMPRESSION SET Max. @ 50% (% height loss) Dow Method | 10 | 10 | 10 | N/A | 15 |
| THICKNESS Min. (inches) ASTM D3676-78 | 0.100 | 0.100 | 0.070 | N/A | 0.100 |
| COMPRESSION RESISTANCE Min. @ 25% (PSI) Dow Method | 5 | 7 | 12 | N/A | 5 |
| FOAM/PRECOAT DELAMINATION RESISTANCE (pli) Min., ASTM D3676-78 | 2.0 | 2.5 | 2.5 | 3.0 | 1.5 |
| EDGE RAVEL (lbs.) Min., (Dow Method) | 2.0 | 2.5 | 2.5 | 2.5 | 1.5 |
| IMPERMEABILITY National Health Service Patient Area Requirement for the United Kingdom | N/A | N/A | PASS | PASS | N/A |
| Typical End Uses³ | Office and clerical areas, lounges in health care centers, school classrooms, dormitories, stores, convention center auditoriums, and hotel corridors. | Office building cafeterias, lobbies, corridors in health care centers, school corridors and cafeterias, ticket areas, major aisles in retail stores, sports club locker rooms, convention center lobbies, restaurant and hotel lobbies. | Hospital corridors, patient areas, banks, lobbies, libraries, bank teller stations, casinos, supermarkets, major aisles in retail stores, cafeteria surfaces and other end uses under Class III where spillage and roller traffic is a concern and some cushion properties are needed. | Community centers, churches, hospital corridors, patient areas and lobbies, libraries, banks, bank teller stations, casinos, athletic surfaces and cafeteria surfaces and other end uses under Class II, III, and IV where spillage and heavy roller traffic is anticipated. | Any room of an owner-occupied single family dwelling. THE ENHANCER carpet backing is FHA certifiable. |

¹A 10% manufacturing tolerance for this specification is allowed on all classes, EXCEPT CLASS IV where density is a minimum.

pattern, with severe dirt, grit, twisting, turning, heavy rowing and spillage anticipated.

Class IV is for extra heavy use. THE ENHANCER is a high performance noncushioned backing system. TacFast is an installation system now available in THE ENHANCER line that offers the ease of a hook and loop approach to attach the carpet to the floor. The TacFast versions replace the nonwoven polyester scrim secondary with a knitted tricot scrim that becomes the “loop” component of the hook and loop installation system. Physical properties of the various classes of THE ENHANCER carpet backings are shown in Table 10.2.^{10,16}

Other materials that compete with polyurethane in the contract market are SBR latex, PVC and EVA. SBR latex was the only foam in the carpet business before other polymers were developed.^{10,17 - 10,18} PVC has a much larger market share than EVA, but has had problems passing smoke-emission tests in some areas. The physical properties for both PVC and EVA are very comparable to those of polyurethanes.

CARPET TILES



Figure 10.2
Typical Application For
Carpet Tiles

Two other carpet products with attached cushions are carpet tiles and some lines of residential carpet. The carpet-tile area is the fastest growing segment of the contract carpet market. Tile is also one of the most difficult products to make. The application for carpet tiles is illustrated in Figure 10.2. Carpet tiles need to lie flat on the floor and not grow or shrink. Maintaining dimensional stability is of the utmost importance to the success or failure of a carpet tile program. Due to the inherent stresses imposed by typical tentered processes, most commercial tile programs now are produced on belted ranges. Additionally, gauge control is made more critical in the tile product due to the desire for “seamless” appearance of the installation. Thickness control of the carpet/cushion composite must be maintained to within +/- 15 mils to be viable for this application.

The majority of the carpet tile market is currently supplied by Milliken, Interface, Collins and Aikman and Shaw Industries. These mills account for approximately 85% of the entire commercial contract carpet-tile business. PVC backing has performed well in the marketplace, but has been discontinued in some parts of Europe due to the chlorine content. Milliken is aggressively pursuing growth in the tile market with Comfort Plus featuring THE ENHANCER attached cushion.

RESIDENTIAL ATTACHED CUSHION

Another significant product is the attached cushion for residential carpet. This market segment is heavily influenced by price and has migrated toward lower cost materials. The preferred product is the chemically blown polyurethane system produced by The Textile Rubber Company. Their process yields a product with densities of approximately 2.5 pounds per cubic foot. This product is less durable than the mechanically frothed systems, but does meet the needs of the residential market. The formulations used with this technology resemble those used in the molded foam industry and are based upon polymeric MDI. Latex precoats used with these formulations yield adequate tuft binds for the intended market.^{10,19} A typical formulation listing is given in Table 10.3.

Table 10.3 Chemically Blown Carpet Foam

| Component | pphp |
|---------------------|------|
| VORANOL 9741 Polyol | 50 |
| VORANOL 9543 Polyol | 50 |
| Water | 2 |
| Amine Catalyst | 0.4 |
| Tin Catalyst | 0.4 |
| Silicone | 0.15 |
| Polymeric MDI | 50 |

Most of the carpet installed in residential areas comes with a separate pad made of virgin or rebonded foam.

TECHNOLOGY COMPARISON

Of the various processes, Textile Rubber's chemically blown polyurethane attached cushions have the biggest price advantage. The total raw material costs are virtually equivalent to those of a latex foam. This technology can also be used to produce a low-cost cushion thicker than any other, yielding the perception of better value and comfort.

Latex foam has the advantage of having the lowest raw material cost. Not only does it start with a relatively low-cost latex polymer, but it can be filled to high loadings (300 parts per 100 parts rubber). However, at high loadings, durability is an issue. The density of foams made from both latex and mechanically frothed systems are about 12-30 lb/ft³.

Advantages of the Dow mechanically frothed system over both competitive technologies are improved durability and appearance retention. Dow's resource commitment to the floor coverings industry is discussed in Reference 10.20.

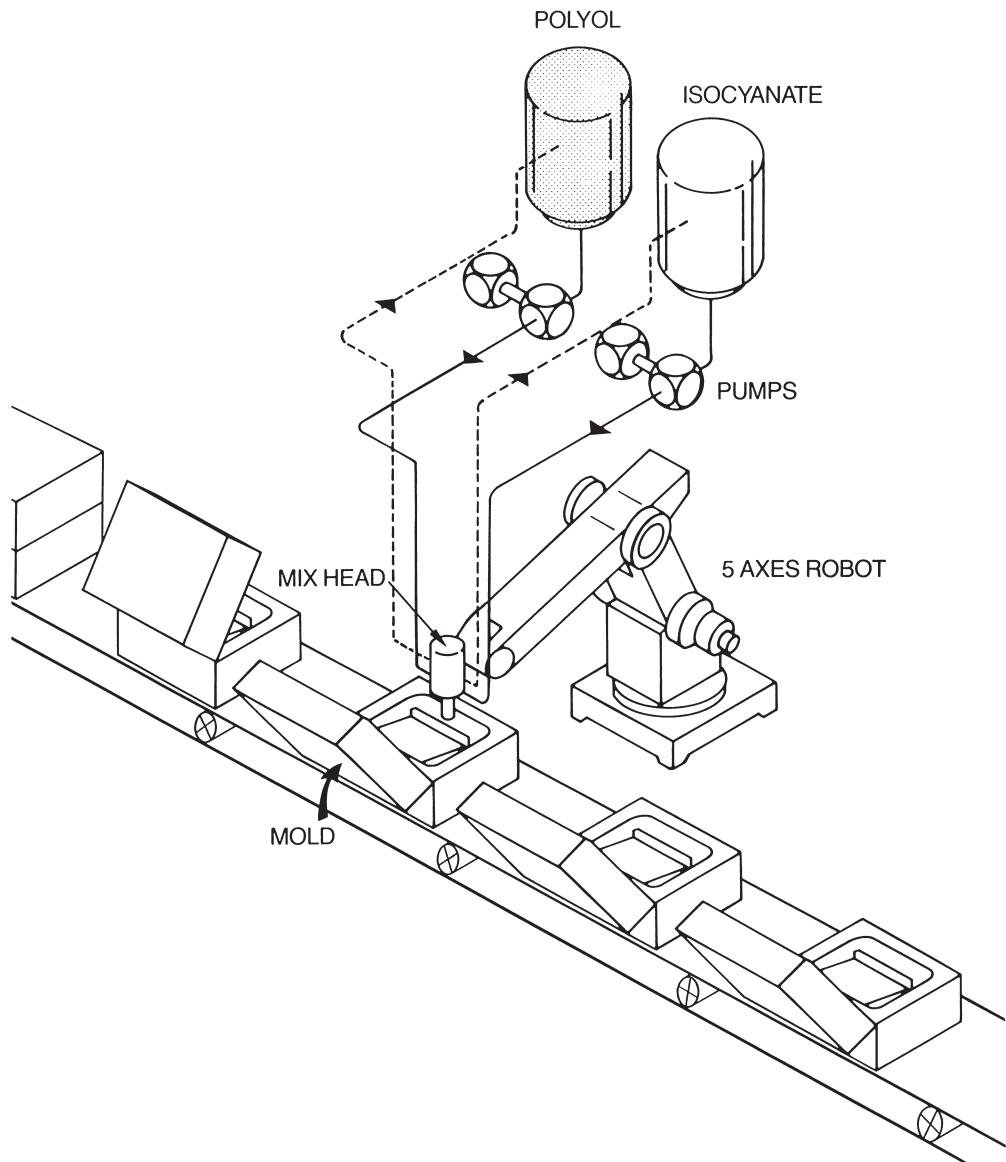
References

- 10.1 Buist, J.M. "The properties of Polyurethanes and their applications"; *Plast. Inst. Trans.* **1959**, 27, 13-27.
- 10.2 Editorial, "Big market is emerging in carpet underlays"; *Mod. Plast. Intl.* **1973**, June, 14-17.
- 10.3 Cravens, T.E. "Urethane Sponge Carpet Backing"; *Proceedings of The Carpet Rug Institute Annual Meeting, Hilton Head South Carolina, 1975.*
- 10.4 Editorial, "Carpet backing with pu foam"; *Plast. Rub. Wkly.* **1975**, March 7, 25-26.
- 10.5 Marlin, L.; Durante, A.J.; Schwarz, E.G. "Mechanically frothed urethane: a new process for controlled gauge, high density foam"; *J. Cell. Plast.* **1975**, 11/6, 317-322.
- 10.6 Kallert, W. "Urethane Foam For Carpet Backing"; *J. Coated Fab.* **1975**, 4, 272-278.
- 10.7 Bobe, J.; Hurd, R.; Woods, G. "The Backing of Carpets with Urethane Foams"; *Proceedings of the SPI-4th International Cellular Plastics Conference*; Society of The Plastics Industry: New York; 1976, 290-295.
- 10.8 Hurd, R. "New Applications For Polyurethanes"; In *Developments In Polyurethane - I*, Buist, J.M., Ed.; Applied Science: London, 1978, 211-222.
- 10.9 Editorial, "Mechanically foamed urethane moves into market for floor-covering backing"; *Mod. Plast. Intl.* **1978**, August, 12-13.
- 10.10 Bez, W.; Quack, G. "Polyurethane and Latex Foam Carpet Backing Today"; *Cell. Polym.* **1983**, 2, 31-53.
- 10.11 Berthevas, P. "Mechanical Frothing Process Develops New Applications for Polyurethanes"; *Cell. Polym.* **1985**, 4, 179-193.
- 10.12 *THE ENHANCER®; end use market report featuring THE ENHANCER® carpet backing*, The Dow Chemical Company; Form No. 109-854-88.
- 10.13 *THE ENHANCER® is the answer*, The Dow Chemical Company; Form No. 109-898-88.
- 10.14 Gavin, K. "Urethane Backs Provide Cushion Underfoot"; *Floor Cov. Wkly.* **1990**, June 11.
- 10.15 *THE ENHANCER® Carpet Backing*; The Dow Chemical Company; Form No. 109-805-88.
- 10.16 *THE ENHANCER® Carpet Backing*; The Dow Chemical Company; Form No. 109-633-86.
- 10.17 Fitzgerald, P.L. "Integral Latex Foam Carpet Cushioning"; *J. Coat. Fab.* **1977**, 7, 107-120.

- 10.18 Brentin, R.P. "Latex Coating Systems For Carpet Backing"; *J. Coat. Fab.* **1982**, 12, 82-91.
- 10.19 Ward, D. "Fresh Opportunities For Polyurethane Backing Process"; *Textile Month* **1980**, September, 23-26.
- 10.20 *Dow Polyurethanes: Innovative Research for the Floor Covering Industry*; The Dow Chemical Company; Form No. 109-923-489.

Chapter 11

Molded Foams



In contrast to the large buns produced in conventional slabstock foam, molded foams are made one at a time in production plants specifically designed for repetitive production of discrete foam shapes. These plants often operate 2 or 3 working shifts per day and may produce more than one style of part.

Chapter 11

Molded Foams

R. Herrington, R. De Genova, F. Casati, M. Brown

Since polyurethane foams expand and flow during the foaming reaction, many commercial products can be made by molding foam to size and shape in closed molds. It is estimated that 20 percent of total flexible foam production worldwide involves one of the molding techniques. Molded foams find application in all forms of transportation seating and trim parts, as well as in some upholstered furniture,^{11.1-11.2} bedding, packaging and novelty items.

Basically, foam molding involves pouring the reacting mixture into a suitable mold, closing the mold and allowing the foam to fill the mold. Details of the various foaming processes were discussed in Chapter 5. In addition to replicating the internal dimensions of the mold, the final product can also permanently record its part or style number and can incorporate physical inserts of various types. The typical methods of constructing a final automobile seat assembly have been reviewed.^{11.3}

If the mold is lined with a preformed plastic skin or textile fabric, dispersed foam will adhere to it and simplify the assembly requirements of many composite products. Technology for directly foaming onto a cover material preformed into a seat cushion mold has existed since 1955.^{11.4-11.7} Recent developments in vacuum-assisted foam-in-place technology for auto seating are discussed in References 11.8-11.19. Alternative schemes for bonding the cover fabric to the foam pad have been developed.^{11.20-11.24}

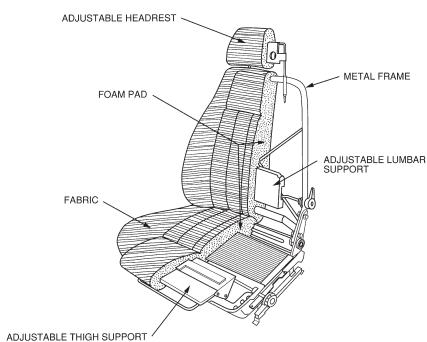
Closed molding is considerably more complicated than slabstock foam production. Factors which contribute to that complication include a higher reactivity formulation, pour-pattern limitations, the discrete size of each individual shot, the need to open and close a mold lid mechanically, the choice of release agent, mold temperature latitudes and the available curing cycle. Foam formulations used for molding and for slabstock differ mainly with respect to the catalyst packages and composition of the polyols. Generally, higher-molecular-weight, more reactive polyols are used for molding so that foams with good cure and rapid property development can be produced.

The two major molding techniques in the polyurethane industry today are the ‘hot-cure’ and the ‘HR’ or cold cure processes. As the name implies, hot-cure molding involves the application of high temperature to the mold during the cure cycle. This is necessary to drive the foam reaction to a sufficient degree of cure to permit the foam to be demolded in a timely manner and subjected to additional downstream fabrication steps. The newer HR foam molding process utilizes higher-reactivity ingredients so that less oven curing is needed.

Most molding is done in cast-aluminum molds, but there has been some use of reinforced-epoxy molds. Molds are usually made in two sections, with provision for mechanically opening and closing the lid.

For hot-molded foams, the lids contain many vent holes and generally “float” under restrained conditions. HR foam molds have less venting and must be constructed to withstand higher internal mold pressures. Heavier construction and tight seals are normally required. The importance of mold release cannot be overemphasized. Polyurethanes are excellent adhesives and will stick to bare metal. Molds are usually designed to allow about 1-2% shrinkage of the foam part after manufacture. It is best for the inner surface of the mold to have a mill run or other nonpolished surface to allow for good retention of the release agent. Additional mold construction details were discussed in Chapter 5. Nonmetallic molds have proven useful in molding furniture cushions.

SEATING FOAMS



In the area of transportation seating, flexible foams have become the material of choice not only because of the economies offered by large-scale molding operations but also because the cushioning and vibration damping characteristics of a foam can be easily adjusted to fit the requirements of the many different types of public and private transportation. Figure 11.1 illustrates the use of molded flexible foams in automotive seating applications.

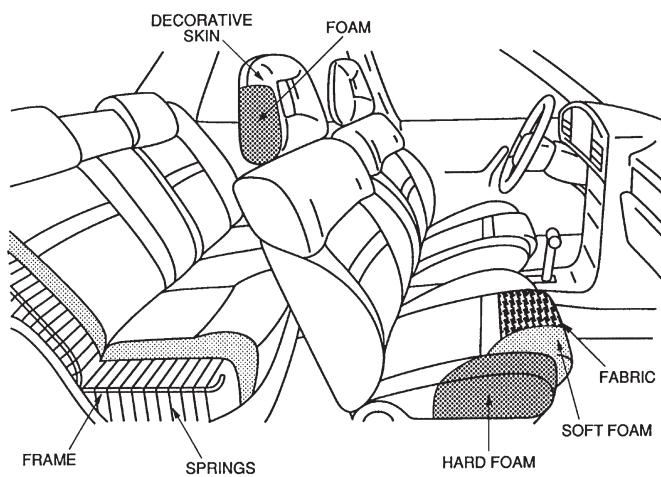


Figure 11.1 Typical Seating Applications for Flexible Foam

Worldwide, the older hot-molded foam technology is still in use. On the North American continent, the HR foam technology is dominant. One reason for that dominance, is a lower energy requirement. Figure 11.2 compares typical energy usage for alternative molding processes.

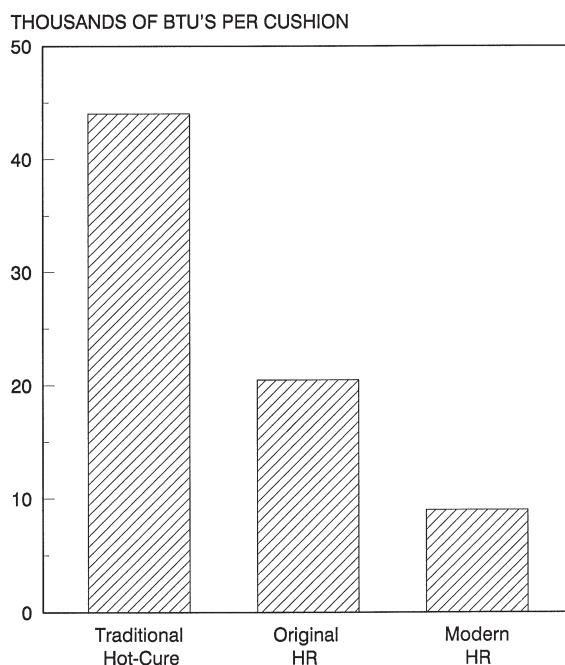


Figure 11.2
Energy Requirements of Molded Foam Processes
(Reconstructed from Reference 11.25)

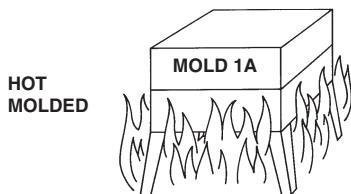
HOT-MOLDED FOAMS

The most important application for hot-molded foam is as a contoured cushion laid atop tensioned springs in automotive seating. In general, formulations for hot-cure foams are based on nominal 3000-molecular weight ethylene-oxide-capped triols. Diols are often added for those applications requiring higher strength properties. For higher loads, it is common to blend in the filled or copolymer polyols discussed in Chapter 2. Alternatively, higher-functionality blended initiators have been used to produce higher-load-bearing foams. Typical hot-molded foam formulations are given in Table 11.1. If the foam is required to meet a flammability testing specification, a flame-retarding additive would be required.

Table 11.1 Typical Hot-Molded Foam Formulations

| Component | Parts by Weight | | |
|---------------------------|-----------------|------|----------|
| | Soft | Hard | Backrest |
| VORANOL CP-3111 Polyol | 80 | — | 92 |
| SPECFLEX NH 104 Copolymer | 20 | 100 | — |
| SPECFLEX NK 916 Additive | — | — | 8 |
| OSI RS 204 | 1.0 | — | — |
| Tegostab B4900 | — | 0.8 | 1.0 |
| Niax A-1 | 0.10 | 0.04 | 0.08 |
| Dabco 33-LV | — | 0.10 | 0.08 |
| Dabco XDM | 0.40 | — | 0.13 |
| Stannous Octoate | 0.05 | 0.09 | 0.13 |
| Water | 2.4 | 2.1 | 3.5 |
| VORANATE T-80 TDI Index | 100 | 100 | 98 |

With the use of the SPECFLEX NH-104 copolymer polyol and the SPECFLEX NK-916 softening additive, the foam producer has the capability to make a wide range of both single and dual-hardness foams.^{11,26} The hot-molded foam process was discussed in Chapter 5. Mold temperature at pour is a critical variable. Optimum mold temperatures often fall in the range of 95–115°F (35–46°C). Lower temperatures result in a soft, densified foam core. When the mold gets too hot, the skin becomes loose and flaky, resulting in a poor overall cosmetic appearance. In the oven, sufficient heat must be applied to raise the temperature of the inner surface of the mold quickly up to about 250°F (120°C). This temperature approximates the exothermic reaction temperature of the interior of the foam, allowing sufficient cure for the foam to be demolded in 10 to 15 minutes. Cycling the molds down to the pour temperature and back up to the cure temperature is costly in terms of both energy and time.

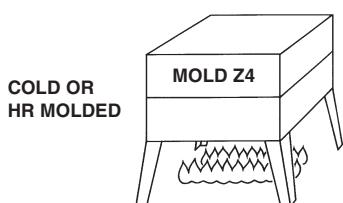


For more details of the hot-molding process and characteristics of the foams, see References 11.27–11.30. The most recent developments in hot-molded foam are discussed in References 11.31–11.36.

HR FOAMS

The term ‘HR’ is an abbreviation for the words ‘high resiliency’. As it applies to foams, it refers to foams having dropping-ball-type resiliency test values significantly greater than those obtained with the conventional hot-molded or slabstock foams. One definition of HR foams requires that those foams possess a resiliency greater than 60%.^{11,37} Technology extending the achievable range of resiliency up to 70% has been reported.^{11,38} These foams have been referred to as the Extra-High-Resiliency (XHR) grade.

Today, the term HR foams is also generally taken to encompass the foams earlier referred to as cold-cure foam. HR molded foams offer several advantages:



1. Their support factor (ratio of 65% IFD to 25% IFD) is superior to that of conventional slab or hot-molded foams.
2. The amount of energy required to accelerate foam cure and develop final properties is less.
3. These foams can be formulated more easily to meet the requirements of various small-scale flammability tests.

An improvement in support factor means that a foam can offer higher load bearing at the use deflection and still maintain its soft initial feel. A typical HR foam shows a support factor around 2.2 to 3.0 or higher, while a conventional hot-cure foam has a support factor in the range of 1.7 to 2.0. Brown has described layered HR foam technology giving support factors as high as 5.0.^{11,3}

Some of the early history of HR molded foams in North America is recorded in References 11.39–11.40. The first HR foams appeared during the 1960s. These foams were based on ethylene-oxide-tipped polyether triols in combination with reactive diamine cross-linkers and various isocyanate compositions. Copolymer or grafted polyols were introduced for this application in the late sixties. Both technologies could produce foam meeting the various automotive specifications; but when the most popular diamine cross-linker was listed as a possible carcinogen in the early seventies, the copolymer polyol technology became dominant.

HR molded foams are typically made by the processes described in Chapter 5. HR foams are often made from specially formulated two-component systems. The base polyether triols used generally fall in the molecular-weight range of 4000 to 6000 and have 5 to 25% end capping with ethylene oxide to give primary hydroxyl contents ranging from about 65 to 90%.^{11,39} The comparative reactivity data presented in Figure 11.3 show that this variation in primary hydroxyl content is a fundamental way of designing the desired reactivity into a polyol (see Chapter 2 for a discussion of the test method).

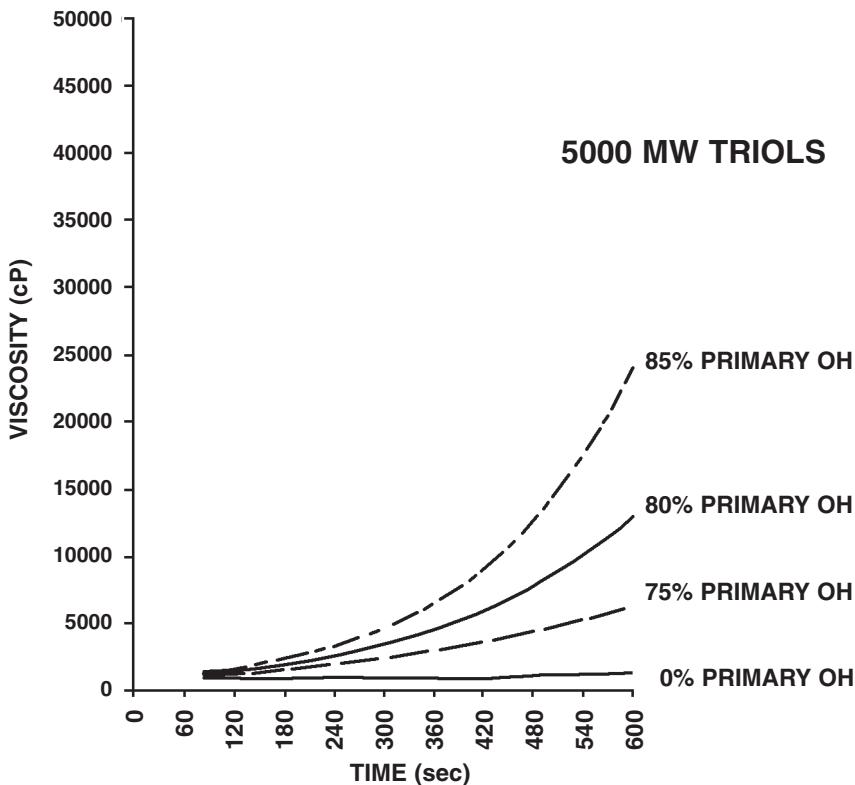


Figure 11.3
Comparative BVT Type Reactivity Data for
Polyols Used in Making HR Molded Foams

With more reactive polyols, the rate of gellation in HR foams is faster than in conventional foams. This translates into the need for less gellation catalyst than is used in slabstock and hot-molded foam. It also allows the use of (and, in some cases, the absolute need for) more blowing catalyst to accelerate the foam expansion reaction. The faster rate of polymer formation and the restricted expansion provided by the mold produces a foam containing a higher population of intact cell-walls when conventionally demolded. Because of this, and in contrast to hot-molded foam, HR foams must be crushed soon after demold to avoid shrinkage as the foam cools down. It is possible to formulate more or even perfectly open-celled foam, but such foams often border on instability, and most foam manufacturers choose to run tighter formulations. As long as the closed-cells can be adequately crushed open, it is safer to run a tight foam than to risk catastrophic foam instability.

Recent advances in HR polyol technology include higher functionality products for improved productivity^{11,42-11,43} and higher solids copolymer

polyols.^{11,44} Higher molecular weight polyols are reported to be helpful in attaining resiliency values over 70%.^{11,45} Liquid carbon dioxide has been successfully used to lower foam density in both TDI and MDI based formulations.^{11,46} Primary and secondary amine-capped-polyether polyols have also been used successfully to prepare a polyurea-type HR molded foam.^{11,47-11,50}

HR foams generally require less active silicone surfactants and in many cases require only cell-size-regulating types of surfactants. A typical low-density all-TDI based HR seating foam formulation is presented in Table 11.2.

Table 11.2 Typical Low-Density HR Seating Formulation

| Component | Parts by Weight |
|---------------------------|-----------------|
| SPECFLEX NC 630 Polyol | 70 |
| SPECFLEX NC 710 Copolymer | 30 |
| DC-5043 | 0.75 |
| DC-5169 | 0.25 |
| Diethanol Amine, pure | 1.5 |
| Dabco 33-LV | 0.25 |
| Niax A-1 | 0.08 |
| Water | 4.0 |
| VORANATE T-80 TDI | 100 Index |

On a global basis, approximately 15% of all HR molded seating foam is made with a blend of TDI with one of the polymeric forms of MDI. A common ratio is 80 weight percent TDI, 20 weight percent polymeric MDI. A typical formulation for this grade of foam is presented in Table 11.3.

Table 11.3 Typical HR Seating Formulation Based On Blended TDI/PMDI Isocyanates

| Component | Parts by Weight |
|---------------------------|-----------------|
| SPECFLEX NC 630 Polyol | 70 |
| SPECFLEX NC 710 Copolymer | 30 |
| Tegostab B-4113 | 0.6 |
| Tegostab B-8708 | 0.4 |
| Dabco 33-LV | 0.3 |
| Niax A-1 | 0.1 |
| Water | 3.5 |
| SPECFLEX TM-20 Isocyanate | 100 Index |

In traditional HR foam chemistry, the soft-segment portion of the foam matrix is a polymer containing urethane linkages resulting from the reaction of polyol with isocyanate. Polyurea structures result from the reaction of formulation water with isocyanate. For foams made from toluene diisocyanate and diethanol amine cross-linker (as in Table 11.2), it is

generally conceptualized that these reactions lead to a two-phase morphology consisting of discrete hard-segment domains dispersed within a continuous soft-segment polymer phase.^{11.51-11.52} An additional reinforcing phase may be present if the foam has been formulated to contain particulate fillers. Figure 11.4 offers a conceptual representation of such a system.

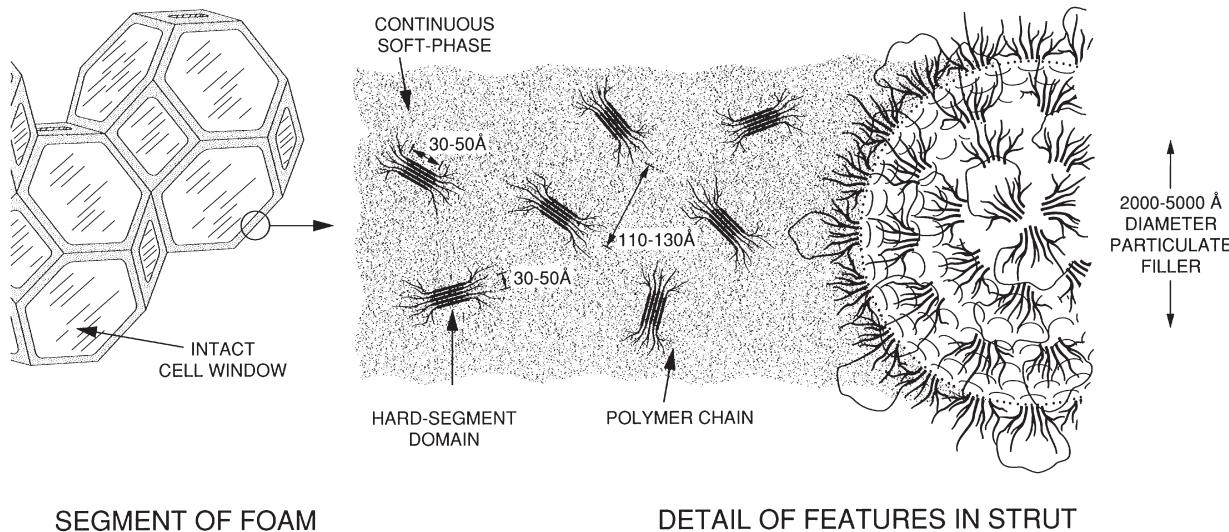


Figure 11.4 Conceptual Morphology of HR Foams

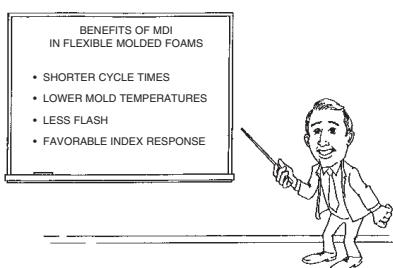
In the figure, the hard-segment domains are represented by the clustered straight lines. Our best estimates of physical dimensions for these structures are indicated.^{11.53} These features are tied into the matrix by covalent attachment to or entanglement with polymer chains (the wiggly lines) that are shown fading off into the continuous soft-segment phase. A size range for traditional styrene/acrylonitrile type copolymer polyol filler particles is also given.

Prior to discussing general seating foams in more detail, three special classes of foam receiving notable recent attention will be discussed below.

ALL-MDI FOAM

Commercially useful seating foams can be made from either TDI or MDI-based technology. The competition between the two technologies began early and continues today.^{11.54-11.64} An excellent comparison of the two foam types has been presented.^{11.65}

Some of the advantages of MDI-based systems are: shorter production cycles, utilization of lower mold temperatures, reduction in waste foam from mold vents and seals, and the higher inherent rate of foam cure. MDI-based foams cure so quickly that traditional forms of auxiliary curing heat are often not needed. The higher rate of cure reduces the time a given shot of foam must remain in the mold before it can be demolded and sent for further fabrication. Demold times of as little as ninety seconds have been observed. Quality



checks can be performed sooner, and it is not uncommon for MDI-based foam pads to be fabricated into covers and shipped within a few hours. All this increases production capabilities and reduces the need for large inventories of foam pads at various stages of cure.

MDI-based foams can be made on any of the molded foam production equipment described in Chapter 5. Two component systems are generally used with both sides specially formulated for the intended application. The base polyols used are blends of ethylene-oxide-capped triols and diols. Triols in the molecular-weight range of 4000 to 7000 are the most useful. Typical diols range from 2000 to 4000-molecular-weight. The isocyanate side is frequently a blend of a polymeric MDI with a prepolymer or with the pure 2,4' or 4,4' MDI isomers. A typical starting formulation is presented in Table 11.4.

Table 11.4 Typical All-MDI Based HR Foam Formulation

| Component | Parts by Weight |
|-----------------------------------|-----------------|
| VORANOL CP 4711 Polyol | 98.0 |
| VORANOL CP 5021 Polyol | 2.0 |
| Tegostab B-4113 | 1.0 |
| Diethanol Amine, 85% | 0.8 |
| Dabco 33-LV | 0.55 |
| Niax A-1 | 0.1 |
| Water | 3.4 |
| SPECFLEX NE-106 Isocyanate, Index | 80-110 |

Fast viscosity increase is a characteristic of MDI-based systems that often leads to in-mold flowability problems. Accurate temperature control of the process streams is helpful in minimizing flowability problems. Functionality and pure isomer content are the main chemical variables that affect foam flowability. The low free NCO content of MDI-based isocyanates compared to TDI, results in a reduced blowing efficiency. Figure 11.5 illustrates the typical density differences seen when the same amount of water is used in each type of foam.

Efforts to reduce the blowing deficiency with new catalysts and surfactants have been reported.^{11.66 - 11.67} Further density reduction efforts should be aided by use of the new liquid carbon dioxide auxillary blowing agent technology.^{11.68}

Another useful feature of MDI-based foams is their strong response to widely varying isocyanate index. Figure 11.6 compares the typical index response of TDI-based foam systems to that for MDI-based systems.

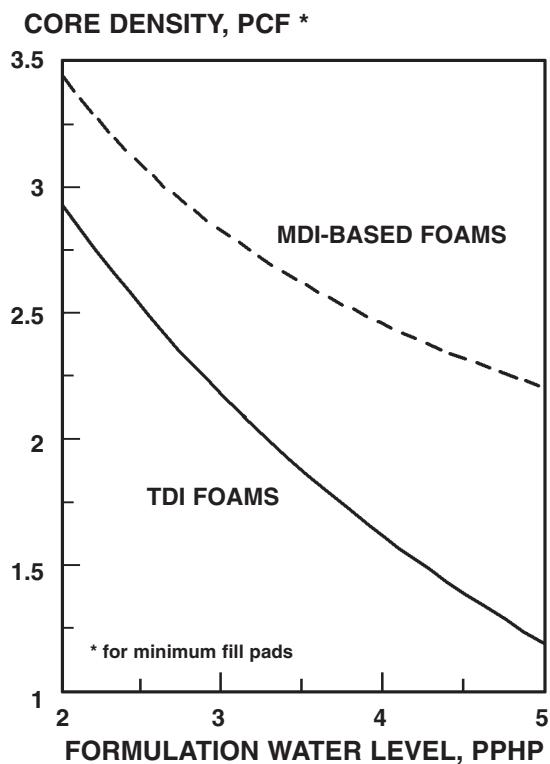


Figure 11.5 Typical Density Differences In All-Water Blown Foams

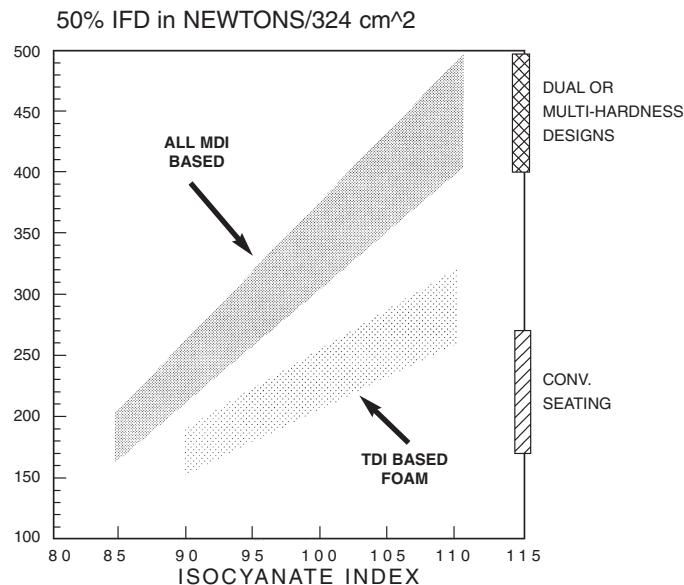


Figure 11.6 Typical Index Response in Foams Made with TDI and MDI Type Isocyanates

Clearly, a given MDI-based system has a greater capability than a TDI-based system to satisfy a wide range of customer load-bearing specifications. Reference 11.69 details how this strong index response can have serious negative effects on other important foam properties. References 11.70-11.74 discuss the utilization of MDI's favorable load-to-index response for the preparation of dual-hardness foams.

DUAL-HARDNESS FOAMS

Dual or multihardness foams are a special class of HR molded foams that are used almost exclusively for automotive seating. Automotive seating designers now believe that optimum support and long-term comfort can best be obtained with seats having various zones of different hardness foam. Sitting pressures vary across the surface of a seat, and designers have found that dual or multihardness foam technology gives them a way to tailor the load-bearing strength in areas needing more or less support. Car seats provide support for the human body under both static and dynamic conditions. It has been reported that sitting forces need to be distributed for optimum comfort in such a way that the load on wide areas of the skin is kept below about 1 pound per square inch. Seating engineers say that pressures above this level decrease blood circulation and contribute to driver weariness. In addition, a large degree of side support is needed to hold driver and passenger in place while the car is being turned.

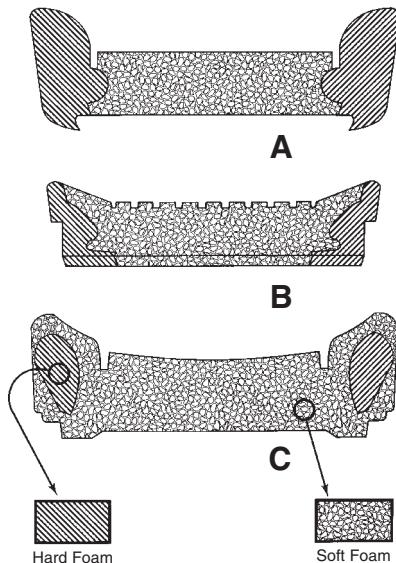


Figure 11.7 Alternative Designs for Side-Support Types of Dual-Hardness Foams

Several alternative designs for the side-support-type of dual-hardness foam are shown in Figure 11.7. Design "C" is an example of the side-roll encapsulation technology.^{11.75-11.77} in which a core of hard foam is surrounded by a softer foam. This is accomplished in essence by dispensing the hard foam into the already rising soft foam. Advantages and more details of this technology are available in References 11.78-11.79.

Traditionally, a measure of localized support has been accomplished by embedding a heavy wire frame in the seat cushion. This technique involved manual placement of the wire prior to foaming and a host of hidden costs associated with producing, shipping, storing and handling a wide variety of wire-insert designs. Even with the most complicated wire designs, structural support was generally limited.

The concept of multihardness foams is to replace the wire with machine dispensed foam of a higher hardness than that used in other areas of the pad. A simplified example is shown in Figure 11.8.

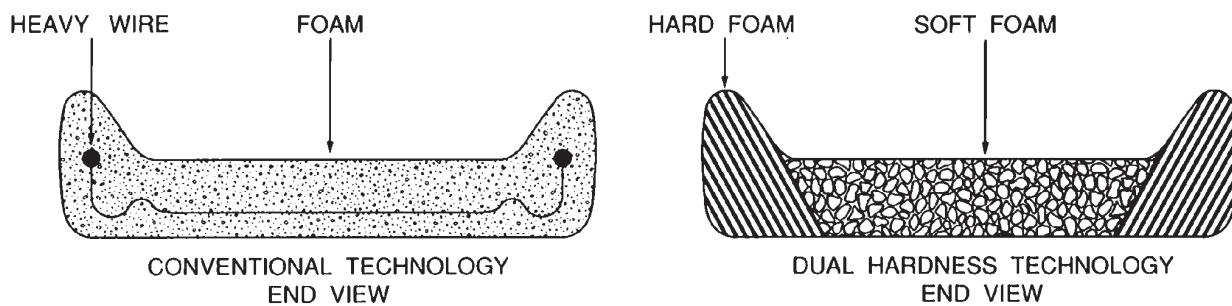


Figure 11.8 Basic Concept of Wire Replacement with Multihardness Foams

For instance, some seating designs may be more comfortable when one sits directly on a relatively softer section of a seat that is surrounded by relatively harder sections. In other seat designs, more than two regions having different hardness may be present. In general, seat designers prefer the hard sections to

be 2 to 4 times as firm as the softer sections. Another concept for improving comfort and overall seating performance is illustrated in Figure 11.9.

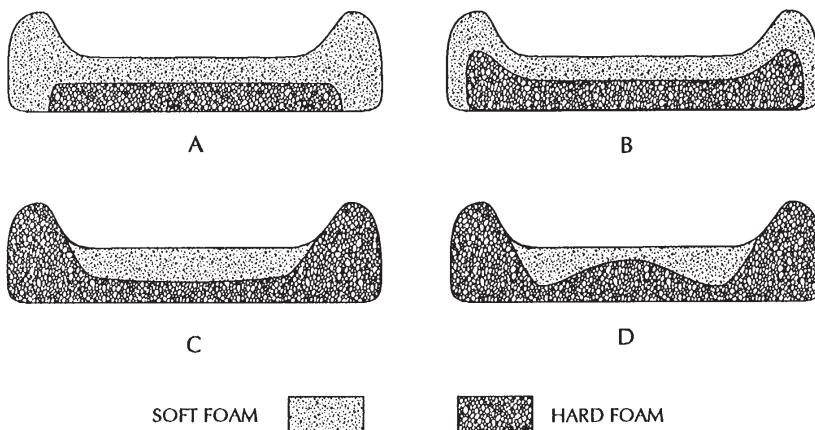


Figure 11.9 Concepts for The Layered Foam Technology

In this technology, both a soft and a hard foam are dispensed into the mold in such a way that a layer of soft foam is *in situ* bonded on top of a layer of hard foam.^{11.80} Brown described the performance advantages^{11.81-11.82} and the technology has been successfully combined with the encapsulated side-roll process mentioned earlier.^{11.83}

Dual-hardness technology is in production today globally and is expected to grow as design, cost and processing requirements increase. Table 11.5 lists the candidate chemical technologies and their present limitations.

Table 11.5 Technologies for Dual-Hardness Foams

| Technology | Disadvantage |
|-------------------------|---|
| High CPP Concentration | None. Today's Production Standard |
| Cross-Linker & Index | Formulation Cost Foam Properties |
| All-MDI Foam | Density Penalty |
| Preformed Foam Inserts | Labor Costs |
| Encapsulated Side-Rolls | Multiple Shots Long Pour Times Mold Design Considerations |
| Layered Foam | Long Pour Times Mold Design Considerations |

The above technologies also vary in the complexity of the hardware required. Good reviews of the various mechanical processes can be found in References 11.70-11.74. The high copolymer polyol option is rapidly

becoming the dominant technology. Example starting formulations for this technology are given in Table 11.6.

Table 11.6 Typical Dual-Hardness Formulations
Based On Copolymer Polyol and TDI

| Component | Parts by Weight | |
|---------------------------|-----------------|-----------|
| | Soft | Hard |
| SPECFLEX NC 632 Polyol | — | 30 |
| SPECFLEX NC 700 Copolymer | 20 | 70 |
| SPECFLEX NC 635 Polyol | 80 | — |
| Dabco 5164 | 0.6 | 0.6 |
| Diethanol Amine, 85% | 0.8 | 0.6 |
| Glycerine | 0.5 | 0.7 |
| Niax A-300 | 0.2 | 0.2 |
| Niax A-400 | 0.2 | 0.2 |
| Dabco 33-LV | 0.2 | 0.2 |
| Water (added) | 3.8 | 2.8 |
| VORANATE T-80 TDI | 100 Index | 100 Index |

Additional reviews of the all-MDI foam option are provided in References 11.84-11.86.

FAST-DEMOLD FOAM

This special area of HR molded foam technology addresses the desire of some foam producers to be able to demold a finished foam part 2 to 3 minutes after it is poured. Further, that part should be sufficiently cured to allow immediate downstream processing into the finished seat assembly. The desired mechanical process would involve shorter molding lines, possibly carousel-type, running at higher speeds and with little or no auxiliary heating.

Much work has been done on developing a chemical system to meet the above requirements. With careful attention to catalysts, TDI or blended TDI/Polymeric MDI-based systems have been successful.^{11.87-11.89} Higher functionality polyols and copolymer polyols have been developed that offer a faster rate of cure without introducing excessive foam tightness.^{11.42-11.43} MDI-based systems are also successful, but often fall short of foam density requirements.

PROCESSING AND PROPERTIES IN MOLDED FOAMS

The ability to quantify processability and the resultant physical properties of a polymer system is of extreme importance in assessing the commercial potential of a candidate product early in its life. Commercial acceptance of any new product depends in part on its price, the attainable performance features and the processability of the material. One definition of

processability might be the overall ease with which a product can be acceptably produced in a commercial facility given its normal day-to-day variations in equipment and people performance. A number of terms commonly used to describe performance characteristics of molded foams will be discussed below.

MOLDED FOAM PADS

In molded foam production, each part has a specified finished weight. This part weight is directly related to the overall density of the molded foam and to the core density. Load-bearing measurements are normally conducted on the whole foam pad, while other physical properties are determined using samples taken from the cut foam. In conducting comparative evaluations, it is important to prepare samples at the correct part weight (and hence at the correct molded and core densities).

Experimentally, foams are often produced at varying additive and/or index levels. Controlling part weight when the throughput of one or more process streams is changed requires adjusting the shot timer to reflect the new total liquid throughput. Throughput numbers are available from the calibration data. Shot timers are normally adjustable to a hundredth of a second, so it is a fairly simple task to produce foams of the desired weight. An example calculation would proceed as follows:

Total liquid throughput: 23.500 kg/min

Shot time: 3.30 seconds

Foam weight: 1,225 grams

New total throughput: 23.100 kg/min (e. g., index lowered)

Desired foam weight: 1,225 grams

New shot time: ?

The new shot time is obtained by multiplying the old shot time by the ratio of the old throughput to the new throughput:

New shot time = old shot time x (old/new throughput)

For the present example:

New shot time = $3.30 \times (23.500/23.100)$ seconds

New shot time = 3.36 seconds

A simple check is to note that a higher throughput should require less time for a given weight foam while a lower throughput will require a longer shot time. In actual practice, small corrections to this result are usually needed to compensate for changes in flash and other extrusion weight resulting from changes in total gas evolution.

Foams are also known to gain weight as they cool down after production. Normally the weight gain will be less than about 2%, but it is important to know a formulation's characteristic weight gain so that part weight can be adjusted on the day of production. It is also well known that the physical

properties of a foam develop over the first few days after production. The growth of properties can often be influenced by catalysis and cure history. Typical information of this type is presented in Figure 11.10. Such information often proves valuable in situations where the foam must be tested or shipped very soon after manufacture.

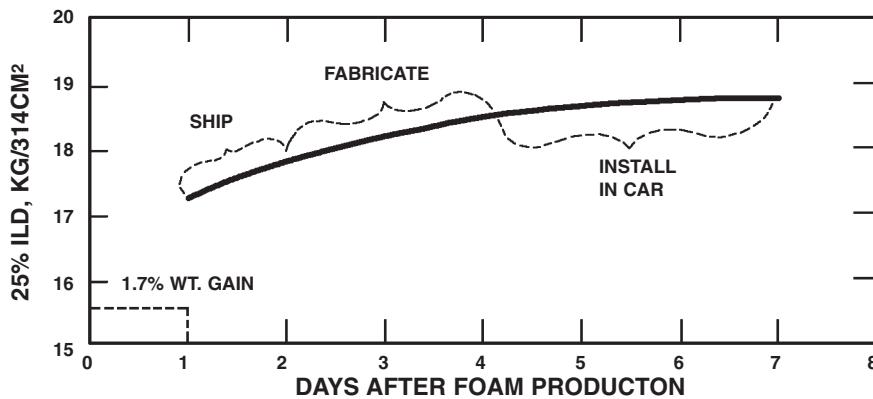


Figure 11.10 Weight-Gain and Load-Bearing Growth with Time for a 3 pcf (48 kg/m^3) Density HR Molded Foam

QUANTIFICATION OF PROCESSING

Over the years, several testing procedures have been developed to aid in quantifying some of the processing characteristics observable in molded foams. Several of these procedures are detailed below.

Mold-Temperature Latitude

In this testing scenario, it is desired to establish between what upper and lower extremes of mold surface temperature a cosmetically acceptable foam pad can be produced. Process conditions in real-world production plants vary widely, and it is useful to know the limitations of any candidate system. Sensitivity to mold temperature is studied by pouring a constant shot of foam into a freshly waxed mold at surface temperatures varied across a normally applicable range; e.g., 120-170°F (49-77°C). Repetitive pours are conducted at roughly 5°F (3°C) intervals until the limits are found.

After pouring, the mold lid is closed, the fill time noted and the foam allowed to cure according to the desired cycle. After cure, the mold is opened, the foam removed and the show surface rated for overall quality. Only two grades of surface quality are noted: excellent and poor. Poor surfaces have obvious defects, such as loose or torn skin, excessive subsurface voids, craters, or other cosmetic defects. An excellent surface shows no defects whatsoever. Figure 11.11 illustrates a convenient way to report the data.

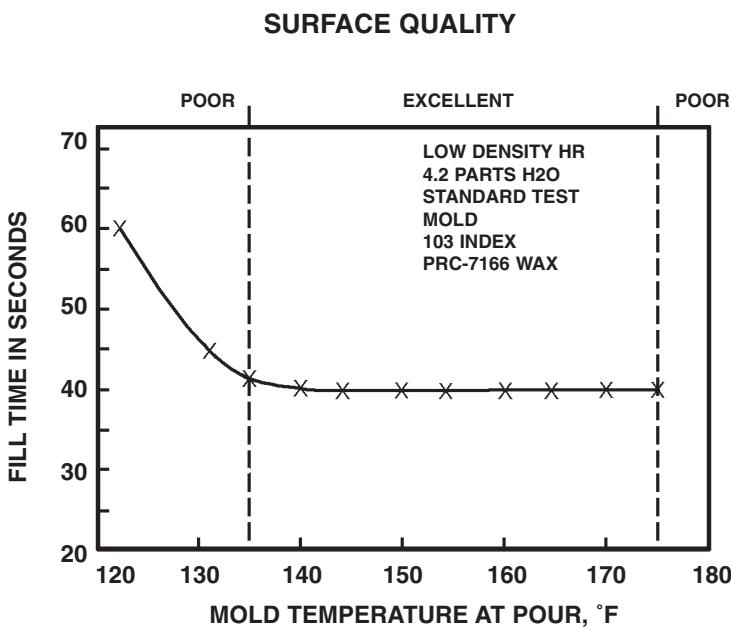


Figure 11.11 Typical Mold-Temperature-Latitude Data

A cooler mold normally results in a slower fill time. Fill time is an important parameter for which acceptable values can vary from plant to plant or in the same plant running at varying conditions. The critical factor is that the mold lid can be closed and locked in time to accommodate the rising foam. On the cool side of the graph, the limiting temperature is that at which cold collapse appears. On the hot side, the limiting temperature is indicated by sizable areas of small regular subsurface voids on the show surface. Day-to-day reproducibility of this test for a given foam system often varies plus or minus 5°F (3°C) on either end.

The pads prepared in the mid-range of a mold temperature latitude study are suitable for determining foam physical properties. The example data in Figure 11.12 show that choice of mold can have an effect on the resultant data. Thin, wide tools such as automobile seat backs often give narrower latitudes than thick section molds.

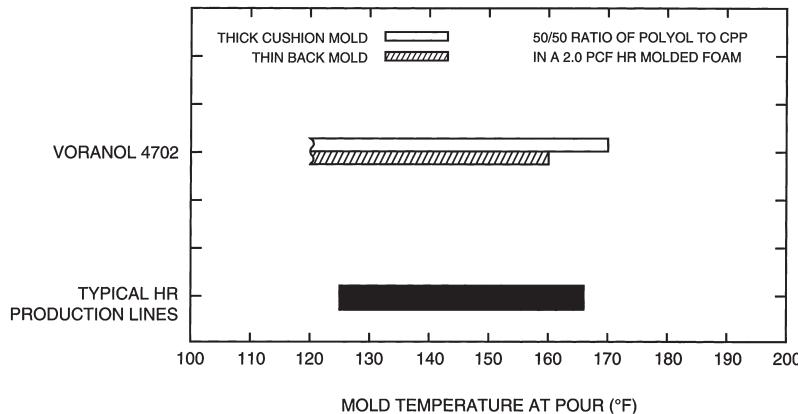


Figure 11.12 Typical Mold-Temperature-Latitude in Thin and Thick Molds

Foam Cure

For a foam formulation to be commercially viable it must demonstrate an adequate level of ‘cure’ at several critical points in the manufacturing process. Table 11.7 presents some practical examples of foam cure assessment.

Table 11.7 Practical Examples of Foam Cure

| Judged At | Affecting |
|---------------------|-----------------------------------|
| Mold Fill | Bulk Stability, Flash |
| Part Demold Station | Green Strength and Fingerprinting |
| Crusher Station | Hot Set |
| Shipping Station | Short Term Static Fatigue |

The extent of cross-linking or cure at the moment of mold fill directly affects the amount of polymer that escapes the mold through vent holes and parting lines. If this is excessive, valuable material is wasted and additional trimming and cleanup labor may be needed. The flowing polymer may also transfer physical strain forces back into the mold, causing damage (e.g., shear collapse or vent instability) to the still-reacting cellular mass.

At the demold station, the foam must have enough green strength to resist tearing and fingerprinting. Physical tears can occur when a person or machine removes the foam pad from the mold with less than optimal care. Tears can usually be repaired off-line at some additional expense. Fingerprinting results when the foam is not yet strong enough to rebound from indentations caused by grasping the foam pad and pulling it from the mold.

In passing through mechanical roller types of crushing machines, the foam is subjected to intense pressure over short time periods. Inadequate cure at this stage often gives rise to internal tears, densification and loss of dimension. Wrinkles may also appear on the exterior of the pad, detracting from the cosmetic appearance of the part.

At the shipping station, multiple pads are often compressed into a shipping container for delivery to the seat assembly plants. Variable time periods are involved before the pads are released from this compression. A foam with inferior cure may exhibit a permanent loss in dimension when removed from the shipping container.

The overall cure of a foam is affected by both the inherent chemistry and by the amount of additional energy contributed by component temperature, stirring and thermal (e.g., oven) exposure. Excessive humidity in the ambient atmosphere can adversely affect foam cure and properties. Some success has been reported in microwave curing of molded foams.^{11.90-11.101}

Historically, cure data have been reported using manual ‘squeeze-the-foam’ tests, which are highly subject to operator technique and interpretation. No specific test for quantifying the antitearing or green strength of a molded

foam has ever been reported. The phenomena of fingerprinting, hot set and short-term fatigue can be simulated using an “initial compression set” type of testing procedure shown in Figure 11.13.

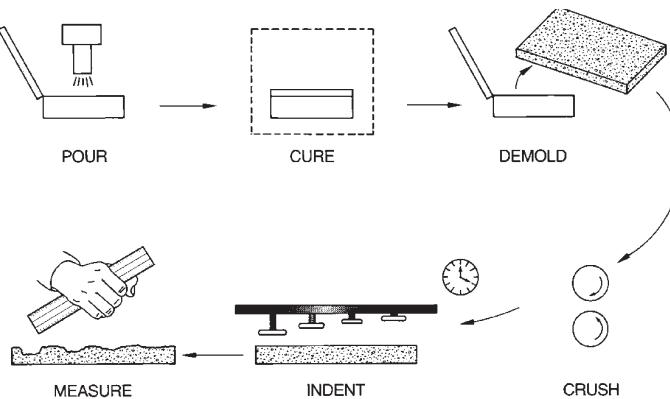


Figure 11.13 The Hot Set Cure Test

Foams prepared in the normal manner are dispensed using a simple line pour into a 15 x 30 x 2.5 inch thick mold. The mold is closed and clamped, and the foam is cured according to the desired cycle. Upon demold, the foam pad is immediately given a roller crush at a 1/2-inch gap and placed beneath the indenter jig. The four indenter feet are adjusted to regionally deflect the foam part to 1", 3/4", 1/2" and 1/4" residual thicknesses. Four replicate pads are prepared and tested at varying times so that the data form in Table 11.8 can be filled in.

Table 11.8 Cure Data Form

| Deflection to: | 1" | 3/4" | 1/2" | 1/4" |
|----------------|----|------|------|------|
| Time (sec) | | | | |
| 15 | A | B | C | D |
| 30 | E | F | G | H |
| 45 | I | J | K | L |
| 60 | M | N | O | P |

Where A, B, C, etc., are the minimum residual thicknesses remaining at each test location. The undepressed thickness of the foam is also recorded.

After deflection, the pads are allowed to recover for a minimum of 4 hours before cutting and measurement of residual thickness in each test area. Percent compression set values are then calculated for each test condition and a total cumulative % Hot Set number calculated.

From general experience, the amount or degree of hot set is dependent upon both the severity of regional deflection and the amount of time that deflection is held. For instance, shallow deflections for long periods of time or severe deflections for short periods usually result in little, if any, hot set. However, as both the degree and time of deflection increase, hot set also increases in magnitude. This response may be attributed to the increasing probability that residual primary reactions in the foam core are more likely to occur as both

time and degree of deflection increase. As a consequence, the amount of foam set increases. To demonstrate this response, Table 11.9 presents some typical percent set and a total hot set cure number for a 2.0 pcf (32 kg/m^3) HR molded foam.

Table 11.9 Typical Percent Hot Set Cure Data

| Time (Sec.) | Compressed To | | | |
|-----------------------|---------------|------|------|------|
| | 1" | 3/4" | 1/2" | 1/4" |
| 15 | 4 | 5 | 7 | 14 |
| 30 | 9 | 13 | 14 | 30 |
| 45 | 11 | 16 | 18 | 32 |
| 60 | 16 | 20 | 29 | 52 |
| Total % Hot Set = 290 | | | | |

The individual percent set values are calculated according to the following equation:

$$\% \text{ Hot Set} = \frac{T_O - T_R}{T_O} \times 100 \quad (11.1)$$

where T_O is the thickness of an undeflected area of the pad and T_R is the residual thickness for the test area being considered.

Example data showing the utility of this test procedure for studying the effects of oven residence time on foam cure are presented in Figure 11.14.

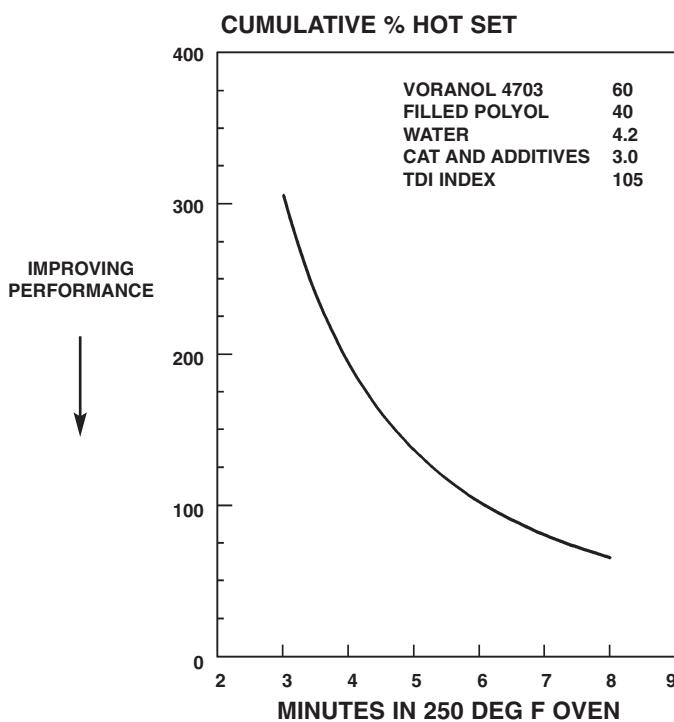


Figure 11.14 Use of Hot Set Cure Data in Studying Effect of Oven Residence Time on Cure

Similar cure tests are in use by other workers.^{11.56,11.66-11.67} Measuring the “Hot IFD” of a freshly demolded foam can also be taken as a measure of cure.^{11.38}

Foam Stability

Good stability in the early stages of the foam reaction is required for the production of defect-free parts. The difficulty of maintaining adequate stability increases as foam density decreases.

One common measure of foam stability is the free-rise bucket test illustrated in Figure 11.15.

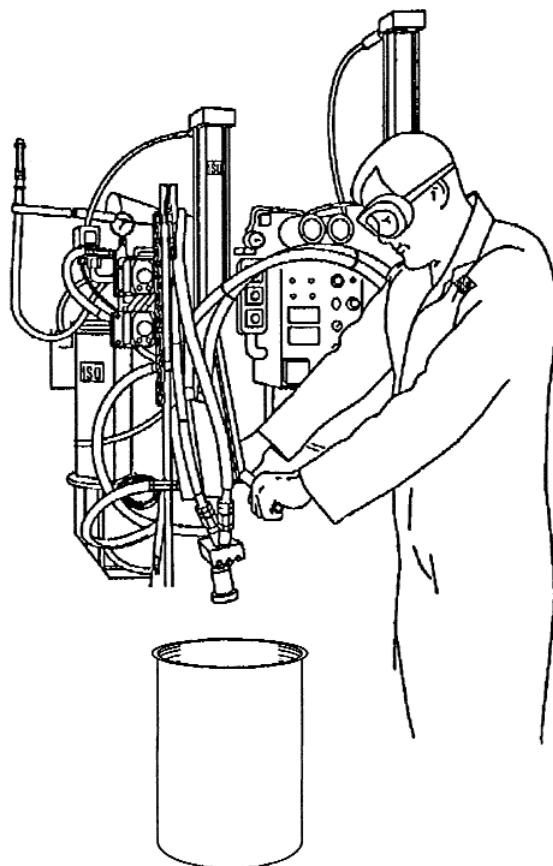


Figure 11.15 Bulk Stability Test

In this test, a 22.7 liter (five imperial gallons) plastic bucket receives a shot from the foam dispensing machine. The shot size is sufficient to totally fill the bucket with at least a 10 centimeter (3.9 inch) crown of foam above the lip of the bucket. Typical data recorded would include time to reach the lip, maximum and final foam height and an internal foam stability rating.

The internal stability rating is obtained by cutting the cured foam and ranking the severity of voids on a 1 to 10 scale. A perfect foam would receive a 10 rating while a collapsed foam would be rated at 1. Figure 11.16 is taken from a recent study^{11,42} and contains examples of the cut and graded foams.

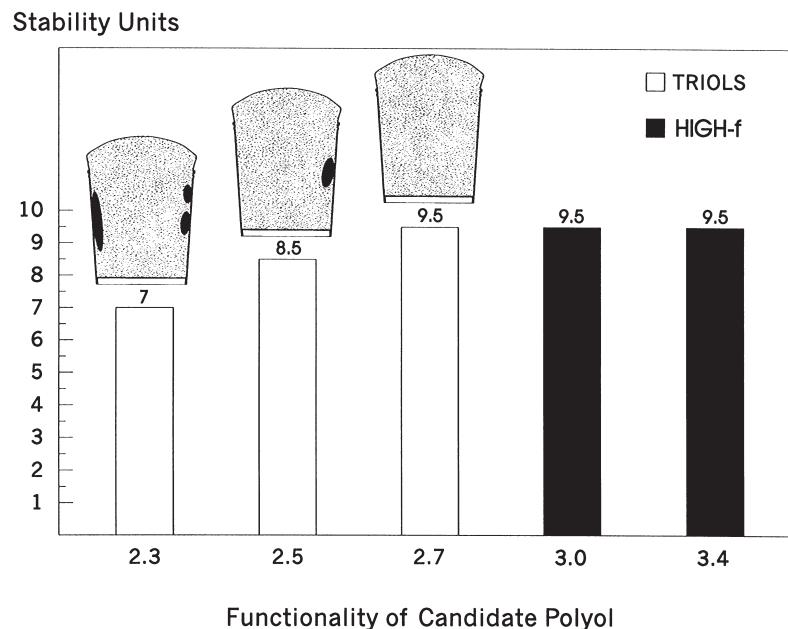


Figure 11.16 Comparative Bulk Stability Performance

This example data clearly shows the bulk stability improvements found in a series of foams made with increasing functionality base polyols.

In-Mold Flowability

Lack of stability in a molded foam is normally evidenced as shear collapse, vent instability, or other subsurface voiding. Figure 11.17 illustrates the areas of a foam that are typically subject to shear collapse and voiding.

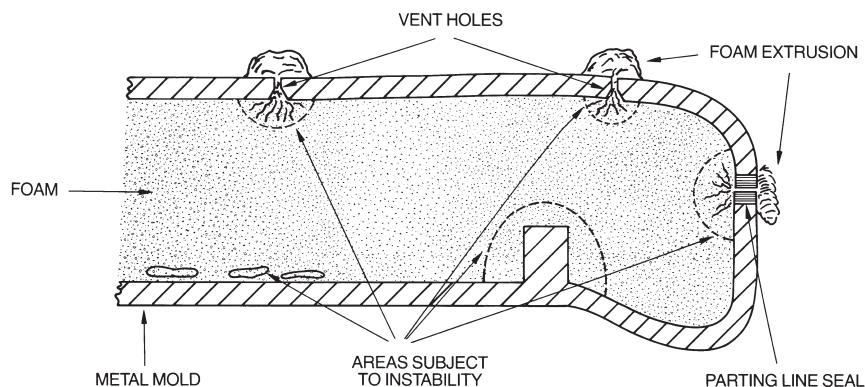


Figure 11.17 Foam Instability Example

The severity of such instability is often related to the complexity of the mold and density of the foam. Lower-density foams are much more prone to instability, particularly when foamed into wide, thin molds with internal inserts or ridges.

The phenomenon can be caused by purely chemical factors such as a catalyst imbalance or a combination of chemical and mechanical factors. In foam production, the mixed ingredients are dispensed into the mold in a manner

commonly referred to as the pour-pattern. From this initial distribution the liquid/foam mass must flow to fill the mold volume. An imbalance in the blowing/gelling ratio at this point can lead to catastrophic results. In the case of excessive blowing, the force of the expanding gases exceeds the strength of the growing polymer so that a propagating area of cell coalescence occurs. If the polymer growth rate is excessive, the foaming mass may lack sufficient fluidity to move (under the motive power supplied by the expanding gases) and fill the mold. Strain forces may be set up in the polymer, which likewise destroy the desired cellular structure. The preparation of free-rise cup foams has proven helpful for adjusting catalysts to obtain a balanced blow/gel ratio. Also, if the gel time for a particular formulation is too slow, extrusion at the vents or parting line can transfer strain forces back into the mold and cause destabilization of the foam in areas such as those shown in the above figure.

Pour pattern is one mechanical factor that can completely override all chemical factors. A grossly incorrect pour pattern, e.g., all liquid dispensed in one confined area of a mold, can cause even the best formulation to exhibit processing problems.

Shear collapse problems are most often seen in production molds that are wide and thin, contain internal rails or inserts and are designed to vent at the parting line. Many seat backs are produced in this type of mold at as low a density as possible. Since actual production tools are not always available to work with and change so often it is impossible to establish a long term database, the following stability/flowability test procedure has been established.

Foams are prepared in the normal manner and dispensed into a long, thin mold as conceptualized in Figure 11.18. A simple one spot pour at the indicated position is used.

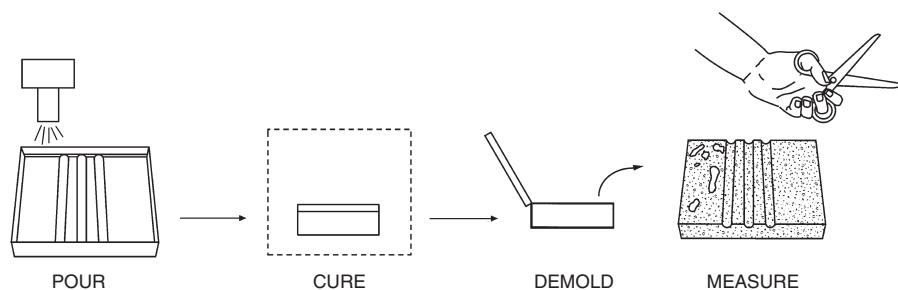


Figure 11.18 Stability Testing Scenario

After pouring, the lid is closed and locked, and the foam is allowed to cure for the desired cycle. From the pour spot, the foam must travel over three separate humps as it moves to fill the mold.

To calculate a percent instability ranking, the pad is laid on a light box or other convenient back-lighting source. The visible void areas are marked so that they may be transferred to a piece of tracing paper the same size as the foam pad. By weighing the paper and then weighing the cut out void areas, % instability can be calculated according to the following equation:

$$\% \text{ Instability} = \frac{\text{Void Area Weight}}{\text{Total Area Weight}} \times 100 \quad (11.2)$$

A larger number would indicate more instability. More exacting procedures for quantification of the void areas, such as with a planimeter or computerized image analysis, may also be used. Several detailed studies of foam flow phenomena are available.^{11.102-11.105}

Even when all the influences mentioned above have been considered, instability may still be present for other reasons. Surfactant and cross-linker levels may not be optimized. Contaminants can be present, or the timing of cell-opening may be incorrect. Part weight can also have an influence on stability as shown by the data in Figure 11.19. Here a given foam system was used to produce parts ranging from underfill to gross overpacking, with the indicated instability results.

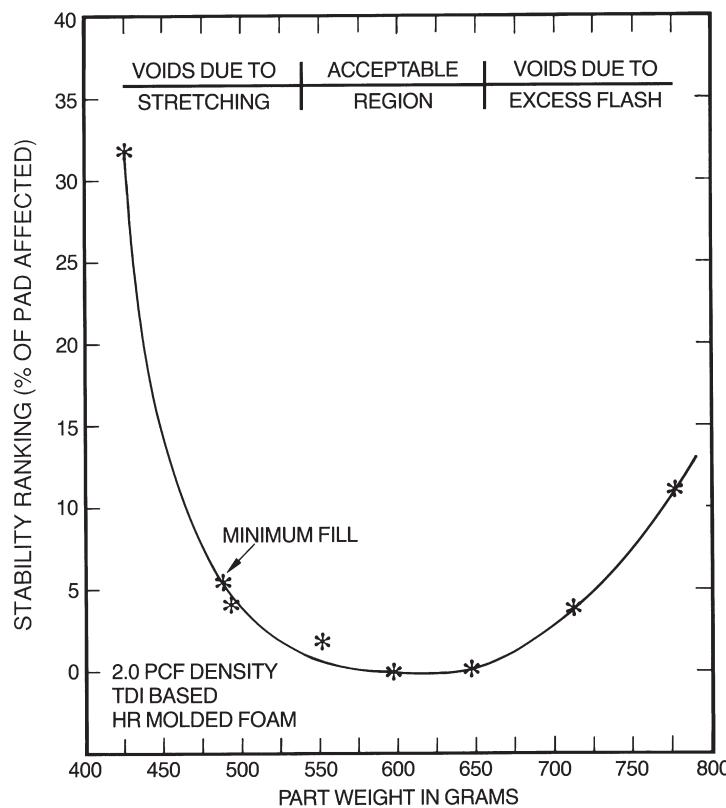


Figure 11.19 Typical Effect of Part Weight on Stability of Low-Density HR Molded Foam

Methods of ranking foam stability by quantifying levels of vent collapse have been reported.^{11.56, 11.106-11.108}

Foam Shrinkage

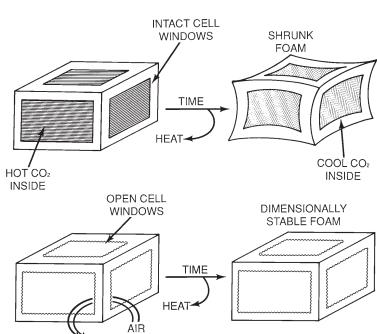


Figure 11.20 Simplified Model for Foam Shrinkage

All molded flexible polyurethane foams will shrink 2 to 3 volume percent during curing. To compensate for this, molds are cut appropriately larger than the dimensions of the final part. Uncontrollable shrinkage beyond this small amount is of utmost concern to foam producers.

Many molded foam producers believe that overall foam moldability is better with a tight formulation than with a more open one. One consequence of running a tight formulation is the danger of excessive foam shrinkage if the cell-walls are not adequately opened by crushing (Figure 11.20). Shrinkage in a flexible foam results when a large population of foam cells with intact windows remains at the end of foam manufacture. Just after production, such cells are filled with hot, pressurized carbon dioxide gas. As the foam cools, two things happen: the internal gas pressure diminishes, and the carbon dioxide diffuses out of the cells roughly fifteen times as fast as air diffuses into the cells.^{11.109} The net result is reduced internal pressure in the cell which, when taken over a population of closed-cells, causes the foam to shrink and lose physical dimensions.

Many of the factors affecting cell-opening and shrinkage in flexible foams were discussed in Chapter 3. Table 11.10 lists the most common influences on shrinkage in HR molded foams. The indicated references will provide more details of the individual factors.

Table 11.10 Factors Influencing Shrinkage in HR Molded Foams

| Factor | Reference |
|---------------------------|-----------|
| Blow/Gel Reaction Balance | 11.110 |
| Surfactancy | 11.111 |
| Component Functionality | 11.112 |
| Copolymer Polyol Use | 11.113 |
| Additives | 11.114 |
| Isocyanate Composition | 11.70 |

Shrinkage is most reliably reported as simply a percentage of the original molded height. The shrinkage test procedure is presented in Figure 11.21.

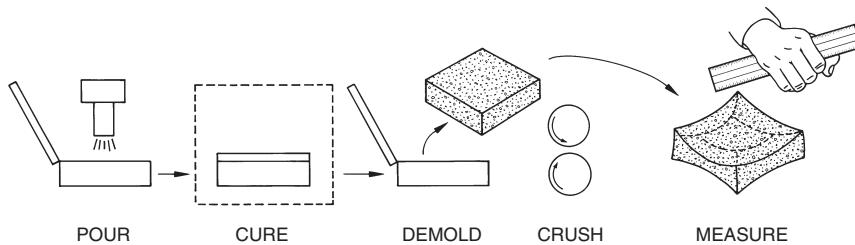


Figure 11.21 Shrinkage Testing

Foams are prepared in the normal manner, carefully removed from the mold, and allowed to stand uncrushed overnight. Then each pad is cut through the area of maximum shrinkage and the remaining thickness at that point is measured to the nearest millimeter. Percent shrinkage is then calculated using the expression:

$$\% \text{ Shrinkage} = \frac{T - \text{Remaining Foam Height}}{T} \times 100 \quad (11.3)$$

where T is the original foam thickness. Accuracy of the physical measurement is typically plus or minus 1%, but statistical studies have shown the shrinkage phenomenon itself to be no better than about plus or minus 5%. Figure 11.22 presents typical shrinkage data illustrating the effect of varying total catalyst package concentration in a low-density HR molded foam.

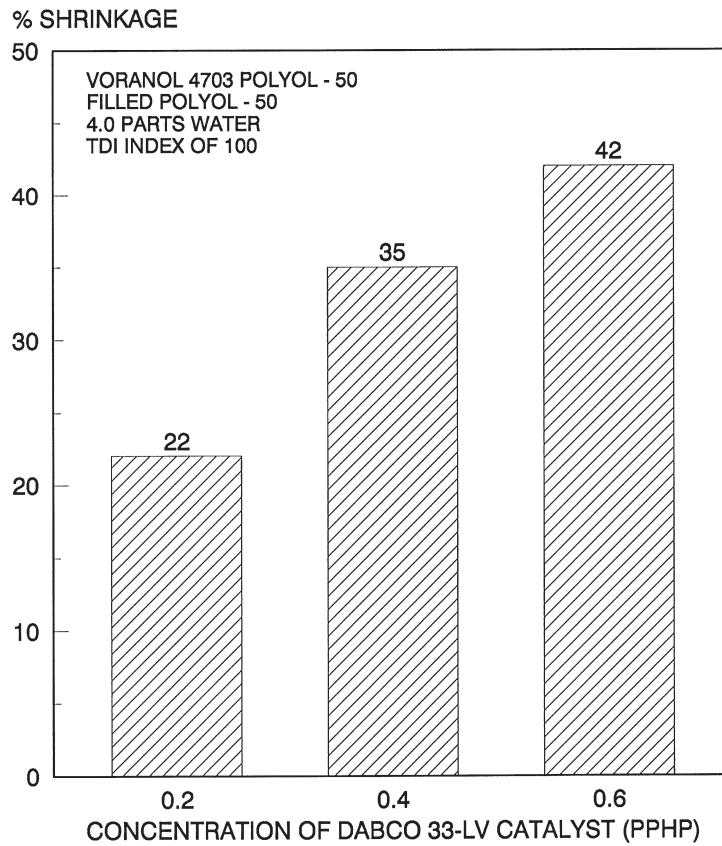


Figure 11.22 Effect of Varying Catalyst Package on HR Molded Foam Shrinkage

Foam Tightness

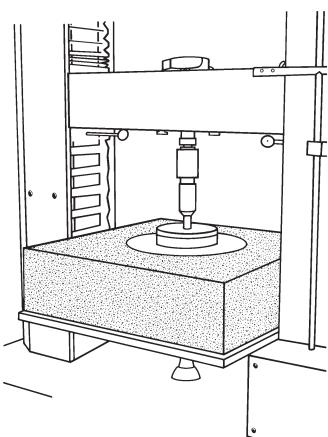


Figure 11.23
Force-To-Crush Test

Assessments of tightness in an HR molded foam are too often subjective in nature. Typically, after a foam is removed from the mold, a person will squeeze or crush the foam by hand and record a subjective tightness rating based on the ease or difficulty of crushing. Obviously such ratings will vary from person to person. The practical concern is whether the foam will survive the crushing event. If the foam is too tight, the stress forces inside the foam may exceed the tensile strength of the “green” foam resulting in a physical splitting apart of the foam pad as it goes through the rollers. This gross splitting results in a foam that must be scrapped.

Conventional force-measuring machines, such as the Instron brand testing machine, (see Figure 11.23) can be used to quantify foam tightness in a Force-To-Crush test. In a typical procedure, foams are prepared in the normal manner, cured for the desired cycle, and then removed from the mold with care. The uncrushed pad is quickly placed in the force measuring machine and deflected to a desired thickness. Preload height, instantaneous peak load and load decay are the basic data available. The example data in Figure 11.24 are again taken from Reference 11.42.

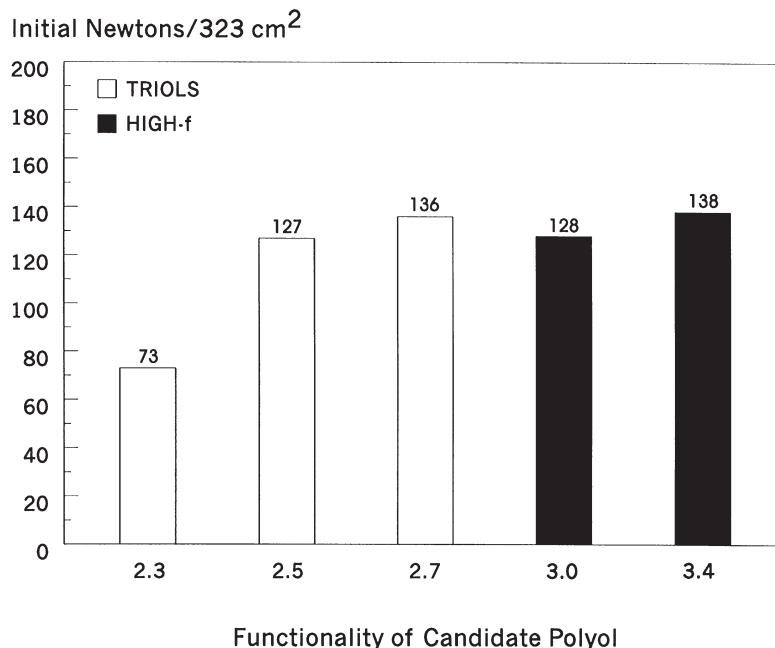


Figure 11.24 Comparative Foam Tightness

Within the family of conventional triols, the peak load was found to increase as the functionality and the reactivity of the polyol increased. No further loss in performance was seen by using either of the higher functionality polyols studied. Comparable force-to-crush tests have been described by others.^{11.115-11.117}

PHYSICAL PROPERTY STUDIES

A full set of foam-physical-property data is generally required for a complete evaluation of any candidate foam system. Some 12 or more discrete physical property tests are done on each foam pad submitted for testing. The testing process is time-consuming and costly, but necessary for a complete analysis of a foam's performance potential. Additional testing may be required to satisfy customer requests for information not provided by normal testing.

Physical Properties Versus Isocyanate Index

The first study that should be done when evaluating a new foam system is a look at how the foam physical properties vary across a wide index (or additive of interest) range. The practical range of index for TDI-based molded foams has historically been approximately 90-110. Foams produced outside these limits often suffer deficiencies in properties or processability. The discussions below illustrate the responses of common foam properties to changes in index.

Figure 11.25 shows the typical response of 25% and 65% IFD load-bearing values to increasing index and copolymer polyol concentration. The response is typical of TDI-based flexible polyurethane foams: load bearing increases as either factor increases. Data of this type are helpful in routinely preparing foams that meet the intended application specifications. Load bearing can also be influenced by many other factors.

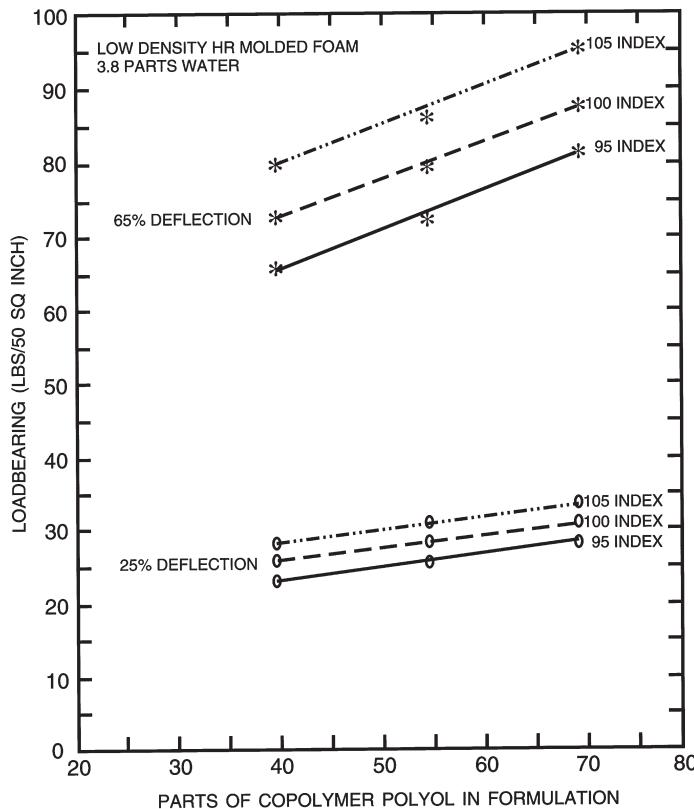


Figure 11.25 Load-Bearing Increases with Index and CPP Level

If part weights are controlled in the desired range, the density and resiliency properties are normally constant across an index range. The compression set properties of a foam are often the most difficult to control. Typical responses for a low-density foam are shown in Figure 11.26.

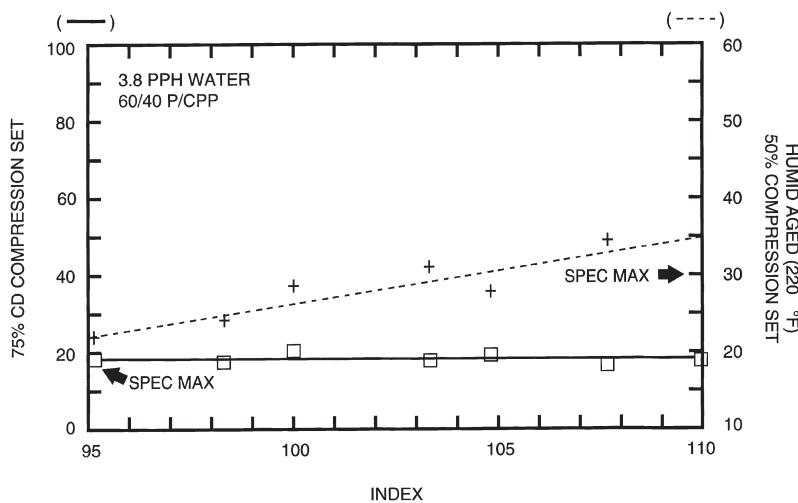


Figure 11.26 Typical Compression Set Data for Low-Density HR Foam

Collectively, the tensile, tear and elongation properties are referred to as the strength or mechanical properties. Figure 11.27 shows that these properties often diminish with the increasing cross-linking that results from higher indexes.

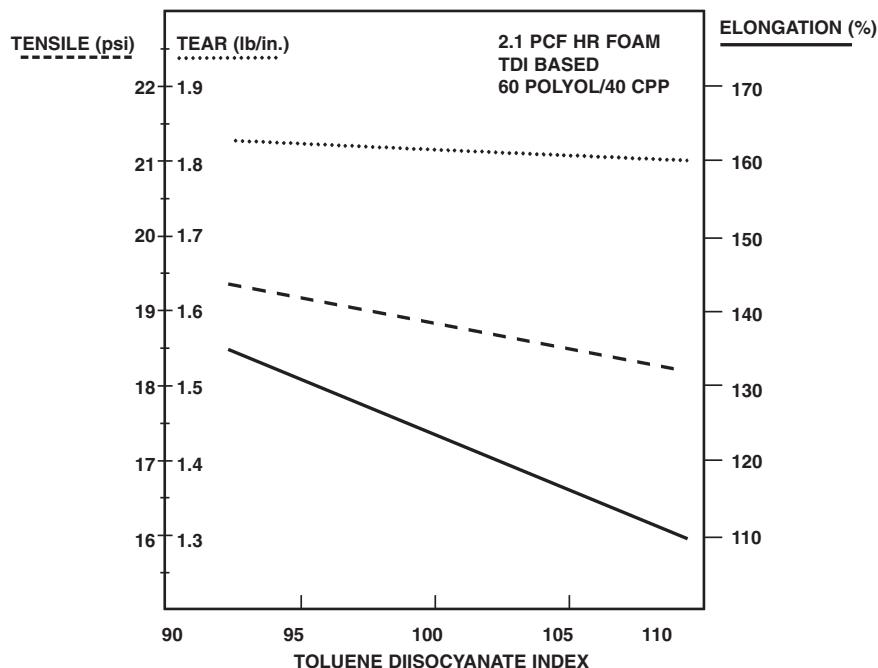


Figure 11.27 Typical Mechanical Properties for Low-Density HR Molded Foam

Packing Level

Packing level studies are often done to determine the effect of varying part weight on foam physical properties. As discussed earlier, each production part has a specified design weight. In practice, however, part weights can vary due to any number of process-induced variables. Some of these variables include molds that differ slightly from design volume, shot times shorter or longer than optimum, incorrect pour pattern (resulting in excessive extrusion through some vent holes) and leaking parting line seals. A typical response curve for load bearing versus part weight is given in Figure 11.28. Other physical properties are typically less affected than load bearing.

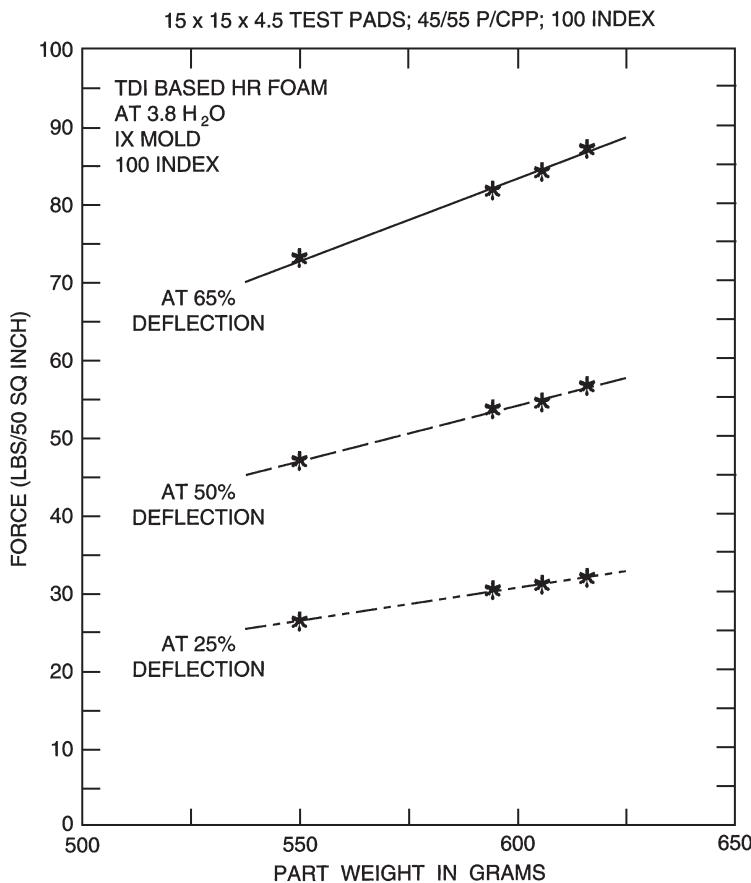


Figure 11.28 Foam Load Bearing Varies with Part Weight

Other workers have also found packing to be an effective way to adjust load bearing.^{11.118-11.121}

Fatigue In Molded Foam

Fatigue in flexible molded foams is defined as the loss of load-bearing capacity with use. In severe cases, fatigue can also be evidenced as a loss in seat cushion thickness. The general observation is that when a foam is subjected to either a static or dynamic load, the load-bearing capacity after such loading will be lower than that measured before loading. After an adequate period of rest, the foam may regain most but not all of its original

strength. A typical automotive seat cushion is exposed to high static and dynamic loads over widely varying frequency, temperature and humidity conditions.

Numerous standard laboratory tests exist, and all the car manufacturers have durability tests for their final seat assemblies. Some claims of correlation between these controlled testing procedures and real world performance have been reported.^{11.122-11.123}

Accelerated fatigue testing has become more important as seating designs have evolved. In the older topper-pad-and-springs seat constructions, a fatigued foam usually just resulted in a more uncomfortable but still serviceable seat. In the newer seats, where the support mechanism depends largely on a given thickness of foam to hold the occupant in the design position, foam failure leads to a more unacceptable condition. A review of foam fatigue can be found in Chapter 8.

Comfort of Automobile Seats

The automobile seat is the major element of contact between the occupant, the vehicle and ultimately the road surface. Its function is to position the occupant in a designed space so that the necessary tasks of operating (or simply using) the vehicle can be performed effectively. A successful design should also provide a measure of comfort and styling for the enjoyment of the occupants.

Vibrations transmitted through the seat assembly^{11.124} have the potential to reduce driver performance;^{11.125-11.126} contribute to driver and passenger discomfort;^{11.127} and may contribute to long term health effects.^{11.128-11.129}

The concept of comfort in an automobile seat and technology for its quantification has been evolving since the early 1920's.^{11.130-11.139} Keegan^{11.140-11.141} and Hall^{11.142} have discussed the practical difficulties of designing a comfortable automobile seat. A number of reviews are available^{11.143-11.149} and major development programs continue today.^{11.38,11.150-11.156}

Comfort is a very difficult criterion to measure. Most researchers give an essential definition of comfort as the absence of discomfort. The operational aspects of seat comfort have been particularly difficult to define. Runkle has identified the major elements of seat comfort and found that at least 50% of a comfort rating resulted from subjective rather than actual performance issues.^{11.157}

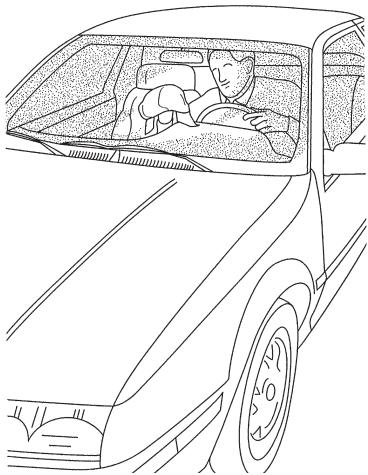
To assess the contribution of foam to overall seat comfort, the foam industry has developed a number of performance tests intended to indicate the suitability of a given foam grade for use in an auto seat. Some of the tests believed to be important in assessing a foam's contribution to comfort include:

- Foam density.
- Hardness and support factor.
- Resilience.

- Airflow.
- Compression set.
- Fatigue.
- Vibration dampening.

Automotive OEM seating specifications have historically been written around these test criteria.

Fogging



Every driver has experienced the fogging phenomenon and car manufacturers have become increasingly concerned about its effect on driver visibility. The problem is most acute when the incidence of light into the vehicle is the most intense as in the case of direct sunlight or on-coming headlights.

Fogging has been defined as the undesirable deposit of a light-scattering film on the interior glass surfaces of a vehicle.^{11.158} The problem began with the introduction of vinyl materials into the passenger compartment in the late 1950s. Phthalate type plasticizers and other ingredients in plastic trim components contributed to the fog film and the famous new car smell.^{11.159-11.160}

The mechanism of film formation is thought to involve the continuous condensation of volatile ingredients contained within many of the components inside the vehicle. The high interior temperatures reached in parked vehicles (see Figure 12.1) provides a driving force for this event.

Samples of these films have undergone chemical analysis and a number of molecules traceable back to flexible polyurethane foam have been found:^{11.161-11.162}

- Catalysts (both the amine and the carrier liquid)^{11.163-11.166}
- Flame retardants^{11.167-11.168}
- Antioxidants (mainly BHT)^{11.169}
- Silicone surfactants^{11.170-11.172}
- Pigment carriers
- Lactones in polyester polyols^{11.173-11.175}

The experimental measurement of fogging is discussed in Chapter 7.

References

- 11.1 Stewart, D. A.; Westfall, P. M.; Quarles, P. D. "Molded Furniture Foam"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 90-93.
- 11.2 Chadwick, F.; McCune, L. "Low Density Molded Foams for Furniture Applications"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 33.
- 11.3 Brown, M.J. "High Sag Factor Foams Boost Comfort and Performance of Car Seats"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 463-467.
- 11.4 Abernathy, H. H. "Isocyanates and Their Reaction Products"; *Rub. World 1955*, 131/6, 765 - 769.
- 11.5 Wall, J. R. "Adaptability of the Physical Properties of Urethane Foam to the Design of Seat Cushions"; a paper given before the Cellular Plastics Division, Society of The Plastics Industry, Inc., Detroit, June, 1960.
- 11.6 Healy, T.T. "Applications of Polyurethane Foam In The Motor Industry"; In *Polyurethane Foams*, Healy, T.T., Ed.; Illiffee Books: London, 1963, 75-92.
- 11.7 Bishop, A. C. "In Situ Foam Moulding For Car Seats"; *Plast. Rub. 1970*, 1/9, 381.
- 11.8 Zick, J. "Upholstery Parts Made by the Foam-In-Place Vacuum Process"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 570-573.
- 11.9 Bayer, H.G. "A Device for the Direct Foam-In-Cover Production of Textile-Fabric Covered Molded Parts, Especially Seat Cushions and Seat Back Rests"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 574-577.
- 11.10 Ostertag, B. "Back-foaming of Car Seats on a Carousel Unit"; *Kunststoffe 1987*, 79/11, 1144-1145.
- 11.11 Zick, J. "In-Mould Foam Fabric System for the European Ford Fiesta-Materials and Processing Characteristics"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 211-215.
- 11.12 Ostertag, B. "Integrated Seat Production for Ford Europe"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 209-210.
- 11.13 Heiberger, R.; Dipietrantonio, B.F.; Katz, J.J. "All-MDI Flexible Foam: First North American Pour-in-Place Automotive Seating"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 44-49.
- 11.14 Pierkes, L. "Modular control systems for PUR-processing"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990; 126-130.
- 11.15 Deno, L. "Automotive seating – the growing appeal of foam-in-fabric"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990; 142-144.
- 11.16 Schneider, F. W.; Grasse, H. "Pour-in-Place Automotive Seating An Established Technology"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990; 149-154.

- 11.17 Schneider, F. W.; Grasse, H.; Gillham, M. "High Volume Pour-in-Place Seating Production Equipment"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 32-39.
- 11.18 Gill, W. A.; Good, R. M.; Hawker, L. E. "Flexible Pour-in-Place Foam Based on TDI"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 40-45.
- 11.19 Murray, D.; Deno, L.; Katz, J. J. "Automotive Seat Production Using the Pour-in-Place Technology"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 172-176.
- 11.20 Patent U.S. 4,692,199, E.F. Kozlowski, E.R. Kruger to Lear Siegler, Inc., September 8, 1987.
- 11.21 *Seating Technology*, Fall 1994; Lear Seating Corporation.
- 11.22 Gabriele, M.; Monks, R. "New Polymers and Processes For Plastics in Automotive"; *Plast. Tech.* **1992**, 38/4, 15-23.
- 11.23 *Trim Retention Bonding*; The Woodbridge Group; 1993.
- 11.24 Andrew, G.D.; Boyer, T.C.; Olari, J.R. "Unique Water Based Release Agents For Foam-To-Fabric Automotive Seat Applications"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 480-486.
- 11.25 Patten, W.; Seefried, C.G. Jr.; Whitman, R.D. "A Rapid Demolding Process for High Resilience Polyurethane Foam"; *J. Cell. Plast.* **1978**, 14/2, 99-101.
- 11.26 Pique, S. "A Versatile and Comprehensive Approach to CFC-Free Polyurethane Hot-Molding"; *Conference Papers, UTECH 96*; Crain Communications: London, 1992; 272-276.
- 11.27 Saunders, J.H.; Frisch, K.C. *Polyurethanes Chemistry and Technology, Part II. Technology*; Interscience: New York, 1964; 99-107.
- 11.28 Woods, G.W. *Flexible Polyurethane Foams Chemistry and Technology*; Applied Science: New Jersey, 1982; 152-158.
- 11.29 Knibbe, D.E. "A Chemical and Physical Comparison of Polyurethane Hot Cure and Cold Cure Molding"; *J. Cell. Plast.* **1985**, 21/4, 264-268.
- 11.30 Freitag, H. A.; Volland, A. "Flexible Polyurethane Molded Foam"; In *Polyurethane Handbook*, Oertel, G., Ed.; Hanser: New York, 1985, 201-222.
- 11.31 Mispreuve, H.; Duff, A.; Gansow, M.; Fangaretti, A. "Recent Developments in Hot Moulding Polyurethane Flexible Foam Technology for Automotive Seating"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 559-563.
- 11.32 Duff, A.; Gansow, M. "Polyurethane Foam Chemistry for Automotive Seating"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 420-425.
- 11.33 Hasegawa, N.; Hayashida, S.; Morita, H.; Yamaguchi, Y.; Doi, T. "A New Polyol for Hot Cure Molded Foam with Improved Resilience"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 426-430.

- 11.34 Nishioka, T.; Matsubara, K.; Sakai, S.; Kita, M. "A New System for Hot Molded Flexible Foam"; *Proceedings of the SPI-32nd Annual Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1989, 16-20.
- 11.35 Hayashida, S.; Horie, A.; Morita, H.; Yamaguchi, Y. "The New Polyol for CFC Free Hot Molded Foam Using High Mold Temperature Process"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1982, 575-578.
- 11.36 Lambach, J. L.; Gill, W. A. "Hot Foam Replacement with Non-CFC HR Foam"; *Proceedings of the SPI-33rd Annual Polyurethane Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1990, 165-171.
- 11.37 "Standard Specification for Flexible Cellular Materials - High Resilience Polyurethane Foam (HR)"; *Annual Book of American Society for Testing and Materials Standards, Volume 09.02*, D 3770 79; ASTM: Philadelphia, 1990, 372-373.
- 11.38 McEvoy, J.; Thakurta, K.; Pique, S.; Bladon, J. "Extra-High Resilience, TDI-based, Polyurethane Flexible Foams for High-Comfort, High-Durability Automotive Seating"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 504-511.
- 11.39 Musgrave, I. "Modern Methods of Moulding Urethane Foams"; *J. Cell. Plast.* **1969**, 5/4, 225-231.
- 11.40 Editorial, "Cold-cure urethane is on the rise"; *Mod. Plast.* **1961**, 48/6, 44-45.
- 11.41 Fabris, H. J. "High Resilience Polyurethane Foams"; In *Advances In Urethane Science and Technology*, Frisch, K. C.; Reegen, S. L.; Eds.; Technomic: Lancaster, Pa., 1974, 108-129.
- 11.42 Khameneh, K.N.; Cosman, J.P.; Hunter, D.G. "A New Generation of High-Productivity Polyols for HR Molded Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 253-260.
- 11.43 Pique, S. "Low-Density, High-Resilience Foams for Automotive Seating, Based on TDI"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 8.
- 11.44 Berthevas, P.R.; Hamada, S. "Low Viscosity/High Solids Copolymer Polyols for Low Density High Resilience Moulding"; *Proceedings of the PU China Conference*; Crain Communications: London, 1995.
- 11.45 Hatano, S.; Yasuda, N.; Hayashida, S.; Takeyasu, H.; Kozawa, S. "High Molecular Weight Polyols for Automotive HR Foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 112-116.
- 11.46 Noakes, C.W.; Casagrande, G. "Liquid CO₂ Blown Foam for Automotive Flexible Moulding"; *Conference Papers, UTECH 96*; Crain Communications: London, 196; Paper 11.
- 11.47 Patent U. S. 3,179,606 W.E. Prescott and S.P. Edwards to The Dow Chemical Company, April 20, 1965.
- 11.48 Priester, R.D.; Peffley, R.D.; Turner, R.B.; Herrington, R.M. "High Resiliency Polyurea Foam - An Improved Flexible Foam Matrix"; *Proceedings of the SPI-32nd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 21-28.

- 11.49 Humbert, H.; Klockemann, W. "PUREA Foam-A Superior HR-Flexible Foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 117-120.
- 11.50 Grigsby, R.A. "Water Blown Polyuea Foam"; *Proceeding of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 344-351.
- 11.51 Priester, R.D.; Turner, R.B. "The morphology of flexible polyurethane matrix polymers"; In *Low density cellular plastics, Physical basis of behaviour*; Hilyard, N.C.; Cunningham, A., Ed., Chapman and Hall: London, 1994.
- 11.52 Dounis, D.V.; Wilkes, G.L. "A Structure-Property Comparison Between Flexible Molded Polyurethane Foams and Conventional Slabstock Polyurethane Foams"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 353-361.
- 11.53 Creswick, M.W.; Lee, K.D.; Turner, R.B.; Huber, L.M. "Urea Domain Structures in Polyurethane Foams"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 11-17.
- 11.54 Wood, A. S. "MDI-based flexible PUR Foam looks like a real winner"; *Mod. Plast. Intl.* **1984**, 14/3, 36-39.
- 11.55 Buethe, I.; Reichel, C. J.; Taylor, J. D. "Flexible Polyurethane Molded Foams Based On MDI"; *J. Cell. Plast.* **1984**, 20/4, 285-290.
- 11.56 Volland, R.; Lindsey, J.; Schoberth, W. "A Technical Update On MDI Based Molded Flexible Foams"; *J. Cell. Plast.* **1984**, 20/6, 416-422.
- 11.57 Haggerty, T. I.; Katz, J. J.; Watts, A.; Brooks, M. F. "All-MDI Flexible Foam - Advantages In Single And Dual Hardness Automotive Seat Molding"; *J. Cell. Plast.* **1985**, 21/4, 269-276.
- 11.58 Reichel, C. J.; Berkowski, L. A.; Taylor, J. D. "Lower Density MDI Based Flexible Molded Foams"; *J. Cell. Plast.* **1986**, 22/4, 287-294.
- 11.59 Carey, D. G.; Turner, R. B. "Low Density Urethane Foam for Automotive Seating Using Low Functionality MDI and Polyol"; *J. Cell. Plast.* **1989**, 25/4, 353-370.
- 11.60 Thoen, J.; Elwell, R.; Sewell, R.; Broos, R.; Pellacani, L.; Pedroni, L.; Bergianti, G. "Replacement of Chlorofluorocarbons in All MDI Automotive Seating Foams"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 100-107.
- 11.61 Huygens, E.; Leenslag, J.W.; Murty, V.S. "Recent Advances in All-MDI Flexible Moulded foam"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 467-477.
- 11.62 Wolf, K.D. "MDI-Based Flexible Moulded Foam with Low Density for Automotive Seating"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 6.
- 11.63 Tan, A.; Deno, L.; Leenslag, J.W. "Low Density All-MDI Polyurethane Foams for Automotive Seating"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 7.
- 11.64 Tan, A.; Deno, L.; Leenslag, J.W. "Low Density All-MDI Polyurethane Foams for Automotive Seating"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 518-524.

- 11.65 Obata, M.; Utsumi, H.; Ohkubo, K.; Uneo, K.; Sakai, S. "A New All Water blown MDI based Flexible Moulded Foam System"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 406-412.
- 11.66 Yoshimura, H.; Okuzono, S.; Arai, S.; Lowe, D. W. "Innovative Tertiary Amine Catalyst Systems for CFC Free All MDI Based HR Foam"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 10-18.
- 11.67 Muha, K.; Harakal, M. E. "New Surfactant and Catalysts for All Water Blown MDI Cold Cure Molded Foam"; *Proceedings of the SPI-33rd Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990; 2-9.
- 11.68 Fiorentini, C.; Taverna, M.; Luca, J. "Liquid Carbon Dioxide Blown Molded Foams: the Technology and Initial Applications"; *Proceedings of the 1995 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1995, 476-480.
- 11.69 Cavender, K. D.; Hawker, L. E. "New Considerations in Isocyanate Selection for Automotive Seating Foam"; *Proceedings of the SPI-32nd Annual Polyurethane Technical/Marketihg Conference*; Technomic: Lancaster, Pa., 1989; 594-601.
- 11.70 Buethe, I.; Reichel, C.J.; Taylor, J.D. "Flexible Polyurethane Molded Foams Based on MDI"; *Proceedings of the SPI-6th International Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983; 156-160.
- 11.71 Haggerty, T.I.; Katz, J.J.; Watts, A.; Brooks, M.F. "All-MDI Flexible Foam-Advantages in Single and Dual Hardness Automotive Seat Molding"; *Proceedings of the SPI-28th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1984, 70-76.
- 11.72 Volland, R.; Lindsey, J.; Schoberth, W. "A Technical Update on MDI Based Molded Flexible Foams"; *Proceedings of the SPI-28th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1984, 86-91.
- 11.73 Allen, R.C.; Reid, G.E.; Jasenak, J.R. "Practical Applications for MDI Flexible Molded Foams"; *Proceedings of the SPI-30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 256-261.
- 11.74 Pham, T.; Van Assche, J.; Watts, A.; Lockwood, R.J. "MDI Based Flexible Foam: A Status Report on World Developments"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 532-537.
- 11.75 Patent U.S. 4,714,574, R.J. Tenhagen to BP Chemicals Ltd., December 22, 1987.
- 11.76 Patent U.S. 4,965,029, W.A. Lidy and R.J. Tenhagen to Polyol International BV, October 23, 1990.
- 11.77 Patent U.S. 5,273,695, M.J. Brown and W.A. Lidy to The Dow Chemical Company, December 28, 1993.
- 11.78 Brown, M.J. "The Industrial Production of Dual Hardness Foam Seats Using Polymer Polyols, Robots and Unmodified Moulds"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 538-543.
- 11.79 *Dow Automotive, Passion For Performance, Automotive Seating, A Total Solutions Package*; The Dow Chemical Company: Form No. CH 500-012-E-1292.
- 11.80 Patent Canadian 2,012,410, M.J. Brown and W.A. Lidy to Polyol International BV, November 15, 1994.

- 11.81 Brown, M.J. "Layered Foam Boosts Comfort and Performance of Car Seats"; *Conference Papers, UTECH 92*; Crain Communications: London, 1992; 67-70.
- 11.82 Brown, M.J. "High Sag Factor Foams Boost Comfort and Performance of Car Seats"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992; 463-467.
- 11.83 Brown, M.J.; Bocquel, P.; Corelli, B.; Gatouillat, G.; Lidy, W.A.; Thanh, H.P. "Multi-Hardness seating using polymer polyol technology"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988, 68-71.
- 11.84 Woods, G. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science Publishers: London, 1982; 151-173.
- 11.85 Freitag, H. A.; Volland, A. "Flexible Polyurethane Molded Foam"; In *Polyurethane Handbook*, Oertel, G., Ed.; Hanser: New York, 1985, 201-222.
- 11.86 Woods, G. *The ICI Polyurethanes Book*; John Wiley and Sons: New York, 1987; 71-84.
- 11.87 Patten, W.; Seefried, C.G.; Whitman, R.D. "A Rapid Demolding Process for High Resilience Polyurethane Foam"; *J. Cell. Plast.* **1978**, 14/2, 99-101.
- 11.88 Petrella, R.G.; McGovern, M. J. "Fast Demold Catalyst for TDI Based Molded Foam"; *Proceeding of the SPI-30th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 138-144.
- 11.89 Pauperio, A.; Noakes, C.; Bagnariolli, E.; De Almeida, N. "Fast Demold, Dual Hardness Foam for General Motors of Brasil"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 338-342.
- 11.90 Killen, D.; Blackwell, J.B.; Waldron, K.C. "Processing Machinery For Polyurethane Foams"; In *Polyurethane Foams*, Healy, T.T., Ed.; Iliffe Books: London, 1963, 29-54.
- 11.91 Lanigan, W.J. "Microwave curing of flexible polyurethane foam mouldings"; *British Plast.* **1963**, 36, Oct, 562-565.
- 11.92 Editorial, "Microwave Power For Fast Curing"; *Rub. Plast. Age* **1963**, 44/5, 525.
- 11.93 Parkinson, J.C. "Moulding flexible polyurethane foam"; *British Plastics* **1964**, 37/3, 146-147.
- 11.94 Stoltion, R.E.; Wilkinson, W.V. "Epoxide resin moulds for forming and curing polyurethane foam by means of microwave energy"; *Int. Plast. Eng.* **1964**, Oct, 315-316.
- 11.95 Blackwell, J.B.; Killen, D. "Multi-Magnetron and Phenolic Moulds — A New Concept in Flexible Foam Moulding"; *J. Cell. Plast.* **1965**, 1/2, 285-290.
- 11.96 Buist, J.M. "Moulding of flexible urethane foam"; *Rubber Journal* **1966**, 148/3, 26-34.
- 11.97 Hoskins, A. "Microwave Curing of Cellular Plastics"; *Polymer Conference Series*, Wayne State University, 1967.
- 11.98 Rajan, R. "Microwave Curing Of Polyurethane Foams For Automotive Applications"; *J. Cell. Plast.* **1968**, 4/4, 304-308.
- 11.99 Benning, C.J. *Plastic Foams: the physics and chemistry of product performance and process technology, Volume 11: Structure Properties, and Applications*; John Wiley and Sons: New York, 1969, 163.

- 11.100 Buist, J.M.; Woods, G. "Moulding of Flexible Urethane Foam"; *Trans. Inst. Rub. Ind.* **1965**, 41/1, T1-T23.
- 11.101 Maxey, E. M. "Recent Advances In Flexible Urethane Foams"; In *Advances In Urethane Science And Technology, Volume 1*, Frisch, K. C.; Reegen, S. L., Eds.; Technomic: Lancaster, Pa., 1971, 176-180.
- 11.102 Lindt, J.T.; Kostrzewski, W. "Flow Mechanics of Polyurethane Foam Formation"; In *Urethane Chemistry and Applications*; Edwards, K.M., Ed.; ACS Symposium Series 172, 1981, 167-178.
- 11.103 Bessette, M.D.; Sundstrom, D.W. "Rheology Of Model Polyurethane Foams"; *Polym. Proc. Eng.* **1985**, 3(1 & 2), 25-35.
- 11.104 Kostrzewski, W.; Lindt, J.T. "Flow Characterization Of A Chemically Blown Polymeric Foam III"; *J. Polym. Eng.* **1986**, 6/1-4, 187-199.
- 11.105 Tillotson, R.; Patrick, M.A. "Mathematical modelling of polyurethane foam flow"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988; 230-235.
- 11.106 Leung, S.K.; Patten, W. "New Cell Opening Surfactant for HR Molded Foam"; *Proceedings of the SPI-32nd Annual Polyurethane Technical/ Marketing Conference*; Technomic: Lancaster, Pa., 1989; 619-622.
- 11.107 Koshute, M.A. "Advances in PHD Polyol technology for Automotive Molded Flexible foam"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa.; 1991, 121-126.
- 11.108 Brune, A.; Klietsch, J.; Zellmer, V. "Design of New Stabilizer for HR-Moulded Foam"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 12.
- 11.109 Frensdorff, H.K. "Polyurethane Foams; Stability, Collapse, Shrinkage"; *Rubber Age* **1958**, 812-818.
- 11.110 Malwitz, N.; Manis, P.A.; Wong, S.W.; Frisch, K.C. "Amine Catalysis of Polyurethane Foams"; *Proceedings of the SPI-30th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1986, 338-353.
- 11.111 Battice, D.R.; Lopes, W.J. "New Cell Opening Surfactants for Molded High Resiliency Polyurethane Foam"; *Proceedings of the SPI-30th Annual Technical/Marketing Conference*; Technomic; Lancaster, Pa., 1986, 145-148.
- 11.112 Turner, R.B.; Nichols, J.B.; Kuklies, R.A. "The Influence of Viscosity in Cell Opening of Flexible Molded Foams"; *Proceedings of the SPI-31st Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1988, 18-21.
- 11.113 Cloetens, R.; Lidy, W.A.; Phillips, B.D.; Thomas, D.B. "Polymer Polyols—Properties and Application"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 480-489.
- 11.114 Suh, K.W.; Webb, D.D. "Cellular Materials" In *Encyclopedia Of Polymer Science And Engineering, Second Edition, Volume 3*; John Wiley & Sons: New York, 1985; 4.
- 11.115 Derderian, E.J.; El Ghobary, H.; Esposito, G.; Muller, L. "Cell-Opening, Low Fugitivity, Delayed-Action Catalysts for HR Molded Foam"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 274-279.

- 11.116 Brune, A.; Klietsch, J.; Zellmer, V. "Design of New Stabilizer for HR-Moulded Foam"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 12.
- 11.117 Burkhart, G.; Klietsch, J.; Zellmer, V. "New Surfactant for High Resiliency Moulded Polyurethane Foam Improves Processing"; *Proceedings of the SPI/ISOPA Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 127-131.
- 11.118 Wolfe, H.W. "Designing High Resilience Molded Foams"; *J. Cell. Plast.* **1973**, 9/3, 134-138.
- 11.119 Patten, W.; Seefried, C.G. "High Resiliency Urethane Foams for Automotive Seating Applications"; *J. Cell. Plast.* **1976**, 12/1, 41-48.
- 11.120 Draganski, R.S. "Principles of High Speed Automotive Urethane Seat Molding"; *J. Cell. Plast.* **1978**, 14/5, 281-286.
- 11.121 Webb, D.D. "Composite Flexible Molded Urethane Foam"; *Proceedings of the SPI-26th Annual Technical Conference*; Technomic: Lancaster, Pa., 1981, 105-108.
- 11.122 Hartings, J.W.; Hagan, J.H. "Fatigue Investigations of Urethane Seat Pads,"; *J. Cell. Plast.* **1978**; 14/2, 81-86.
- 11.123 Ashe, W.A.; Grace, O.M.; Otten, J.G. "BASF Wyandotte Pounding Fatigue Apparatus"; *Proceedings of the SPI-25th Annual Urethane Division Technical Conference*; Technomic: Lancaster, Pa., 1979, 107-112.
- 11.124 Griffin, M.J. "The Evaluation of Vehicle Vibration and Seats"; *Applied Ergonomics* **1978**; 9, 15-21.
- 11.125 Griffin, M.J. "Occupational Human Vibration"; In *Occupational Ergonomics*; Bhattacharya, A.; McGlothlin, J.D.; Eds.; Marcel Dekker: New York, 1996, 605-626.
- 11.126 Hanes, R.M. "Human Sensitivity To Whole-Body Vibration In Urban Transportation Systems: A Literature Review"; *Applied Physics Laboratory Report TPR-004*; The John Hopkins University: Silver Springs, Maryland, 1970.
- 11.127 British Standards Institution "Measurement and Evaluation of Human Exposure to Whole-Body Vibration and Repeated Shock"; BS 6841, 1987.
- 11.128 Griffin, M.J. *Handbook of Human Vibration*; Academic Press: London, 1990.
- 11.129 Goldman, D.E.; von Gierke, H.E. "Effects Of Shock And Vibration On Man"; In *Shock and Vibration Handbook*; Harris, C.M.; Crede, C.E., Eds.; McGraw-Hill: New York, 1961, 44.1-44.51.
- 11.130 Anon. "Riding Comfort Factors"; *SAE Journal* **1924**, 14/3, 335-337.
- 11.131 Lay, W.E.; Fisher, L.C. "Riding Comfort and Cushions"; *SAE Journal* **1940**, 47/5, 482-496.
- 11.132 Paton, C.R.; Pickard, E.C.; Hoehn, V.H. "Seat Cushions and the Ride Problem"; *SAE Journal* **1940**, 47/1, 273-283.
- 11.133 Versace, J. 'Measurement Of Ride Comfort'; Proceedings of the SAE Automotive Engineering Congress and Exposition, Detroit, Michigan, 1963; Paper No. 638A; SAE: Warrendale, Pa.

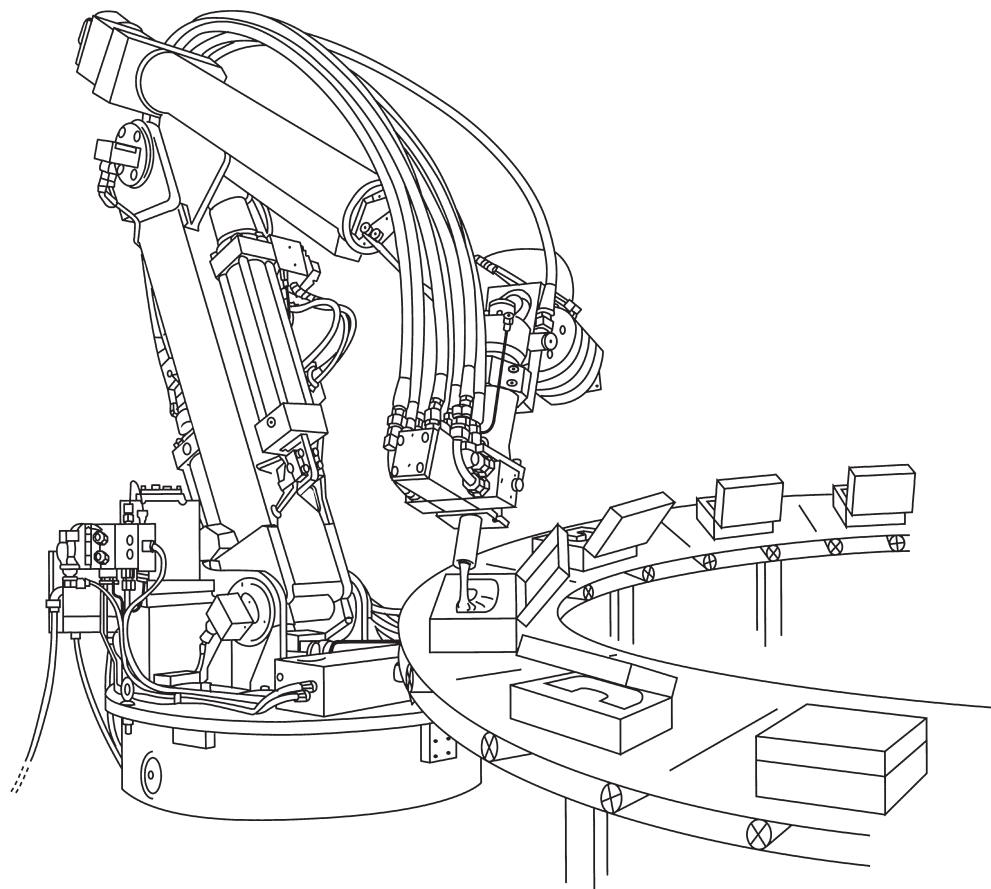
- 11.134 Their, R.H. "Measurement of Seat Comfort"; *Automotive Engineer* **1963**, February, 64-66.
- 11.135 Smith C.C.; Kwak, Y.K. "Identification of the Dynamic Characteristics of a Bench-Type Automotive Seat for the Evaluation of Ride Quality" *Trans. ASME J. Dynamic Systems, Measurement and Control* **1978**, 100/3, 42-49.
- 11.136 Varterasian, J.H. "Measuring Automobile Seat Ride Comfort"; Proceedings of the SAE International Congress and Expositon, Detroit, Michigan, 1982; Paper No. 820309; SAE: Warrendale, Pa.
- 11.137 Kamijo, K.; Tsujimura, H.; Obara, H.; Katsumata, M. "Evaluation of Seating Comfort"; Proceedings of the SAE Passenger Car Meeting, Troy, Michigan, 1982; Paper No. 820761; SAE: Warrendale, Pa.
- 11.138 Editorial, "Measuring Seat Comfort" *Auto. Eng.* **1993**, July, 25-30.
- 11.139 Thakurta, K.; Koester, D.; Bush, N.; Bachle, S. "Evaluating Short and Long Term Seating Comfort"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1995; Paper No. 950144; SAE: Warrendale, Pa.
- 11.140 Keegan, J.J. "Evaluation and Improvement of Seats"; *Ind. Med. Surgery* **1962**, 31/4, 137-148.
- 11.141 Keegan, J.J. "Designing Vehicle Seats For Greater Comfort"; *SAE Journal* **1964**, 72/9, 50-55.
- 11.142 Hall, M.A.W. "Back pain and car-seat comfort" *Appl. Erg.* **1972**, 3.2, 82-91.
- 11.143 Jones, J.C. "Methods and Results of Seating Research"; *Erg.* **1969**, 12/2, 171-181.
- 11.144 Oliver, R.J. "A Study of the Comfort Characteristics of Production Car Seats"; The Motor Industry Research Association, Report # 1970/12, Lindley, England, September 1970.
- 11.145 Leatherwood, J.D. "Vibrations Transmitted To Human Subjects Through Passenger Seats And Considerations Of Passenger Comfort"; *NASA Technical Note TN D-7929*; National Aeronautics and Space Administration: Washington, D.C., 1975.
- 11.146 Habsburg, S.; Middendorf, L. "What Really Connects in Seating Comfort? Studies of Correlates of Static Seat Comfort"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1977; Paper No. 770247; SAE: Warrendale, Pa.
- 11.147 Maertens, D. "Automotive Seating Comfort Criteria"; GM-10 Report, Third Edition, January 25, 1988.
- 11.148 Viano, D.C.; Andrzejak, D.V. "Research Issues on the Biomechanics of Seating Discomfort: An Overview with Focus on Issues of the Elderly and Low-Back Pain"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1992; Paper No. 920130; SAE: Warrendale, Pa.
- 11.149 SAE, *Seat System, Comfort and Safety*; SP-963; SAE: Warrendale, Pa., 1993
- 11.150 Schreffler, R. "Take A Seat"; *Auto. Ind.* **1993**, June, 23.
- 11.151 Keebler, J. "Hot Seat, Supplier spends billions to search for ways to improve customer comfort"; *Auto. News*, Oct. 25, 1993.
- 11.152 Editorial, "What's New In Seating"; *Fleet Owner* **1993**, December, 96.

- 11.153 Editorial, "What is comfort? Static and dynamic versions differ"; *Urethanes Tech.* **1994**, 11/5, 30.
- 11.154 Sawyer, C.A. "In Search of the Perfect Seat"; *Auto. Ind.* **1994**, February, 136.
- 11.155 Hughes, I. "Which automotive seat cushioning is best?-a benchmarking exercise"; *Urethanes Tech.* **1995**, 12/1, 30-34.
- 11.156 Blair, G.R.; Horn, R.J. "Fleet Durability Testing of Moulded Polyurethane Foam and Competitive Automotive Cushions"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 5.
- 11.157 Runkle, V.A. "Benchmarking Seat Comfort"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1994; Paper No. 940217; SAE: Warrendale, Pa.
- 11.158 "Standard Test Method for Determination of Fogging Characteristics of Vehicle Interior Trim Materials"; American Society for Testing and Materials, D 5393-93; ASTM: Philadelphia, 1993.
- 11.159 Somers, N.; Mulrenin, E.A. "General Motors Fog Test (GM9305P) Modified for Improved Repeatability"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1992; Paper No. 920502; SAE: Warrendale, Pa.
- 11.160 Maxwell, J. *Plastics in the automotive industry*; Woodhead Publishing Ltd.: Cambridge, 1994, 72.
- 11.161 Editorial, "Research Suggests That PU May Cause Fogging"; *Eur. Plast. News* **1995**, 22/1, 20.
- 11.162 Myers, J. "Efforts to curb auto VOC emissions focus on PUR"; *Mod. Plast.* **1995**, June, 17-18.
- 11.163 Jensen, T.E.; Richert, J.; Carter, R.O.; McCallum, J.B.; Henrickson, D.R. "Volatile Present in Low Density Polyurethane foams: Composition and Methods of Analysis"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1987; Paper No. 870316; SAE: Warrendale, Pa.
- 11.164 Diblitz, K.; Hoell, D. "Incorporable Amine Catalysts for Flexible Foams without Fogging"; *Conference Papers, UTECH 92*; Crain Communications: London, 1992; 80-85.
- 11.165 Diblitz, K.; Diblitz, C. "THANCAT DA Line-Highly Effective Catalysts for All-Water-Blown HR Foam"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 348-358.
- 11.166 Yoshimura, H. "Characterization of New Amine Catalysts for all Water blown Flexible Foams"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994; Paper 12.
- 11.167 Blundell, C.; Wuenstenen, J. "The Fogging Performance of Flame Retardants in Flexible Polyurethane Foam"; *Conference Papers, UTECH 92*; Crain Communications: London, 1992; 76-79.
- 11.168 Baatz, G.; Franyutti, S. "Low-Fogging Polyester-Based Flexible Foams"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994; Paper 9.
- 11.169 Hill, R.A. "New Antioxidant Package for Polyether Polyols, with Reduced Fogging Behaviour"; *Proceedings of the SPI-34th Annual Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 459-462.

- 11.170 Brune-Fisher, A.; Burkhardt, G.; Zellmer, V. "New Concepts in Designing Silicone Surfactants for HR-Molded Foams"; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 267-273.
- 11.171 Brune, A.; Klietsch, J.; Zellmer, V. "Design of New Stabilizers for HR-Moulded Foam"; *Conference Papers, UTECH 96*; Crain Communications: London, 1996; Paper 12.
- 11.172 Harakal, M.E.; Grabowski, W.; Desnier, M.C. "Reduced Fogging, FR and Non-FR, Polyester Urethane Silicone Surfactants"; *Proceedings of the 1996 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1996, 380-382.
- 11.173 Soler, J.; Monso, J.M.; Duocastella, L. "Low Fogging Flexible Polyurethane Foams Based on Polyolesters"; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 552-557.
- 11.174 Soler, J.; Monso, J.M.; Duocastella, L. "Low Fogging PU Foams based on Polyester Polyols"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994; Paper 8.
- 11.175 Editorial, "A clear view of fogging"; *Urethanes Tech.* **1995**, 11/6, 16.

Chapter 12

Specialty Molded Foams



Specialty molded foams include the semiflexible, semirigid and integral-skin classifications. In recent years, these classes of foams have seen significant volume growth in automotive and recreational applications.

Chapter 12

Specialty Molded Foams

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Specialty molded polyurethane foams include semiflexible, semirigid and integral-skin foam technology areas. These foams bridge the range of resilience and hardness between the softer foams for seating applications and rigid foams for insulation. An important property of these foams of intermediate flexibility is their low resilience/elasticity which results in a slow rate of recovery after deflection. The combination of higher load bearing and slow recovery gives these foams good shock-absorbing characteristics. The principles and mechanisms of energy absorption by cellular polymers are discussed in References 12.1-12.18. Specialty molded foams have found widespread use in automotive applications like integral skin foams for steering wheels and in headliners. Finally, specialty molded foams have been utilized for meeting new government safety regulations. These newer applications include supplemental inflatable restraint (SIR) doors, knee bolsters, door panels for side-impact and pillars for head-impact requirements.

For this chapter, molded semiflexible foams will be defined as those which have higher hardness, higher density and lower resilience characteristics than typical molded seating foams. The key automotive application areas for semiflexible foams are instrument panels, door panels, arm rests, headliners, NVH and other interior trim parts.

Semirigid molded foams have more of a rigid character and may not recover 100% after deformation. These include molded foams for impact energy management applications. Semirigid foams find use in door panels for side-impact, pillars for head-impact, knee bolsters and in bumper applications.

Integral-skin foams have an attached, densified outer skin which is produced during manufacture. These foams had previously required the use of halogenated hydrocarbon or other volatile solvents to produce the gas used for polymer expansion and skin formation. Technology to produce these foams using all-water-blown chemistry is available today.

Specialty molded foams are required to meet the stringent foam physical property requirements of the OEMs (Original Equipment Manufacturers). The specialty molded foams must also meet additional specifications and

processing requirements of the molder. The industry demands for improved productivity, lighter weight, lower cost and part consolidation has provided many new opportunities and challenges for specialty molded foams. The finished composite parts (i.e., vinyl skin, foam and substrate) must also meet stringent quality control requirements for dimensional stability, hardness, color stability, fit-and-finish and foam-related defects. Specialty molded foam parts for automobile interiors must also meet tough specifications for window fogging, discoloration (staining) and embrittlement due to the high temperature exposures encountered in the interior of automobiles. Typical temperature exposures are illustrated in Figure 12.1.

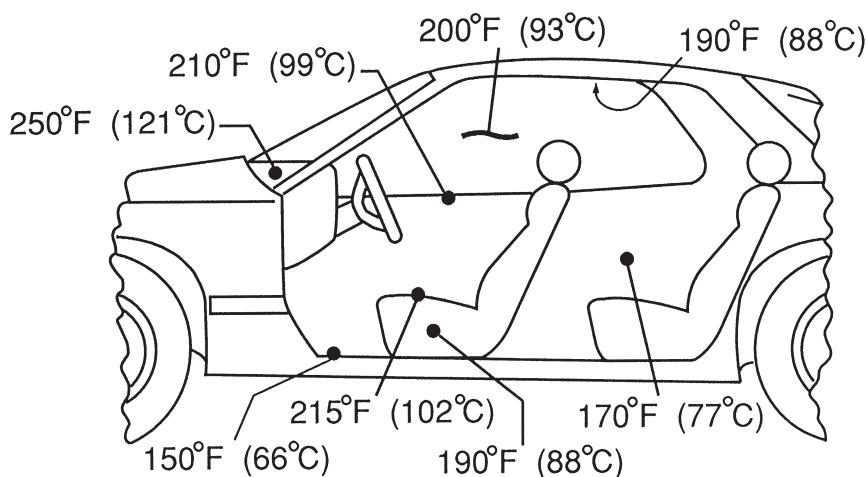


Figure 12.1 Typical Temperatures Found In A Parked Car In The Southern United States (compiled from References 12.19-12.25)

Specialty molded foams is one of the most challenging areas in the polyurethane industry. Manufacturing specialty molded foams is one of the most complex areas in the automotive market due to the complexity of the foam chemistry, the processing and the diversity of parts made. The need to manufacture consistent quality parts is complicated by the use of a variety of substrates (inserts), skins, fabrics and mats which are incorporated during the manufacturing of the composite parts. In addition, complicated and intricate mold geometry's make flowability, foam stability and internal foaming pressure critical processing parameters. Finally, the multiplicity of composite parts combined with different processing requirements present great challenges in troubleshooting the specialty molded foam process. Figure 12.2 is a cause-and-effect diagram which illustrates some of the factors affecting the quality of specialty molded parts.

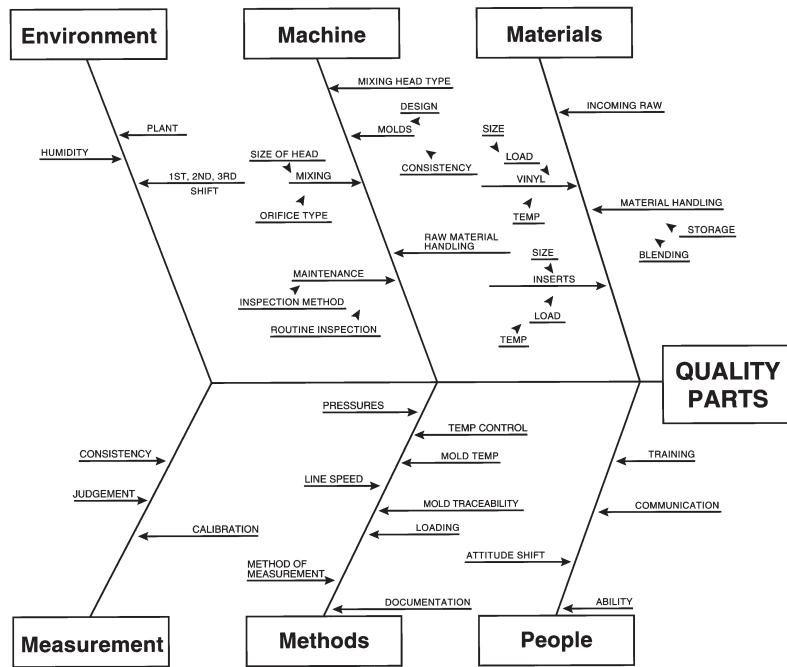


Figure 12.2 Cause-and-Effect Diagram for the Production of Specialty Molded Parts

Applications for specialty molded foams include automobile interiors and exteriors, furniture, packaging, crash helmets, protective sportswear, bicycle seats, motorcycle seats and toys. The focus of this chapter concerns the automobile industry's usage of specialty molded foams. Some of the typical automotive application areas for specialty molded foams are shown in Figure 12.3.

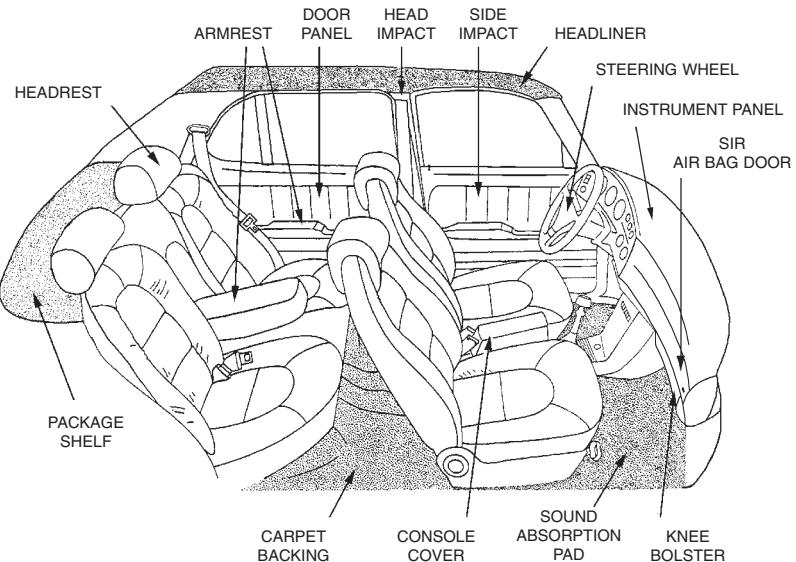


Figure 12.3 Typical Automotive Uses for Specialty Molded Foam

Reviews of the large and complicated field of specialty molded foams can be found in References 12.26-12.34.

SEMIFLEXIBLE FOAMS

In recent years, semiflexible molded foams have been utilized for many applications in the automotive area. The major applications are instrument panels and interior trim parts. Semiflexible foams are almost all water-blown and, like molded foams, have over 90% open-cell structure. The openness of semiflexible foams is critical, since most finished parts cannot be crushed after demold to eliminate shrinkage. Semiflexible foams usually have a higher hardness and a lower resilience than molded seating foams. However, like flexible foams, they recover completely over time from high levels of compression.

The manufacture of most semiflexible foam parts is very complex and involves the merging of five distinct processes as shown in Figure 12.4.

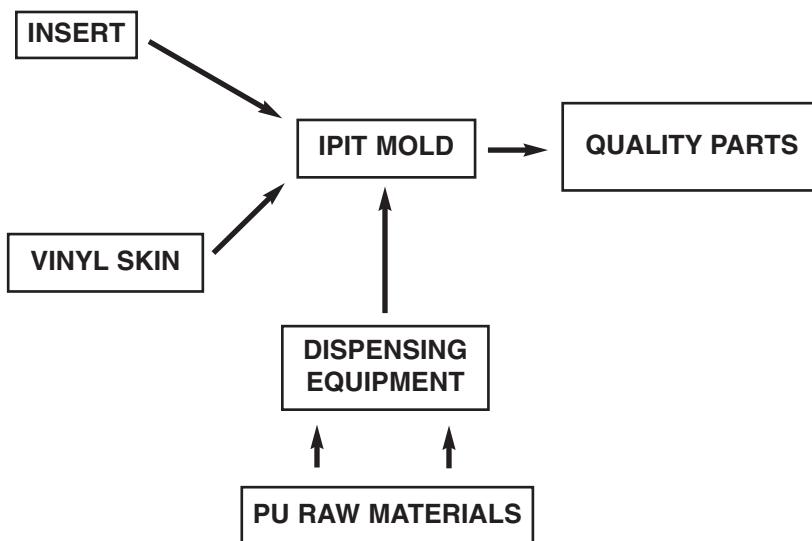


Figure 12.4 Simplified Semiflexible Foam Process Diagram

If foam-related defects are discovered in semiflexible foam parts, the polyurethane foam chemicals or the assembly process are often held accountable. Foam-related defects in the finished parts are usually addressed by modifying the processing conditions on the line or by modifying the polyurethane chemical formulation. Historically, the molds, and foam dispensing equipment (all parts of the foam assembly process) are usually not considered to be the cause of the foam-related defects. Moreover, the skin and substrate (insert) are rarely considered during troubleshooting to be the cause of the foam-related defects. Later in this chapter (Figures 12.8 and 12.9) data is presented to show how the vinyl skin and the insert were the major contributor in foam-related defects on actual instrument panel production lines. During the final inspection of the composite parts, root cause analysis and troubleshooting of foam related defects must also include the foam molds, skin, insert, foam dispensing equipment, plant personnel, the plant environment and the polyurethane chemicals. In order to identify and correct the actual production line problem, and not just treat symptoms, extensive root cause analysis and troubleshooting emphasis must be placed on the entire semiflexible foam process.

CHEMISTRY

A typical semiflexible foam formulation is presented in Table 12.1.

Table 12.1 Typical Semiflexible Foam Formulation

| Component | Parts by Weight |
|---------------------------|-----------------|
| SPECFLEX NC 630 Polyol | 80.0 |
| SPECFLEX NC 710 Copolymer | 20.0 |
| Cross-linker | 1.5 |
| Water | 2.2 |
| Catalyst | 0.6 |
| Black Colorant | 0.3 |
| Adhesion Promoter | 2.0 |
| Cell Opener | 1.0 |
| Polymeric MDI, Index | 105 |

The two main components are the base polyol and copolymer polyol (CPP). The base polyol is utilized at levels between 70-100%. The nominal molecular weight of base polyols range from 4500 to 6000 for triols and 2000 to 4000 for diols. Ethylene-oxide-capped polyether polyols have replaced most polyester polyols as the base polyol. The primary hydroxyl content is usually greater than 75% and the capping range is typically 10-20%.^{12,35} The other major component in the polyol blend is the CPP. Levels of 0-20% are common. The base polyol and CPP are blended with low-molecular-weight cross-linkers. Cross-linkers are traditionally used to build hardness and promote faster demold. The level of cross-linker may vary depending on hardness requirements of the finished parts. Cross-linkers usually reduce the flowability and increase the density (fill weights) of the parts. An alternate approach for increased hardness in semiflexible foams while offering processing advantages (see Table 12.2) over increased levels of cross-linker is to use higher levels of CPP in the formulations. The overall pluses and minuses for the addition of CPP and cross-linkers to a standard semiflexible foam formulation are seen in Table 12.2.

Table 12.2 Effect Of Cross-linkers vs CPP On Processability

| PROPERTY | CPP | CROSS-LINKER |
|------------------------|----------|--------------|
| Processing Latitude | Improved | Varies |
| Demold Time | Faster | Faster |
| Foam Openness | More | Less |
| Hardness(at = density) | Higher | Higher |
| Compression Sets | Higher | Lower |
| Iso Consumption | Lower | Higher |

Water levels are chosen to give free rise densities from 3 to 6 pounds per cubic foot (48-96 kg/m³). Packing factors of 1.5 to 2.0 are typically used to produce molded densities of 4.5 to 12.0 pounds per cubic foot (72-192 kg/m³).

Cell-openers are utilized from 1 to 2 parts per hundred in semiflexible foams to reduce the internal foam pressure during the cure cycle and thus reduce pressure-relief voids and “parting lines”. They also provide open cell structure to control shrinkage, but may also reduce the hardness of the parts.

Typically, the effect of silicone surfactants is to tighten up the foam and provide improved cell-size regulation and stability control along with improved compatibility of the blended formulation. The increased tightness of the foams reduces the tendency to exhibit extrusion-collapse voids. However, if utilized at too high a concentration, silicone surfactants can cause pressure-relief voids, parting lines and blown covers. Surfactants are utilized from 0.0 to 0.5 parts per hundred in semiflexible foam formulations. Levels will vary, depending upon processing needs, mold design and skin quality. Adhesion of the foam to lower-quality vinyl skins may be adversely affected by the use of high levels of silicone surfactants.

Adhesion promoters can be added, depending upon the quality of the vinyl skin, to improve adhesion between the polyurethane foam and the vinyl skin. Polyester polyols ranging in molecular weight from 500 to 2000 are useful at the 1-4 parts-per-hundred level. Higher molecular weights show better adhesion but have poorer phase stability and shelf life. Usage above 3 parts per hundred lowers the overall foam system reactivity.

The catalysts employed in semiflexible foams are predominately blends of tertiary amines. Tertiary amines provide the optimum physical properties and line processing characteristics. However, tertiary amine catalysts create concern with respect to vinyl skin discoloration. To reduce the levels of tertiary amine catalysts in foam formulations and thus improve staining, the industry is moving to reactive amine catalysts, metal catalysts and/or organic salt type catalysts. The levels of catalyst vary, depending upon demold time, physical property and processing requirements. Amounts range from 0.2 to 1.5 parts per hundred parts polyol. The effect of catalyst level on the rise profile of a typical semiflexible foam is shown in Figure 12.5.

Semiflexible foam formulations may also include carbon black or liquid-type dyes. Dyes are preferred in semiflexible foam formulations because of the ease of handling and reduced wear on equipment. However, dyes are more expensive than carbon black especially if very dark parts are required. Usage levels range from 0.3 to 1.0 parts per hundred parts polyol. Aesthetically, this is done so that any foam exposed to sunlight will not change color dramatically in areas visible to the automobile occupant.

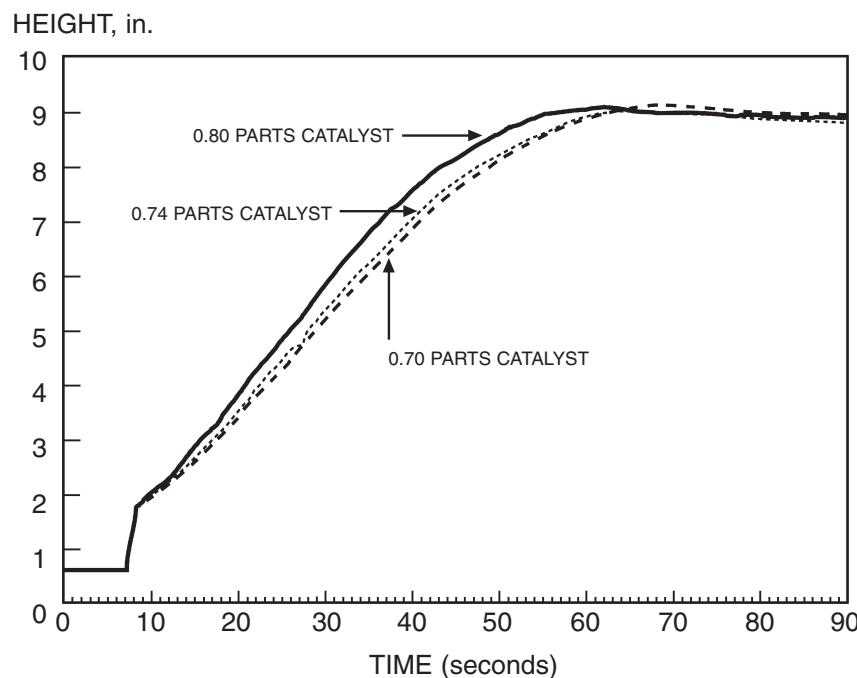


Figure 12.5 Catalyst Effects On Rise Profile

Semiflexible polyurethane foams are made by the reaction of an isocyanate and a blended polyol formulation. Polymeric methylene diphenyl diisocyanate (MDI) is the preferred choice. Polymeric MDI (PMDI) has gradually replaced toluene diisocyanate-based prepolymers. The functionality and general performance properties of selected polymeric MDIs are given in Table 12.3.

Table 12.3 Effect of Polymeric MDI Functionality on Processing

| PMDI | FUNCT. | FLOWABILITY | HARDNESS | CURE |
|-----------|---------|-------------|----------|------|
| PAPI 4094 | 2.2-2.3 | High | Low | Slow |
| PAPI 4901 | 2.2-2.4 | Med | Med | Med |
| PAPI 4095 | 2.3-2.5 | Med | Med | Med |
| PAPI 4027 | 2.6-2.8 | Low | High | Fast |

Since hardness, flowability and cure are the critical processing parameters in all semiflexible foams, the choice of the polymeric MDI depends upon the application and processing conditions encountered. The typical index ranges for semiflexible foams are from 80 to 110. The effect of varying the PAPI 4901 isocyanate index on the rise profile of a semiflexible foam is shown in Figure 12.6.

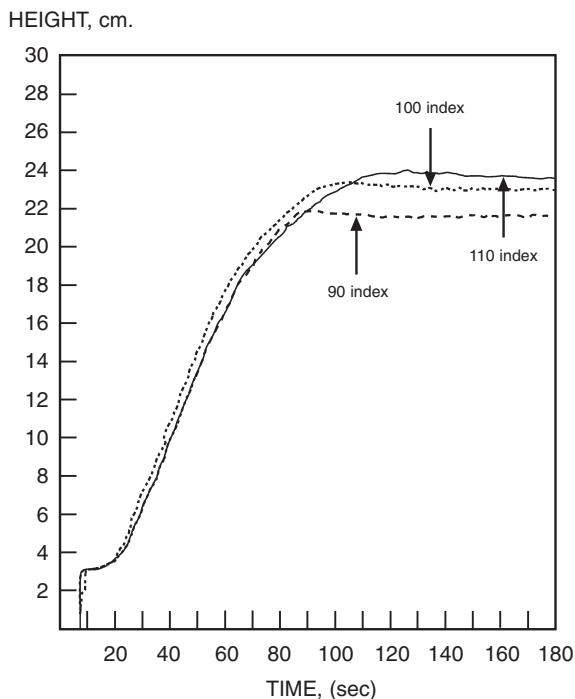


Figure 12.6 Index Effects On Rise Profile

The final composition of a semiflexible foam formulation varies because of the complexity of the overall foam process (see Figure 12.4) and the diversity of the applications for the final part.

CHEMICAL IMPACT ON SEMIFLEXIBLE FOAM PROCESSING

The quality and type of the vinyl skin mainly effects the adhesion, hardness and staining characteristics of the finished part. The substrate mainly effects the flowability, internal foaming pressure, adhesion and dimensional stability of the finished part. However, the vinyl skin and substrate in the foaming tool can also contribute to foam-related defects. If the vinyl skin and substrate in the foaming tool allows for foam leakage then extrusion collapse voids are the usual foam-related defect. The overall tightness of the foam formulation may need to be increased to reduce the possibility of extrusion-collapse voids. Chemical changes to the formulation such as addition of silicone surfactant, increased gelling catalyst or an increase in the cross-linker may be needed to improve foam stability.

Pressure relief voids, parting lines or blown covers at demold can occur on instrument panel (IP) parts even if minimum foam leakage is seen from the IP tool. This occurs when the internal foam pressure is too high or if the foam leakage (venting) occurs after the foam's gel point and during peak pressure build in the foaming tool. Internal mold pressures typically range from 5 to 20 psi (34-138 kPa). If pressure related problems are present, the internal foam pressure in the molds needs to be reduced. Chemical changes to reduce internal molding pressures include the addition of a cell-opener, increase in the CPP, reduced silicone surfactant, reduced cross-linker or a reduction in the

gelling catalyst concentration. Solutions to extrusion and pressure-related foam defects without making chemical changes to the formulation are discussed in the semiflexible foam section of the Troubleshooting Guide.

The type of machine, mold and processing conditions employed on the line also affect the composition of the semiflexible foam formulation. Semiflexible foams must flow throughout the part and cure sufficiently for demold. The semiflexible foam requires excellent flowability to facilitate processing in intricate molds, while the demold times vary from 1-6 minutes. Careful adjustment of the formulation is required to fill a 1300-gram one-minute demold instrument panel compared to a 200-gram 4mm thick door panel or glove-box door part which has a six-minute demold cycle. In many cases, the processing requirements for flowability and tightness vary from part-to-part even on the same production line.

Open-pour molds usually require delayed cream times to allow for mold closure prior to significant foaming of the polyurethane chemicals. On low-pressure continuous transport lines, the cream time of the foam should be longer than the longest pour-to-pour time. This is required to improve the cleaning of the head during solvent flushing at the end of the pour pattern. For high-pressure closed-pour systems, the cream time should be a minimum of 1.5 times the longest shot time. In situations where multiple shots are made into the same mold, the cream time needs to be delayed beyond the end of the last shot to minimize foam-related defects as explained in the Troubleshooting Guide. Whether open or closed-pour processing is being utilized, liquid foam material should never be dispensed on top of rising foam. Single-shot pours are preferred over multiple shots into the same mold.

The liquid components are metered into the mixing head at temperatures from 65 to 105°F (18 to 40°C) and are usually temperature controlled only at the run tank. As a result, the plant environment and the length and placement of piping can change the component stream temperatures to the mix head. The reaction profile of the foam system can be greatly affected. The effect of component temperature on the reaction profile of a semiflexible foam formulation is illustrated in Figure 12.7. This sensitivity can result in foam-related defects corresponding to temperature swings of the plant environment. If the component temperatures can be controlled at the mix head, the reactivity profile of the formulation can be adjusted to yield the desired processing window for the production line. Controlling the component stream temperatures is one critical item often overlooked during the production of semiflexible foam parts.

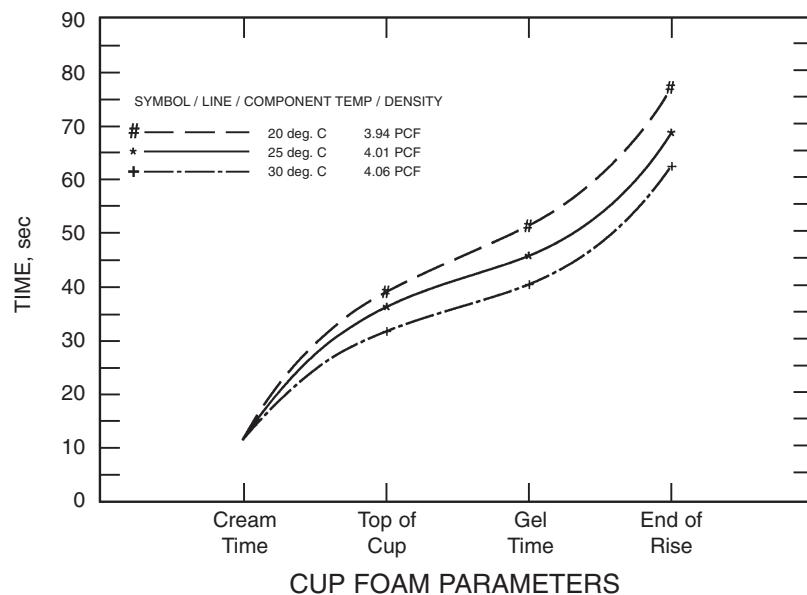


Figure 12.7 Effect of Component Temperature on Semiflexible Foam Reaction Profile

FOAM ASSEMBLY PROCESS

The molds, mixing equipment and processing conditions vary greatly throughout the semiflexible foam industry. Most of the molds used for the production of semiflexible foams are constructed of aluminum, steel, epoxy or epoxy-faced aluminum. The mold designs also vary throughout the industry, and both open and closed-pour molds are utilized.

Open-pour molding can utilize a simple one spot-pour or can be complex enough to require robotic pour patterns so the pattern can be repeated from mold-to-mold and part-to-part. Closed-pour molds have either single or multiple pour holes. Both open and closed-pour molds are found on stationary, “over-under”, carousel and racetrack lines. Demold times vary from 1-6 minutes, depending upon the production line requirements.

Mold temperatures of 65 to 130°F (18 to 55°C) are typical. Mold temperatures on the production line have been noted to cycle 20°F (10°C) during daily operation. This large swing in mold temperatures has been documented to be the assigned cause for an increase in foam related defects on the production line. One of the reasons for this large swing in mold temperatures is that the semiflexible foam reaction is very exothermic and requires little external heat on the molds for curing the parts after production starts. As a result, most molds are not adequately equipped with the necessary heating at start up and after breaks or cooling capacity once production is running to give good temperature control. As the industry moves to faster demold times and lower-density formulations, mold temperature control will need to be improved to avoid the manufacture of parts with foam related defects.

Mold leakage (extrusion) of the polyurethane foam material varies greatly, from 0 to over 20%. The design and workmanship of the molds, the substrate and the vinyl skin have an effect on the amount of extruded material. Water-based mold release is commonly applied to the mold to help in demold due to flash. A thin sheet of polyethylene film is sometimes placed on the back of the substrate to reduce the amount of foam flash onto the mold surface and to aid demold.^{12,36}

The size and multiplicity of the parts being produced in semiflexible foams are numerous. The weight of foam being poured in semiflexible parts varies from 30 grams of foam in a horn pad to 1500 grams of foam in an instrument panel. Interior trim parts on the same processing line can vary in fill weights from 30 grams to 400 grams, and also have different processability and physical property requirements.

The foam metering and mixing equipment can create or worsen foam-related defects in semiflexible foam parts. Inconsistent metering (ratio/index) and mixing deficiencies can cause a variety of foam defects. Differences in the molds, processing line conditions and problems with the foam machines make troubleshooting foam-related defects on the foam assembly process very complex. However, equal emphasis must be placed on all five processes involved in the production of semiflexible foam parts. Therefore, attention to the tools, foaming equipment, the chemical formulation, vinyl skin and substrate process is necessary for consistent production of quality semiflexible foam parts.

Skin Process

The vinyl skins utilized in automotive interior trim applications are produced by several different procedures.^{12,37-12,41} The most common are:

- Vacuum forming,
- Dry powder slush molding,
- Dry powder rotocasting,
- Liquid plastisol - rotocasting,
- Liquid plastisol - wet slush,
- Injection molding.

Critical issues common to all the processes used in the manufacture of vinyl skins are adhesion, staining (discoloration), window fogging and brittleness.^{12,42-12,47} Skins made from a sprayed, two-component polyurethane system or a TPU (Thermoplastic Polyurethane) powder slush system have been reported to overcome many of these concerns.^{12,48-12,53} The new polyurethane skin technologies provide soft touch, low gloss, consistent color and ten year durability for instrument panel and other interior trim parts.

In North America, the vacuum-forming process was dominant until the mid-1990's. The advantages of this widely practiced process included lower tooling costs, improved staining properties, higher adhesion values and superior

physical properties. The specifications for semiflexible foam parts are becoming more stringent as the more aerodynamic design of automobiles increases thermal and ultraviolet exposure of instrument-panel and interior-trim parts. These concerns are evidenced by the interior-temperature data presented earlier in Figure 12.1. In the future, improved glass for windshields and doors may help reduce the interior temperatures currently being experienced in today's automobiles.

Vacuum-forming vinyl skins is gradually being replaced by the powder slush molding process. The powder slush process offers new process technology, lower overall skin cost, good staining properties and good physical properties. For these reasons, powder slush molding of skins is gaining acceptance in the marketplace as the manufacturing process of choice for automotive vinyl skin production. The other new process for the manufacture of instrument panel and interior trim parts is polyurethane skins. The two major types of polyurethane skin processes are the powder slush thermoplastic polyurethane process and the polyurethane spray skin process. Both of these relatively new processes have gained acceptance at the OEMs and are in limited production on specific platforms.

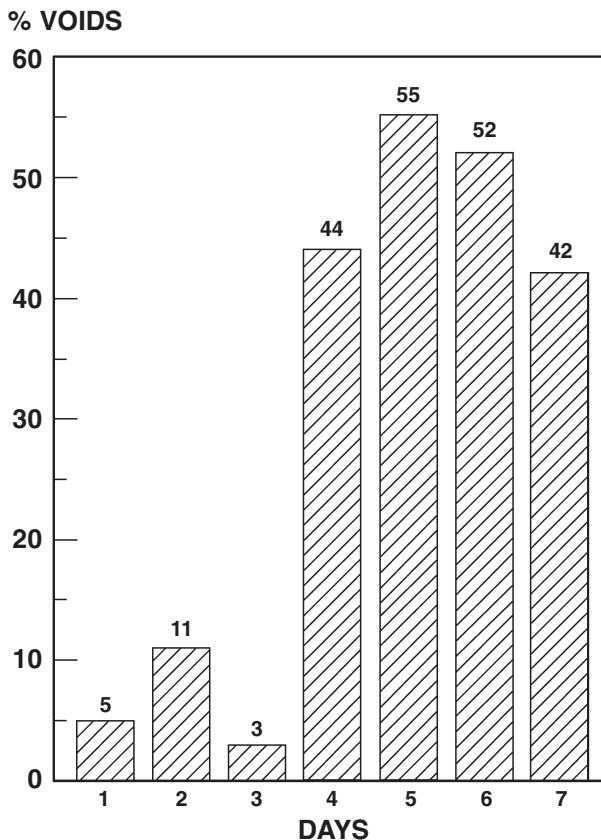


Figure 12.8 Vinyl Skin Thickness Effects Instrument Panel Foam Void Results

Equally important to the production of quality parts is the dimensional consistency of the vinyl skin. If the skin thickness varies as a result of process variables during skin production, foam voiding down stream in the foam assembly process can occur. Figure 12.8 illustrates how an 0.3 millimeter

thickness change in the vinyl skin (occurring on day 4) resulted in a 40% increase in foam voids in the finished instrument panel part. This average thickness change of 0.3 millimeters (over the entire surface of the vinyl skin) also reduced the overall weight of the skin by approximately 20%. Retooling of the foaming molds to improve the foam shut-off was required to correct this seemingly small change in vinyl thickness.

Substrate Process

The substrate (insert) is the main structural component in instrument-panel or interior-trim parts. The substrate is designed to be the main energy-absorbing device during impact. Engineered thermoplastics (ETP) and some thermoset resins have essentially replaced metal, compressed wood-pulp fiber and cardboard. Compared to these materials, plastic materials are lighter in weight and equal or superior in strength properties. They also allow for the consolidation of parts and processing steps.

As with vinyl skin manufacturing, the quality of the substrate affects the quality of the parts produced downstream in the foam assembly process. Figure 12.9 illustrates the effect reworked substrates had on the foam void rate. The foam void rate was 40% during the study. Eighty-eight percent of the foam voids were on reworked substrates; only 12% occurred on parts manufactured with new substrates. Thus, a 35% increase in foam voids could be attributed to the reworked substrates. The reworked substrates decreased the sealing between the vinyl skin and the substrate in the foaming step. The increase in the amount of flash resulted in higher foam-related defects in the instrument panel parts.

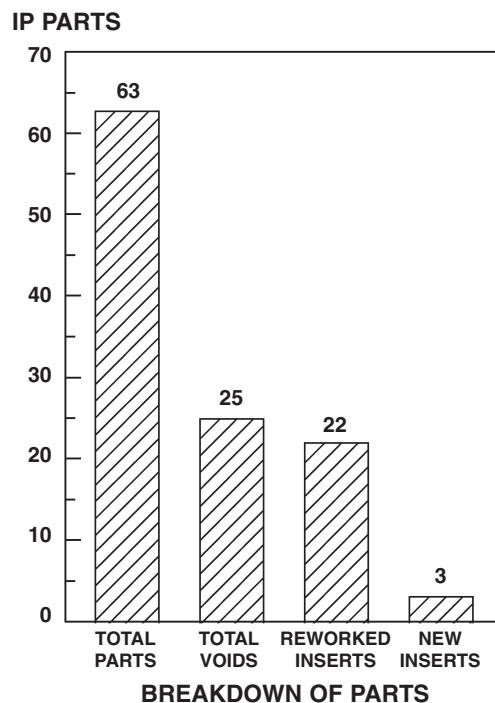


Figure 12.9 Effect of Reworked Inserts on Foam Related Defects In Instrument Panel Parts

SEMIFLEXIBLE FOAM APPLICATIONS AND PROCESSING

INSTRUMENT PANELS

The automotive instrument panel (IP) generally encompasses the upper crash pad, the instrumentation cluster, the passenger side inflatable restraint (PSIR), glove box, knee bolster and center console area in the front compartment of the automobile. This usually does not include the steering wheel assembly. The soft IP platform is the largest volume application for the use of polyurethane foam in the semiflexible foam market. The two dominate processes for the manufacture of soft PU foamed IP parts in the industry are the open-pour and closed-pour processes.

OPEN-POUR INSTRUMENT PANEL PROCESS

The open-pour process for the manufacture of instrument panels is the original method for the manufacturing of IP parts. In North America, most transnational molders utilize the open-pour process to manufacture these parts. The process starts by securing the insert at the top of the foaming tool and placing a skin (show surface down) in the bottom cavity of the foaming tool. The liquid chemicals are then dispensed (by a pour pattern) into the bottom of the foaming tool directly onto the underside of the skin. The foam can be dispensed through a variety of high-pressure or low-pressure mixheads. The high-pressure mixheads are the dominate type used in the industry. The mixed foam chemicals can be dispensed onto the skin in a consistent pattern by robot, xyz turntable or in some cases, manually by an operator. A consistent pour pattern is critical to eliminate foam-related defects and minimize part weight. After the chemicals are poured onto the skin, the lid holding the insert is closed onto the bottom cavity of the foaming tool and secured with clamps. The foam must flow and fill the cavity created between the insert and the skin. Critical processing requirements for the foam chemicals are delayed cream time, stability, low-pressure build, good flowability and good final cure. At the specified demold time the clamps are released and the lid of the foaming tool is opened leaving the finished composite IP part in the bottom cavity of the tool. Demold times vary from 2 to 6 minutes. Molded densities range from 4.5 to 12 lb/ft³ (72-192 kg/m³). After a new insert is loaded onto the top cavity of the foaming tool, the finished IP part is removed for inspection, trimming and additional build-up. The critical specifications for composite IP parts include hardness, staining, fogging, dimensions and adhesion.

CLOSED-POUR INSTRUMENT PANEL PROCESS

The closed-pour process is the newer method to manufacture IP parts. The same steps as for open-pour process are utilized in loading the insert and skin into the foaming tool. However, the foaming tool is closed and clamped before the mixed liquid foam chemicals are dispensed into the cavity between the insert and the skin. High-pressure mixheads are used exclusively for this manufacturing process. Two methods are commonly used to dispense the foam chemicals into this cavity. One method is to dispense down a pour hole

through the top mold lid and the substrate. Another method is to utilize runners or diverters to dispense the foam chemicals between the skin and the substrate usually along the windshield edge. The critical processing parameters for the foam chemicals are flowability, adhesion, cure, stability and low-pressure build. In addition, flow rate, diverters, sealing and venting are critical process parameters for the elimination of air traps. At demold, the clamps are released and the lid of the foaming tool is opened leaving the finished composite IP part in the bottom cavity of the tool. Demold times vary from 1 to 2 minutes. Molded densities range from 6 to 12 lb/ft³ (96-192 kg/m³). After a new insert is loaded onto the top cavity of the foaming tool, the finished IP part is removed for inspection, trimming and additional build-up. The same critical specifications as for open-pour processing listed above apply to the closed-pour IP process.

Although the closed-pour process has been utilized for the manufacture of IP parts for many years, only recently has the process gained wide acceptance and utilization. The increased preference for closed-pour IP production includes lower cost and increased productivity. Closed-pour IP production has faster demold times and requires fewer foaming tools to produce the same number of IP parts compared to an open-pour carousel or racetrack production line. In the past, RIM type 50 ton clamps were utilized for closed-pour IP production. Today most closed-pour tools are of similar design to the “clam shell” type tools used for open-pour IP production. The capital investment costs for closed-pour production lines are usually higher than the simpler open-pour lines, but this would appear to be less of a significant factor than the savings gained through increased productivity. Finally, foam related defects seem to be fewer in number on closed-pour IP parts compared to open-pour IP parts. However, the options to correct foam related defects are more limited on closed-pour IP parts than on open-pour IP parts. Hence, involvement by knowledgeable foam process personnel during the early design stages of either open-pour or closed-pour IP platform parts is critical to eliminate foam related problems which may occur later during production start-up.

SEAMLESS PSIR DOOR INSTRUMENT PANEL PROCESS

In the future, seamless PSIR IP parts may become the dominate style of design. The soft foam seamless PSIR IP can utilize either the open or closed-pour manufacturing processes. However, the seamless PSIR door IP parts will require the foam system to have improved physical properties over conventional foam systems in production today. Depending upon the design of the seamless PSIR IP, the foam may require higher adhesion, elongation and tear properties than conventional foams utilized in the industry today for conventional IP parts. The design of the seamless PSIR IP is critical in determining the demands placed upon the foam to meet the stress of air bag deployment. The seamless PSIR IP part has growing acceptance because it eliminates the visual air bag door on the passenger side of the IP. Basically, the seamless PSIR IP is being driven by parts consolidation for lower cost, improved productivity and improved visual aesthetics to the consumer. The Seamless PSIR IP also offers minimum loss in design freedom for the design engineers. Both hard plastic and soft seamless PSIR IP parts in the

production and overall cost, safety and aesthetics will determine which will be the dominate choice for manufacturing new IP platforms.

INTERIOR TRIM

Applications for foam in automotive interior trim (IT) has grown dramatically in diversity and volume in the last 10 years. Applications for foam include arm rests, door panels, headliners, headrests, console covers and air bag doors. In addition, integral skin foams are utilized for steering wheels. Finally, energy management foams are utilized for knee bolsters, side-impact and head-impact applications.

ARM RESTS / HEAD RESTS

The arm rests and head rests (AR/HR) are commonly molded with semiflexible foam. The volumes of foam for these applications are smaller than with the instrument panel parts but the number of platforms and interiors with foamed AR/HR is larger. Most of the AR/HR are molded with vinyl skins. Some however, are molded and then inserted into traditional cut-and-sewed cloth covers. This is especially true for head rests and arm rests on the side of bucket seats away from the door of the vehicle. A small number of AR/HR are foamed in the fabric. These parts require a very fast cream time for the foam system and may require more expensive barrier films to prevent the liquid foam chemicals from “wetting” the cloth. The same processing requirements and diversity of processing equipment as with IPs are found in the manufacture of AR/HR parts. The critical processing requirements for the AR/HR parts are stability, low-in-mold pressure build and cure. The AR/HR parts must meet a variety of hardness and compression set specifications. This can be especially challenging when multiple AR/HR parts are being produced on the same production line.

DOOR PANELS

The production of soft molded foam door panels is less utilized than other conventional methods of interior door production. The foamed door panels may use the same foam for the door panel and the arm rest, or mold the arm rest separately to be added on to the door panel at a later step. In addition, side-impact foam can be molded into the door panel or also added later. Finally, the growing use of low-density RIM for door applications also allows for the incorporation of soft foam for the arm rest to consolidate parts for improved productivity. The critical processing requirements for soft door panel foam are staining, adhesion and flowability. If arm rests are molded in place with the same foam system then hardness and compression set requirements will also need to be considered for the door panel foam system.

HEADLINERS

Automotive headliners have changed drastically over the last 10 years.^{12,54} Headliners have gone from a simple decorative and aesthetic cover for the sheet metal roof to a critical piece of the acoustical package with integration into the overall structural roof system. Simple flat cardboard and shoddy fiber composites are being replaced with fiberglass and molded or thermoformable foam composites.^{12,55-12,56} These “sandwich” designs add structural as well as acoustical properties for the headliner. In addition, these polyurethane composites can be supplied as a modular part directly to the OEM assembly process. A variety of different manufacturing processes are currently utilized by the automotive industry to manufacture headliners. The use of polyurethane chemical components (i.e. Polymeric MDI) as well as formulated foam systems are utilized to produce headliners. The critical processing requirements are cure (open time and demold), flowability (wet out), adhesion and hardness (including structural modulus). In the future, headliners will incorporate more electrical components, possibly the communication system and the HVAC system by means of the A and B pillars.

OTHER INTERIOR TRIM PARTS

Specialty molded semiflexible foams are also used to produce several other categories of automotive interior parts. These would include supplemental inflatable restraint (SIR) air bag doors, glove box doors and console covers. Due to the safety requirements for air bag doors, the foam systems for these applications are usually not made with the same type of foam systems as instrument panels, arm rests or door panels. Early platform designs required the foam to have high-elongation, tear and adhesion properties. For these reasons, polyol blends containing high levels of chain extenders and the use of MDI prepolymers was required to meet the early design specifications. Today, additional deployment testing and modifications to the structural design of the SIR door and housing has reduced the physical property requirements. Today, many SIR doors are manufactured with the same foam system as the IP. In the future, seamless PSIR door IP parts may replace the separate SIR door commonly seen today. The critical processing requirements are adhesion, staining, physical properties and hardness.

Numerous small interior parts are manufactured with semiflexible foam. Glove box doors, console covers and interior trim pieces are manufactured to add soft luxurious aesthetics to the interior of the automobile. The critical processing requirements are hardness and cure.

APPLICATIONS FOR SEMIRIGID FOAMS

IMPACT ENERGY MANAGEMENT

Another special class of molded foams are used for impact energy management applications. These foams are more semirigid in nature in that they are more like rigid foams and may not fully recover like other flexible resilient foams. Typically these foam systems have a high capacity for energy absorption.^{12.57-12.62} Application areas include side-impact,^{12.63} knee bolsters,^{12.64} head-impact^{12.65} and bumpers. Molded foam cores or parts can be supplied to simply insert into the designated application area or molded in place with the door panel, pillar or bumper. Figure 12.10 illustrates the use of semirigid foam in a bumper system.

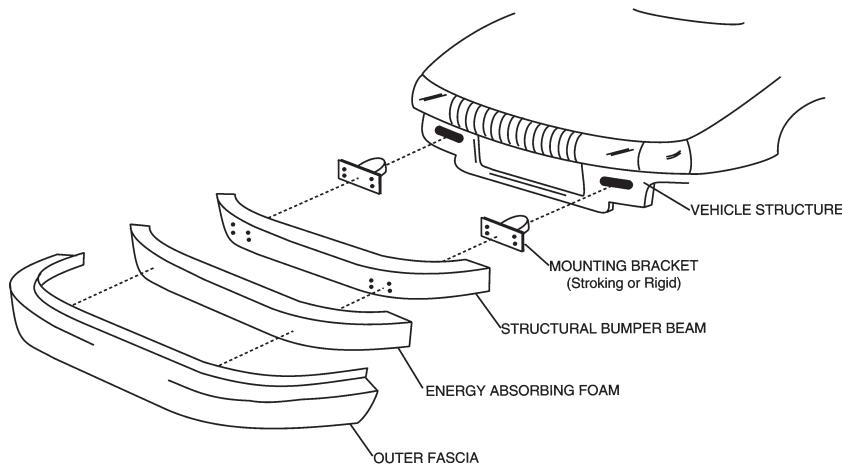


Figure 12.10 Typical Construction Features of an Automobile Bumper

Some of the legislative and technical developments leading to the successful use of polyurethane foams in this application are detailed in References 12.66-12.76.

Basic formulation ingredients are the same as detailed above for semiflexible foams. Cross-linker and copolymer polyol levels are generally increased to maximize foam hardness and energy dissipation characteristics. Copolymer polyols are especially useful in developing these properties at economical foam densities. The typical influences of formulation variables on the properties and processing of energy management foams are detailed in References 12.77-12.78.

APPLICATIONS FOR INTEGRAL-SKIN FOAMS

Molded foams having an attached, densified outer skin of polyurethane are produced in the integral-skin process. In this technology, the gas used for polymer expansion comes from volatilization of solvents or more recently from just the traditional water-isocyanate reaction. A cross-section of an integral-skin foam will reveal a regular cellular core that changes to a denser and less cellular structure in areas near the outer skin. The skin itself is made of the same polymer, but is noncellular and nonporous. Skin thickness typically ranges from one to five millimeters (0.04-0.2 inch).

Color-coated integral-skin foams are used in steering wheel center pads, head rests, spoilers and similar light-contact automotive interior trim and external applications. Parts with more rigorous handling requirements such as steering wheels and furniture trim are made with internally pigmented formulations. Typical properties for three general classes of flexible integral-skin foams are given in Table 12.4.

Table 12.4 Example Integral-Skin Foam Properties

| Property | Low-Density | High-Density |
|--|-----------------|----------------------|
| Overall Density, pcf kg/m ³ | 8-14 128-224 | 40-50 640-800 |
| Core Density, pcf kg/m ³ | 5-12 80-192 | 35-45 560-720 |
| Hardness at 25% def. psi kn/m ² | 1-10 7-70 | 200-800 1380-5520 |
| Tensile, psi kg/cm ² | 50-125 3.5-9 | 200-600 14-42 |
| Elongation, % | 100-200 | 100-200 |
| Application Area | auto interiors | auto exteriors |

Reviews of this complex segment of polyurethane foams are given in References 12.79-12.87.

FORMULATION TECHNOLOGY

A basic formulation listing for integral-skin foam is presented in Table 12.5.

**Table 12.5 Formulation Ingredients
For Integral-Skin Foam**

| Component | Parts by Weight |
|-----------------------|-----------------|
| Polyether Polyols/CPP | 100 |
| Chain Extenders | 5-30 |
| Cross-linkers | 1-10 |
| Amine Catalysts | 0.1-2.0 |
| Tin Catalysts | 0-0.05 |
| Pigment/Stabilizers | 0-10 |
| Blowing Agents: | |
| HFC 134a | 2-4 |
| Pentane | 4-6 |
| Water | 0.3-0.6 |
| Isocyanate Index | 80-110 |

The basic properties of the foam and its integral-skin are matched to the intended application by proper choice of the polyols, copolymer polyols, chain extender, cross-linker and the functionality of the isocyanate. Variations in the final molecular weight per cross-link (M_c) can change the foam from rigid, to semirigid and ultimately to flexible in nature. Numerical M_c values in the range of 300 to 800 give rigid foams, M_c of 800 to 2000 are semirigid foams and M_c above 2000 are flexible foams.

The polyols used are ethylene-oxide-capped so that the basic polymer matrix can be formed quickly. Copolymer polyols are used for additional hardness and cell-opening. The most common chain extenders are low-molecular-weight diols or diamines. Applications requiring a soft foam with a flexible skin, utilize the diol chain extenders. Diamines give harder foams with a tough outer skin. The diamines also increase the rate of polymer cure and allow faster demolding of the part. Cross-linker and catalyst concentrations are adjusted to give a formulation the required flow and cure characteristics. Demold times of less than 90 seconds are currently running in production.

For good skin formation, care must be exercised to prevent atmospheric moisture pickup during handling and formulating of the various raw materials. Historically Freon 11, trichloroethane and pentane were the preferred blowing agents. New all-water-based integral skin foam systems are now commercially available.^{12.88-12.96}

The preferred polyisocyanates are those based on MDI. Higher mechanical properties are obtained with the more expensive urethane and uretonimine modified forms of pure MDI. Adequate results for most applications can be

obtained with one of the polymeric forms of MDI. Optimum properties for any given application are usually obtained by experimentation to find the proper balance of all formulation ingredients.

THE INTEGRAL-SKIN FOAM PROCESS

This process produces in one operation, a molded part with both a foam core and a high-density-exterior, finishable skin. Essential steps in the process are listed below:

- Clean and prepare the mold,
- Attach inserts and fasteners,
- Apply mold-release system,
- Apply in-mold coating if desired,
- Condition mold to proper temperature,
- Mix and dispense chemicals,
- Cure for desired cycle,
- Demold and post cure,
- Trim and finish.

Key features within the above steps will be discussed below.

Molds

Simple or complex mold shapes may be used. If the molds are engraved or textured, the pattern will be transferred to the molded part. Molds must be sturdily constructed and able to withstand internal pressures up to 20 psi (138 kPa). Cast aluminum molds with good seals and a high heat removal capacity are preferred. Provision for gas venting must be made, but only minor extrusion of the polymer can be tolerated. Parting lines should be placed in non-show-surface areas of the part. A single filling port with a tight sealing plug is recommended.

Molds must be perfectly cleaned and treated with a release agent and any desired in-mold coating.^{12.97} Some success has been reported with an internal mold release.^{12.98}

Mold Temperature Effects

Accurate mold temperature control is essential for reproducible production of integral-skin foams. Each different formulation will have an optimum mold temperature latitude that must be established by experimentation. If mold temperature is too low, surface voids appear in the skin layer. At excessive temperatures, the skin layer becomes undesirably porous. In general, the mold temperature should be as low as practical for fast cycle times and blemish-free surfaces. Mold temperatures in the range of 100-150°F (38-66°C) are typical.

Dispensing The Mixture

Conventional metering and mixing equipment is used to dispense integral-skin foams. Special precautions must be taken to design and size the mixing head for minimum entrainment of air into the mixed ingredients. Mixer outlet nozzles should be large enough to minimize splashing and air entrainment during the pour. Entrained air is a major source of skin surface defects.

Machine output should be set so that the total required shot of ingredients can be delivered in less than one-half the formulation cream time. Single shot pours are generally preferred. Final skin formation is aided if the mold is overpacked by a factor of 20 to 100%. The percent overpack is calculated as the overfill weight divided by the weight of material required to just fill the mold.

Skin Formation

Various proposed mechanisms for skin formation have been reviewed and further developed by Campbell.^{12,99-12,100} The essential observations suggest that the mold is first filled with foam that has a minimal skin layer. Then, because of heat conduction to the mold and increasing internal pressure within the overpacked mold, a dense skin is formed by condensation of the blowing agent near the mold wall. The dynamic process of skin formation continues until the polymer gels or the mold pressure decreases.

Higher mold temperatures produce thinner skins. Thicker skins are obtained by lowering mold temperatures or increasing the percentage of overpack.

Demold and Post Cure

The exothermic heat of reaction in integral-skin foams is enough to cure the polymer in as little as two minutes. After demold, a surface of the part must be punctured to allow gas to escape and to prevent shrinkage. At this stage of production, the foam still contains blowing agent and other vapors, which may be undesirable for the subsequent finishing steps. These vapors are conveniently removed by post-curing the parts in a hot-air oven.

Final Finishing

After post-cure, the parts are trimmed and any residual mold release removed. If the parts have been prepared with a suitable color pigment or an in-mold transfer coating, the process is complete. Alternatively, the parts can be solvent-cleaned in preparation for color coating.

The color coatings of choice have historically been the solvent-borne polyurethane elastomers. When properly applied, these products offer excellent color retention in a tough, wear-resistant film that is generally stronger than the integral-skin itself.

References

- 12.1 Rusch, K.C. "Load-Compression Behavior of Flexible Foams"; *J. Appl. Polym. Sci.* **1969**; 13, 2297-2311.
- 12.2 Austin, C.E.; Buesking, G.O.; Lutz, J.B. "Instrument Panel Impact Characteristic Studies - G Loadings, and Force - Deflection Analyses"; Proceedings of the SAE International Engineering Congress, Detroit, Michigan, 1969; Paper No. 690067; SAE: Warrendale, Pennsylvania.
- 12.3 Green, S.J.; Schierloch, F.L.; Perkins, R.D.; Babcock, S.G. "High-velocity Deformation Properties of Polyurethane Foams"; *Exp. Mech.* **1969**; March, 103-109.
- 12.4 Rusch, K.C. "Load-Compression Behavior of Brittle Foams"; *J. Appl. Polym. Sci.* **1970**; 14, 1263-1276.
- 12.5 Meinecke, E.A.; Schwaber, D.M. "Energy Absorption in Polymeric Foams. I. Prediction of Impact Behavior from Instron Data for Foams with Rate-Independent Modulus"; *J. Appl. Polym. Sci.* **1970**; 14, 2239-2248.
- 12.6 Hilyard, N.C.; Djiauw, L.K. "Observations on the Impact Behavior of Polyurethane Foams; 1. The Polymer Matrix"; *J. Cell. Plast.* **1971**; 7/1, 33-42.
- 12.7 Meinecke, E.A.; Schwaber, D.M.; Chiang, R.S. "Impact Analysis for Cellular Polymeric Materials"; *J. Elastoplast.* **1971**; 3/1, 19-27.
- 12.8 Hilyard, N.C. "Observations on the Impact Behavior of Polyurethane Foams; II. The Effect of Fluid Flow"; *J. Cell. Plast.* **1971**; 7/2, 84-90.
- 12.9 Rusch, KC. "Impact Energy Absorption by Foamed Polymers"; *J. Cell. Plast.* **1971**; 7/2, 78-83.
- 12.10 Schwaber, D.M.; Meinecke, E.A. "Energy Absorption in Polymeric Foams. II. Prediction of Impact Behavior from Instron Data for Foams with Rate-Dependent Modulus"; *J. Appl. Polym. Sci.* **1971**; 15, 2381-2393.
- 12.11 Rao, P.M.; Hofer, K.E. "The Mechanical Behavior of Flexible Polyurethane Foams under High Rate Loading"; *J. of Mat., JMLSA* **1971**; 6/3, 704-717.
- 12.12 Cousins, R.R. "A Theory for the Impact Behavior of Rate-Dependent Padding Materials"; *J. Appl. Polym. Sci.* **1976**; 20, 2893-2903.
- 12.13 Lockett, F.J.; Cousins, R.R.; Dawson, D. "Engineering basis for selection and use of crash padding materials"; *Plast. Rub. Proc. Appl.* **1981**; 1/1, 25-37.
- 12.14 Kurauchi, T.; Norio, S.; Osami, K; Noboru, K. "Mechanism of high energy absorption by foamed materials -foamed rigid polyurethane and foamed glass"; *J. Mat. Sci.* **1984**; 19, 871-880.
- 12.15 Lin, J.G.; Manson, JA. "Analysis of Dynamic Mechanical Response of Some Energy-Absorbing Polyurethanes: A New Approach"; *Conference Proceedings, Society Of Plastics Engineers 44th Annual Technical Conference and Exhibit*, SPE: Brookfield Center, Co., 1986, 518-521.
- 12.16 Yossifon, S.; Szanto, M. "Dynamic Compression Characteristics of Flexible Foams. I. Similarity Model, Analysis, and Experiments"; *J. Appl. Polym. Sci.* **1987**; 34, 2025-2036.
- 12.17 Gibson, L.J.; Ashby, M.F. "Energy Absorption In Cellular Materials"; In *Cellular Solids*, Gibson and Ashby, Eds.; Pergamon Press: New York, 1988, 212-240.

- 12.18 Miltz, J.; Ramon, O. "Energy Absorption Characteristics of Polymeric Foams Used as Cushioning Materials"; *Polm. Eng. Sci.* **1990**; 30/2, 129-133..
- 12.19 Chiou, J.P. "Application of Solar-Powered Ventilator in Automobiles"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1986; Paper No. 860585; SAE: Warrendale, Pennsylvania.
- 12.20 Weibner, R.; Adler, J. "Plastics for the Interior Trim of Passenger Cars-Present Situation and Trends for the Future"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1987; Paper No. 870305; SAE: Warrendale, Pennsylvania.
- 12.21 Young, P.; Bernardi, R. "Auto Solar Control"; Proceedings of the SAE international Congress and Exposition, Detroit Michigan, 1988; Paper No. 880050; SAE: Warrendale, Pennsylvania.
- 12.22 Avar, G.; Thompson-Colon, J. "The Influence of Polyurethane Foam on the Heat Staining of Instrument Panels"; Proceedings of the SAE International Congress and Exposition, Detroit Michigan, 1988; Paper No. 880507; SAE: Warrendale, Pennsylvania.
- 12.23 Wigotsky, V. "Creativity and Economy"; *Plast. Eng.* **1989**; 45/9, 23-30.
- 12.24 Tilton, H. "Automotive Plastics Winning Over Detroit"; Chemical Marketing Reporter, February 12, 1990, SR16.
- 12.25 Editorial "How Hot Was It?"; *Popular Science* **1993**; 243/2, 32.
- 12.26 Sandridge, R.L.; Morecroft, A.S.; Hardy, E.E.; Saunders, J.H. "Properties of a Semiflexible Urethane Foam System"; *J. Chem. Eng. Data* **1960**; 5/4, 495-498.
- 12.27 Saunders, J.H.; Frisch, K.C. *Polyurethanes Chemistry And Technology, Part II. Technology*; Interscience: New York, 1964, 164-166.
- 12.28 Huester, P.K; Huntington, D.P. "One-Shot Semirigid Foam System Process and Properties"; *J. Cell. Plast.* **1965**; 1/2, 301-310.
- 12.29 Wirtz, H. "Semirigid Urethane Foams in the Automotive Industry"; *J. Cell. Plast.* **1966**; 216, 324-331.
- 12.30 Ryall, B.; Griffiths, P.G. "One shot semi-rigid PU foam moulding developments"; *Brit. Plast.* **1970**; June, 101-104.
- 12.31 Grant, B.R. "Room Temperature Cure Semirigid Foams for Molded Parts Based on Hylene TRF"; *J. Cell. Plast.* **1971**; 7/1, 43-48.
- 12.32 Ganster, O. "Semi-Rigid Moltopren And Bayflex For Safety Parts In The Automobile"; *Int. Prog. In Urethanes* **1975**; 1, 116-121.
- 12.33 Schafer, H. "Semi-Rigid Polyurethane Molded Foams"; In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: New York, 1985, 223-233.
- 12.34 Woods, G. *The ICI Polyurethanes Book*; Wiley and Sons: Chichester, England, 1987, 85-100.
- 12.35 Fabris, H. J. "High Resilience Polyurethane Foams"; In *Advances In Urethane Science And Technology*; Frisch, K.C.; Reegen, S. L.; Eds.; Technomic: Lancaster, Pa., 1975, 108-129.
- 12.36 Woods, G. *The ICI Polyurethanes Book*; Wiley and Sons: Chichester, England, 1987, 87.

- 12.37 Torres, A. F. "Slush Moulding Of Plastisol Automotive Instrument Panel Fascia"; *Proceedings of SPE National Technical Conference*; SPE: Brookfield Center, Co., 1974, 20-21.
- 12.38 Schafer, H. "Semi-Rigid Polyurethane Molded Foams"; In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: New York, 1985, 224.
- 12.39 Nagase, T.; Kato, T.; Takamatsu, S. "Powder Slush Molding For Automotive Interior Parts"; Proceedings of the SPE Automotive Plastics Retec '87, Dearborn, Michigan 1987; SPE: Brookfield Center, Co., 384-386.
- 12.40 Fujii, Y.; Matsuura, I.; Wakatsuki, A. "Poly (Vinyl Chloride) Powder Molding Technology"; *Conference Proceedings, Society Of Plastics Engineers 46th Annual Technical Conference and Exhibit*, SPE: Brookfield Center, Co., 1988, 862-864.
- 12.41 O'Malley, M.; Eller, R. "New Developments in Materials and Fabrication Processes for Automotive Interior Trim Skin Materials"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1989; Paper No. 890588; SAE: Warrendale, Pennsylvania.
- 12.42 Lord, E.M.; Kishbaugh, L.; Russel, J.; Arthur, J. "Instrument Panel Weatherability"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1988; Paper No. 880506; SAE: Warrendale, Pennsylvania.
- 12.43 Avar, G.; Thompson-Colon, J. "The Influence of Polyurethane Foam on the Heat Staining of Instrument Panels"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1988; Paper No. 880507; SAE: Warrendale, Pennsylvania.
- 12.44 Bartels, H. "Amine-free foam filling for slush-moulded PVC dashboards"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988, 83-85.
- 12.45 Lord, E.M.; Kishbaugh, L., Russel, J. Arthur, J. "Instrument panel weatherability"; *Auto. Polym. Des.* **1989**; 8/4, 14-20.
- 12.46 Hunter, D.; Magnusson, B. "Polyurethane foam catalysts for applications in non-staining instrument panels"; *Auto. Polym. Des.* **1990**; 10/1, 2-11, 27.
- 12.47 Irvine, J.L. "The Discoloration of Vinyl Instrument Panels by Polyurethane Foam Backing"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1991; Paper No. 910359; SAE: Warrendale, Pa.
- 12.48 Peters, G.; Dupont, E.; Verwilst, J. "Light-Stable Polyurethane as a Competitor for PVC in Automotive Interior Trim"; *Conference Proceedings, Society Of Plastics Engineers 46th Annual Technical Conference and Exhibit*, SPE: Brookfield Center, Co., 1988, 851-857.
- 12.49 Peters, G. "A New Method of Producing Interior Trim Using a Light-Stable Polyurethane Skin"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1988; Paper No. 880340; SAE: Warrendale, Pa.
- 12.50 Verwilst, J. "Colo-Fast LM and Colo-Fast Spray New Developments In Polyurethane Technology"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 176-178.
- 12.51 Schneider, F.W.; Grasse, H. "Processing PUR Economically"; *Kunststoffe* **1992**; 82/10, 42-43.

- 12.52 Karwan, T.; Peters, G.; Long, R.; Verwilst, J. "State of the Art: Polyurethane Skin Technology for Automotive Interior Trim"; *Proceedings of the SPI 1994 Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1994, 618-624.
- 12.53 Karwan, T.W.; Long, R.; Peters, G.M. "A Production Proven Polyurethane Skin Technology for Interior Trim Parts"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1995; Paper No. 950442; SAE: Warrendale, Pa.
- 12.54 Gardner, C. "Headliners - Rising To The Occasion"; *Inside Automotives 1994*; December, 19-23.
- 12.55 Schmutzler, K.; Jung, L.; Schlotterbeck, D.G.; Lutter, H.D. "Thermoformable Polyurethane Foam for the Manufacture of Headliners"; *Proceedings of the SPI 1991 Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1991, 266-271.
- 12.56 Fair, D.L. "Formable Polyurethane Foam Composites for Automotive Applications"; *Proceedings of the 1995 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1995, 427-430.
- 12.57 Thompson-Colon, J.A.; Huber, M.; Liddle, J.W. "Fundamental Studies of Polyurethane Foam for Energy Absorption in Automobile Interiors"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1991; Paper No. 910404; SAE: Warrendale, Pa.
- 12.58 Rossio, R.C.; Vecchio, M.; Abramczyk, J. "Polyurethane Energy Absorbing Foams for Automotive Applications"; Proceedings of the 1992 SPI Polyurethanes Technical/Marketing Conference; Technomic: Lancaster, Pa., 1992, 438-448.
- 12.59 Naik, B.G. "New Polyurethane Energy Management Foams for Improved Auto Interior Safety"; *Proceedings of the 1993 SPI Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1993, 425-432.
- 12.60 Syrowik, G.F.; Huber, M.A.; Sounik, D.F.; Gansen, P. "Energy-Absorbing Polyurethane Foam to Improve Vehicle Crashworthiness"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1995; Paper No. 950553; SAE: Warrendale, Pa.
- 12.61 Yu-Hallada, L.C.; Kuczynski, E.T.; Weierstall, M. "Polyurethane: The Material of Choice for Occupant Protection and Energy Management"; *Proceedings of the 1995 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1995, 390-396.
- 12.62 *Enerflex EA Foams, Energy Absorbing Polyurethane Foam*; Corporate Brochure: The Woodbridge Group, Troy, Mi., 1995.
- 12.63 Clavel, P.; LeBerre, D.; Kaeser, R.; van Ballegooie, P.; Mispreuve, H. "Polyurethane Foams for Side Impact Protection of Automobiles"; *Proceedings of the 1993 SPI Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1993, 412-419.
- 12.64 McCullough, D.W.; Pakulsky, B.R.; Liddle, J.W. "Polyurethane Foam for Automotive Knee Bolsters"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1992; Paper No. 920336; SAE: Warrendale, Pa.
- 12.65 Kerman, M. "Dynamic Force Deflection Curves of Cellular Plastics Versus Impact Head Shapes"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1996; Paper No. 960158; SAE: Warrendale, Pa.

- 12.66 Weller, P.A; Silverwood, H.A.; Scrivo, J.V. "Energy Management with Urethane Bumpers"; *Proceedings of the SPI-18th Annual Technical Conference*; Technomic: Lancaster, Pa., 87-94.
- 12.67 Barnatt, A. "Recent Developments in Polyurethanes"; In *Developments with Thermosetting Plastics*; Whelan, A.; Brydson; Eds., Wiley and Sons: New York, 1975, 82-85.
- 12.68 Weller, P. A.; Scrivo, J. V. "Davisorb Bumpers Reduce Weight and Damage"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1977; Paper No. 770308; SAE: Warrendale, Pa.
- 12.69 Ferrari, R. J. "The Development and Design of RIM Parts for Automotive Applications"; In *Reaction Injection Molding*; Becker, W. E., Ed., Van Nostrand: New York; 1979, 134-135.
- 12.70 Short, E. "The Design and Manufacture of Energy Absorbing Bumper Systems"; *Eur. J. Cell. Plast.* **1979**; 2/1, 33-40.
- 12.71 Thornton, P.H. "Energy Absorption by Foam Filled Structures"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1980; Paper No. 800081; SAE: Warrendale, Pennsylvania.
- 12.72 Weller, P.A. "A Soft and Low-Weight Energy-Absorbing Bumper System"; Proceedings of the SPI/FSK International Conference on Cellular and non cellular Polyurethanes, Strasbourg, France, 1980; Hanser: Munich, 173-185.
- 12.73 Lampinen, B.E.; Jeryan, R.A. "Effectiveness of Polyurethane Foam in Energy Absorbing Structures"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1982; Paper No. 820494; SAE: Warrendale, Pennsylvania.
- 12.74 Schumacher, W. "Polyurethane Foams to Improve Shock Absorption and Assembly of New Bumper Systems"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987, 248-251.
- 12.75 Kath, H.; Avar, G.; Thompson-Colon, J.A. "Energy Absorbing Polyurethane Foams for Modular Bumper Concepts"; *Proceedings of the SPI-32ndAnnual Polyurethane Technical Marketing Conference*; Technomic: Lancaster, Pa., 1989, 587-593.
- 12.76 Rusch, K.C. "An Overview of Automotive Plastic Bumpers"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1990, Paper No. 900420; SAE: Warrendale, Pennsylvania.
- 12.77 Oosterhof, H.A.; Dawson, J.W. "Chemical Formulation And Energy: Absorption Characteristics Of Polyurethane Automotive Fenders"; *J. Cell. Plast.* **1978**; 14/2, 106-112.
- 12.78 Brasington, R.D.; Clutton, E.Q. "Formulation considerations in the production of moulded energy managing PU foams"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988, 98-104.
- 12.79 Wirtz, H. "Integral Skin Foam - A Progress In Urethane Molding"; *Proceedings of the SPI - 2nd International Cellular Plastics Conference*; SPI: New York, 1968, Section 5-D, 1-9.
- 12.80 Zwolinski, L.M. "Molded Integral-Skin Urethane Foam"; *SPE Journal* **1969**; 25, 24-27.

- 12.81 Grieve, R.L.; Bonk, H.W.; Nadeau, H.G. "The Development of Integral Skin Molded Urethane Foams for the Automotive Industry"; *J. Cell. Plast.* **1969**; 5/6, 358-363.
- 12.82 Whitman, R.D. "How To Make Integral-Skin Urethane Foam"; *Plast. Tech.* **1970**; 16/2, 44-48.
- 12.83 Rice, D.M. "Integral Skin Foams Based on Polymeric Isocyanates"; *J. Cell. Plast.* **1971**; 7/1, 16-22.
- 12.84 Fabris, H.J. "Integral Skin Flexible Foams"; In *Advances In Urethane Science and Technology*; Frisch, K.C.; Reegen, S.L.; Eds.; Technomic: Lancaster, Pa., 1973, 203-220.
- 12.85 Wirtz, H. "The Application of the RIM Process in Europe"; In *Reaction Injection Molding*, Becker, W. E., Ed.; Van Nostrand: New York, 183-191.
- 12.86 Woods, G.W. *Flexible Polyurethane Foams, Chemistry and Technology*; Applied Science: New Jersey, 1982, 181-190.
- 12.87 Weber, C. "Flexible Polyurethane Integral Skin Foams"; In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: New York, 1985, 325-331.
- 12.88 Andreola, P.; Valcarenghi, A. "New Technologies to overcome the CFC problem for integral skin foams production"; *Conference Papers, UTECH 90*; Crain Communications: London, 1990, 52-55.
- 12.89 Hass, J.D.; Reichel, C.J.; Cole, E.W.; Krueger, D.C.; Markovs, R.A. "Integral Skin and Shoe Soles - Alternate Blowing Methods"; *Proceedings of the SPI - 33rd Annual Polyurethane Technical/Marketing Conference*, Technomic: Lancaster, Pa., 1990, 197-200.
- 12.90 Scarpatic, M.; Brown, B.W.; Harrison, R.P.; Zagata, B.J. "Water Blown - Integral Skin Foams for Steering Wheel Applications"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1991; Paper No. 910525; SAE: Warrendale, Pa.
- 12.91 Scarpatic, M.; Harrison, R.P.; Zagata, B.J. "CFC-Free Integral Skin Foams for Steering Wheels"; *Proceedings of the Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 436-439.
- 12.92 Fangareggi, A.; Guidetti, G.; Pedroni, L. "New Approach to CFC Free Steering Wheels"; *Proceedings of the Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991, 450-455.
- 12.93 Wada, H.; Hasegawa, N.; Fukuda, H.; Takeyasu, H. "All Water Blown Integral Skin Foam"; *Proceedings of the 1992 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 449-454.
- 12.94 Amato, T.A.; Cassidy, E.F.; Christfreund, A.; Dobinson, D.; Randall, D. "Development of CFC-Free Integral Skin Foam for Steering Wheels"; *Proceedings of the 1992 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 455-458.
- 12.95 Zagata, B.; Hartings, J. "Polyurethane Water Blown Steering Wheel - Total Performance"; *Proceedings of the 1994 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1994, 610-617.

- 12.96 Ueda, H.; Sakai, M.; Inoue, H.; Koga, N.; Soo, C.Y. "All-Water Blown Integral Skin Foam for Automotive Steering Wheels"; *Proceedings of the 1994 SPI Polyurethanes Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1994, 625-630.
- 12.97 Brix, H.; Schroder, W. "Methods for In-mould Coating of Polyurethane Mouldings for the Automotive Industry"; *Kunststoffe* **1987**; 77/9, 832-836.
- 12.98 Pauperio, A.; Santos, R.N. "Development Of Integral Skin Foams Based On Modified Isocyanate With Self-Releasing Characteristics"; *Proceedings of the SPI-30th Annual Polyurethane Technical Marketing Conference*; Technomic: Lancaster, Pa., 1986, 240-243.
- 12.99 Campbell, G.A. "Polyurethane Foam Process Development. A Systems Engineering Approach"; *J. Appl. Polym. Sci.* **1972**; 16, 1387-1402.
- 12.100 Campbell, G.A. "Integral-Skin Foam. A Mechanism for Skin Formation"; *J. Appl. Polym. Sci.* **1972**; 16, 1735-1748.

Chapter 13

Noise and Vibration Control



There are dozens of pathways for noise and vibration to enter a typical passenger compartment. The NVH grades of foam are useful in reducing the environmental harshness felt by the occupants and thereby contribute to a more comfortable ride.

Chapter 13

Noise and Vibration Control

R. Herrington, P. Berthevas

Noise has been defined as the presence of unwanted sound. Early work revealed that conventional flexible slabstock polyurethane foams have excellent airborne sound absorption properties. Airflow, cell-size and density are the main factors influencing the effectiveness of sound absorption provided by simple cut sheets of foam.^{13.1-13.2} Increasing cell count improves sound absorption at all frequencies. Optimum airflow through the cells was found to be between 0.1 and 1.0 cubic feet per minute (at 0.5-inches of water pressure). Increasing foam density generally improves sound absorbance, but to a lesser degree than the previous two factors. The effects of foam thickness, cutting profile and surface treatment have also been studied.^{13.3}

The fundamental mechanisms and experimental methods of measuring sound absorption by flexible foams are reviewed in References 13.4-13.12. A review of the patent literature prior to 1986 is available.^{13.13} The physiological effects of noise and vibrations on humans have been described.^{13.14-13.18}

AUTOMOTIVE APPLICATIONS

Noise and vibration control are important functions for many trim parts in the modern automobile. As cars have become smaller and lighter, noise has become a major consumer concern. Interior noise levels in the range of 60-70 decibels have been reported.^{13.19-13.26} Noise and vibrations present inside the automobile combine to present a level of environmental harshness that contributes to occupant discomfort. The grades of specialty molded foams that are helpful in reducing this harshness are called noise and vibration harshness (NVH) foams.

Competitive and legislative pressures have combined recently to prompt many car manufacturers to upgrade their noise and vibration reduction packages. In Europe, the large number of small, comparatively noisy vehicles in use has prompted the European Union to implement new legislation reducing the permissible level of “pass-by” noise. Around the globe, similar legislation already exists or is proposed in most developed countries.^{13.27} To

address this requirement, many new car and truck models will insulate noisy mechanical parts with shields padded on the noise receiving side with molded NVH foam. Commercial examples of this application have been presented.^{13,28} The myriad of potential NVH foam applications is illustrated in Figure 13.1.

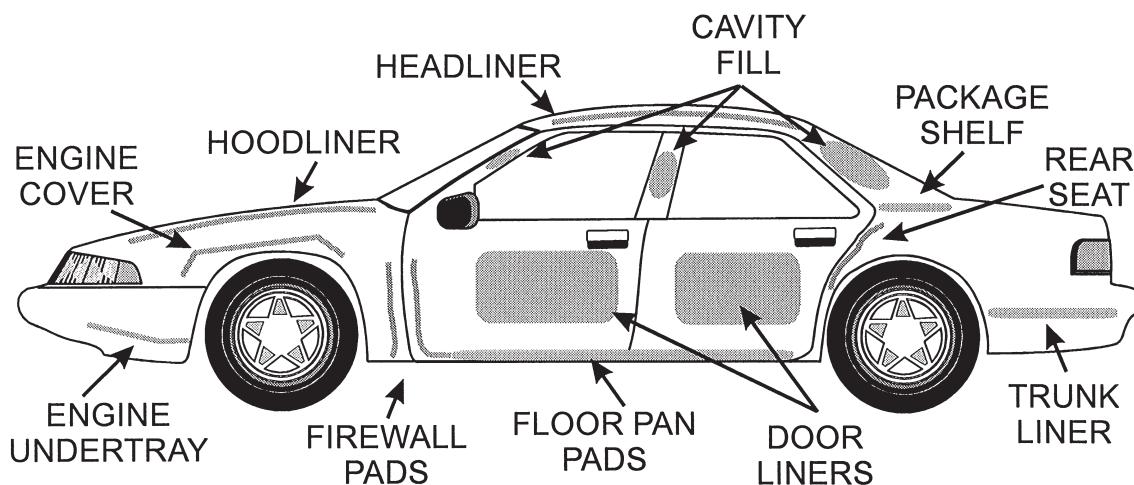


Figure 13.1 Application Areas for NVH Foams

In the early days of the automobile industry, natural products like straw, felt and even peat moss were used to provide a measure of harshness reduction. By the 1950's, fiber pads made of resinated fiber felt (usually reclaimed cotton and synthetic fibers) were the preferred material for NVH applications. By the late-1970's, cut slabstock and rebonded polyurethane foams were being used in some applications.^{13,29}

With each of these early technologies, the final part was often just a flat cut sheet of material that required significant labor to produce and install in the car. Fit to the body contours was often poor resulting in the need for more hand labor to cut-out certain areas and build up others. Acoustic performance was reduced by the poor fit, the presence of cut-outs and by compression of the material occurring during final installation and use.

By the mid-1980's, some automobile manufacturers had begun to eliminate these problems with flexible foams molded to fit the exact shape of each application. This reduced labor costs, trimming scrap and made it possible to improve long-term acoustic performance. MacFarland has recently listed over 40 major car and truck platforms that are now using molded NVH foams for dash mat and carpet underlay applications.^{13,30} Recent advances in cutting and contouring technology have won new applications for conventional slabstock foams.^{13,31} An overall comparison of various performance criteria for alternative NVH materials is presented in Table 13.1.

Table 13.1 Performance Criteria for Alternative NVH Materials
(after MacFarland 13.30)

| | Cotton Felt | Slabstock Foams | Molded Foams |
|----------------------|-------------|-----------------|--------------|
| Acoustic Performance | 1 | 1 | 1 |
| Ease of Installation | 3 | 2 | 1 |
| Part Cost | 2 | 1 | 3 |
| Part Weight | 3 | 1 | 2 |
| Compression Set | 3 | 1 | 1 |
| Fogging Contribution | 3 | 2 | 1 |
| Recyclability | 2 | 2 | 2 |
| 1 = best performance | | | |

Molded NVH Foams

Soft, cold-cure type HR foams have been developed for many NVH applications. For applications requiring high-damping factors, the viscoelastic type foams have proven useful. Typical raw materials used in each type of foam are illustrated in Table 13.2.

Waddington and Duff have reported that the viscoelastic type of NVH foams can be successfully prepared using polyols obtained from recycled automobile seats.^{13.32}

Table 13.2 Typical Formulation Ingredients and Properties
For NVH Foams

| Components | HR Molded Foam | Viscoelastic Foam |
|-----------------------------------|----------------|-------------------|
| VORANOL CP-6001 Polyol | 100 | 80 |
| VORANOL CP-700 Polyol | 0 | 20 |
| VORANOL CP-5021 Polyol | 2.5 | 6-15 |
| Water | 3-4 | 3-4 |
| Catalysts and Surfactants | 1-1.5 | 1-1.5 |
| SPECFLEX NS 540 | | |
| Isocyanate, Index | 70-100 | 70-100 |
| Properties | | |
| Demold Time, seconds | 45-90 | 60-130 |
| Molded Density, kg/m ³ | 45-80 | 55-100 |
| Dynamic Modulus, kPa | 40-400 | 60-550 |
| Damping Factor | 0.15-0.25 | 0.33-1.0 |
| 40% CLD Hardness, kPa | 2-18 | 5-15 |
| Elongation, % | 100-150 | 100-150 |
| Tensile Strength, N/m | 100-200 | 100-300 |
| 50% Compression Set, % | 5-12 | < 20 |

Many applications require these foams to be molded into a large surface area part (typically 1 to 5-square meters), containing no internal voids or air-traps and with thicknesses varying from 1 to 150-millimeters across the part. Such parts are very difficult to mold and require rigorous formulations with excellent flowability. Depending on the complexity of the part and the manufacturing process, demold times typically vary from 45 to 180-seconds. Table 13.3 presents a comparison of physical and acoustic properties for the main classes of NVH materials. Efforts are now underway to lower molded foam density and to improve acoustic performance using for example, the new liquid carbon dioxide auxiliary blowing agent technology.

Table 13.3 Acoustic and Physical Properties for Common NVH Materials

| | Cotton Felt | Slabstock Foam | Rebonded Foam | Molded Foam |
|----------------------|-------------|----------------|---------------|-------------|
| Density, g/l | 50-1000 | 25-60 | 60-120 | 45-100 |
| Compression Set, % | 20-100 | 5-20 | 5-40 | 5-20 |
| Elongation, % | < 50 | 50-300 | > 50 | 100-150 |
| Dynamic Modulus, kPa | > 20 | > 20 | > 20 | > 20 |
| Damping Factor | 0.05-0.2 | 0.1-1.0 | 0.05-0.2 | 0.15-1.0 |

In many cases, improved insulation against noise and vibration can be achieved by combining the soft foam (often called the spring in conceptual models) with a heavy layer (the mass in models).^{13.33} The combination can involve two or more separate parts installed in the same application area or one composite part in which the NVH foam has been molded directly onto the back of the heavy layer. In some cases, the heavy layer will have been previously bonded to a decorative layer visible to the automobile occupants. This is an excellent way to consolidate parts and simplify installation into the automobile. Total acoustic performance of the assembly or the composite part is influenced by; the accuracy of fit to the application area, foam thickness, the softness of the foam, the airflow resistance of the foam and by the characteristics of the heavy layer.^{13.34}

Numerous pathways for sound propagation into the passenger compartment have been detailed.^{13.35-13.43} One pathway that can be influenced by the use of NVH foams is the transmission of sound and vibrations through the engine bulkhead and the floor pan. An acoustical barrier system for that application is conceptualized in Figure 13.2.

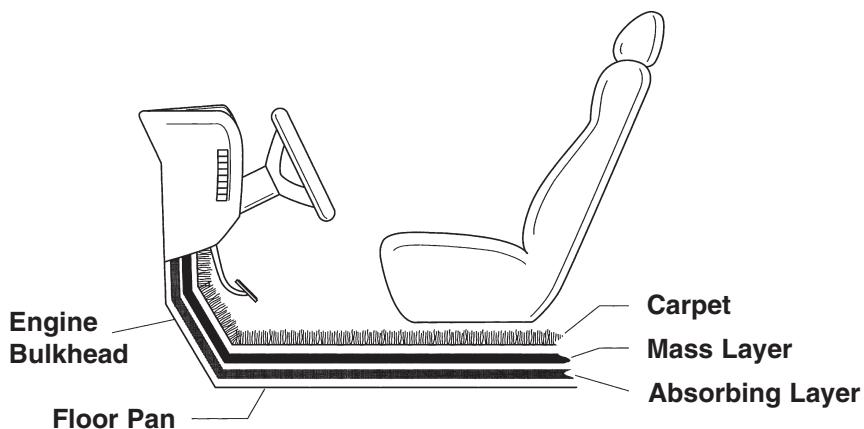


Figure 13.2 Typical Acoustical Barrier System
For A Passenger Automobile

In that system, a soft noise-and-vibration-absorbing foam layer is placed in direct contact with the acoustic sources. The next layer is a heavy mass composite, which is then topped with the final carpet. The carpet is often thermoformed to fit the contours of the floor pan and engine bulkhead. The system could consist of three separate parts or of one composite assembly. A comprehensive study of this NVH application is available.^{13.44}

Sound and Vibration Absorption

Sound is originated by vibrations from some source. In the automobile, these sources can include vibrating body panels, the engine, the suspension and the exhaust system. The wind and other outside sources can also contribute to the noise level inside the passenger compartment.

When a sound falls on a surface, its energy is partially reflected and partially absorbed. In the above application, the soft sound-absorbing foam layer is used to reduce the intensity of vibrations reaching the passenger compartment. The characteristic of materials that defines how well they do that job, is the sound absorption coefficient, α . This coefficient is defined as the ratio of energy absorbed by the surface to the energy incident upon the surface. It is calculated according to the following equation:

$$\alpha = 1 - (v/I) \quad (13.1)$$

where, v is the reflected sound energy and I is the incident sound energy.

Numerical values for α range between 0 and 1, with higher values indicating better performance. This number is typically reported as a function of frequency as illustrated in Figure 13.3.

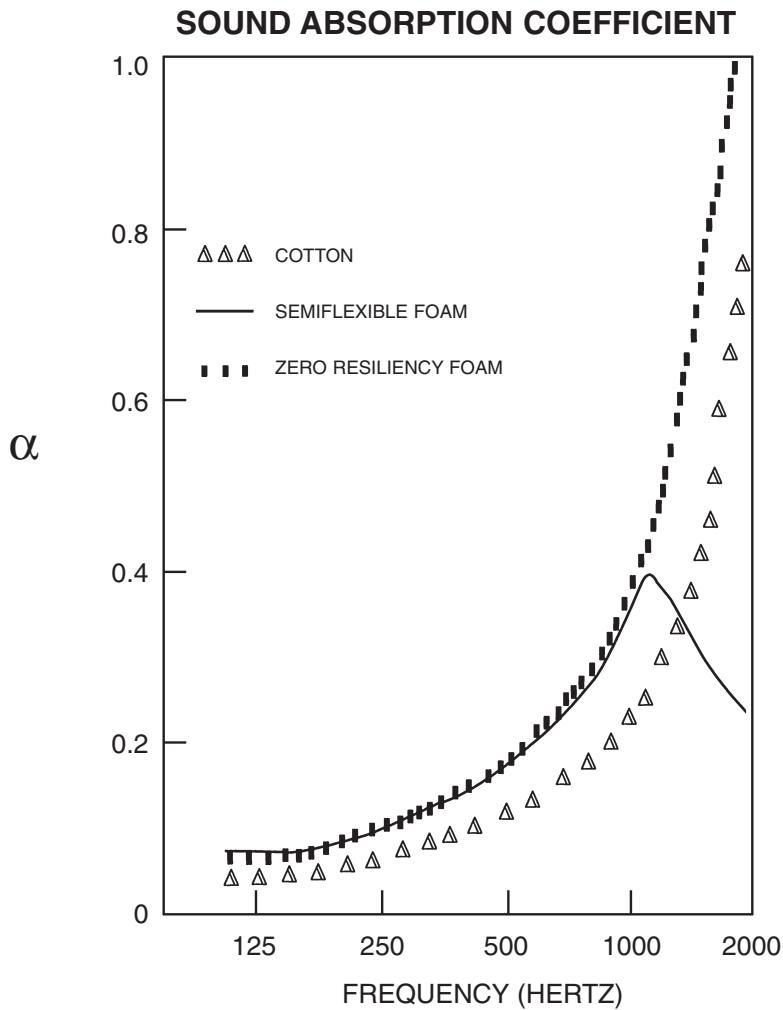


Figure 13.3 Typical Sound Absorption Coefficients for Selected Padding Materials (Compiled from References 13.46, 13.50)

The traditional material for this application has been a resinated, pliable felt made from reclaimed cotton and synthetic fibers (fiber pads). Good sound absorption at a low raw-material cost were the main advantages. The principal disadvantage was the high labor costs associated with fabricating and installing the final pad.

Various processes now exist that allow polyurethane foam to be molded directly onto the backing of a carpet.^{13.45-13.46} These processes offer the following advantages:

- Acoustic pad molded to fit shape of car,
- Easier, faster installation,
- Integration of other parts,
- Capability to vary thickness where needed.

Enhanced performance has been found with composites of polyurethane foams with other polymers.^{13.47-13.49}

In the present application, it is also desired for the foam layer to reduce the vibrations reaching the carpet's attached heavy-mass layer. Excessive vibrations of that mass layer could result in noise in the passenger compartment.

Generally, vibrations in the range of 50 to 300-Hertz are of most interest. The ability of materials to absorb vibrations is described by a composite loss factor term, η_c . Details of the procedure and calculations leading to the final η_c number are given by Zwinselmann and Bachmann.^{13.50} Higher numbers indicate better performance. Figure 13.4 shows typical performance for several alternative padding materials.

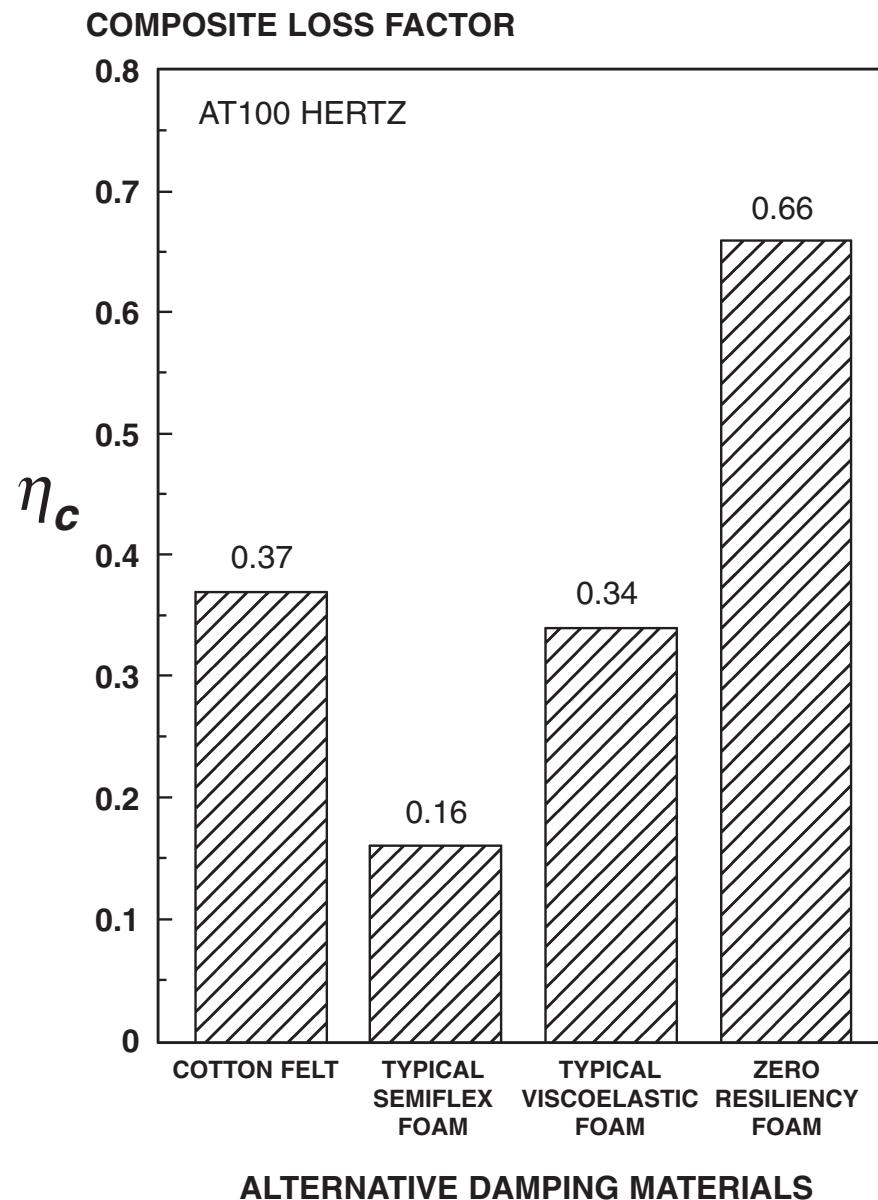


Figure 13.4 Vibration Damping Performance Of Selected Materials
(Compiled from References 13.46, 13.50)

Cotton felt is the accepted baseline of performance. Conventional molded foams can appear somewhat inferior in simple flat surface controlled vibration tests, but do offer major processing, installation and long-term performance advantages. Molded viscoelastic foams can be expected to perform about as well as cotton felt. A real performance improvement can be seen with the use of zero-resiliency foam.

The Sound Barrier

The function of the heavy-mass layer is as a sound barrier. This layer may be attached to the back of the carpet, or simply be laid between the carpet and floor. Effective barrier materials have a property called transmission loss. This characteristic is the ability to resist the flow of vibrational energy through the material. The major basis for a high transmission loss is mass.^{13.51-13.52} Thus, the traditional products used in this application have been highly filled bitumen, rubbers, thermoplastics or, more recently, polyurethanes.^{13.45}

In one typical process, a highly filled, specially formulated thermoformable polyurethane heavy layer is knife coated onto the back of a special grade of carpet. After curing, the carpet/heavy layer composite is cut and thermoformed to match the exact contours of the floor pan. The heavy layer is generally applied in thickness less than about 4 millimeters (0.15 inch) and at coverage in the range of 4-8 kg/m² (118-236 oz/yd²).

An alternative process uses discontinuous RIM molding technology to attach a heavy filled polyurethane mass layer to a previously thermoformed carpet. This process has the advantage that it allows the positioning of a heavy layer of any needed thickness only at those points where sound absorption help is needed.

The polyurethanes offer improved fogging and heat resistance compared to the thermoplastic alternatives.

References

- 13.1 Ball, G.L.; Schwartz, M.; Long, J.S. "The Sound Absorption Properties Of Urethane Foams"; *Official Digest Federation of Societies for Paint Technology* **1960**; 32/425, 817-831.
- 13.2 Buist, J.M.; Gudgeon, H. *Advances in Polyurethane Technology*; Maclaren and Sons: London, 1968, 159-162.
- 13.3 Imai, Y.; Asano, T. "Studies of Acoustical Absorption of Flexible Polyurethane Foam"; *J. Appl. Polym. Sci.* **1982**; 27, 183-195
- 13.4 Moore, R.S. "Sound Absorption" In *Encyclopedia Of Polymer Science And Technology* 1970, 12, 700-724.

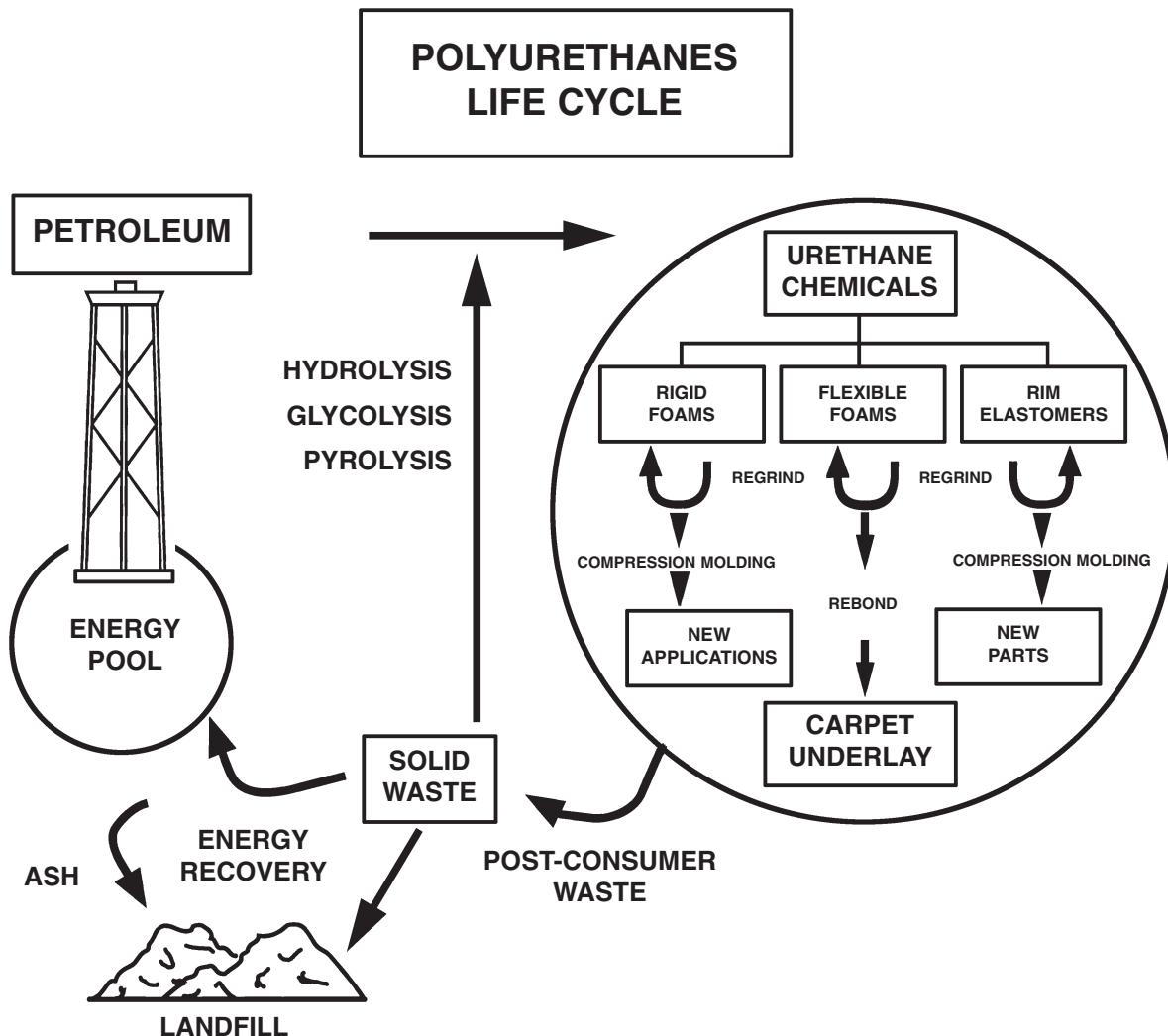
- 13.5 Ludman, W.R. "The Practical Application of Flexible Polyurethane Foams in Sound Insulation"; *Proceedings of the Plastics and Rubber Institute Urethanes Group Conference, London*, 1976, GI-G4.
- 13.6 Kingsbury, H.B.; Cho, K.; Powers, W.R. "Dynamic Complex Modulus of Polyurethane Foams"; *J. Cell. Plast.* **1978**; 14/2, 113-117.
- 13.7 Eeckhaut, G.; Pham, T.; Lockwood, R.J. "Improved Sound Insulation in Motor Vehicles"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 708-711.
- 13.8 Gahlau, H.K. "Advanced Noise Control in Automotive Engineering"; *Proceedings of the SPI/FSK Polyurethanes World Congress*; Technomic: Lancaster, Pa., 1987; 712-726.
- 13.9 Lee, J.R. "Automotive Sound Insulation - The Role Of Polyurethanes"; *Conference Papers, UTECH 88*; Crain Communications: London, 1988, 81-82.
- 13.10 Corsaro, R.D.; Sperling, L.H.; Eds. *Sound and Vibration Damping with Polymers, ACS Symposium Series 424*; American Chemical Society: Washington, DC., 1990.
- 13.11 Lutter, H.D.; Mertes, J.; Zschiesche, R. "PUR Flexible Foam with Sound Absorbing Properties"; *Proceedings of the Polyurethanes World Congress 1991*; Technomic: Lancaster, Pa., 1991; 252-256.
- 13.12 Lauriks, W. "Acoustic characteristics of low density foams"; In *Low density cellular plastics, Physical basis of behaviour*; Hilyard, N.C.; Cunningham, A.; Eds.; Chapman and Hall: London, 1994, 319-361.
- 13.13 *Polymers in Vibration Damping and Soundproofing*; PB86-858966; National Technical Information Service: Springfield, Va., 1986.
- 13.14 Goldman, D.E.; von Gierke, H.E. "Effects Of Shock And Vibration On Man"; In *Shock and Vibration Handbook*; Harris, C.M.; Crede, C.E., Eds.; McGraw-Hill: New York, 1961, 44.1-44.51.
- 13.15 McCormick, E.J. *Human Factors Engineering*; McGraw-Hill: New York, 1964, 474-483.
- 13.16 Kryter, K.D. *The Effects of noise on Man*, Academic Press: New York, 1970.
- 13.17 Miller, J.D. "Effects of Noise on People"; *J. Acou. Soc. Am.* **1974**; 56/3, 729-764.
- 13.18 Griffin, M.J. *Handbook of Human Vibration*; Academic Press: London, 1990.
- 13.19 Bryan, M. E.; Tempest, W.; Williams, D. "Vehicle noise and the passenger"; *Appl. Ergonom.* **1978**; 9/3, 151-154.
- 13.20 Winklhofer, E.; Thien, G.E. "A Review of Parameters Affecting the Noise and Vibration in Diesel Powered Passenger Cars"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1985; Paper No. 850966; SAE: Warrendale, Pennsylvania.
- 13.21 Kryter, K.D. *The Effects of noise on Man*, Academic Press: New York, 1970.
- 13.22 Miller, J.D. "Effects of Noise on People"; *J. Acou. Soc. Am.* **1974**; 56/3, 729-763.
- 13.23 Howell, T.M.; Schumacher, R.F. "Vehicle Sound Measurement - 20 Years of Testing"; Proceedings of the SAE International Congress and Exposition, Detroit Michigan, 1985; Paper No. 850969; SAE: Warrendale, Pennsylvania.

- 13.24 Bagga, K.S.; Repick, E.P. "Development of an Interior Sound Level Measurement Procedure for Light Vehicles - SAE J1477"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1985; Paper No. 85-0994; SAE: Warrendale, Pennsylvania.
- 13.25 "Measurement of Interior Sound Levels of Light Vehicles", SAE Recommended Practice SAE J1477, January 1986; SAE: Warrendale, Pennsylvania.
- 13.26 Stacy, J.M. "The Development of a Unique Australian Car"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1987; Paper No. 871260; SAE: Warrendale, Pennsylvania.
- 13.27 Jost, K. "Measuring vehicle pass-by noise"; *Auto. Eng.* **1995**; March, 28-32.
- 13.28 Costa, C.E.T.; Pauperio, A. "Development of a High Filled Semirigid System for the Automotive Sound Insulation"; *Proceedings of the SPI-32nd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1989, 579-586.
- 13.29 Wehrenberg, R.H. "Materials that control Noise"; *Mat. Eng.* **1981**; 94/4, 51-60.
- 13.30 MacFarland, D.R. "Cost Effective Molded Polyurethane Foam for Automotive Acoustical Carpet Underlay and Dash Insulators"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1994; Paper No. 940700; SAE: Warrendale, Pennsylvania.
- 13.31 Grande, J.A."Novel PUR foam-backed carpet to appear in new GM minivans"; *Mod. Plast.* **1996**; October, 30-31.
- 13.32 Waddington, S.; Duff, A.W. "Polyurethane Automotive Seating Finds New Life in Moulded Vehicle Acoustics"; *Proceedings of the Polyurethanes World Congress 1993*; Technomic: Lancaster, Pa., 1993; 558-563.
- 13.33 Waddington, S. "CFC-Free Polyurethane Foams for Enhanced Noise Reduction in Automotive Applications"; *Conference Papers, UTECH 92*; Crain Communications: London, 1992, 72-75.
- 13.34 Cunningham, A.; Duggan, N. "Advances in Polyurethane for use in Acoustic Applications for the Automotive Sector"; *Conference Papers, UTECH 94*; Crain Communications: London, 1994, Paper 7.
- 13.35 Apps, D.C. "Automobile Noise"; In *Handbook of noise Control*, C.M. Harris, Ed.; McGraw-IEH: New York, 1957, Chapter 31.
- 13.36 Priede, T.; Jha, S.K. "Low Frequency Noise in Cars"; *J. Auto. Eng.* **1970**; July, 17- 21.
- 13.37 Jha, S.K.; Priede, T. "Origin of Low Frequency Noise in Motor Cars"; *Proceedings of the 14th FISITA Conference*, London, 1972, 46-55.
- 13.38 Peart, J.R.; Huber, T.V. "Vehicle Sound Package-Art or Science?"; Proceedings of the SAE National Automobile Engineering Meeting, Detroit, Michigan, 1972; Paper No. 720508; SAE: Warrendale, Pennsylvania.
- 13.39 Jha, S.K. "Characteristics and Sources of Noise and Vibration and Their Control in Motor Cars"; *J. Sound Vib.* **1976**; 47/4, 543-558.
- 13.40 Nefske, D.J.; Howell, L.J. "Automobile Interior Noise Reduction using Finite Element Methods"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1978; Paper No. 780365; SAE: Warrendale, Pennsylvania.

- 13.41 Betzhold, C.; Gahlau, H. "Quiet Automobiles Despite Lightweight Construction"; *SARIRSA* **1990**; 5, 215-220.
- 13.42 Yamazaki, I.; Inoue, T. "An Application of Structural-Acoustic Coupling Analysis to Boom Noise"; *Proceedings of the SAE Passenger Car Meeting and Exposition, Dearborn, Michigan*, 1989; Paper No. 891996; SAE: Warrendale, Pennsylvania.
- 13.43 Lim, T.C.; Steyer, G.C. "Hybrid Experimental-Analytical Simulation of Structure-Borne Noise and Vibration Problems In Automotive Systems"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1992; Paper No. 920408; SAE: Warrendale, Pennsylvania.
- 13.44 Cunningham, A.; Hilyard, N.C. "PU Automotive Carpet Composites for Vehicle Interior Noise Control: Physical Basis of Behaviour"; In *Advances In Urethane Science and Technology, Volume 13*; Frisch, K.C.; Klempner, D., Eds., Technomic: Lancaster, Pa., 1996, 1-52.
- 13.45 Berthevas, P.R.; Fanget, A.; Gatouillat, G. "The Development of a Sound Insulation Package for Car Floor Coverings Using a Combination of Polyurethane Technologies"; *Proceedings of the SPI/FSK Polyurethanes World Congress, Aachen, West Germany*, 1987; Technomic: Lancaster, Pa., 1987; 701-707.
- 13.46 McCullough, D.; Gansen, P. "Viscoelastic MDI-Based Polyurethane Foam for Sound and Vibration Dampening in Automobiles"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1990; Paper No. 900093; SAE: Warrendale, Pennsylvania.
- 13.47 Chen, A.C.F.; Williams, H.L. "Studies of Polymeric Systems for Absorbing Airborne Sound"; *J. Appl. Polym. Sci.* **1976**; 20, 3387-3402.
- 13.48 Klempner, D.; Wong, C.L.; Ashtiani, M.; Frisch, K.C. "Sound Attenuation of Interpenetrating Polymer Network Foams"; *J. Appl. Polym. Sci.* **1986**; 32, 4197-4208.
- 13.49 Tong, S.; Tsai S.; Chen, J.; Wu, P. "Studies of Phenol-formaldehyde/Polyurethane Hybrid Foam for Sound Absorption Material"; *Conference Proceedings, Society of Plastics Engineers 46th Annual Technical Conference and Exhibit*; SPE: Brookfield Center, Co., 1988, 699-702.
- 13.50 Zwinselman, J.J.; Bachmann, W.D. "Polyurethane Foams for Sound and Vibration Dampening in Automotive Applications"; *J. Cell. Plast.* **1988**; 24/3, 274-283.
- 13.51 Schwartz, M.; Gohmann, E.J. "Influence of Surface Coatings on Impedance and Absorption of Urethane Foams"; *J. Acous. Soc. Am.* **1962**; 34/4, 502-512.
- 13.52 Wehrenberg, R.H. "Materials that control Noise"; *Mat. Eng.* **1981**; 94/4, 51-60.

Chapter 14

Recycling



Resource conservation and environmental concerns require all of us to consider recycling and resource management as integral parts of our business practice. This chapter focuses on the technologies that have been developed for the recycling of polyurethane flexible foams. These include material recycling, such as regrind incorporated into new foam or rebond for carpet underlay; feedstock recycling through hydrolysis, pyrolysis or glycolysis; and thermal recycling through combustion with energy recovery.

Chapter 14

Recycling

W. Farrissey, J. Fosnaugh

Polyurethanes, in common with most plastics, are petroleum-based materials. As outlined in the polyurethanes life cycle graphic, the petroleum-derived polyurethane precursor chemicals are converted into rigid and flexible foams, RIM and cast elastomers and the various other products which make up the polyurethane industry today.^{14.1} Although polyurethane flexible foam is classed as a thermoset polymer, and thermoset polymers historically have not generally been associated with recycle activities, in reality, a great deal of recycling of flexible foams does occur. The graphic introducing this chapter illustrates that virtually all of the process scrap from flexible slabstock foam cutting operations and from molded foam seating production is recycled by a rebonding process into high quality carpet underlay. Other technologies for recycling of both process scrap and post-consumer scrap have been developed, including chemical recovery via pyrolysis, hydrolysis, or glycolysis; material recovery through the use of regrind and energy recovery.

The ultimate goal of these various technologies is to conserve and recover as much of the energy and resources invested in polyurethane materials as possible.

This chapter will discuss the various recycle strategies listed in Table 14.1. These include material recycling; such as the foam rebond and regrind processes; chemical recycling via polymer breakdown through hydrolysis, glycolysis or pyrolysis; and energy recovery through various combustion technologies.

Table 14.1 Recycle Technologies

| Technology | References |
|-------------------------------|----------------------|
| Material | |
| Rebond | 14.2-14.5, 14.7-14.9 |
| Regrind | 14.6 |
| Chemical | |
| Hydrolysis | 14.11, 14.12-14.19 |
| Glycolysis | 14.1, 14.20-14.34 |
| Pyrolysis | 14.35-14.45 |
| Energy | |
| High Temperature Gasification | 14.47 |
| Rotary Kiln/Fluidized Bed | 14.46 |

MATERIAL RECYCLING

Polyurethane foam in automotive seats is likely to be the first major plastic resin to be recycled from end-of-life vehicles.^{14.48} The reason is because the foam is advantaged at the critical steps in the recycling process.

1. Polyurethane foam is universally used and easy to identify in seats.
2. A significant quantity can be recovered from each vehicle (20 lbs/all seats).
3. Low cost to process into a product that can be sold (shredding).
4. Large market and demand for the recycled material (carpet underlay).
5. Relatively high price offered for the recycled foam.

The critical issue remaining, which has been preventing wide spread recycling, is the high cost of foam removal from the vehicle. This cost is no higher than the removal of any plastic part and points out the necessity to develop new designs that yield foam more readily and to improve auto dismantling efficiency by modifying the current auto scrapping infrastructure.

The conversion of flexible polyurethane foam into cushioning generates 8-12% waste depending on the shape of the foam blocks, and the complexity of the cut parts. Molded seat cushion production generates some scrap as well. All of this scrap, plus some imported material, is used in the production of rebonded carpet underlay pads. About 280 million pounds per year of North American flexible foam scrap is consumed in this way. In addition, approximately 120 million pounds of scrap foam was imported for this application in 1989.^{14.2}

As with all scrap recycle processes, the first step in the reuse of flexible foam scrap is separation of the foam from any contaminants such as wire, fabric and any other debris. The foam is then chopped into pieces of suitable size and coated with binder. Typically, the binder is an isocyanate prepolymer prepared from toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) with less than a stoichiometric amount of a polyether polyol.^{14.3} These types of prepolymers contain excess isocyanate functions which react with steam in the curing step to complete the polymerization. Amounts of binder of 10-20% by weight of foam are used. After addition of catalyst and thorough mixing, the foam/binder mixture is placed in a mold, compressed and kept compressed during cure with heat and steam.^{14.4-14.5} Semicontinuous and also continuous processing, as illustrated in Figure 14.1, may be used. By varying the degree of compression, foam densities of 2.5-6.2 lb/ft³ (40-100 kg/m³) can be prepared.

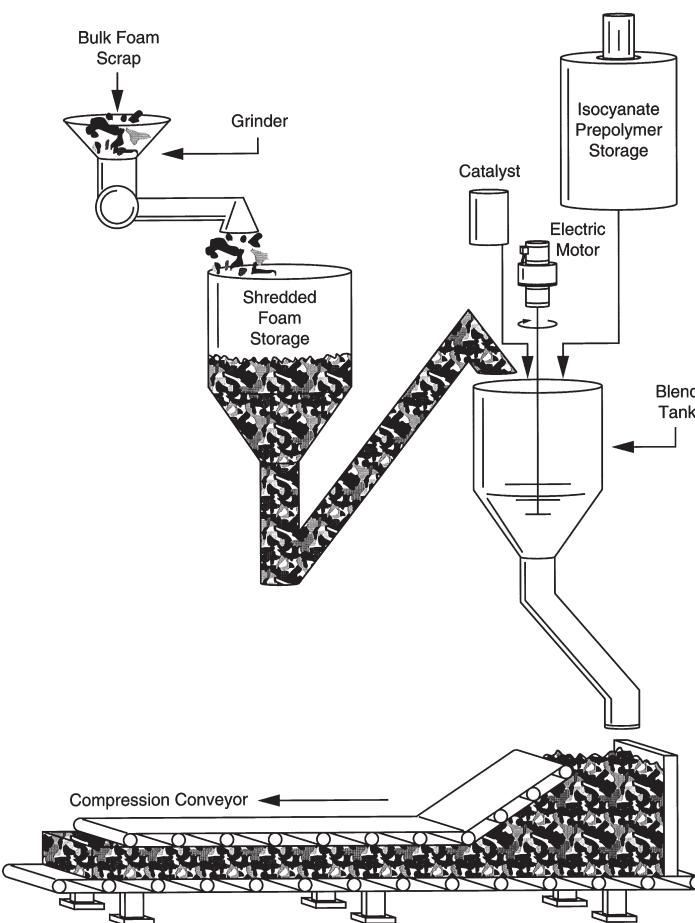


Figure 14.1 Manufacture Of Rebonded Foam

Another potential technology for the utilization of scrap flexible foam involves recycle of the comminuted or pulverized scrap back into the foam formulation. In a process described by Baumann and coworkers, the scrap foam is first ground at cryogenic temperatures to a suitable powder.^{14,6} The powder is then mixed with polyol, at levels of 15-20 parts per hundred of polyol. A typical formulation is listed in Table 14.2.

Table 14.2. Typical Formulation
Using Ground Foam

| Material | pbw |
|---------------------------|-----------|
| Polyol | 100.0 |
| Ground Foam | 15.0 |
| X345 Additive | 0.75 |
| Water | 5.2 |
| Fluorocarbon 11 | 3.0 |
| Silicone Surfactant | 1.2 |
| DABCO TL Catalyst | 0.2 |
| Stannous Octoate Catalyst | 0.15 |
| 80:20 TDI | 115 Index |

The blended polyol/ground foam slurry can be handled on typical slabstock foam processing equipment. For optimum performance, adjustments to catalyst and isocyanate levels are necessary. The mechanical and physical properties of the foam made with regrind, listed in Table 14.3, are comparable to those of control materials.

Table 14.3 Physical Property Comparison (Grade 1130)

| Property | Control | Experimental with 15% Addback |
|-----------------------------|---------|-------------------------------|
| Density, lb/ft ³ | 1.17 | 1.14 |
| IFD 25% | 30.5 | 30.0 |
| IFD 65% | 58.9 | 57.9 |
| Support Factor | 1.93 | 1.93 |
| Breathability | 5.0 | 4.0 |
| Tensile, psi | 12.3 | 13.7 |
| Tear, lb/in | 1.7 | 1.8 |
| Elongation, % | 114 | 121 |
| 90% Compression Set, % | 5.8 | 6.1 |
| Resilience, % | 42 | 42 |

Additional studies have been completed by the Polyurethane Recycle and Recovery Council-(PURRC), incorporating regrind into both slabstock and seat foam.^{14.49}

The cost of pulverizing the foam presents the biggest challenge towards sustainable recycling. PURRC has funded several studies to understand and to improve pulverization economics. Several processes have been studied and evaluated for effectiveness in molded foam, including Air Swept Pulverizers, Cryogenic Hammer Mills, Ball Mills, Two Roll Mills, Solid State Extrusion and Pellet Mills.^{14.50}

One pulverization process, the two roll mill, has been commercialized by Hennecke in Germany, under the name GRINDFLEX technology. They claim up to 30% powder in the polyol stream is possible using their equipment.^{14.51}

An evaluation has been made to estimate the cost of recycling polyurethane foam from scrapped cars back into new seat cushions using the regrind concept.^{14.52} The study assumed the two roll mill process would be used to pulverize the recovered seat foam. The study concluded that a 15% recycled content product would be 1% lower in cost than 100% virgin product, depending on the size of the operation.

Nissan is recycling scrap foam and polyvinyl chloride (PVC) skins from its seating and interior trim operations.^{14.7} The finely ground scrap is subjected to an air separation step to remove the lower-density foam from any PVC material as diagrammed in Figure 14.2.

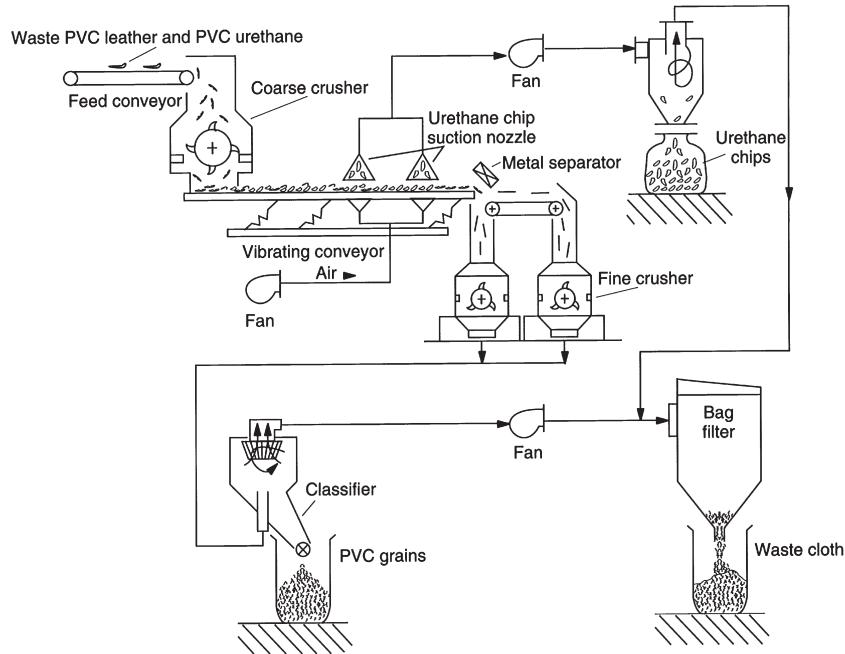


Figure 14.2 Nissan Process For Scrap Foam Recovery

Then it is rebonded and molded into headrests and armrests. The recovered PVC is also reused to produce trunk mats (see Figure 14.3).

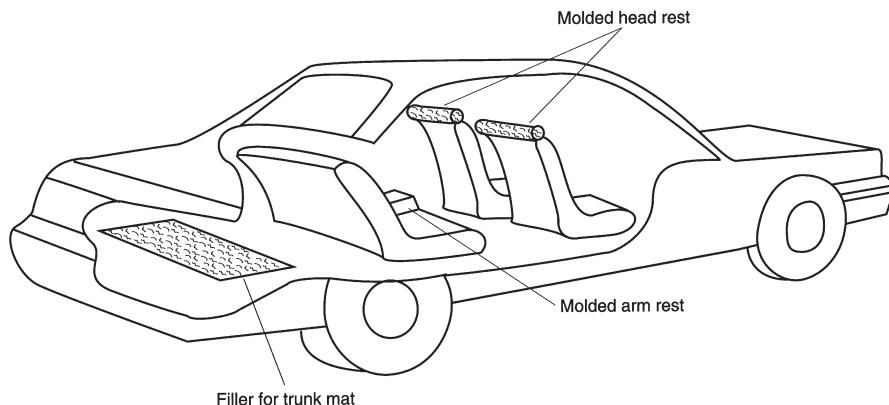


Figure 14.3 Applications For Recovered Materials

Although recycle of flexible foam process scrap is highly successful, the situation with post-consumer flexible foam waste is fairly limited to recovered carpet underlay. Some attempts have been made to rebond scrap from used bedding and car seats.

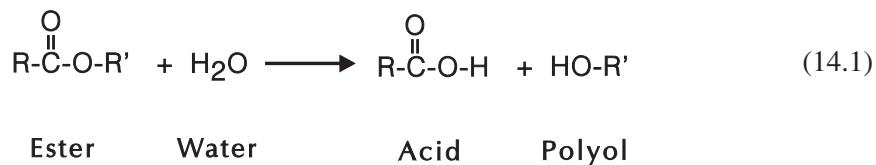
A study commissioned by PURRC demonstrated that foam from automobile seats could be removed in an average of 12 minutes and from mattresses in 4-8 minutes. PURRC and the American Plastics Council have sponsored several studies to define the removal of foam from automobiles and the viability of the rebonded product in new carpet underlay and NVH

applications in the car. One study, commissioned by PURRC demonstrated that the foam removed from end-of-life vehicles could be manufactured into 100% recycled content carpet underlay. The carpet underlay was tested by an independent laboratory and found to be comparable in performance and long term durability to conventional carpet underlay.^{14.53}

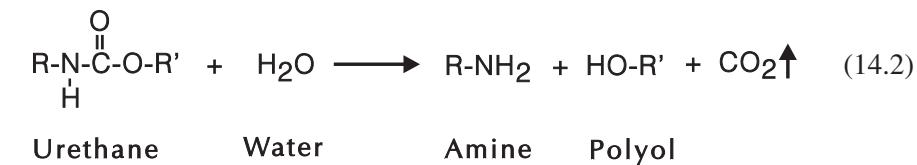
CHEMICAL RECYCLING: HYDROLYSIS/GLYCOLYSIS/PYROLYSIS

Polymers containing carbonyl functions can be cleaved back to monomers by hydrolysis or glycolysis. For polyesters such as polyethylene terephthalate, hydrolysis merely reverses the polycondensation reaction which formed the polymer initially. For polyurethanes, the situation is more complicated, in that one of the polymer building blocks, the polyisocyanate monomer, is not obtained. Rather the product of its reaction with water, the polyamine is produced along with the polyol. Carbon dioxide is evolved as a hydrolysis byproduct. Of course, the polyamine can be converted back to the polyisocyanate if desired. These reactions are illustrated in Equations 14.1 and 14.2.

For polyester polymers:

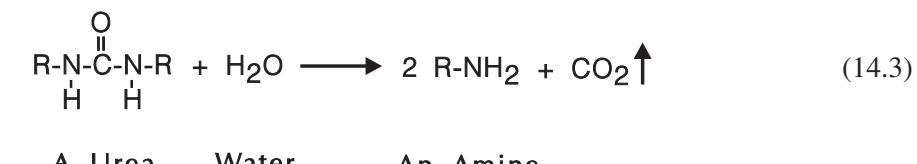


For polyurethane polymers:



The situation for polyurethanes is further complicated by the presence of other hydrolyzable functions in the polymer, e.g., the urea functions in flexible foams. Fortunately, as described in References 14.10 and 14.11, these groups can be hydrolyzed back to an amine and carbon dioxide. Equation 14.3 illustrates the process.

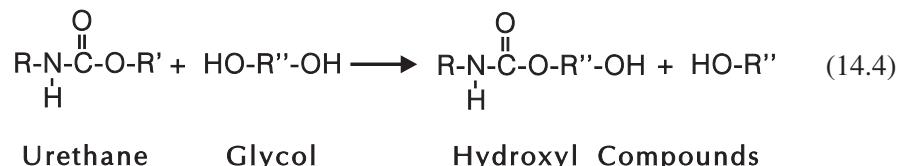
For polyurethane/polyurea polymers:



The appeal of the hydrolysis method for breaking down polyurethanes, especially from sources where both urethane and urea linkages may be present, is the simplicity of converting everything to the diamine plus the polyol. The major disadvantage is that the diamine and polyol must be separated before either is reused.

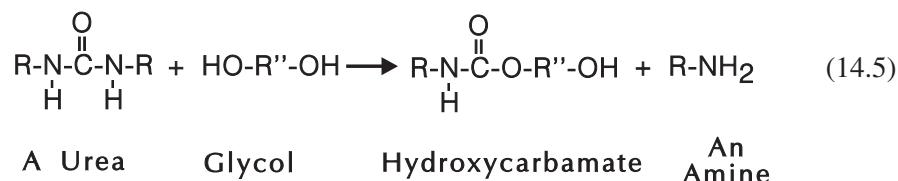
Glycolysis of polyurethanes, on the other hand, converts everything to a mixture of polyhydroxy compounds which can be used directly without further separation.^{14,10} The process is illustrated in Equation 14.4.

For glycolysis of polyurethanes:



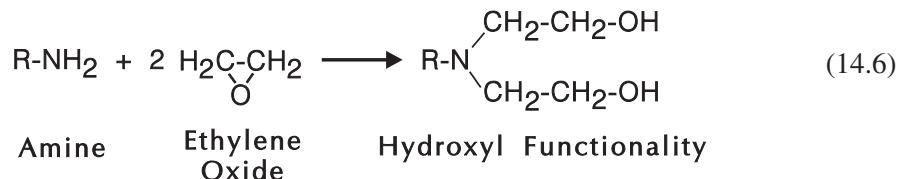
The situation gets more complicated when urea functions are involved. In this case, amino-functional moieties are produced along with the hydroxycarbamates, as shown in Equation 14.5.

For glycolysis of polyureas:



Even in this case, however, separation can be avoided by converting the amine-terminated functions to hydroxyl functions by reaction with ethylene (or propylene) oxide.^{14,10} Note that in Equation 14.6, the ethoxylation (or propoxylation) increases the functionality of the system by converting an amino function to two hydroxyl functions. Both hydrolysis and glycolysis have been explored at some depth and will be discussed more fully below.

Ethoxylation of amines:



STEAM HYDROLYSIS

Equation 14.2 illustrated that flexible polyurethane foam can be hydrolyzed by high-pressure steam to give a polyamine, polyol and carbon dioxide. General Motors Research Laboratories has published most of the available information on this process.^{14.12-14.14}

High-pressure steam will hydrolyze flexible foam rapidly at temperatures of 450-600°F (232-315°C). The diamines can be distilled and extracted from the steam stream, and the polyols can be recovered from the hydrolysis residue. The hydrolysis temperature did have an effect on the polymer quality and yield. An optimum polyol yield was found at a foam degradation temperature of 550°F (288°C). Table 14.4 shows that the recovered polyol could be used in a flexible foam recipe at the 5% level with excellent results.^{14.12}

Table 14.4 Flexible Foam Physical Properties

| Property | Control | Recycled Polyol |
|----------------------------|---------|-----------------|
| Density, kg/m ³ | 41.6 | 42.6 |
| Tensile, kPa | 160.0 | 165.0 |
| Tear, N/m | 405.0 | 382.0 |
| Elongation, % | 160.0 | 167.0 |

In the continuous recycle process shown in Figure 14.4, residence times of 10-30 minutes at 550°F have given 60-80% yields for recovered polyol.^{14.15} Also, a twin-screw extruder has been described as a reactor for continuously hydrolyzing foam-scrap. Temperatures and residence times are similar.^{14.16-14.17}

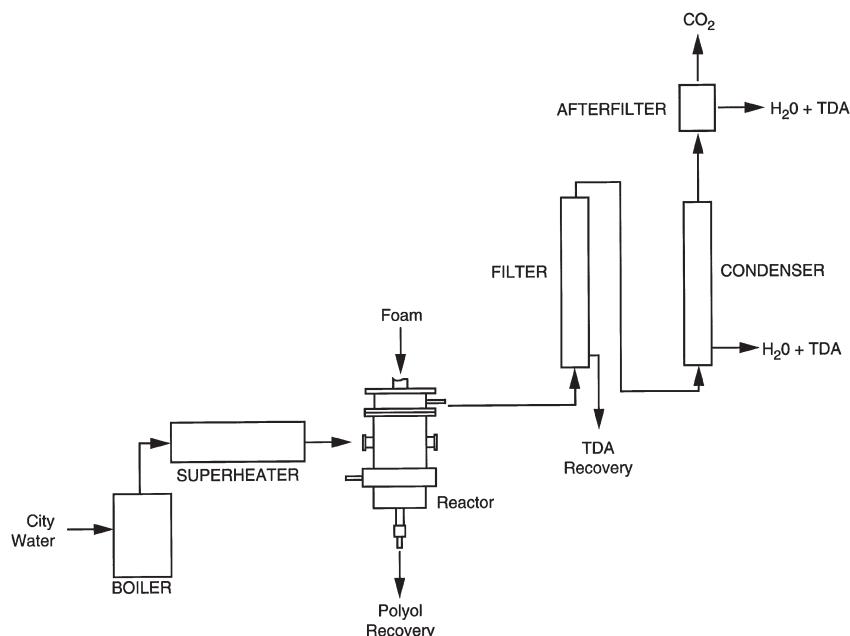


Figure 14.4 Continuous Reactor For Hydrolysis Of Polyurethane Flexible Foam

Ford Motor Company researchers have explored the hydrolysis of polyurethane seat cushioning materials at somewhat lower temperatures than the General Motors study. A systematic kinetic study showed that the rates of formation of the 2,4 and 2,6 isomers of toluene diamine (TDA) and polyether polyol followed pseudo-first-order kinetics. Yields of TDA, isolated from the reaction mixture by vacuum distillation, were 65-80% and varied with reaction conditions.^{14,18}

A variation of the high-pressure steam hydrolysis was examined using diethylene glycol as solvent.^{14,11} Temperatures of 374-428°F (190-220°C) were required for reasonable rates of hydrolysis. Use of a small amount (0.1% by weight of glycol) of lithium hydroxide greatly accelerated foam degradation and reaction times of a few minutes could be obtained at 338-374°F (170-190°C). Kinetic analysis of the catalyzed hydrolysis suggested a complex reaction scheme, with two reactions proceeding at different rates, both producing toluene diamine as the product. It was surmised that the faster reaction might be the hydrolysis of the urethane linkages and the slower one the urea linkages. The presence of the glycol solvent complicates product isolation from the reaction mixture. The procedure adopted was extraction of the polyol with hexadecane. Evaporation of the hexadecane yields a high quality polyol which could replace up to 50% of the virgin polyol in a seating formulation. Capital and operating costs were estimated for a plant to consume 4 million pounds (1800 metric tons) of waste foam per year in a two-shift operation. Approximately 1080 tons or 2.4 million pounds of polyol could be produced.^{14,19} A diagram of the plant is illustrated in Figure 14.5.

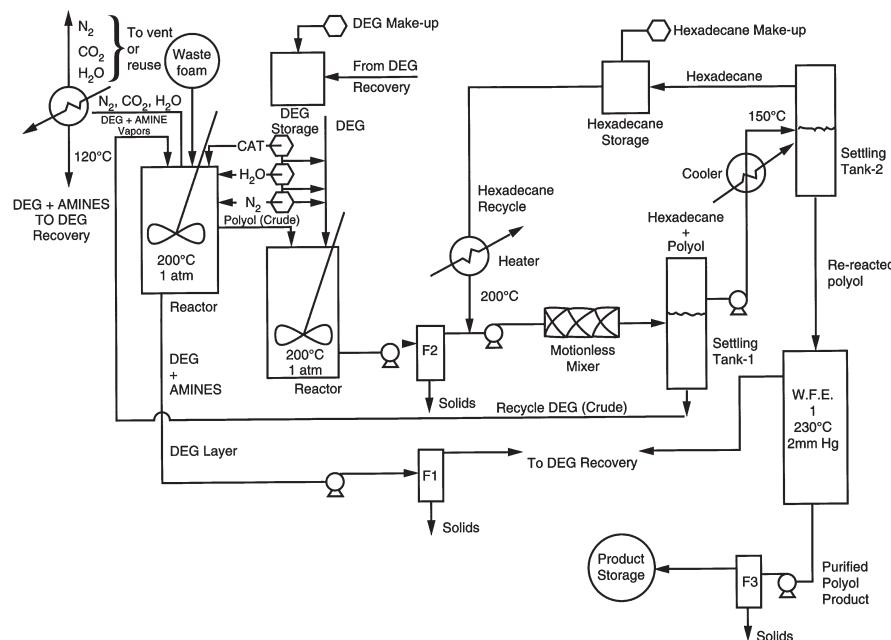


Figure 14.5 Polyurethane Foam Hydrolysis Plant

The hydroglycolysis procedure was applied to flexible foam obtained from an auto shredder operation. The dark colored foam contained some water, volatile hydrocarbons, oil, finely divided glass, metal and plastic debris. However, the polyol recovered from this contaminated foam could be used as a replacement for 5-10% of the virgin polyol in foam formulations.

A considerable amount of research and development effort has been expended on the hydrolysis of polyurethane foams^{14.27-14.31} including production facilities at the million pound per year level.

GLYCOLYSIS

As described above, hydrolysis of polyurethanes and polyureas produces both a polyol and a diamine, which require separation prior to reuse. Glycolysis of polyurethanes, on the other hand, can yield a mixture of polyols (Equation 14.4), which can be reused directly. A series of papers and patents by Upjohn (Dow) have shown the utility of this approach.

Scrap from a variety of sources: rigid foam,^{14.10,14.20} flexible foam,^{14.10,14.21} RIM,^{14.22} and microcellular elastomers^{14.23-14.26} have been digested with glycols to yield reusable polyols. As noted in Equation 14.5, urea linkages can lead to polyamine formation, which can be converted to polyol with alkylene oxide. The process consists of digesting the ground material with an equal weight of a 90/10 mixture of di-(alkylene) glycol/diethanolamine at 374-410°F (190-210°C), for several hours. After cooling and reaction with propylene oxide, the polyol mixture is filtered to remove insoluble materials and is ready for use.

The polyols produced by this method have fairly low equivalent weights (95 +/5) and are most suitable for rigid foams. The reclaimed polyols could be substituted for up to 70% of the virgin polyol in typical rigid foam formulations.^{14.23-14.26} To reuse these polyols in flexible foam formulations would require considerable chain extension with alkylene oxide.

The perception remains that the processes are too costly relative to virgin polyol production. However, work sponsored by Ford Motor Company, Europe, has described a recovery process which yielded acceptable polyol at claimed costs 30% less than new polyol. Studies at the Technical University, Aalen, where the process was developed, utilizes a pilot facility to recover polyols from automotive seating by glycolysis.^{14.32-14.34} A schematic of the process is shown in Figure 14.6.

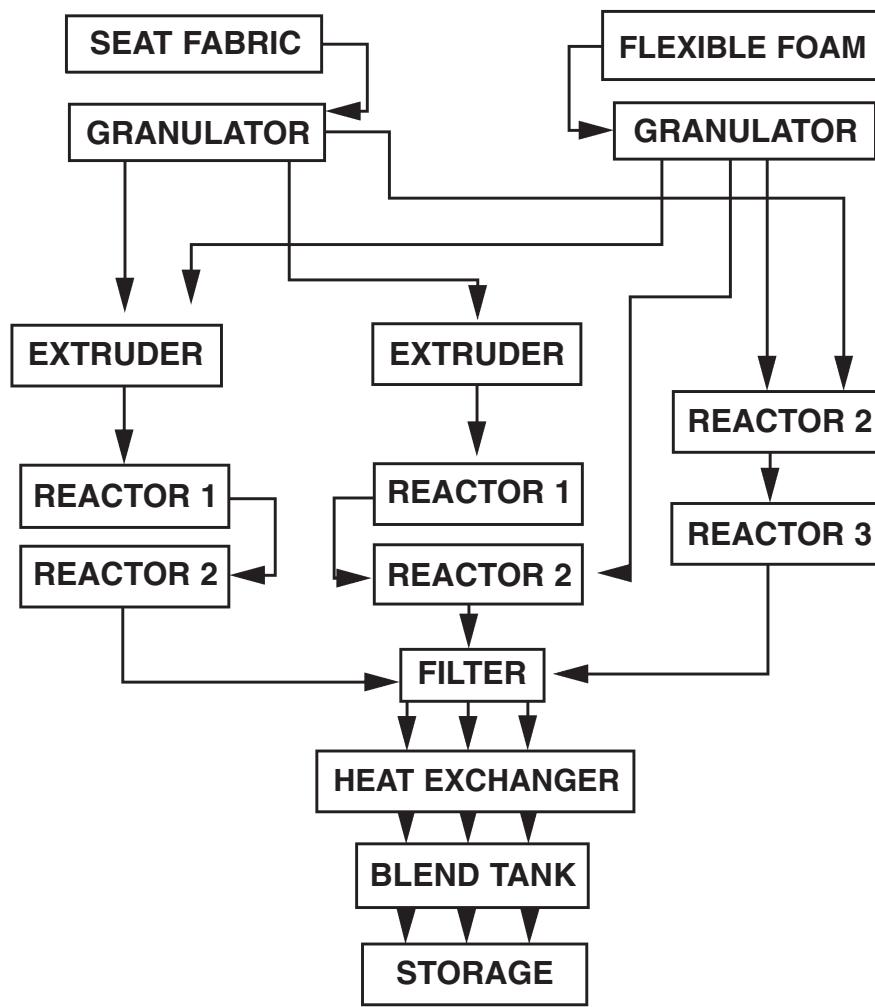


Figure 14.6 Flow Diagram Of Alcohlysis Pilot Plant

The pilot facility has an output capacity of 90 kg/hr of polyol. At a ratio of flexible foam to polyester of 1.5:1 and a ratio of scrap to added glycol of 2:1, a polyol of the following properties was obtained:

Table 14.5 Analysis of Recovered Polyol

| | |
|---------------------------|------|
| Viscosity (mPa s) | 5500 |
| Hydroxyl Number (MgKOH/g) | 380 |
| Acid Number (MgKOH/g) | 1.5 |
| Water Content, % | 0.1 |
| Aromatic Amine Content, % | 0.5 |

More recently, two new glycolysis processes have been developed which produce two distinct layers of glycolate, each layer being quite different in functionality. The Dow Chemical Company developed the “tandem” process by subjecting the polyurethane scrap to an alkanolamine in a 15:1 to 50:1 ratio at elevated temperatures. For instance 1 m³ of foam would be “dissolved” in one liter of alkanolamine. A metal hydroxide is used as a catalyst. The second step is to react the mixture with either ethylene oxide or propylene oxide. The resultant glycolate forms two layers. The top layer, about 30% of the volume, is basically the same polyol that was used in the original polyurethane foam formulation.

The bottom layer is a high functional polyol that has been successfully tested in the production of rigid foam double band laminate applications. Both MDI and TDI based foams can be recycled using this technology.^{14.54-14.55} With further processing, polyols from this technology were found useful in foams designed for automotive NVH applications.^{14.56}

ICI has developed the “split phase” glycolysis process for MDI-based foams. This process relies on the use of prepolymers to eliminate the concern of residual aromatic amines.^{14.57}

PYROLYSIS

In addition to chemical treatment, thermal energy can be used to break down polymers to recover chemical values. In general, only vinyl addition polymers yield appreciable amounts of monomer via “unzipping” or depolymerization mechanisms.

The pyrolysis of polyurethane materials has been examined in some detail. Pyrolysis conditions have ranged from 482-2192°F (250-1200°C), and have included inert as well as oxidative atmospheres.^{14.35-14.40} Pyrolysis of polyurethanes based on polypropylene glycol (PPG) and toluene diisocyanate (TDI) in an inert atmosphere at 392-482°F (200-250°C), occurs by random scission of urethane bonds to isocyanate and hydroxyl.^{14.41-14.43} At higher temperatures, scission of the polyether chains occurs to yield a variety of oxygenated products. Under similar conditions, flexible foams lose most of their nitrogen at about 572°F (300°C), concurrent with the loss of about one-third of their mass. For rigid foams, the higher the temperature, 392-932°F (200-500°C), the greater the nitrogen and weight loss. At 392-572°F (200-300°C), rigid polyurethane foams produce isocyanate and polyol in about equal proportions. Other studies have indicated polyureas from TDI-based flexible foams and polycarbodiimides from diphenylmethane diisocyanate-based rigid foams.^{14.44} Above 1112°F (600°C), both the polyureas and polycarbodiimides decompose further to nitriles, olefins and aromatic compounds.

Braslaw and coworkers have examined the plastic mixture from automotive waste under pyrolytic conditions.^{14.45} The product composition was about 45% char (25% expected based on nonvolatile content), 35% liquid, and 20% gas, at a final temperature of 1022-1112°F (550-600°C). Attempted scale-up experiments gave disappointing results, with a much higher gas-to-liquid weight ratio. In the authors’ opinion, the high nitrogen and sulfur content of the liquids would make them less desirable as a fuel.

ENERGY RECOVERY

Polyurethane materials, in common with many petroleum-derived plastics, contain a considerable amount of recoverable thermal energy, about 12,000-14,000 BTU/lb (28-32Mj/kg). Several trials have been conducted recently to determine the type of equipment necessary to recover this energy from reaction injection molding (RIM) polyurethane scrap parts and from the mixed plastics residue from automotive shredder operations. For RIM materials, both rotary kiln and fluidized bed combustors performed well.^{14,46} For the auto shredder residue, High-Temperature-Gasification technology such as that diagrammed in Figure 14.7 was employed. Combustion of the generated fuel gas gave good energy recovery and stack gas emissions were well below permitted levels.^{14,47}

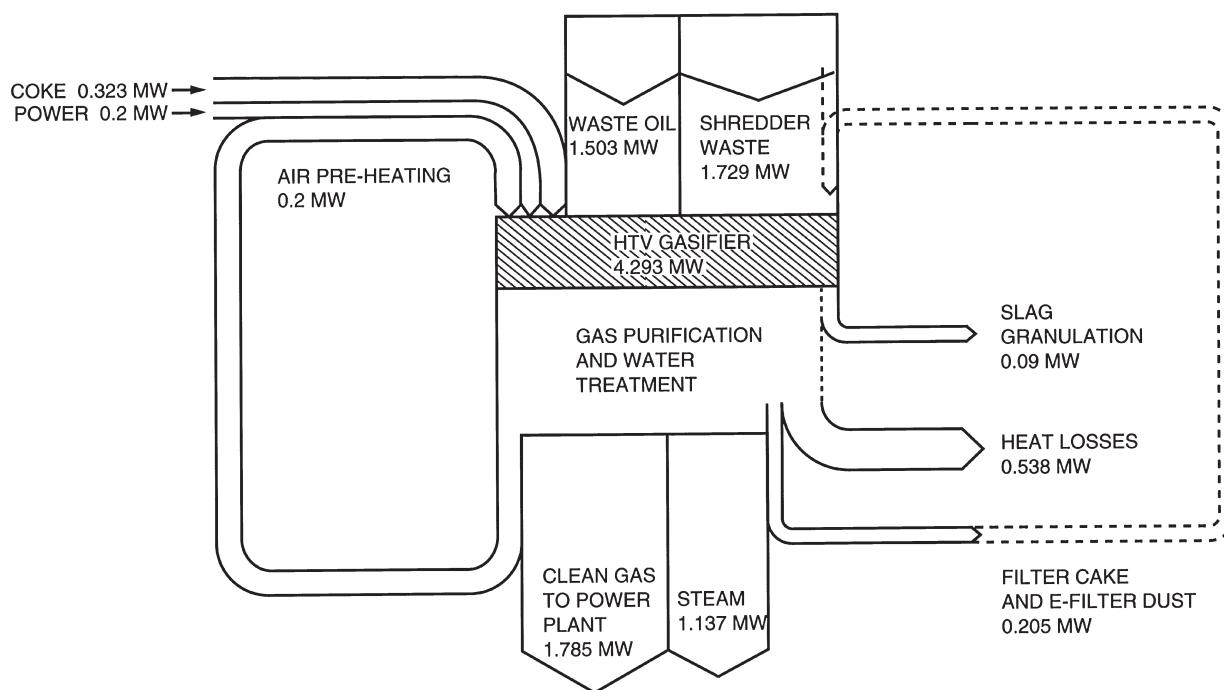


Figure 14.7 Voest-Alpine High-Temperature Gasification Schematic

INDUSTRY EFFORTS

The formation of PURRC (Polyurethane Recycle and Recovery Council) by the Polyurethane Division of the Society of the Plastics Industry underscores the importance of the recycle issue to the industry.^{14,48} This industry group sponsors recycle programs in flexible and rigid foams. The flexible foam programs are focused on post-consumer scrap, and include the separation and recycle of flexible foam from automotive shredder operations, the evaluation of energy recovery options, and the possibilities for adding scrap regrind to flexible slabstock and molded foam production.

PURRC membership includes all of the major suppliers to the polyurethane industry. Members who currently send representatives to PURRC meetings and are active in project management are The Dow Chemical Company, Bayer, BASF Corporation, ICI Americas, Inc., and ARCO Chemical Co.

The American Plastics Council (APC), whose 27 members represent most of the major plastic resin manufacturers in N.A., have also sponsored several recycling studies involving polyurethane foam from mattresses, automotive seats and automotive shredder residue (ASR).

Finally, the Vehicle Recycling Partnership (VRP), which is a part of U.S. Council for Automotive Research (U.S.CAR), facilitates several studies involving PURRC and APC representatives. These studies include seat foam recycling into acoustical applications, Instrument Panel (IP) recycling, and modifying designs to assist the recycling of seats and instrument panels from end-of-life vehicles.^{14.59}

References

- 14.1 Gum, W.F. "Polyurethane Material and Chemical Recycling Alternatives"; *Proceedings of the SPI-33rd Annual Polyurethane Technical/Marketing Conference*; Technomic:Lancaster, Pa., 1990.
- 14.2 Hull & Co. *End Use Market Survey of the Polyurethane Industry in the United States and Canada*, May 29, 1990: prepared for the Society of the Plastics Industry, Inc., Polyurethane Division.
- 14.3 Saunders, J.H.; Frisch, K.C. In *High Polymers, Vol. XVI, Part II*; Interscience: New York, 1964, 849.
- 14.4 Roegler, M. "Slabstock Foams"; In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: Munich, 1985, 176-177.
- 14.5 Woods, G. *The ICI Polyurethanes Book*; Wiley: New York, 1987, 203-204.
- 14.6 Baumann, B.D.; Burdick, P.E.; Bye, M.L.; Galla, E.A. "Recycling Flexible Foam: A Novel Technology Produces A Quality Product with Improved Economics"; *Proceedings of the SPI-6th International Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1983, 139-141.
- 14.7 Miyama, S. "Recycling of Waste PVC Leather and PVC Urethane in the Automotive Industry"; *Conservation and Recycling* **1987**, 10/4, 265-272.
- 14.8 Kettemann, B.U.; Melchiorre, M.; Munzmay, T.; Rashofer, W. "Recycling of Contaminated PU"; *Kunststoffe* **1995**, 85/11, 33-35.

- 14.9 Editorial “Recycling Company Squeezes New Life Into Old Foam Stuffing”; *Charlotte Observer*, March 26, 1990.
- 14.10 Ulrich, H.; Odinak, A.; Tucker, B.; Sayigh, A.A.R. “Recycling of Polyurethane and Polyisocyanurate Foam”; *Polym. Eng. Sci.* **1978**, 18/11, 844-848.
- 14.11 Gerlock, J.; Braslaw, J.; Zimbo, M. “Polyurethane Waste Recycling 1. Glycolysis and Hydroglycolysis of Water-Blown Foams”; *Ind Eng. Chem. Proc. Des. Dev.* **1984**, 23, 545-552.
- 14.12 Campbell, G.A.; Meluch, W.C. “Polyurethane Foam Recycling”; *Environ. Sci. Tech.* **1976**, 10/2, 182-185.
- 14.13 Meluch, W.C.; Campbell, G.A., U.S. Patent 3,978,128, (1976).
- 14.14 Campbell, G.A.; Meluch, W.C. “Polyurethane Waste Disposal Process Development: Amine Recovery”; *J. Appl. Polym. Sci.* **1977**, 21, 581-584.
- 14.15 Salloum, R.J. “The Recycling of Polyurethane Foam”; *Proceedings of the SPE ANTEC*; Society Of Plastics Engineers: Brookfield Center, Ct.; 1981, 491-494.
- 14.16 Grigat, E.; Hetzel, H., U.S. Patent 4,051,212, (1977).
- 14.17 Niederdellmann, G.; Roemer, N.; Schenk, J.; Hetzel, H.; Grigat, E., U.S. Patent 4,399,236, (1983).
- 14.18 Mahoney, L.R.; Weiner, S.A.; Ferris, F.C. “Hydrolysis of Polyurethane Foam Waste”; *Environ. Sci. Tech.* **1974**, 8/2, 135-139.
- 14.19 Braslaw, J.; Gerlock, J.L. “Polyurethane Waste Recycling .2. Polyol Recovery and Purification”; *Ind. Eng. Chem. Pro. Des. Dev.* **1984**, 23, 552-557.
- 14.20 Frulla, F.F., Odinak, A.; Sayigh, A.A.R., U.S. Patent 3,709,440, (1973); and U.S. Patent 3,738,946, (1973).
- 14.21 Tucker, B.; Ulrich, H., U.S. Patent 3,983,087, (1976).
- 14.22 Ulrich, H.; Tucker, B.; Odinak, A.; Gamache, A.R. “Recycling of Thermoset Elastomers”; *Elast. Plast.* **1979**, 11, 208.
- 14.23 Simioni, F.; Bisello, S.; Cambini, M. “Polyols from Rigid Foam Scrap”; *Macplas 8*, **1983**, (47), 52.
- 14.24 Simioni, F.; Bisello, S.; Tavan, M. “Polyol Recovery from Rigid Polyurethane Waste”; *Cell. Polym.* **1983**, 2, 281-283.
- 14.25 Simioni, F.; Modesti, M.; Navazzio, G. “Polyols from Microcellular Elastomer Scrap”; *Macplas 12*, **1987**, (88), 127-129.
- 14.26 Simioni, F.; Modesti, M.; Brambilla, C.A. “Polyester Polyols from Microcellular Elastomer Scrap for Rigid Polyurethane and Polyisocyanurate Foam Production”; *Cell. Polym.* **1989**, 8, 387-400.
- 14.27 Sheratte, M.B. “Chemical Reclamation of Polyurethane and Polyisocyanurate Foams”; *Proceedings of the SPI-20th Annual Technical Conference*; Technomic: Lancaster, Pa., 1977, 59-60.
- 14.28 Kinstle, J.F.; Forshey, L.D.; Valle, R.; Campbell, R.R. “Chemical Intermediates from Scrap Polymers via Hydrolysis”; *Polymer Preprints* **1983**, 24/2, 446-447.
- 14.29 Ulrich, H. “Recycling of Polyurethane and Isocyanurate Foam”; In *Advances in Urethane Science and Technology*, Vol. 5; Frisch, K.C.; Reegen, S.L., Eds.;

Technomic: Lancaster, Pa., 1978, 49-57.

- 14.30 Chapman, T.M. "Models for Polyurethane Hydrolysis under Moderately Acidic Conditions: A Comparative Study of Hydrolysis Rates of Urethanes, Ureas, and Amides"; *J. Polym. Sci. A. Polym. Chem.* **1989**, 27, 1993-2005.
- 14.31 Grigat, E. "Hydrolysis of Plastics Waste"; *Kunststoffe* **1978**, 68/5, 281-284.
- 14.32 Bauer, G. "Recycling of Polyurethane Wastes and Mixed Polymer Wastes by Means of the Alcoholysis Reaction"; *RECYCLE 1990*, Davos, Switzerland, May 29-31, 1990.
- 14.33 Bauer, G., German Patent 2,738,572.
- 14.34 Bauer, G., Europe Patent 948.
- 14.35 Madorský, S.L.; Straus, S. "Thermal Degradation of Polyethylene Oxide and Polypropylene Oxide"; *J. Polym. Sci.* **1959**, 36, 183-194.
- 14.36 Rapp, N.S.; Ingham, J.D. "Polymer Degradation. I. Column Elution Fractionation and Thermal Degradation of Polyoxypolyethylene Glycol/Toluene Diisocyanate (PPGTDI) Polymers"; *J. Polym. Sci.* **1964**, A/2, 689-704.
- 14.37 Ingham, J.D.; Rapp, N.S. "Polymer Degradation. II. Mechanism of Thermal Degradation of Polyoxypolyethylene Glycol/Toluene 2,4-Diisocyanate Polymer (POPGTDI) and a Block Polyether Glycol-TDI Polymer"; *J. Polym. Sci.* **1964**, A/2, 4941-4964.
- 14.38 Tilley, J.N.; Nadeau, H.G.; Reymore, H.E.; Waszeciak, P.H.; Sayigh, A.A.R. "Thermal Degradative Behavior of Selected Urethane Foams Related to Variations of Constituents II. Chemical Reactions in Urethane Decomposition"; *J. Cell. Plast.* **1968**, 4/2, 56-66.
- 14.39 Levin, B.C., National Bureau of Standards Report; NBSIR 853267, (1986).
- 14.40 Maya, P.; Levin, B.C. "A Review of the Literature on the Gaseous Products and Toxicity Generated from the Pyrolysis and Combustion of Rigid Polyurethane Foams"; *Fire Mater.* **1987**, 11, 129.
- 14.41 Wooley, W.D.; Fardell, P.J. "The Prediction of Combustion Products"; *Fire Res.* **1977**, 1, 11-21.
- 14.42 Wooley, W.D. "Nitrogen-Containing Products from the Thermal Decomposition of Flexible Polyurethane Foams"; *Br. Polym. J.* **1972**, 4, 27-43.
- 14.43 Wooley, W.D.; Fardell, P.J.; Buckland, I.G. "The Thermal Decomposition Products of Rigid Polyurethane Foams under Laboratory Conditions"; *Fire Research Note No. 880*, July, 1971.
- 14.44 Chambers, J.; Jiricny, J.; Reese, C.B. "The Thermal Decomposition of Polyurethanes and Polyisocyanurates"; *Fire Mater.* **1981**, 5, 133-141.
- 14.45 Braslaw, J.; Gealer, R.L.; Wingfield, R.C. "Hydrocarbon Generation During the Inert Gas Pyrolysis of Automobile Shredder Waste"; *Polymer Preprints* **1983**, 24, 434.
- 14.46 Myers, J.I.; Farrissey, W.J. "Energy Recovery Options for RIM Polyurethanes"; Proceedings of the SAE International Congress and Exposition, Detroit, Michigan, 1991, Paper Number 910583; SAE: Warrendale, Pa.
- 14.47 Freimann, P., Voest-Alpine report on "High Temperature Gasification of

- Shredder Residue”; Dow Automotive Group, Horgen, Switzerland, (1989).
- 14.48 Fosnaugh, J. “Polyurethanes May Lead In Recycling Race - Viewpoint”; *Automotive and Transportation Interiors* 1994, May, 76.
- 14.49 Quinlan, J.J. “PURRC Flexible Foam Task Group: Recycling Automotive Seating - An Update”; *Proceedings of the AUTO RECYCLE ‘93 Conference*; Schotland Business Research Inc.: Princeton, NJ., 1993, 113-128.
- 14.50 Gibala, D.; Robbins, J. “Effect of Post-Consumer Automotive Seating Granulate on TDI-Based Flexible Foam Properties”; Polyurethanes Division of SPI, PURRC.
- 14.51 Hennecke Corporation Product Brochure Pi 113.
- 14.52 Hall, G.A. “Economic Recycling of Automotive Polyurethane Seats”; *Proceedings of the 1994 SPI Polyurethanes Conference*; Technomic: Lancaster, Pa., 1994, 453-458.
- 14.53 Wasilczyk, G.J., Cerabona, T.J. “Developing a Viable Polyurethane Waste Management Plan: A PURRC Update”; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 196-204.
- 14.54 van der Wal, H.R. “New Chemical Recycling Process for Polyurethanes”; *Proceedings of the SPI-34th Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1992, 560-564.
- 14.55 van der Wal, H.R. “New Perspectives for the Chemical Recycling of Polyurethanes”; *Conference Papers, UTECH 94*; Crain Communications: London, 1994, Paper 53.
- 14.56 Waddington, S.; Duff, A.W. “Polyurethane Automotive Seating Finds New Life in Moulded Vehicle Acoustics”; *Proceedings of the Polyurethane World Congress 1993*; Technomic: Lancaster, Pa., 1993, 558-563.
- 14.57 Hicks, D.A. “Polyurethanes Recycling and Waste Management”; *Conference Papers, UTECH 94*; Crain Communications: London, 1994, Paper 51.
- 14.58 Noble, H.L. “Overview of Polyurethane Solid Waste Issues”; *Proceedings of the SPI-33rd Annual Polyurethane Technical/Marketing Conference*; Technomic: Lancaster, Pa., 1990.
- 14.59 Poston, I.E. “An Update On VRP Programs At The Vehicle Recycling Development Center”; *Proceedings of the AUTO RECYCLE ‘95 Conference*; Schotland Business Research Inc.: Princeton, NJ., 1995, 11-26.

Appendix A

Glossary

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This section attempts to list and define most of the more common terms used in the field of flexible polyurethane foams. Some terms have a scientific derivation, others have a more colorful origin in the art and technology of foams.

A-SIDE The isocyanate portion of a foam formulation. The opposite applies in Europe.

ACID NUMBER This number expresses the amount of acidic residual material in the polyol. It is reported in terms of the number of milligrams of potassium hydroxide required to neutralize the acid present in one gram of a sample. The number is useful as a correction factor in calculating hydroxyl numbers. The specifications for VORANOL® polyols list the maximum acid number as 0.10 milligrams KOH per gram of sample.

ADDITIVE A material used to modify the properties, processing or end use of a base polymer. The amount of additive used is usually expressed in parts per hundred (by weight) of the major resin in the polymer formulation.

ADDUCT Isocyanate reacted with VORANOL® polyols at low temperature to produce a reactive material containing isocyanate groups. See PREPOLYMER.

AEROSOL A suspension of extremely fine liquid droplets in a gas, usually air.

AEROTHENE® Registered trademark of The Dow Chemical Company for a line of specially inhibited 1,1,1-trichloroethane solvents.

AIR BAG In molded foams, this term refers to an extreme case of pocketing or void formation in which an intact outer skin is formed, but the interior of the molded part is one continuous void.

AIRFLOW Cubic feet per minute of air that can be drawn through a 2"x 2"x 1" section of foam at 0.5-inch water pressure.

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| AIR INJECTION | The practice of injecting very small amounts of compressed air into the mixing chamber or into the polyol stream prior to the mixing chamber in order to decrease the average cell diameter in the final foam. |
| AIR TRAPS | Voids in molded foam parts caused by encapsulation of air pockets during mold fill-out. These voids have smooth, shiny surfaces. |
| ALIPHATIC | A term used to describe a chain-like molecule made up of carbon and hydrogen atoms. |
| ALLOPHANATE | A compound formed from the reaction of a urethane group with an isocyanate at elevated temperatures. A potential cross-linking reaction. |
| AMINE | A class of compounds used as catalysts in polyurethane foam reactions. Amines are characterized by having N, NH or NH ₂ groups in the molecule. |
| AMORPHOUS | Having no crystalline structure. |
| ANISOTROPIC | Having different properties when tested along different axes. |
| ANTIOXIDANTS | Materials added to a foam formulation to improve the resistance of the foam to oxidative type reactions. |
| ANTISTATIC AGENTS | Additives which can impart a degree of electrical conductivity to a foam and thus prevent the accumulation of electrostatic charges. |
| AROMATIC | Loosely, a term used to describe molecules that include at least one benzene-like ring. |
| ASR | The abbreviation for automotive shredder residue. The material remaining after scrapped cars are passed through shredders and metals removal processes. |
| ASTM | The abbreviation for American Society for Testing and Materials. |
| AUXILIARY BLOWING AGENT | A low boiling liquid added to assist foaming by generating gas beyond that resulting from the isocyanate-water reaction. |
| B-SIDE | In North America, the active hydrogen (polyol, water, amine, etc.) portion of a foam formulation. (In Europe, the isocyanate portion of a foam formulation). |
| BACKBONE | That portion of a molecule that is relatively nonreactive compared to the reactive end groups attached to it. |
| BACKCOATING | The application of a material to the back of a carpet in order to anchor the tufts. |
| BACKING | The material that forms the back of the carpet. |
| BACK PRESSURE | The pressure (usually higher) in a line upstream of a restrictive device such as a valve or orifice. |

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| BALL REBOUND TEST | A method for comparing the resilience of flexible foams. A steel ball of specified mass is dropped from a fixed height onto a foam sample and the height of the ball rebound is recorded. The rebound height is divided by the original height to give a percentage. |
| BARRIER COATING | Usually a lacquer-based coating sprayed into a mold prior to foaming which adheres to the foam, providing a base for further finishing steps. |
| BASAL CELLS | Larger, irregular cells found just under the show-surface skin of a molded foam part. |
| BIURET | A compound formed from the reaction of an isocyanate group with a urea group. A potential cross-linking reaction. |
| BLEND | A uniform combination of two or more materials. |
| BLOCK | See BUN. |
| BLOW OFF | See HEALTH BUBBLES |
| BLOWING AGENT | A gas, or substance capable of producing a gas, used in making foamed materials. |
| BLOWING REACTION | One of several reactions occurring during formation of a foam. That chemical reaction resulting in the release of carbon dioxide. |
| BO | An abbreviation for butylene oxide. |
| BOARD FOOT | A standard measure of foam which equals to a square foot of material one inch in thickness. |
| BOARDINESS | A term describing foam that feels stiff and not flexible and yet is still in the flexible foam category. A typical foam of this type would require a small force to cause an initial deflection and very little more force to deflect to about 50% of its thickness. |
| BOARD STOCK | Flat sheets of flexible foam cut from large blocks or buns of foam. |
| BOILING AND FLASHING | Boiling is said to occur in the foaming reaction when the rate of formation and/or release of the blowing agent is much greater than the polymerization rate. The result will be a vigorous evolution of gas from the liquid material, which may result in foam collapse. |
| BOTTOM CAVITATION | A deficiency in excessively stable slabstock foams wherein the bulk of the bun separates from a thin bottom layer of foam and rises up to form an irregular-shaped void area. |
| BOTTOMING | The characteristic of some flexible materials, especially polyesters, to support an initial load with a small amount of deflection but virtually collapse under any additional load. After this severe compression, any additional load will cause little further deflection. |

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| BOX FOAM | Generally, any foam of approximately 1 cubic foot or larger volume produced in the laboratory using custom-built semiautomatic mixing equipment. |
| BUN | A segment of foam cut off from continuously produced slabstock type of foam. |
| CALIBRATION | The weighing of carefully timed dispenses of chemicals from the metering ports of the mixing head in order to set an exact component ratio or an exact throughput of all chemicals. |
| CAPPED POLYOL | Refers to a polyol in which the terminal end groups are different from those making up the bulk of the polyol. For example, an ethylene-oxide-capped polyoxypropylene (PO) polyol. |
| CARPET | The word for a soft floor covering fabric. |
| CATALYST | A substance that changes the rate of a chemical reaction. |
| CAVITATION | The formation of cavities or voids within a liquid handling system. |
| CELL | The individual cavities in the skeletal structure of a foam formed by the nucleation and growth of bubbles within the reacting liquid. |
| CELL COUNT | In foams, this means the number of individual cells per unit length. |
| CELL MEMBRANE | The thin, intact film that forms the bubble walls in closed cell foam. Also called cell windows. |
| CELL OPENER | A compound added to a foam formulation for the specific purpose of increasing the population of open cell-windows. Successful cell-opening is evidenced by higher airflow and decreased foam shrinkage. |
| CELL OPENING | In foamed materials, this phrase means the breaking of intercellular membranes present when individual cells cluster together to form a foam. |
| CELL SIZE | The average diameter of the bubbles (or pores) in the final foam. |
| CELL STABILIZER | A substance which helps the formation of fine, uniform cells in a foam by inhibiting the coalescence of small bubbles. |
| CELL WINDOW | See CELL MEMBRANE. |
| CENTIPOISE | One-hundredth of a poise. A poise is the unit of viscosity in the metric system. |
| CFC | Chlorofluorocarbons. Compounds comprised of carbon, fluorine, chlorine and hydrogen that are used as auxiliary blowing agents in polyurethane foams. |

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| CHAIN EXTENDERS | Short-chain reactive molecules joining diisocyanates in a linear fashion to form crystalline hard segments that modify the properties of a polyurethane. |
| CHEMTREC | Chemical Transportation Emergency Center. A program which provides immediate round-the-clock emergency information about cleanup and the potential health and environmental hazards, to carriers and fire and police crews responding to transportation accidents involving chemicals. |
| CLAMPING PRESSURE | That force needed to keep a mold closed during foam rise. |
| CFD (Compression Force Deflection) | A measure of the load-bearing ability of a foam. It is the force exerted against a flat compression foot larger than the specimen to be tested. The value can be expressed at 25%, 40%, 50% and/or 65% compression. |
| CLOSED CELLS | A foam structure in which each individual cell has intact cell membranes so that there are no open passageways for airflow. |
| CLOSED POUR | The case in molded foam production in which the mold lid is closed and locked and the foaming mixture is introduced through one or more special ports in the lid of the mold. |
| CLOUD POINT | The temperature at which a polyol first starts to come out of an aqueous solution. This is normally indicated by the appearance of a milky-white color in the solution. |
| CO₂ BLOWN FOAM | Foam in which all the gas for expanding the reaction mix comes from the reaction of water with isocyanate. Sometimes called an all-water blown foam. |
| COARSE CELLS | Large cells averaging no more than 20 to 30 cells per lineal inch. |
| COLD COLLAPSE | Shallow, roughly circular, localized depressions with a thin, loose skin appearing on the show surface of a molded foam part. This cosmetic defect results when the mold temperature is too low. |
| COLD CURE | See COLD MOLDING, see HIGH RESILIENCE. |
| COLD MOLDING | Molding process for the production of high-resilience foam in which the foam is cured at or near ambient temperature. |
| COLLAPSE | The sudden loss of height occurring after a foam has partially or completely expanded. |
| COLOR | All polyols have color intensity analysis. There are two general types: <ul style="list-style-type: none">• APHA color — commonly used for flexible polyols.• GARDNER color — used for rigid polyols. |
| COLORANT | Dyes or pigments added to impart color to the final foam. |

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| COMFORT | The absence of discomfort. |
| COMPATABILIZER | Special molecules that allow two or more nonmiscible ingredients to come together and give one clear, homogeneous liquid phase. |
| COMPONENT | A separately metered stream of liquid that will be introduced into the mixing head. |
| COMPRESSION SET | A measure of the deformation of a foam after it has been held compressed under controlled time and temperature conditions. The standard conditions are 22 hours at 70°C. In the test, foam is compressed to a thickness given as a percentage of its original thickness. Compression set is most commonly expressed as a percentage of original compression. |
| CONTINUOUS SLAB | The production of a continuous seamless loaf of foam by laying down a uniformly distributed layer of mixed materials on a conveyor belt moving beneath a mixing head at such speed as to form a stable rising front of foam. |
| CORE | The internal portion of a molded foam, free of any skin. |
| CORE DENSITY | The density of the foam at or near the center of the final foamed shape. |
| CPP | An abbreviation for copolymer polyol. |
| CPR (CONTROLLED POLYMERIZATION RATE) | Refers to residual basicity in the polyol. It is ten times the number of milliliters of 0.01N HCl necessary to neutralize 30 grams of polyol. |
| CREAM LINE | The point on a continuous foam slab conveyor where the mixed liquid becomes cloudy and begins to expand. |
| CREAM TIME | The time between the discharge of the foam ingredients from the mixing head and the beginning of the foam rise. At this point, the surface of the liquid will change color, usually turning lighter as a result of saturation of the liquid with evolving gas. |
| CREEP | The degree of compression or height loss that occurs when a flexible foam cushioning material is subjected to a static load over a defined time period. |
| CROSS-LINK DENSITY | The average molecular weight per cross-link. |
| CROSS-LINKER | Molecules that tie chains together to form branched chains or polymer networks. |
| CROSS-LINKING | The formation of chemical bonds between different polymer chains. |
| CRUDE ISOCYANATE | An undistilled isocyanate mixture containing several different isomers or polymeric forms of the intended compound. |
| CRUSHING | Usually a mechanical or vacuum-assisted procedure to open the closed cells of a cold-cure or high-resilience foam after demolding. |

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| CUP FOAM | Generally the volume of foam resulting from mixing 100-300 grams of ingredients together in the laboratory using simple air or electric-driven stirrers. |
| CURE | A term referring to the process whereby chemical reactions approach completion. At 100% completion, a foam should have 100% of the physical properties attainable with that particular formulation. Because 100% cure is not always reached in a practical period of time, see CURE TIME. |
| CURE OVEN | An oven into which foams are placed in order to achieve a desired level of accelerated cure. |
| CURE TIME | The length of time required for sufficient reaction completion to develop a desired level of polymer strength and dimensional stability. |
| CUSHION BACKED CARPET | A carpet that has a cushion or padding as an integral part of its backing. |
| CYCLE | The time for all operations in a manufacturing process to occur once. Usually measured as the time span between a given step and the subsequent repetition of that step. |
| DEAD FOAM | Foam that has a low resilience and only slowly regains its original shape after deformation. |
| DEFASHING | The process used to remove flash on a molded foam. See FLASH. |
| DEMOLD TIME | The time between the discharge of the foam ingredients from the mixing head and the time at which a molded object may be removed readily from the mold without tearing or altering its shape and without post-expansion. |
| DENSITY | Density is the weight per unit volume of the foam normally expressed in kilograms per cubic meter (kg/m^3). The general range of polyether flexible polyurethane foams is 16 to 64 kg/m^3 . This density is not a measure of firmness as it is with latex rubber foams. Density is an important factor, however, in that for a given load-bearing requirement, a higher density foam generally gives better quality and performance. |
| DENSITY, CORE | The density of the foam at or near the center of the final foamed shape. |
| DENSITY, OVERALL | The average density of the entire foam item including any molded skin. |
| DENSITY GRADIENT | Variations in density within a foam sample due to physical problems of heat loss, surface wetting or shearing of the foam during movement. Most foams show a density gradient from the geometric center to the outer skins. |
| DIISOCYANATE | A compound containing two isocyanate groups per molecule. A class of monomers used in preparing polyurethanes. |
| DIMER | A substance formed from two molecules of a monomer. |

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| DIOL | A polyol having two reactive hydroxyl groups per molecule. |
| DISCOLORATION | The gradual yellowing of foam due to a photochemical reaction. It is faster in sunlight than in artificial light, although it occurs in both. Fresh foam may discolor in the center of the block as a result of thermal or chemical events |
| DOCTOR | In carpet processing, to spread a puddle of froth or mixed components evenly across the width of a carpet with the aid of a metal drawdown bar. |
| DOMAIN | A region in a polymer matrix which contains molecular structures of a similar type. |
| DRY HEAT AGING | A procedure in which the physical properties of flexible foams are determined after purposely exposing samples to a specified elevated temperature at ambient relative humidity. |
| DURABILITY | As applied to flexible foams, the term refers to how well a foam retains its load bearing capacity with use. Most measures of durability are done with laboratory-scale tests which often have imperfect correlation to real world experiences. |
| ELEPHANT HIDE | A subjective test to determine the amount of surface wrinkling that occurs as a foam specimen is compressed. |
| ELONGATION | Percentage of original length that a standard sample of foam will stretch before the breaking point is reached. |
| ENERGY MANAGEMENT FOAM | Semirigid foams designed for impact, sound or vibrational energy absorption. |
| ENTRAIN | To disperse a material such as a gas into a carrier liquid. The gas may be uniformly dispersed, but not necessarily totally dissolved. |
| EO | An abbreviation for ethylene oxide. |
| EQUIVALENT WEIGHT | Mass of polyol per reactive hydroxyl. |
| $\text{Equivalent Weight} = \frac{\text{Molecular Weight}}{\text{Number of Reactive Sites}} = \frac{\text{mol wt}}{f}$ | |
| | One equivalent weight of polyol will completely react with one equivalent weight of isocyanate. |
| EXOTHERM | The heat liberated by the foam-producing reactions. This heat accelerates the foaming process. |
| EXTRUSION COLLAPSE | Shallow voids and/or shear collapse on molded foam parts caused by excessive extrusion of foaming material from the mold cavity. The void area often contains strings of polymer. |

FATIGUE A measurement of the loss in load bearing under simulated service conditions, generally expressed as a percentage load loss. The two most common fatigue tests are:

Static Fatigue. In this test, the foam is compressed to 25% of its original thickness for 17 hours at room temperature. IFD (Indentation Force Deflection) losses are calculated as percentages of original values.

Dynamic Fatigue. There are a number of roller-shear tests that use the same basic equipment. A roller, longer than the foam width, is rolled back and forth across the foam. The roller is mounted in an offset position to impart a shearing action. Tests vary in use of constant deflection settings.

FEEDSTOCK A raw material supplied to a processing or refining plant.

FILLER Any substance added to a foam to influence bulk, weight, strength, or price. Common fillers include carbon, clay, calcium carbonate and glass fibers.

FINE CELLS A term used to describe foam with a cell count of 80 or more per lineal inch.

FINGERNAIL TEST A subjective test to determine the recovery of flexible foam when it is indented with a fingernail or sharp object.

FINGERPRINTING A condition in molded foams in which the pad retains evidence of where the operator grasped it during demolding.

FLAME LAMINATION The practice of bonding flexible foam to a fabric by melting one surface of the foam with radiant heat and quickly pressing it to the fabric before the melted material resolidifies.

FLAME RETARDANT A substance purposely added to inhibit the spread of a flame applied to the final foam.

FLAPPER SPLITS Semicircular tears in the top skin of slabstock foam that develop just past the peak rise point and are usually associated with internal splits.

FLASH A thin section of surplus material formed when foam forces itself into crevices between mating mold surfaces.

FLASHING A condition during which there is a continual release of tiny gas bubbles from the surface of a freshly dispensed foaming mixture. It resembles boiling to some extent, but the bubbles are so tiny that no collapse occurs and foaming proceeds normally as soon as the material viscosity has increased to the point at which all gas is trapped.

FLASH POINT The temperature at which a liquid gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid.

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| FLEX FATIGUE | The loss of physical properties of a foam undergoing continuous flexing of a specified magnitude, duration and rate. |
| FLOATING LID | A special lid used on some types of flexible foam cushion molds. The lid is suspended above the foam at a position near the desired maximum rise and is free to float on the surface of the rising foam against the gradually increasing compression of springs. Used mainly for hot-molded foam. |
| FLOWABILITY | Ability to fill a defined cavity with the lowest possible density. |
| FLUOROCARBON | The general family of fluorinated hydrocarbons which find use as auxilliary blowing agents. |
| FOAM | A lightweight cellular material resulting from the introduction of gas bubbles into a reacting polymer matrix. According to ASTM D 1566-82, a flexible foam is one that does not rupture when a 20 x 2.5 x 2.5 centimeter piece is wrapped around a 2.5 centimeter diameter mandrel at a uniform rate of 1 lap in 5 seconds in an ambient temperature of 15-25°C. |
| FOAM ASSEMBLY PROCESS | In semiflexible polyurethane foams, the process of injecting polyurethane foam producing chemicals between the vinyl skin and the substrate. This process includes the foam dispensing equipment, molds and processing line. |
| FOAM FATIGUE | The loss of physical properties of a foam article in use. The most noticed problem is the softening of cushions. |
| FOAM-ON-FABRIC | The practice of pouring foam directly onto the back of special upholstery fabrics that have been preloaded into a mold. |
| FOGGING | The undesirable deposit of a light-scattering film on the interior glass surfaces of vehicles. |
| FORMULATED SYSTEM | A chemical system for producing foam which consists of only two materials. One part is referred to as the isocyanate side and is usually the 'pure' isocyanate with no additives. The second part is often called the resin side and usually consists of blended polyol(s), catalysts, surfactants and other desired additives. |
| FORMULATION | The list of chemicals to be used in the preparation of a foam. |
| FREE NCO | Isocyanate content of a substance that is available for further reaction. This can be either free monomer, as TDI or MDI, or as unreacted isocyanate groups in a polymer or prepolymer. |
| FREE RISE | The unhampered expansion of a foam in a container with no top. |
| FREE RISE TIME | The time at which a freely rising foam stops expanding. Usually determined by close physical observations. |

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| FRIABLE | A term used to indicate the crumbling, flaking, or powdering of a foam when the surface is rubbed. |
| FROTHING | A foaming technique in which a blowing agent is replaced by air or other gases that are mechanically whipped into the polyurethane mixture using a high-shear mixer. |
| FUNCTIONALITY | The number of reactive groups/sites per molecule. |
| GAS LOSS | The weight loss during foam production calculated by subtracting the total weight of the foam produced from the total weight of chemicals dispensed. In most cases, the mass loss is as carbon dioxide from the water-isocyanate reaction. In other cases it may be necessary to include the loss of auxiliary blowing agents. |
| GEL | An intermediate state of cure in thermoset reactions in which the material goes from a liquid to a soft, rubbery mass. |
| GEL POINT | That stage of the polyurethane producing reactions at which a distinct crosslinked polymer network is formed. |
| GEL TIME | The time between the discharge of the foam ingredients from the mixing head and the point at which the foam has developed enough gel strength to resist light impressions and is dimensionally stable. |
| GELLING REACTION | One of several reactions occurring during formation of a foam. That reaction between polyols, crosslinkers and isocyanates leading to the formation of larger molecules, increased viscosity and eventually to a high-molecular-weight macro molecule. |
| GLASS TRANSITION TEMPERATURE | A characteristic temperature at which, for example, a foamed plastic becomes flexible as a result of the onset of segmental motion of the polymer chains. |
| GLYCOLYSIS | The partial breakdown of polymers in the presence of a glycol. |
| GREEN STRENGTH | Initial strength properties of the demolded part. |
| GREIGE GOODS | The carpet fibers and primary backing. Pronounced “gray” goods. |
| GUIDE FACTOR | The ratio of an indentation value; e.g., the 25% or 65% IFD, to density. This term is useful in determining the relative firmness of foams with different densities. The closer the densities, the better the comparison. When densities are different, the foam with the highest guide factor has the cost advantage, but not necessarily the performance advantage. Another term for guide factor is normalized IFD. |
| GURLEY DENSOMETER | A device for measuring the flow of air through the surface skin of a molded foam. |

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| HAND | A subjective description of the feel of the foam as the hand is rubbed lightly over the surface. If the foam is harsh or rough to the touch, it is described as having poor hand. Good hand means a velvet feeling. |
| HARDNESS | See CLD and ILD. |
| HARD SEGMENTS | That portion of a polyurethane polymer resulting from the reaction of isocyanate molecules with water, amines and other low-molecular-weight chain-extending compounds. Hard-segments have glass transition temperatures above ambient temperatures and so impart stiffness to the material. |
| HARDNESS INDEX | A term used in some specifications for the 50% IFD value. |
| HEAD | Short for MIXING HEAD. |
| HEALTH BUBBLES | Small gas bubbles that break through the top skin of a free-rise flexible foam just past the point of peak rise. Often referred to as blow-off. An event generally taken to mean that the resultant foam will be open-celled and generally of good quality. The word is a direct translation of a German phrase brought to the USA with early technology. |
| HIGH RESILIENCE | High-resilience (HR) molded polyurethane foams are based on the reaction of higher-molecular-weight polyols (4,500-7,000), either with polymeric isocyanates, with blends of distilled and polymeric isocyanates, or with 80/20 TDI or 65/35 TDI. The term "high resilience" results from the improved resilience of these foams compared to that of more conventional hot-molded or slabstock foams. "HR" formulations also are characterized by higher catalyst concentrations (several different catalysts are often used to develop optimum processing and physical properties) and the addition of special silicone surfactants. |
| | HR molded foams have several advantages: <ol style="list-style-type: none">1.Their sag factor, or modulus (ratio of 65% IFD/25% IFD) is superior to that of conventional hot molded foam.2.The amount of energy required to accelerate foam cure and development of physical properties is considerably lower than that required in hot molding.3.These foams can meet the federal standard MVSS 302 flammability test more easily than conventional foams. |
| | <i>Note: Polyurethane foams will burn. Results of small scale tests do not predict flammability characteristics in a real fire situation.</i> |
| HOT MOLDING | A flexible molded foam production process in which high oven temperatures are used to drive the curing reaction in foams made from relatively low-reactivity polyols. |

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| HOT SET | A permanent loss in dimension resulting when a foam is deflected as in the demolding or roller crushing step. Generally taken to be a measure of foam cure. |
| HUMID AGING | An accelerated aging test conducted under various combinations of high humidity and temperature. |
| HYDROLYSIS | The breakdown of polymers in the presence of water. |
| HYDROLYZABLE CHLORIDE | Labile chloride from chlorine-containing impurities which may be released during urethane-forming reactions. In isocyanates, this comes from carbamoyl chlorides or other carbonyl chlorides. Excess hydrolyzable chloride usually results in reactivity problems. |
| HYDROPHILICITY | The affinity of substances (in this case polyurethane foams) for water. By increasing the ratio of EO to PO in the polymer, the resulting foam can be made more hydrophilic. |
| HYDROXYL GROUP | The combined oxygen and hydrogen radical (—OH) that forms the reactive group on polyol molecules. |
| HYDROXYL NUMBER | This number indicates the number of reactive hydroxyl groups available for reaction. It is expressed as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of the sample. |
| HYDROXYL EQUIVALENT WEIGHT | The number of grams of sample required so that one gram equivalent weight of hydroxyl (17.008) will be present in the sample. |
| HYSTERESIS | This is a measure of the energy lost or absorbed by a foam when subjected to deflection and is typically given by: $\% \text{ Hysteresis} = \frac{\text{Return 25\% IFD Value}}{\text{Original 25\% IFD Value}} \times 100\%$ In another sense, hysteresis is a measure of the ability of a foam to dampen vibrations. It is quantified as the area under a stress-strain curve as a load is applied and then released. |
| ILD (Indentation Load Deflection) | An indication of the load-bearing ability of a foam. The standard test is to depress a 50-square-inch indenter plate into the foam and measure the number of pounds required to achieve a desired deflection. This is described in ASTM Test Method D-1564 and is no longer used as a description of load bearing. |
| IMPINGEMENT | A mixing technique which achieves mixing via high velocity turbulent contact of two or more streams without the necessity of externally applied agitation. |
| IN MOLDING COATING | See BARRIER COATING. |

INDENTATION FORCE DEFLECTION (IFD)

IFD, is one measure of load bearing and is expressed in Newtons per 323 square centimeters at a given percentage deflection of the foam. To obtain the value, a 323-square-centimeter circular plate is pushed into the foam top surface, stopping at a given deflection and reading a force on the scale. For example, a 25% IFD of 133 means that it takes 133 Newtons force to compress a 100-millimeter-thick piece of foam to a 75-millimeter thickness. The higher the force, the firmer the foam. In this test, the foam sample is larger than the circular plate, generally 380 x 380 millimeters for slab foams.

IFD was formerly known as ILD (Indentation Load Deflection) and also sometimes referred to as RMA (Rubber Manufacturers Association), from the same measurement used for latex foams.

INDENTATION MODULUS (IM)

Indentation modulus is the load required to reduce an indentation of 1% between the limits of 20% IFD and 40% IFD. The slope of the line depends on resistance of foam-cell struts to buckling.

INDENTATION RESIDUAL DEFLECTION FORCE (IRDF)

IRDF is another measure of load bearing and is expressed as millimeters at a given loading. The same 323-square-centimeter circular plate is used as for IFD, but now the plate is weighted with a given load. Normal loadings are 4, 5, 110 and 220 Newtons. The original thickness of the foam must be known to make these values meaningful.

This measure is frequently used in automotive foam specifications. There is no ready correlation between IFD and IRDF values.

INSTRUMENT PANEL

The large composite piece extending across the entire front of most automobile interiors. It usually surrounds the instrument cluster and is made in a multistep process involving PVC skins, polyurethane foam and a plastic structural base. Other names for this piece are crashpad and dashboard.

IRGL

Indentation residual gauge load. Now known as IRDF. See INDENTATION RESIDUAL DEFLECTION FORCE.

INITIAL HARDNESS FACTOR (IHF)

Initial hardness factor is the ratio of 25% IFD to the 5% IFD. This factor defines the surface feel. Supple or soft-surface foams will have a high value and boardy or stiff-surface foams will have a low value. Another term for initial hardness factor is comfort factor.

INITIAL SPOT

A condition in molded foam operations where a spot of off-quality foam is found at the point where the first of the liquid mixture was deposited. (This generally appears as a target pattern of rings within rings). This can be due to improper pressure balance, unbalanced discharge velocities, extreme differences in viscosity or an oversized mixing chamber.

INITIATOR

Usually a low-molecular-weight polyhydroxyl or polyamine to which alkylene oxides can be added to form polyether polyols.

INTEGRAL SKIN FOAM

A molded foam having a dense, tough outer skin and a relatively lower density core. The product is achieved in a single pour using a combination of chemical and mechanical aids.

IRREGULAR CELLS

A term describing foam having widely varying cell sizes and presenting a very irregular appearance. Sometimes caused by excessive air introduced to the mixing head.

ISO INDICATOR SOLUTION

Three percent aqueous hydrogen peroxide used to indicate the presence of unreacted isocyanate arising, for example, from poor mixing. When sprayed on the suspect area of a freshly prepared foam, free isocyanate is oxidized to give a visible dark-brown color.

ISOCYANATE

A reactive chemical grouping composed of a nitrogen atom bonded to a carbon atom bonded to an oxygen atom(-N=C=O); a chemical compound, usually organic, containing one or more isocyanate groups.

ISOCYANATE INDEX

A measure of the stoichiometric balance between the equivalents of isocyanate used to the total equivalents of water, polyols and other reactants. The relative amount of isocyanate used as compared with the theoretical requirement. An index of 100 means just enough isocyanate is provided to react with all compounds containing active hydrogen atoms. Normally, a slight excess of isocyanate is used (e.g., index 105).

ISOCYANATE NEUTRALIZER

A combination of materials used in cleaning up isocyanate spills. A typical formula is listed below:

| | Amt, lb |
|-----------------|---------|
| aqueous ammonia | 5 |
| detergent | 2 |
| water | 93 |
| Total | 100 |

ISOCYANURATE

A cyclic trimer formed by reaction between isocyanate groups. This occurs with “leftover” isocyanates that do not find active hydrogen groups, as when the isocyanate index is greater than 100. Isocyanurates are formed purposely to alter the final polymer’s physical properties.

ISONATE®

Registered trademark of The Dow Chemical Company for a range of products based on 4,4'-diphenylmethane diisocyanate.

ISONOL®

Registered trademark of The Dow Chemical Company for a range of specialty polyether polyols.

ISOTROPIC

Having the same properties in all directions.

KNIT LINES

Lines describing where at least two advancing foam fronts have met during later stages of mold fill-out. Knit lines can sometimes be associated with air trapping and/or shear collapse.

LAMINAR FLOW

A smooth, nonturbulent flow of material as it exits a pipe or mixing head.

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| LEAD-LAG | A term used to describe off-ratio flows of components at the instant of starting or stopping a shot. The most common cause of trouble is a lack of proper pressure balance between the pour and recirculate modes. Uneven velocities of discharge from the metering orifices may also cause this problem. |
| LOAD BEARING | A general term, described in various ways by IFD, ILD, IHF, IM, etc. |
| LOI | The abbreviation for limiting oxygen index. |
| LOOSE SKIN | A condition in molded foams in which the outer skin of the part is a loose intact film. Caused most often by a cold mold surface or excessive movement of the foam after the gelation reaction is too far advanced. |
| MASS EFFECT | A term referring to the observable influence that the total amount of dispensed chemicals has on the density, cure time and exotherm of the foam. A small pour generally requires a higher catalyst level and a much more careful control of the environment than a larger pour does. The surface-to-volume ratio of the mold and the mass of the mold also have an influence on foam properties. |
| MASTERBATCH | A premixed system in which the catalysts, blowing agents, fire retardants, and perhaps the surfactant(s) are added to the polyol according to a predetermined formula. Also called “polyol side” (in U.S.A.), cross-linker, or catalyst side. This side does not contain isocyanate. |
| MDI | In the United States, usually the abbreviation for pure diphenylmethane diisocyanate. In other countries, it can be the undistilled mixture of diphenylmethane diisocyanate and higher molecular weight fractions. |
| MIXING | To combine or blend into one mass or mixture so that the constituent parts are indistinguishable. |
| MIXING HEAD | The device that mixes two or more component streams before dispensing the foamproducing mixture to the desired container. |
| MIXING LINES | Visible lines of poorly formed foam. In a cut section of foam, these lines often radiate up from the pour spot to the top skin of the foam. |
| MODULUS | Usually used in polyurethane technology to represent the result of dividing two points on the load deflection curve for flexible foams. An indication of the slope of the load-deflection curve. For flexible foams, the modulus is expressed as the ratio of the indentation load deflection at 65% deflection to the indentation load deflection at 25% deflection. |
| MOLD | Any enclosure in which a polyurethane mixture reacts to give a shaped final article. |

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| MOLD PACKING | The practice of purposely adding more material to the mold than is actually required to just fill it. The extra material serves to accommodate slight changes in material temperatures, mold temperatures and pour patterns. It is also a way to improve load-bearing properties without changing the foam formulation. |
| MOLD RELEASE AGENT | Any material which when applied to the mold surface serves to prevent sticking of the foamed part to the mold. |
| MOLDED DENSITY | The overall density of a foam when expanded and cured in its final shape. |
| MOLDING | The process of making a shaped part by pouring liquid ingredients into a shaped cavity and allowing those ingredients to react and form a solid material that replicates the shape of the cavity. |
| MOLECULAR WEIGHT | Because individual polyol molecules vary in molecular weight, the molecular weight of a given polyol is a weighted average. |
| MOLECULAR WEIGHT PER BRANCH POINT | The weight of polymer per active center or group that can form a cross link. Also called molecular weight per cross link. |
| MOON CRATERING | Small pits on the bun surface usually extending into the upper part of the foam bun. |
| MORPHOLOGY | The physical form or structures in a polymeric material at the microscopic or submicroscopic level, but not at the molecular level. |
| NCO | The chemical symbol for the isocyanate group. |
| NORMALIZED LOAD-BEARING | The practice of recalculating load-bearing for a foam just slightly off of target density. See GUIDE FACTOR. |
| NUCLEATION | The generation of many small bubbles within a liquid. |
| NVH | The abbreviation for noise, vibration and harshness. |
| NVH FOAM | Those foams specially formulated for use in controlling noise, vibrations and harshness. |
| ONE SHOT SYSTEM | A term describing the technique for simultaneous mixing at the machine mixing head of the polyol, isocyanate, catalyst, blowing agent and silicone to make polyurethane foam. No prior reaction product between the isocyanate and polyol is used. |
| OPEN CELL STRUCTURE | A permeable structure (as in flexible foam) in which there is no barrier between cells, and gases or liquids can pass through the foam. Most cell walls have been ruptured. |
| OPEN POUR | The case where the dispensed foaming mixture is placed in an open-top mold or other containment structure. |

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| ORGANOTIN CATALYSTS | A group of catalysts that are noted for their rather specific influence on the gelation reaction. A good balance between blowing and gelation reactions can be achieved by properly combining an organotin catalyst with an amine catalyst. |
| OVERFILL | See MOLD PACKING. |
| PACKING | See MOLD PACKING. |
| PACKING FACTOR | Defined as: $\text{Packing Factor} = \frac{\text{Molded Density}}{\text{Free Rise Density}}$ |
| PAPI® | Registered trademark of The Dow Chemical Company for a range of products based on polymeric methylene diphenyl diisocyanate. |
| PARTICULATE | Composed of fine particles. |
| PEA HOLES | Small spherical voids randomly dispersed throughout a foam. |
| PERCENT HYDROXYL | The weight percentage of OH units in the total weight of the polyol. |
| pH | A measure of the apparent acidity or basicity. This is a simple and fast analysis, but probably leads to more confusion than any other analysis. Three common standards for pH are used in the polyurethane chemical industry: <ol style="list-style-type: none">1. Methanol/water mixture in a 10:1 ratio by weight.2. Isopropanol/water mixture in a 10:6 ratio by volume.3. 5% polyol in water. The first method is the most common to this industry. |
| PLASTICIZER | Materials (usually nonreactive) which can be used to soften a foam. |
| PMDI | The abbreviation for polymeric methylene diphenyl diisocyanate. |
| PO | An abbreviation for propylene oxide. |
| POCKETS | The undesirable formation of large cavities or pockets in the foam structure. Pocketing is usually caused by rapid formation and/or release of the blowing agent before the polymer structure has gained sufficient strength to contain the gas. |
| POLYESTER | A polymeric polyol material containing a number of chemical groups known as ester groups in the main chain or side chains. |
| POLYETHER | Polymeric polyol material containing a number of carbonoxygencarbon links (-C-O-C-), known as ether linkages, in its main chain or side chain. |
| POLYISOCYANATE | A substance containing a number of isocyanate groups attached to a single molecule. |

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| POLYISOCYANURATE | Polymers containing isocyanurate groups; i.e., cyclic trimers of isocyanates. |
| POLYMER | An organic substance composed of repeating chemical units built up into large molecules. |
| POLYOL | Generally, any organic molecule containing a plurality of hydroxyl groups. For polyurethane foams, polyols are usually polyethers (or formerly polyesters) with hydroxyl reaction sites. |
| | They may be filled with rubber particles such as styrene/acrylonitrile polymers (Copolymer Polyols) or urea particles (PHD polyols), or polyurethane particles (PIPA polyols). Inorganic fillers are also used. The reactive sites may also be partially or totally converted to amine groups. |
| POLYURETHANE FOAM | A cellular product produced from the reaction of active hydrogen-containing compounds with blowing agents and polyisocyanates. |
| POLYURETHANES | Generally, a polymer connected by urethane (or carbamate) groups. In polyurethane foams, these may be supplemented by ureas, isocyanurates, ester groups, biurets, allophanates and others. In flexible foams, the most frequently occurring functional group is the ether linkage; the urethane linkage and its supplements are artifacts of curing. |
| PORE SIZE | The number of cells per linear inch. |
| POROSITY | See AIRFLOW. |
| POSTCURE | Time and temperature history of a molded article after removal from a mold. |
| POT LIFE | Total time at which a mixed and reacting system is usable for its intended purpose from the standpoint of pourability (50,000 cps). |
| POUR PATTERN | The geometric manner in which the dispensed foaming mixture is laid down or placed into an open-top mold. In the simplest case, the mixture is poured at one spot and allowed to flow out to fill the mold. Complicated molds often require the mixing head (and perhaps the mold) to be moved in some manner so as to spread the mixture over a wider area of the mold. |
| PPHP | Parts (by weight) per hundred parts of polyol. |
| PRECURE | Time and temperature history of a molded article during its residence in a mold. |
| PREPOLYMER | A reacted, but not completely polymerized product. In the polyurethane industry, this is usually a prereacted product formed by reacting polyol(s) with isocyanates(s). The materials normally contain residual free isocyanate groups for further reaction with more polyol(s) to produce the final polymer. |

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| PRESSURE BALANCE | A condition in molding operations in which the line pressures during the recycle mode are exactly the same as in the pour mode. If these pressures are not in balance, a surge or lag of material into the mixing chamber can occur. Generally, the shorter the shot time, the more critical the necessity for pressure balance. |
| PRESSURE RELEASE COLLAPSE | Shallow surface voids and/or shear collapse on molded foam parts caused by the sudden release of internal mold pressure or failure of the mold to seal. Usually seen with shiny surfaces and a thin surface skin similar to cold collapse. |
| PRIMARY BACKING (Carpet) | The material through which the carpet fibers are tufted. |
| PRIMARY HYDROXYL | The type of reactive end group found in some polyols. Primary hydroxyls react faster than secondary hydroxyls. In general, the higher the percentage of primary hydroxyls, the less catalyst required for curing. |
| PROCESSABILITY | The overall ease with which a product can be acceptably produced in a commercial facility given the normal day-to-day variations in equipment and people performance. |
| PROCESSING LATITUDE | A condition said to exist in foam formulations, or with components, when the normal variations in processing parameters have no adverse affect on foam quality. |
| PURRC | The abbreviation for Polyurethane Recycle and Recovery Council. |
| PYROLYSIS | The decomposition of polymers into liquids and gases by the application of heat. |
| QUASI-PREPOLYMER | Product formed by reacting only a portion of the polyol with all the isocyanate. Contains excess or residual free isocyanate. |
| RATIO | Relative quantities of isocyanate stream to polyol stream on a weight basis. |
| REACTIVITY | A term broadly used to describe the results of empirical/analytical measurements to characterize the rates at which various polyurethane reactions occur. |
| REBONDED FOAM | That foam resulting from a process of adhering small particles of foam back together again to make a useable cushioning product. Various adhesives and bonding processes are used. A typical application for rebonded foam is as carpet underlay. |
| RELAXATION (SIGHING) | When foam rises to a maximum height and then settles back. This is usually caused by poor surfactant activity, incompatible mixing or a too-slow rate of polymerization. |
| RELEASE AGENTS | These are applied to the mold as solution, dispersion or emulsions. After evaporation of the solvent an adherent film is formed, which allows a foam to be demolded easily. |

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| RESILIENCE (or resiliency) | A measure of foam elasticity or springiness. In this test, a steel ball is dropped on the foam and the rebound is expressed as percent resilience. As with recovery, desirable values are dependent on application. With very soft foam, resilience can be misleading because the foam bottoms out under the load of the ball. This gives low resilience values even though the foam is very "lively" or elastic. Ball rebound is another term for this property. |
| RIM | Reaction injection molding: the injection of a high-pressure impingement-mixed stream into a mold or cavity. |
| RISE TIME | The time between discharge of the foam ingredients from the mixing head and the point at which the foam rise is complete. |
| SAG FACTOR | Sag factor is the ratio of 65% IFD to 25% IFD and gives an indication of cushioning quality. A high value indicates resistance to bottoming out. Foams with low sag factors will often "bottom out" and give inferior performance. Other terms for this number are SAC factor and modulus. |
| SCORCH | A yellow or brown discoloration of the foam, particularly in the center. Scorching is caused by excessive heat during the exothermic reaction. It occurs mainly in high-water flexible slabstock formulations. |
| SECONDARY HYDROXYL | A type of reactive alcohol group found in most polyol molecules. Secondary hydroxyls are less reactive than primary hydroxyls. |
| SEMIFLEXIBLE MOLDED FOAMS | These foams are used primarily by the automotive industry in safety padding and interior trim applications. The ability to shape semiflexible foam by closed molding in a cover stock gives automotive stylists and engineers exceptional design freedom and a highly functional end product. |
| SEMIRIGID MOLDED FOAMS | Foams that are friable in nature and do not fully recover after deformation. Both energy management and matt molded foams are included in this classification. |
| SETTLING | The observable and normal loss in height of a free-rise foam at a point in time just after the peak rise. Height loss occurs when the cell-walls rupture and the expansion gas is lost. If a loss in height is not observed, the foam will normally be closed-cell. |
| SHEAR COLLAPSE | Localized loss of molded-foam polymer integrity resulting in a void containing a coarse, stringy polymer mass. |
| SHELF LIFE | The time a material can be stored without losing any of its properties. |
| SIGH BACK | See RELAXATION. |
| SHINERS (In flexible foams) | Intact cell walls as evidenced by reflected light. Noticeable on cut surfaces of finished foam. Shiners indicate unbroken cell walls; i.e., closed cells. |

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| SHOT (of foam) | The total amount of mixed liquids dispensed during one pour cycle. |
| SHRINKAGE | The contraction of curing foam due to the cooling of entrapped gases within the closed-cell walls of a foam mass. |
| SILICONES | Chemicals formed from a combination of silicon and organic molecules that exhibit surface-active properties. These compounds are used to add stability to the liquid foaming mixture so that drainage is retarded and flowability of the mass is improved. |
| SKIN | The higher-density outer surface of a foam usually occurring when the foam surface cools more rapidly than the core. |
| SLAB | A section of foam cut from the interior of a large bun. |
| SLABSTOCK | Refers to polyurethane foam made in the form of a long, continuous block or bun of nominal rectangular cross-section. |
| SMOKING | The visible and excessive release of vapors from a rising foam. |
| SOFT SEGMENTS | That portion of a polyurethane polymer comprised of the higher-molecular-weight polyol chains present as a bulk continuous phase. This phase has a glass transition temperature well below ambient temperature and thus exhibits good flexibility at ambient temperatures. |
| SOFTNESS | A subjective characterization usually determined by squeezing a foam with the fingers or hands. Soft foams generally have open cells, high airflow and small cell size. |
| SOLVENT BURN | Regional surface deterioration on molded foam parts caused by unflashed mold-release solvent attack. |
| SPECFLEX® | Registered trademark of The Dow Chemical Company for a line of formulated polyurethane components intended for use in flexible foams. |
| SPECIALTY MOLDED FOAMS | A class of polyurethane foams which include semiflexible, semirigid and integral skin foam technologies. |
| SPLASHING | Occurs when the mixed liquids are poured into a mold or onto a conveyor. The event may cause the formation of large bubbles, which show up as large cavities or voids in the final foam. |
| SPLITS | The undesirable formation of fissures or cracks in the foam structure. Caused by too-rapid evolution of the blowing agent compared to the polymer buildup. |
| SPOT POUR | The practice of dispensing all of the mixed liquids into one spot in a mold with no attempt to distribute the material. |
| STATIC FATIGUE | The loss in load-bearing properties of a foam subjected to a constant compression. |

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| STATURE® | Registered trademark of The Dow Chemical Company for a line of antistatic additives. |
| STRING TIME | The time between pouring of the mixed liquids and the time that strings of viscous material can be pulled away from the surface of the foam when it is touched with a tool. |
| STRUTS | The structural members of a foamed material. These roughly triangular features contain most of the solid polymer and surround the oftentimes fugitive gas bubbles. |
| SUBSTRATE PROCESS | In semiflexible foams, the process of manufacturing plastic or metal substrates which are the main energy-absorbing and structural components in an instrument panel or other interior trim part. |
| SUMMER SOFTNESS | A condition in which the load-bearing capacity of standard foams produced during the summer months decreases in direct proportion to the amount of airborne moisture available. |
| SUPPORT FACTOR | The ratio of the 65% IFD to the 25% IFD. Seating foams with low support factors may bottom out and be less comfortable. See SAG FACTOR. |
| SURFACE SCORCHING | Shiny, crusty surface areas on molded foam parts with subsurface voids which may break the foam surface. This phenomenon may occur if mold temperatures are too hot. |
| SURFACE SHEAR | Course surface on molded foam parts caused by lateral polymer movement or flow during advanced stages of gelation. A hot mold, underfill condition or a fast gelling reaction can cause this problem to varying degrees. |
| SURFACTANTS | A term to describe substances that provide resilience and stability to thin films and that markedly lower the surface tension of liquids, thus permitting easier bubble formation. |
| SYSTEM | In polyurethane or polyisocyanurate technology, the two or more substances or materials which, when mixed together, react to form a polyurethane or polyisocyanurate polymer. |
| TACK-FREE TIME | The time between the beginning of the foam pour and the point at which the outer skin of the foam mass loses its stickiness or adhesive quality. |
| TACKY SURFACE | A condition of the surface of a free-rise foam during which any object touching the foam surface will stick to it. A stage of cure through which foams pass on their way to final cure. |
| TDI | Toluene diisocyanate. |
| TDI INDEX | This figure indicates the amount of TDI (toluene diisocyanate) available for reaction with the polyol, water and other active-hydrogen sources. An index of 105 indicates that there is 5% excess TDI available over the stoichiometric amount required by the formulation. |

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| TEAR STRENGTH | A measure of the force required to continue a tear in a foam after a split or break has been started and expressed in pounds per inch (lbs/in.). This property is important in determining suitability of foam in applications where the material is sewed, stapled or otherwise anchored to a solid substrate. Also important in demoldability. |
| TENSILE STRENGTH | Tensile strength is a measure of the amount of stress required to break foam as it is pulled apart and is expressed in pounds per square inch (lbs/sq in.). Tensile strength can be used as a control check for quality. One common test is the determination of tensile strength change after heat aging. |
| TERTIARY AMINE | An amine characterized by a molecular structure in which the nitrogen is connected solely to organic radicals and not to any single hydrogen atoms. Tertiary amines are generally more powerful catalysts than either the primary or secondary type of amines. |
| THE ENHANCER® | Registered trademark of The Dow Chemical Company for a line of carpet backing technologies. |
| THERMOPLASTIC | A material capable of melting at elevated temperatures without degradation and regaining its original properties after further processing and recooling. |
| THERMOSET | A material that is cured by temperature and decomposes rather than melts upon application of elevated temperatures. |
| THROUGHPUT | The total flow rate of all components leaving the mixing head. |
| TILE | A module of carpet usually measuring eighteen or twenty-four inches square of extremely dense construction with a heavy reinforced backing. |
| TOPPER PADS | Thin cushions of foam used in various designs of automotive seats to provide a good feel to the seat. |
| TPR | The abbreviation for timed pressure release. A method of cell opening. |
| TRAFFIC | The passing to-and-fro of persons over a carpet. Often used in discussing wear of carpets. |
| TRIMERIZATION | The reaction of three isocyanate groups to form a polyisocyanurate polymer. |
| TRIMMING | A process used to remove the flash from a molded foam pad. |
| TRIOL | A polyol having three hydroxyl groups attached to the molecule. |
| TUFT LOCK (Carpet) | The amount of force needed to pull a tuft of carpet fiber from the foam backing. |
| URETHANE | Generally, the reaction product of an isocyanate and an organic hydroxyl. |

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| UNDERCUTTING | The flow of the liquid reactants under the already creaming/rising foam mass on the conveyor. This may lead to large splits. |
| UNDERFILL | The use of insufficient material to fill the mold adequately. |
| UNSATURATION | There may be small amounts of allyl-or propenyl-type unsaturation in polyols, resulting from propylene oxide isomerization during polyol manufacture. This unsaturation is usually associated with a monohydroxy, hence a chain terminator. Unsaturation is expressed as the number of milliequivalents per gram (meq/g) of polyol sample. |
| URATE TEST | Ultrasonic Rise and Adiabatic Temperature Evaluation Test. A performance test developed by The Dow Chemical Company which characterizes the temperature and rise profile of a wide variety of polyurethane foams. |
| VAPOR PRESSURE | The pressure of a vapor above the liquid from which it formed. Vapor pressure is temperature dependent. |
| VENTING | The controlled release of gases from a mold via slots, holes, etc. |
| VENT HOLES | Small perforations in a mold to permit the escape of air and other gases during expansion of the foam. |
| VINYL SKIN PROCESS | In semiflexible foams, the process of manufacturing the PVC or PVC/ABS skins utilized for the manufacture of interior trim and instrument panel parts. |
| VIRGIN FOAM | Flexible slabstock foam that has not been processed in any manner other than cutting to shape. |
| VISCOSITY | Viscosity is influenced by the molecular weight and molecular structure of the polyol, and is therefore an important physical property. Viscosities of polyols are expressed in centistokes or centipoises. The two are related by the following equation: |
| $\text{Centistoke} \times \text{Density} = \text{Centipoise}$ | |
| VOIDS | The undesirable formation of large cavities or pockets in a foam structure. Voids are usually caused by poor moldability or incorrect mold filling. In the case of foam buns, voids occur when the blowing and polymerization reactions are out of balance. |
| VORANATE® | Registered trademark of The Dow Chemical Company for isocyanates and prepolymers. |
| VORANOL® | Registered trademark of The Dow Chemical Company for polyether polyols. |

WATER Water can exist in a free, nonchemically bound state in a polyol. Manufacturers normally report the water content of each lot of polyol in units of weight percent. The water content should be taken into account when doing foam-making calculations.

WATER BLOWN FOAM Foam in which the gas for expansion is generated entirely by the reaction of water with an isocyanate.

WINDOWS The thin membranes formed between adjacent gas bubbles as those bubbles expand enough to pack into various polyhedral shapes. These features may be present (a closed-cell window) or absent (an open-cell window) depending on the particular foam chemistry used.

WORM HOLES A term that refers to elongated irregular voids in foams that often extend from the bottom of a free-rise foam vertically to the top skin. Minor cases are detectable only by cutting the foam; major cases are accompanied by large internal voids and loss of bun height.

XHR The abbreviation for extra high resilience foam. Generally taken to mean those foams having a ball rebound type of resilience greater than 70%.

Appendix B

Conversion Factors

J. Porter, R. Herrington

INTRODUCTION

The following conversion factors dealing with common US customary, metric and SI (International System of Units) units are for the reader's convenience. This is not a complete listing. A complete conversion table appears in the Annual Book of ASTM Standards, Part 14.02 ASTM designation E 380-91a, "Standard Practice for Use of the International System of Units (SI) (the Modernized Metric System)."

For the reader's reference, the following seven base units are employed in the SI system:^{B.1}

| | |
|---------------------------|----------|
| length | meter |
| mass | kilogram |
| time | second |
| electric current | ampere |
| thermodynamic temperature | kelvin |
| amount of substance | mole |
| luminous intensity | candela |

The most accurate equivalents are obtained by multiplying specified quantities by the complete conversion factor as given in the tables, then rounding off. Converted values should be rounded off the minimum number of significant digits that will maintain the required accuracy.

It should be noted before comparing converted data, that test method procedures vary in different countries and have a subsequent effect on physical property results.

Conversion Table of Units Commonly Used in Polyurethanes

| | To Convert | Into | Multiply By: |
|-----------------------------|----------------------------|---------------------------|--------------------------|
| Airflow | ft ³ /min | liters/sec | 0.4719 |
| | ft ³ /min | m ³ /sec | 0.0004719 |
| Coating | g/m ² | ounces/yd ² | 0.0295 |
| | ounces/yd ² | g/m ² | 33.90 |
| Density | lb/ft ³ (pcf) | kg/m ³ | 16.018 |
| | kg/m ³ | pcf | 0.0624 |
| | pcf | g/cc (g/cm ³) | 0.016 |
| | g/cc | pcf | 62.43 |
| | g/L | pcf | 0.0624 |
| Energy | Joule | ft-lb | 0.7573 |
| | Joule | in-lb | 8.85 |
| | ft-lb | Joule | 1.355 |
| | in-lb | Joule | 0.113 |
| | Btu | Joule | 1.055 x 10 ³ |
| ILD or IFD (LOADBEARING) | lb/50 in ² | N/323 cm ² | 4.448 |
| | N/323 cm ² | lb/50 in ² | 0.225 |
| | lb/50 in ² | kg/323 cm ² | 0.4536 |
| | kg/323 cm ² | lb/50 in ² | 2.2 |
| Length | Angstroms | meters | 1 x 10 ⁻¹⁰ |
| | meters | micron | 1 x 10 ⁶ |
| | micron | Angstroms | 1 x 10 ⁴ |
| Pressure and Stress | lb/in ² (psi) | (kPa)kN/m ² | 6.895 |
| | kN/m ² (or kPa) | lb/in ² | 0.145 |
| | kg/cm ² | kPa | 98.07 |
| | kg/cm ² | psi | 14.223 |
| | psi | kg/cm ² | 0.0703 |
| | psi | Pa | 6895 |
| | Pa | psi | 0.000145 |
| | g/cm ² | psi | 0.01422 |
| | psi | dyne/cm ² | 68965 |
| | dyne/cm ² | psi | 0.0000145 |
| | bar | atm | 0.987 |
| | bar | kg/cm ² | 1.02 |
| | bar | Pa | 1 x 10 ⁵ |
| | dyne/cm ² | atm | 9.869 x 10 ⁻⁷ |
| | psi | atm | 0.068 |
| | Pa | dyne/cm ² | 10 |
| | MPa | psi | 145 |
| | atm | Pa | 1.013 x 10 ⁵ |
| | dyne/cm ² | Pa | 0.1 |

| | To Convert | Into | Multiply By: |
|---------------|------------------------------------|-----------------|----------------------------|
| Tear Strength | lb/in | N/cm | 1.75 |
| | N/cm | lb/in | 0.571 |
| | N/m | lb/in | 0.00571 |
| | lb/in | N/m | 175.1 |
| | lb/in | kg/cm | 0.1786 |
| | kg/cm | lb/in | 5.6 |
| | kN/m | N/cm | 10 |
| | kg/cm | N/cm | 9.798 |
| Temperature | °C | °F | 9/5 (°C) + 32 |
| | °F | °C | (5/9) (°F - 32) |
| | °C | °K | °C + 273.15 |
| Volume | Liter | in ³ | 61.023 |
| | Liter | U.S. gal | 0.264 |
| | Liter | ft ³ | 0.0353 |
| | U.S. fl oz | ml | 29.6 |
| | U.S. fl oz | m ³ | 2.957 x 10 ⁻⁵ |
| | U.S. gallons | liters | 3.79 |
| | liters | m ³ | 0.001 |
| | m ³ | liters | 1000 |
| | Liter | U.S. fl oz | 33.819 |
| | U.S. fl oz | British fl oz | 1.0408 |
| | board foot | m ³ | 2.359 x 10 ⁻³ |
| | centipoise = centistokes x density | | |
| Viscosity | Pascal second (Pa·s) | centipoise | 1000 |
| | centipoise | Pa·s | 0.001 |
| | mPa·s | centipoise | 1 |
| | | | |
| Weight | g | MetricTons | 1 x 10 ⁻⁶ |
| | g | kg | 0.001 |
| | g | oz (avdp) | 0.0352739 |
| | g | pounds (avdp) | 0.0022026 |
| | ounces (avdp) | g | 28.3495 |
| | ounces (avdp) | Metric Ton | 2.83495 x 10 ⁻⁵ |
| | Metric Ton | kg | 1000 |
| | Metric Ton | pounds | 2240 |

References

B.1 Conant, F.S. "Using the SI Units"; *Polym. Eng Sci.* **1977**, 17/4, 222-228.

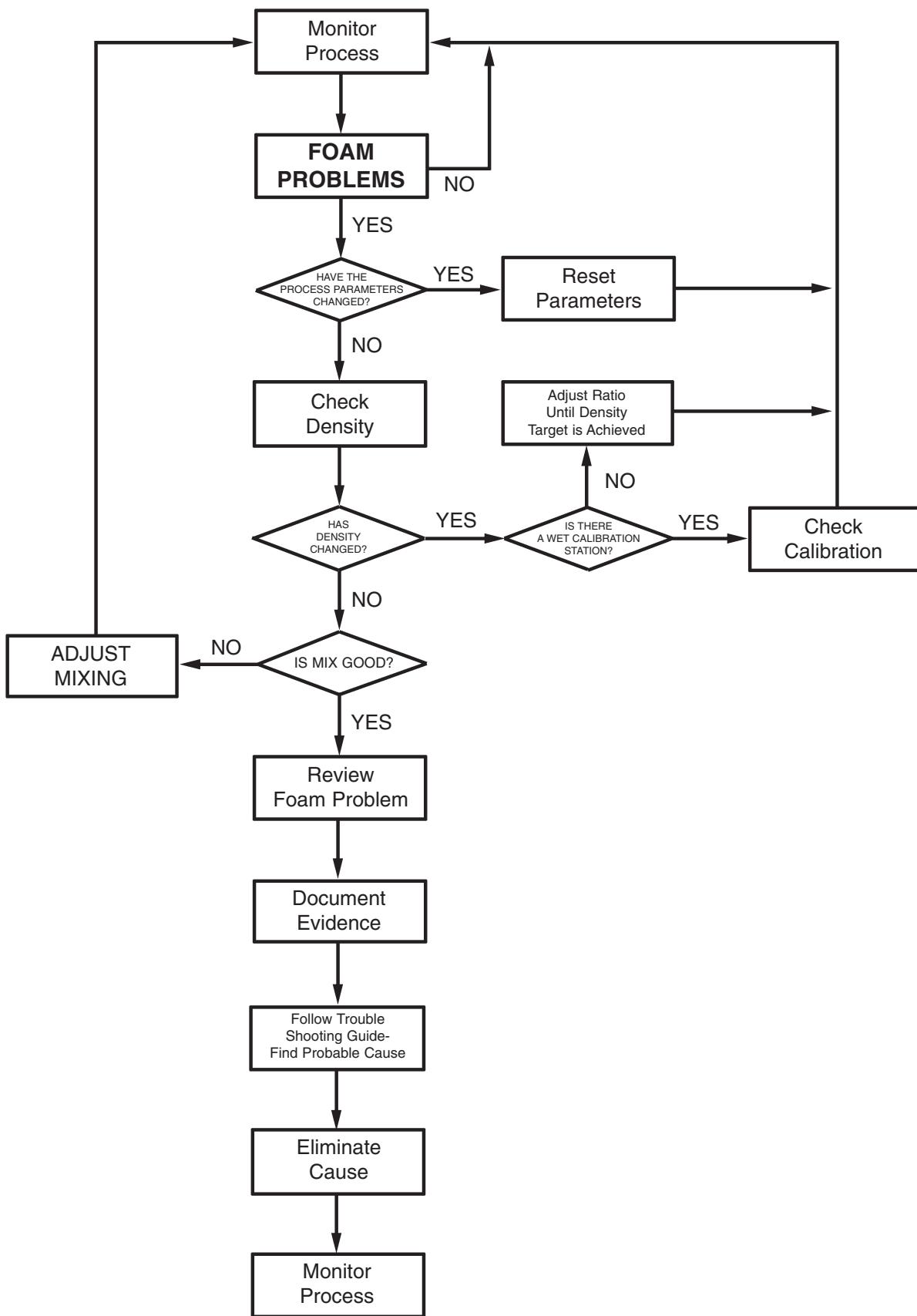


Figure C.1 Flow Chart For Solving Foam Problems

Appendix C

Troubleshooting Guide

**R. Herrington, K. Hinze, S. Burks, L. Shaw, C. Noakes,
F. Polk, R. Autenrieth**

This guide lists the more common processing and physical property deficiencies known to occur in flexible polyurethane foams. The problem areas are listed alphabetically and are split into five sections. First is a general listing of problems common to processing of all types of flexible foams. Next is a listing of items more specific to the making of slabstock foam. The third section details problems more specific to the making of molded foams. The fourth section addresses problems more specific to the field of semiflexible molded foams. A final section addresses problems with some of the physical properties of the final produced foam.

Additional more-specific problems may occur with the various mechanical systems used to shape a rising bun of slabstock foam. In those cases, the manufacturer's operating manual should be consulted. A general scheme for addressing foam problems is presented in Figure C.1.

GENERAL PROCESSING DEFICIENCIES

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|--------------------|--|---|
| Boiling | Large bubbles appear and burst at the surface. | Check surfactant quality and output. Check tin catalyst quality and output. Reduce amine catalyst concentration. Check for contamination with silicone or grease lubricants. |
| Collapse | Foam rises and then falls. | Check surfactant quality and output. Check tin catalyst quality and output. Reduce amine catalyst concentration. Check for contamination with silicone or grease lubricants. |
| Crazy balls | Small liquid bubbles moving rapidly over foam surface. | Increase mixing speed on low-pressure machine. Increase dispensing pressure on high-pressure machine. Minimize splashing during liquid lay-down. |
| Friable | Foam is crumbly with no polymer strength. | Look for errors in metering. Decrease isocyanate output. Check tin catalyst activity. Check polyol reactivity. Increase mixing speed/efficiency. |
| Odor | Finished foam has an objectionable odor. | Use less-odorous amine catalysts. Use less-odorous formulation additives. Allow time for foam to degas. |
| Slow cure | Buildup of polymer strength is too slow. Foam is too weak or too sticky to allow physical handling. Foam bun is dimensionally unstable without side support. | Increase tin and/or amine catalyst concentration. Check for catalyst deactivation. Look for errors in metering. Raise component temperatures. |

| | | |
|--------------------------|--|--|
| | | Improve mixing efficiency. |
| | | Check water quality. |
| Smoking | Excessive isocyanate vapors rise from surface of the foam. | Look for errors in metering. Reduce isocyanate output. |
| Sticky spots | Localized areas of wet, imperfectly mixed ingredients. | Check for lead/lag conditions. Increase mixing efficiency. |
| | | Check component tank levels. |
| | | Look for system contaminants. |
| Tacky bun surface | Surface of foam remains sticky for prolonged time. | Increase total catalyst levels. Check bun storage conditions. See 'Slow cure'. |

SLABSTOCK PROCESSING DEFICIENCIES

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|----------------------------------|--|--|
| Bottom cavitation | Bun has closed cells and bottom is eaten away | Look for errors in metering. Decrease tin catalyst. |
| Bottom-skin densification | Layer of denser foam at bottom of bun. | Increase surfactant level or check for reduced activity. |
| Chimney splits | Mostly vertical splits appearing in combustion modified grade of foam. | Increase cross-linker level. Increase density. Decrease melamine level. |
| Creeping cream line | Cream line moves back toward the pour point. | Speed up conveyor. Increase conveyor angle. Lower amine catalyst level. |
| Flashing, sparklers | Excessive effervescence of top surface of rising foam. | Decrease isocyanate. Decrease surfactant concentration. Decrease amine catalyst. Increase tin catalyst. Look for errors in metering. Decrease component temperatures. |
| Friable skin | Skin is soft and flakes off at the touch. | Increase, change or check activity of amine catalyst. Increase component temperatures. Look for contaminants in system. Add small amount of EO capped polyol. |
| Gross splits | Large vertical or horizontal separations in the bun. | Increase tin catalyst or check for reduced activity. Decrease amine catalyst. Increase surfactant or check for reduced activity. Decrease water level. Check all mechanical factors. |

| | | |
|-------------------------------|---|--|
| Heavy skin | Thick skin of high density. | Increase total system catalysis. Increase isocyanate content. Heat bun surface. |
| Low catalyst tolerance | Foam exhibits excessive sensitivity to changes in tin catalyst concentration. | Increase metered volume of catalyst by using diluted version. Look for errors in metering of all components. |
| Moon craters | Small pits or pockmarks on the bun surface. | Decrease amine catalyst. Decrease or use lower activity surfactant. |
| Narrow tin latitude | Latitude from splits to closed cells is too narrow. | Reduce air entrapment in lay-down. Minimize splashing on lay-down. |
| Pea holes | Small spherical voids randomly dispersed throughout the foam. | See 'Low catalyst tolerance'. Increase surfactant or check for reduced activity. |
| Relaxation | Bun rises to maximum height and then settles back down excessively. | Decrease component temperatures. Reduce air entrapment in lay-down. Decrease mixing speed. Decrease tank agitation. Decrease tank pad pressures. Try anti-air entrainment surfactant. Check for contamination with silicone or grease lubricants. Reduce length of dispensing tube after mixer. Eliminate solid type pigments. |

| | | |
|--------------------------|---|--|
| Shrinkage | Bun contracts upon cooling. | Decrease tin catalyst. Decrease surfactant level. Decrease isocyanate index. Increase amine catalyst. Lower component temperatures. Increase mixer speed. Check air injection. Enlarge mixer outlet nozzle. Decrease dispensing pressure on high-pressure machine. |
| Sighback | Bun rises and then settles back down. | See 'Relaxation'. |
| Small side splits | Small diagonal separations at the corner of the bun. | Increase tin catalyst. Increase isocyanate content. Increase surfactant or check for reduced activity. Check all mechanical factors. |
| Stratification | Irregular density throughout bun. | Look for errors in component metering. Check mechanical factors. |
| Striations | A distinct line of unusual cell structure. | Increase mixing. Check injection nozzles. Minimize splashing at laydown. Check distribution of pigment. Check for foam buildup. Look for contamination. Clean mixing chamber. |
| Undercutting | Liquid reactants flow under the already rising foam mass. | Speed up conveyor. Decrease conveyor angle. Increase catalyst levels. |

Underrunning

See ‘Undercutting’.

See ‘Undercutting’.

Zig-Zag splits

Crumbly, ragged splits throughout the foam or on its sides.

Increase tin catalyst concentration.

Check for reduced tin catalyst activity.

Increase surfactant level.

Look for metering errors in water and isocyanate.

MOLDED FOAM PROCESSING DEFICIENCIES

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|--------------------|--|--|
| Air bag | An extreme case of voiding in which an intact outer skin is formed but the interior of the molded part is one continuous void. | Increase level of cross-linker. Increase the rate of polymer gellation. Decrease the rate of blowing reaction. Reduce the size/number of vent holes. Reduce mold overpacking. Check for contamination with silicone or grease lubricants. |
| Air trap | Voids caused by encapsulation of air pockets during mold fill-out. | Improve pour pattern. Optimize pattern and size of vent holes. Optimize mold tilt. Minimize splashing during liquid laydown. Use alternative amine catalyst system. Use alternative silicone surfactant. |
| Basal cells | Large, irregular cells found just under the show-surface skin. | Check for defoaming contaminant. Check surfactant activity. Utilize surfactant blends. Remove wax buildup. Reduce mold temperature at pour. Buff mold surface with paper towel and rewax Check balance of blow/gel reactions. |
| Blistering | Random small areas of coarse cells and loose skins on show surface of molded part. | Clean and recondition mold. Lower component temperatures. Check release agent application. Try alternative release agent. |
| Blowholes | Small diameter void areas extend well down into finished part. | Reduce air entrapment during liquid laydown. |

Coarse surface cells

Cells on show surface of molded pad are larger than elsewhere in pad.

Decrease ISO pad gas pressure.

Increase mixing efficiency.

Optimize lid-venting pattern.

Reduce mold temperature at pour station.

Check release agent application.

Try alternative release agent.

Remove wax buildup.

Buff surface with paper towel and rewax.

Cold collapse

Shallow localized depressions with a thin, loose skin appearing on the show surface of pad.

Raise mold temperature at pour station.

Select amine catalyst package designed for lower pour temperatures.

Crusher set

Foam pad loses height when processed through roller-type crusher.

Increase cure time prior to crushing.

Increase overall rate of polymer gellation.

Increase functionality of polyol/isocyanate.

Utilize progressive steps of crushing.

Substitute vacuum crushing for mechanical crushing.

Check quality of the water.

Lower component temperatures.

Decrease tightness of the foam.

Crusher splits

Foam physically splits apart during mechanical crushing.

Decrease size/number of vent holes.

Excessive flash

Polymer escapes the mold through vent holes and parting lines to an excessive degree.

Increase clamping pressure on mold parting lines.

Increase rate of polymer gellation.

Decrease total shot size.

Extrusion collapse

Shallow void and/or collapsed areas resulting from excessive flow of material through mold vents and parting lines.

Reduce shot size.

Optimize pour pattern.

Increase rate of polymer gellation.

Reduce rate of blowing reaction.

| | | |
|---------------------------------|---|---|
| Fingerprinting | Upon demold, the pad retains evidence of where the operator grasped it. | Utilize extrusion control insert; e.g., slab foam, fabric, or reticulated foam tape. |
| Gross internal splits | Interior of hot-molded pads shows fissures or tearing apart of the foam. | Increase level or activity of surfactant. Improve mold sealing. Increase in mold cure time. Increase functionality of the polyol/isocyanate. Increase rate of polymer gellation. Check quality of the water. |
| Hard edges | Foam is excessively hard along and near the parting line of the mold. | Increase tin catalyst or check for reduced activity. Restore proper blow/gel balance. Optimize mixing conditions. Optimize pour pattern to minimize foam movement. Check mold factors such as temperature, venting and sealing. |
| Knit lines | Weak joints between two different sections of foam that have flowed together. | Decrease gas and foam extrusion through the parting line. Increase clamping pressure. Increase venting through lid. Improve foam stability. |
| Loose skin | Show surface of the pad has a thin, loose skin. | Optimize pour pattern. Decrease overall rate of system gellation. For hot-molded foam, decrease mold temperature at pour. In HR foam this is caused by too low a mold temperature at pour. |
| Parting line instability | Void areas in the foam pad occurring at or near the mold parting line. | Check efficiency of mold release. Increase clamping pressure along the parting line. Increase overall rate of system gellation. Clean parting line seals. |

| | | |
|----------------------------------|--|--|
| Poor flow | Dispensed material is adequate to fill mold but does so with difficulty. | Improve pour pattern. Lower overall catalysis level. Lower mold temperature at pour. Lower component temperatures. Reduce heat input by mixer. Ensure adequate venting of mold. |
| Poor green strength | Foam pad easily tears upon demold. | Increase wax utilization/efficiency. Increase rate of polymer gellation. Decrease tightness of foam. Increase functionality of polyol/isocyanate. Improve mixing. Check quality of the water. |
| Poor Release | Foam pad sticks to mold surface or is otherwise difficult to remove from mold. | Improve coverage of sprayed release agent. Raise mold temperature at pour. Remove wax buildup. Lower isocyanate index. Try alternative release agent. Increase overall catalysis level. |
| Pressure release collapse | Shallow voids usually on show surface of pad. | Insure proper sealing of the mold. Maintain proper clamping during foam cure. Leave all mold extrusions in place during foam cure. |
| Shear collapse | Localized loss of polymer integrity resulting in voids containing coarse, stringy polymer. | Check balance of blow/gel reactions Check timing of cell-opening. Check efficiency of surfactant. Increase overall system functionality. Increase reactivity of the polyol(s). Optimize pour pattern. |

Shrinkage

Contraction of the finished foam upon cooling.

Ensure good sealing and proper venting.

Adjust part weight to proper range.

Look for particulate contaminants.

Remove wax buildup.

Reduce overall rate of polymer gellation.

Increase amine blowing catalyst concentration.

Decrease component temperatures.

Reduce surfactant concentration or activity.

Increase copolymer polyol concentration.

Utilize cell-opening additives.

Utilize timed-pressure-release technology.

Increase mixer speed on low-pressure machines.

Increase mixer outlet nozzle diameter.

Slow cure

Buildup of polymer strength is too slow.

Increase cure cycle.

Foam is too weak or too sticky to allow physical handling.

Increase overall level of catalysis.

Increase functionality of polyol/isocyanate.

Lower isocyanate index.

Improve mixing.

Check quality of the water.

Solvent burn

Localized areas of deteriorated foam usually on the show surface.

Ensure complete evaporation of the mold release solvent before pouring the foam.

Reduce application rate of mold release.

Check for proper wax atomization.

Select a mold release with a higher volatility solvent.

Buff mold surface with paper towel and rewx.

| | | |
|---------------------------|--|--|
| Surface scorching | Shiny, crusty areas on show surface of pad, with subsurface voids that occasionally break the surface. | Increase wax application rate. Check for proper wax atomization. Decrease mold temperature at pour. Buff with paper towel and rewx. Clean and recondition mold. |
| Surface shear | Coarse cells on show surface. | Decrease overall rate of gellation. Increase shot size. Optimize pour pattern. Reduce mold temperature at pour. |
| Tacky part surface | Foam is too sticky to allow physical handling. | Increase cure cycle. Check polyol and ISO line pressures. Introduce surface-cure type of amine catalyst. |
| Thick skin | The show surface of pad has a thick, hard skin. | Caused in hot-molded foam by too cold a mold temperature at pour. Increase venting to reduce internal mold pressure. Increase silicone surfactant or check for reduced activity. |
| Underfilled mold | Foam mix fails to fill mold. | Check for excessive part weight or packing level. Increase shot size. Optimize pour pattern. Increase blowing catalysis or check for reduced activity. Increase formulation water level. Increase isocyanate index. Increase component temperatures. Increase mold temperature at pour. Reduce extrusion through vent holes. Lower shot size. |
| Vent instability | Voids form immediately under mold vent holes. | |

| | | |
|-----------------------------|--|--|
| | | Utilize extrusion control insert; e.g., slab foam or fabric. |
| | | Increase rate of polymer gellation. |
| | | Decrease rate of blowing reaction. |
| | | Increase surfactant concentration or activity. |
| Visible pour pattern | Surface of pad shows evidence of liquid lay-down pattern. | Avoid splashing during lay-down. |
| | | Change outlet pipe diameter and/or length. |
| | | Clean and recondition mold. |
| | | Check mixing efficiency. |
| | | Increase wax application rate. |
| | | Try alternative mold release. |
| Worm holes | Elongated irregular voids running vertically through the foam. | Check for lead/lag condition. |
| | | Check for dripping contaminant. |
| | | Check water-based mold release system. |
| | | Decrease ISO pad gas pressure. |
| Wrinkling | Crushing step produces wrinkles on the pad. | Increase cure cycle. |
| | | Check polyol and ISO line pressures. |
| | | Increase overall rate of polymerization. |
| | | Decrease foam tightness. |
| | | Utilize progressive steps to final crush thickness. |
| | | Substitute vacuum crushing for mechanical crushing. |
| | | Check quality of the water. |

AUTOMOTIVE SEMIFLEXIBLE FOAM PROCESSING

General

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|----------------------|---|--|
| Blown covers | Degassing under the vinyl skin. | Reduce fill weight. Raise index. Lower mold temperature. |
| Cold collapse | Shallow dish of collapsed foam. Loose skin on top with shiny undersurface. | Raise mold temperature. Heat skins. |
| Dented parts | An imprint or depression in the part. | Clean debris from molds. Clean wax buildup on molds. Clean foam buildup on molds. Check skin quality. Increase packing in the part. |
| Hard to clean | Difficult to pick foam flash off of part. | Reduce index. Reduce fill weight to reduce flash. Wax problem areas. |
| Knit lines | Nonuniform joining of foam fronts. | Decrease component temperature. Increase index. Decrease mold temperature. Use one continuous pour (open pour). Increase throughput (closed pour). Raise fill weight. Use one shot pour (closed pour). |
| Poor adhesion | Vinyl skins peel away from foam without foam tearing. | Raise index; lower fill weights. Reject vinyl skins. (dirty, old or poor quality). Optimize pour pattern. Increase level of adhesion promoter. |

| | | |
|---------------------------|---|--|
| Poor cure | Tacky foam. Poor green strength. Under cure. Fingerprints. | Check ratio; lower index to improve cure. Raise level of gelling catalyst. Increase cycle time. Increase component temperature. Increase mold temperature. |
| Poor metering | Inconsistent hardness. Off index. | Clean filters and orifices. Check tank levels. Slow agitation on day tank. Check for pressure drops in the lines. |
| Rippled vinyl skin | Rippled skin (Inconsistent vinyl thickness). (Large vinyl skin). | Check for pump slippage. Check ratio consistency. Reject the skins. Cure vinyl skin longer to allow proper shrinkage. |
| Shrinkage | Contraction of the foam upon cooling. | Check ratio; raise index. Reduce fill weights. Hand crush parts after demold. Adjust degas timer. |
| Solvent burn | Voids. Coarse, ratty foam. Flaky skin. | Eliminate wet mold release in contact with foam. (Increase wax drying time) Reduce mold release usage. Change to mold release with more volatile solvent. Raise mold temperature. |
| Stratification | Irregular hardness. | Adjust mixing parameters/pressures. |
| Stretching | Large irregular cells (coarse, ratty foam). | Check ratio. Check mixing. Increase fill weight. Optimize pour pattern. |

Tough skin

Thick, hard skin.

Increase nucleation.

Improve mold sealing/venting.

Raise mold temperature.

Reduce fill weight.

Underfill

Underfill (may appear as a void with no vinyl wet-out).

Check consistency of delivery weight.

Increase fill weight.

Increase mold temperature.

Increase index.

Optimize pour pattern.

Increase nucleation.

Voids, Open-Pour

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|------------------------------|--|---|
| Air traps | Smooth rounded void with shiny surface. | <ul style="list-style-type: none"> Reduce splatter from head. Reduce throughput. Optimize mold closure time. Adjust pour pattern. Lower component temperatures. Lower mold temperature. Install or clean vents. Raise index; lower fill weight. <p>Nucleation has been found to both cause air traps and reduce air traps — it is very much part dependent.</p> |
| Extrusion collapse | Hairy/stringy void (coarse, collapsed cells). | <ul style="list-style-type: none"> Reduce agitation in day tank. Improve mold sealing to reduce flash. Lower index. Reduce fill weight to reduce flash. Lower mold temperature. Lower component temperature. |
| Pressure relief voids | <ul style="list-style-type: none"> Smooth, flat void with shiny surface. Similar to snail's trail. | <ul style="list-style-type: none"> Reduce fill weight. Raise index; reduce fill weight. Lower mold temperature. Improve venting of mold. Lower component temperatures. |
| Shear collapse | Coarse ratty foam (irregular cell size). | <ul style="list-style-type: none"> Increase fill weight in area where problem occurs through pour pattern changes. Maintain consistent foam thickness over entire part. Lower mold temperature and component temperature with increased fill weight to avoid underfills. Increase nucleation. Check for hydraulic oil leaks. |

Voids, Closed-Pour

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|--------------------------------|--|---|
| Air trap | Smooth rounded voids with shiny surfaces. | Lower component temperatures. Lower mold temperature. Reduce throughput. Increase fill weights. Clean vents/install vents. Tilt mold to redistribute flow. Reduce splatter from head. Shorten distance from head to substrate. |
| Extrusion collapse void | Hairy, stringy void (coarse collapsed cells). | Reduce flash.(Improve mold sealing). Lower index. Lower mold temperature. Reduce fill weight. Lower component temperatures. |
| Pour-hole voids | Void directly over pour-hole. | Tighten or replace pour-hole valve. Lengthen time between end of pour and valve closure. Improve sealing around pour-hole. Check pour hole alignment. Increase cycle time (See poor cure). Decrease machine throughput. |
| Pressure relief void | Smooth, flat void with shiny surface. Similar to snail trail. | Reduce fill weight. Raise index. Lower mold temperature. Improve mold venting. Lower component temperature. |
| Shear collapse | Coarse, ratty foam (irregular cell size). | Tilt mold to redistribute flow. Increase fill weights. Increase index. Lower mold temperature. Lower component temperature. Maintain consistent foam thickness over entire part. |

PHYSICAL PROPERTY DEFICIENCIES

| <u>Defect</u> | <u>Description</u> | <u>Recommendations</u> |
|---------------------|---|---|
| Airflow low | Foam exhibits low airflow. | <p>Decrease tin catalyst.</p> <p>Decrease amine gellation catalysts.</p> <p>Decrease surfactant or use less potent variety.</p> <p>Utilize or increase cell-opening additive.</p> |
| Boardy feel | Foam feels harsh and unpleasant to the touch. | <p>Utilize foam crushing step during manufacture.</p> <p>Decrease cell-size; e.g., increase surfactant, increase stirrer speed.</p> <p>Decrease total blowing as by reducing water or isocyanate content.</p> <p>Reduce overall cross-linking.</p> |
| Closed cells | Cell-walls remain intact and do not rupture. | <p>Decrease system gellation.</p> <p>Increase system blowing catalysis.</p> <p>Decrease surfactant concentration.</p> <p>Decrease component temperatures.</p> <p>Increase stirrer speed.</p> <p>Increase mixer exit nozzle diameter.</p> <p>Decrease packing in molded foams.</p> <p>Utilize cell-opening additive.</p> |
| Coarse cells | Foam contains large cells. | <p>Check surfactant level and activity.</p> <p>Increase tin catalyst to balance blow/gel reactions.</p> <p>Increase mixer speed on low-pressure machines.</p> <p>Increase outlet pipe diameter on low-pressure machines.</p> <p>Decrease machine throughput on low-pressure machines.</p> <p>Decrease mixing head pressure on high-pressure machines.</p> |

| | | |
|--|--|---|
| Compression sets high | High test values. | Increase throughput on high-pressure machine. Lower component temperatures. Check for contamination. Check dissolved gas in polyol and Iso. |
| Dead foam | Foam has low resiliency and closed cells. | Decrease tin and surfactant levels. Optimize isocyanate index. Increase functionality of polyol/isocyanate. Improve foam airflow. Improve foam cure conditions. |
| Dense foam | Foam density is higher than expected from known formulation. | Reduce tin catalyst. Reduce surfactant level. Decrease cell-size. Lower index. See ‘Closed cells’. |
| Density variation from part to part | Molded foams from one formulation vary from part to part. | Look for errors in metering of components. Check for errors in calibrating water and isocyanate streams. Increase blowing catalyst concentration or check for reduced activity. Increase temperature of mold in molded foams. Decrease packing level in molded foams. |
| Discoloration | Foam is off-color. | Check for constant shot time. Check for constant mold temperature. Verify equal venting and mold sealing. Optimize mixing conditions. Check for consistent pour pattern. Reduce tin catalyst. |

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| | | Look for contaminants in system. |
| Elongation low | Low test values. | See ‘Scorching’. |
| Internal splits | Ragged internal separation of the foam to form void areas. | Decrease isocyanate index. Decrease cross-linker concentrations. Increase mixer speed. Decrease cell-size. Look for errors in component metering. |
| Load-bearing high | Formulation produces higher test values than expected. | Increase tin catalyst. Increase surfactant level. Increase isocyanate index. Decrease blowing catalyst. Lower mixer speed. Reduce nucleating air. Look for errors in component metering. |
| Load-bearing low | Formulation produces lower test values than expected. | Decrease isocyanate index. Look for errors in component metering. Check use level of copolymer polyol. Consider humidity effects. Adjust packing level in molded foams. Increase isocyanate index. Look for errors in component metering. Check use level of copolymer polyol. Lower humidity at curing station. Adjust packing level in molded foams. |
| Pneumatic feel | Foam has poor breathability and feels like a balloon. | Decrease closed-cell content as by reducing catalyst and surfactant. Crush molded foam pads to open cell windows. Utilize cell-opening additive. |

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| Poor cell size | Foam is composed of large cells. | Increase surface porosity of molded foam pads. |
| Poor fingernail | Foam recovers slowly when indented with a sharp object. | See ‘Closed cells’. |
| Poor hand | Foam is rough or harsh to the touch. | See ‘Coarse cells’. |
| Reactivity splits | Smooth gross splits throughout the bun. | Improve foam airflow by decreasing tin catalyst and/or surfactant levels. |
| Scorching | Discoloration and loss of properties in the foam core. | Decrease cell-size. |
| Shiners | Intact cell-walls visible when viewing cut surface of a foam. | See ‘Closed cells’. |
| Stratification | Irregular density throughout the bun. | Decrease isocyanate index. |
| | | Decrease total reactivity of foam system. |
| | | Look for errors in metering isocyanate. |
| | | Look for errors in component metering. |
| | | Reduce formulation water level. |
| | | Check for iron contaminants. |
| | | Reduce bun height. |
| | | Avoid stacking freshly prepared buns. |
| | | Store in a cooled atmosphere. |
| | | Confirm use of antioxidant package. |
| | | Decrease tin catalyst. |
| | | Decrease isocyanate index. |
| | | Decrease surfactant concentration. |
| | | Optimize mixing speed. |
| | | Decrease cell-size. |
| | | See ‘Closed cells’. |
| | | Look for errors or fluctuations in component metering. |
| | | Check all mechanical factors of machine. |
| | | See ‘Undercutting,’ Slabstock Processing Deficiencies. |

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| Surface porosity low | Skin of molded pads has closed cells. | Increase wax utilization rate. Switch to more effective wax composition. |
| Tensile strength low | Test values lower than expected. | Increase mixing speed. Decrease isocyanate index. |
| Voids | Small voids, randomly distributed throughout the foam. | Increase tin catalyst concentration. Increase cell-size as by decreasing mixing speed. Check for contamination by silicone or grease lubricants. See ‘Pea holes,’ Slabstock Processing Deficiencies. |

Appendix D

Catalysts

R. Herrington, J. Porter, F. Casati

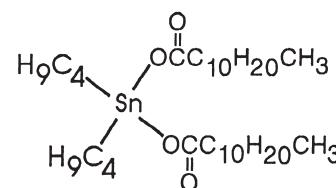
The following is a descriptive list of the most common catalysts used in manufacturing polyurethane foam. Organometallic compounds such as the tin catalysts are primarily used for the gelling reaction, while tertiary amine compounds can have either gelling or blowing effects. The list is by no means complete, but instead is an attempt to expose the reader to the more commercially available catalysts from various vendors. The companies represented in this appendix and their catalyst series trademarks are as follows:

| | |
|----------------------------------|-----------------------|
| Air Products and Chemicals Inc. | DABCO, POLYCAT |
| Cosan Chemical Co. | COCURE, COSCAT, COTIN |
| Enterprise Chemical Corp. | QUINCAT |
| Huntsman Corporation | JEFFCAT |
| Kao Corporation | KAO LIZER |
| Merck & Co. | METASOL |
| Nitroil Europe | PC CAT |
| Rohm & Haas Co. | DMP |
| Shepherd Chemical Co. | BICAT |
| Specialty Products International | SPI |
| Th. Goldschmidt Co. | KOSMOS, TEGOAMIN |
| Toyo Soda Co. | TOYOCAT |
| OSI Specialties-Witco | NIAX |
| Witco Chemical Corp. | FOMREZ, FOMREZ UL |

This appendix lists the catalysts alphabetically by trade name. When possible, the analogous catalysts from different vendors have been cross-referenced. The reader should realize that many other catalysts for polyurethane reactions are known in the art.

The descriptions below have been gathered from various sources and are intended to serve as a starting point only. More detailed information is readily available in the original vendor publications. In all cases a thorough understanding of the toxicology information available through vendor material safety data sheets is required before utilizing these catalysts in foam experiments. Contact the vendors for the latest information on catalyst use and availability.

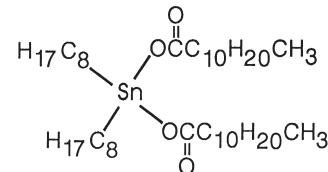
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| BICAT 8 | A bismuth/zinc neodecanoate mixture. |
| BICAT H | 89% Bismuth 2-ethylhexanoate. |
| BICAT V | Bismuth 2-ethylhexanoate/neodecanoate mixture. |
| BICAT Z | A zinc neodecanoate/zinc oxide mixture. |
| COURE 20 | Organomericurial urethane catalyst. Carrier is diethylene glycol monomethyl ether, 25% mercury. |
| COURE 26 | Phenylmercuric acetate, 60% mercury, white powder. |
| COURE 30 | Organomericurial carboxylate urethane catalyst. 60% active ingredient in diethylene glycol, 20% mercury. Same catalyst as COURE 31 and 32 but different carrier. |
| COURE 31 | Organomericurial urethane catalyst. 60% active ingredient in dipropylene glycol, 20% mercury. Same catalyst as COURE 30 and 32 but different carrier. |
| COURE 32 | Organomericurial urethane catalyst. 60% active ingredient in inert material, 20% mercury. Same catalyst as COURE 30 and 31 but a different carrier. |
| COURE 44 | A heat activated organomericurial urethane catalyst. 60% active ingredient in 1,4 butanediol, 20% mercury. |
| COSCAT 83 | Bismuth neodecanoate. More hydrophobic than tin catalysts, but not as active. Catalyzes isocyanate/polyol but not water/iso reaction. Lower toxicity than tin catalysts. |
| COSCAT B-1 | Bis-(dimethylaminoethyl) ether. |
| COSCAT DM-5 | Pentamethyl DETA. |
| COSCAT DM-8 | Dimethylcyclohexylamine. |
| COSCAT DMEA | N,N' dimethylethanolamine. See DABCO DMEA. |
| COSCAT NEM | N-ethyl morpholine. |
| COSCAT NMM | N-methyl morpholine. |
| COSCAT T-33 | 33% triethylene diamine in dipropylene glycol. See DABCO 33-LV, NIAX A-33. |
| COTIN 200 | Dibutyltin dilaurate. |



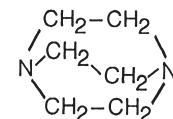
COTIN 222 Organotin carboxylate. Strongly promotes urethane reaction without promoting water/isocyanate reaction.

COTIN 227 Organotin catalyst, dibutyltin diacetate. See FOMREZ SUL-3, TOYOCAT TEDA-T400.

COTIN 430 Organotin catalyst, dioctyltin dilaurate. See FOMREZ UL-38, FOMREZ UL-12.



DABCO CRYSTALLINE Triethylene diamine. Gelation catalyst. Solid crystals.



DABCO 33-LV 33% Triethylene diamine in dipropylene glycol. See TOYOCAT TEDA-L33, NIAX A-33, TEGOAMIN 33.

DABCO 120 Dibutyltin dimercaptide. More reactive than DABCO T-12. Used in spray and slabstock applications for rigid foam as well as in high resilience foam and shoe sole formulations. Good masterbatch stability.

DABCO 125 Dibutyltin biisooctylmaleate. Used in HR molded foam. Provides excellent masterbatch stability in rigid foams. Less reactive than DABCO T-12.

DABCO 131 Dialkyltin dialkylmercapto acid. Less reactive than DABCO T-12. Delayed action gelation catalyst for use in all areas of polyurethanes.

DABCO 1027 37% active amine in monoethylene glycol. Useful for cream and demold time adjustments in microcellular shoe sole foams.

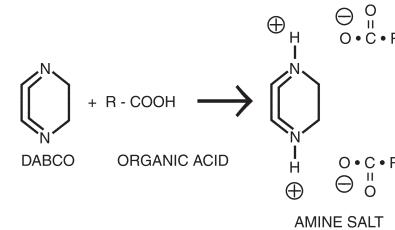
DABCO 1028 30% active amine in 1,4 butane diol. See uses at DABCO 1027.

DABCO 2039 Proprietary catalyst for flexible polyester slabstock foam. Provides minimal odor, reduced plant emissions and reduced fogging.

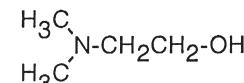
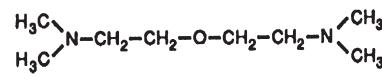
DABCO 2103 50% DABCO 8264 in 3000 MW polyol for slabstock use. See DABCO 8264.

DABCO 7928 Catalyst designed to process continuous block foam on Planiblock, Henneke and Edgemaster foam machines. Intended as the sole catalyst for densities 0.9 PCF to 3.0 PCF.

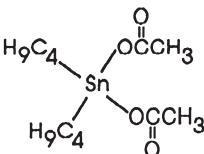
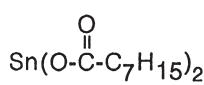
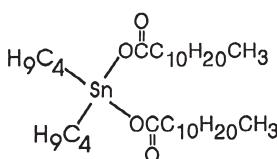
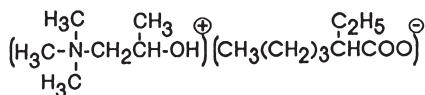
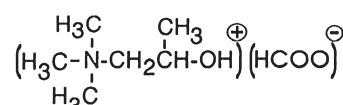
DABCO 8154 Delayed action version of DABCO crystalline. Widely used in all types of polyurethane foam.



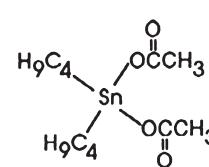
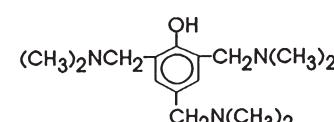
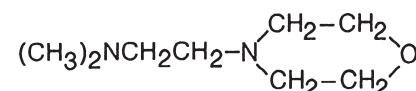
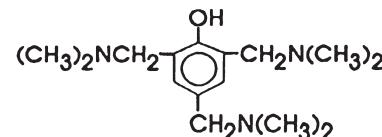
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| DABCO 8264 | Optimized amine catalyst blend for slabstock. Very versatile. |
| DABCO B-16 | 96% N-cetyl, N,N-di-methylamine, 4% isopropanol. Surface cure catalyst. Used to promote good feel in a foam. |
| DABCO BL-11 | 70% Bis (N,N dimethylaminoethyl) ether in dipropylene glycol. Blowing catalyst. See NIAX A-1, TOYOCAT ET. |
| DABCO BL-13 | 23% Bis (N,N dimethylaminoethyl) ether in dipropylene glycol. See NIAX A-1 for applications. |
| DABCO BL-16 | 10% Bis (N,N dimethylaminoethyl) ether in dipropylene glycol. See NIAX A-1 for applications. |
| DABCO BL-17 | Formic acid blocked version of DABCO BL-11. Delayed action catalyst for water/isocyanate reaction in a flexible or rigid polyurethane foam. |
| DABCO BL-19 | 100% Bis(N,N dimethylaminoethyl) ether. Catalyst to promote water-/isocyanate reaction. See NIAX A-99. |
| DABCO BL-22 | Proprietary composition which provides strong blowing, more cell opening, better flowability and a stronger gel than DABCO BL-11. To be used with DABCO 33-LV, in all-water-blown TDI-based molded foams. |
| DABCO BLV | 75% DABCO 33-LV and 25% DABCO BL-11. Standard in industry. Used in melamine modified CMHR and high density foams, slab and molded foam. |
| DABCO CS90 | Offers improved airflow in flexible slabstock foams blown with chlorinated solvent. |
| DABCO DC-1 | Contains a blend of delayed action tin and amine catalysts. Normal initiation with extra-fast cure for use in rigid, semirigid and elastomers (shoe soles). |
| DABCO DC-2 | Contains a blend of delayed action tin and amine catalysts. For rigid foam applications, gives long creams with short cure times. Better cure but less flow than DABCO DC-1. Good for shoe soles. |
| DABCO DMEA | N,N' dimethylethanolamine. Moderately strong blowing catalyst. See NIAX DMEA, JEFFCAT DME. |
| DABCO EG | 33% Triethylenediamine in ethylene glycol. See TOYOCAT TEDA-L33E. |
| DABCO HB | Blend of tertiary amines and butane diol. |



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| DABCO HE | Blend of tertiary amines and ethylene glycol. For microcellular foam systems with polyethers and ethylene glycol. Extended cream, increased flow and decreased demold. For use in shoe soles. Equivalent cream to DABCO EG, but faster demold. |
| DABCO K-15 | 70% potassium octoate in diethylene glycol. Isocyanurate catalyst. |
| | $\text{CH}_3(\text{CH}_2)_3\overset{\text{C}_2\text{H}_5}{\underset{\text{CH}_2-\text{CH}_2}{\text{N}}}-\text{COO}^\ominus \text{K}^\oplus$ |
| DABCO MC | A blended catalyst for use in flexible slabstock foam utilizing methylene chloride as an auxilliary blowing agent. Provides strong cure and minimizes density gradients. |
| DABCO NCM | N-CoCo Morpholine. Moderately slow catalyst providing greater control of the polymerization. |
| | $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \\ \text{R}-\text{N} \\ \\ \text{CH}_2-\text{CH}_2 \end{array} \begin{array}{c} \text{O} \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$ R = C ₁₂ H ₂₅ |
| DABCO NEM | N-ethyl morpholine. Used in polyester foams, allows cure to continue after rise. Good surface cure in HR molded foam. See JEFFCAT NEM, TOYOCAT NEM. |
| | $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2-\text{N} \\ \\ \text{CH}_2-\text{CH}_2 \end{array} \begin{array}{c} \text{O} \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$ |
| DABCO NMM | N-methyl morpholine. See JEFFCAT NMM. |
| | $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \\ \text{H}_3\text{C}-\text{N} \\ \\ \text{CH}_2-\text{CH}_2 \end{array} \begin{array}{c} \text{O} \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$ |
| DABCO R-8020 | 20% triethylenediamine in 80% dimethylethanolamine. For rigid or other foams made with polymeric or crude isocyanates. |
| DABCO S-25 | 25% triethylenediamine and 75% 1,4, butanediol. For RIM applications using 1,4 butanediol as a chain extender. Also used in microcellular foams. See TOYOCAT TEDA-L25B. |
| DABCO SB | Microcellular foam catalyst, used in polyester systems extended with 75% 1,4 butanediol. Extended cream, increased flow, decreased demold. Replacement for DABCO S-25. |
| DABCO SE | Proprietary amine extended with 67% mono ethylene glycol. Microcellular foam catalyst used in polyester systems. Extended cream, increased flow, reduced demold time. |
| DABCO T | N,N dimethylaminoethyl N', methyl ethanolamine. Nonfugitive rigid foam blowing catalyst for use in molded foam or low-density packaging. Premier packaging foam catalyst. |
| | $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$ |

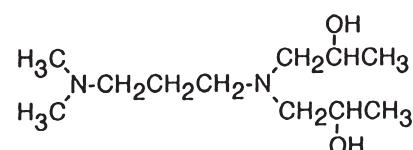
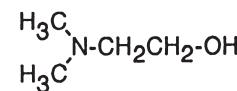
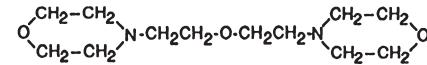
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| DABCO T-1 | Dibutyltin diacetate. See FOMREZ SUL-3, TOYOCAT TEDA-T400, COTIN 227. |  |
| DABCO T-9 | Stabilized Stannous octoate. Mostly for use in one shot polyether slabstock foam. Exposure to air or water can quickly reduce catalytic activity. See KOSMOS 29, FOMREZ C-2, and TOYOCAT TEDA-D007. |  |
| DABCO T10 | 50% stannous octoate (DABCO T-9) in dioctylphthalate. For applications see DABCO T-9, KOSMOS 15, FOMREZ C-4. | |
| DABCO T-12 | Dibutyltin dilaurate. Used in foams, adhesives, sealants and coatings. Performs best in rigid. See FOMREZ SUL-4, KOSMOS 19, TOYOCAT TEDA-T411. |  |
| DABCO T-95 | 33% stannous octoate (DABCO T-9) in dioctylphthalate. See KOSMOS 10. | |
| DABCO TETN | Triethylamine, highly volatile amine catalyst. Acts as a surface cure catalyst and reduces defects associated with lower temperature molds. Balanced blow and gel for molded and slabstock foams. | N-(CH ₂ CH ₃) ₃ |
| DABCO TL | More blow than DABCO 33-LV. For use with methylene-chloride-blown foams. Sole catalyst for a wide variety of slabstock foams. Promotes complete surface cure and early green strength. | |
| DABCO TMR | Quaternary ammonium salt in ethylene glycol. N-hydroxy-alkyl quaternary ammonium carboxylate. Isocyanurate catalyst used with DABCO R-8020 or POLYCATE 8. Reactivity TMR > TMR2 > TMR3 > TMR4. |  |
| DABCO TMR-2 | Slower reaction profile than TMR but gives excellent isocyanurate foam properties. Same as DABCO TMR but formic acid blocked instead of 2-ethyl hexanoic acid blocked. |  |

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| DABCO TMR-3 | Isocyanurate catalyst used for continuous bunstock with long rise rates, rapid cure. See note on reactivity DABCO TMR. |
| DABCO TMR-4 | Isocyanurate catalyst used for pour-in-place. Excellent flow, less prone to deactivate co-catalysts or amine polyols than DABCO TMR-3. |
| DABCO TMR-5 | A reduced odor version of DABCO TMR-2. |
| DABCO TMR-30 | Tris (dimethylaminomethyl) phenol. Phenolic hydrogen very unreactive. Isocyanurate catalyst, but weak. Helps smooth rise profiles. Not a true DABCO TMR catalyst. See DMP-30. Also useful for HR foam. |
| DABCO WT | Delayed-action flexible foam catalyst with strong gel. Not for use with water. Corrosive. |
| DABCO X-543 | Strongly acid-blocked, formulated catalyst. Fast-demold catalyst for HR molded TDI foam. |
| DABCO X-8136 | Delayed action catalyst for energy absorbing applications. |
| DABCO XDM | N,N -dimethylaminoethyl morpholine. Surface cure and gelation catalyst. Helps to prevent cold collapse. Low odor, used in flexible polyester foam. |
| DABCO XED-20A | Catalyst blend containing aliphatic amines and glycols, for use in HR-molded foam made with MDI or TDI/MDI blends. |
| DMP-10 | Mixture of ortho and para dimethylaminomethyl phenol. |
| DMP-30 | 2,4,6 Tris (dimethylaminomethyl) phenol. See DABCO TMR-30 |
| FOMREZ C-2 | Stannous octoate, stabilized. See KOSMOS 29, DABCO T-9, TOYOCAT TEDA-D007. Used in polyurethane and silicone applications. |
| FOMREZ C-4N | 50% stannous octoate in diisononylphthalate. Used in polyurethane and silicone applications. |
| FOMREZ EC-686 | Potassium octoate in diethylene glycol for isocyanurates. |
| FOMREZ SUL-3 | Dibutyltin diacetate. See DABCO T-1, COTIN 227, TOYOCAT TEDA-T400. Best blowing catalyst of the organotin gelation catalysts. |

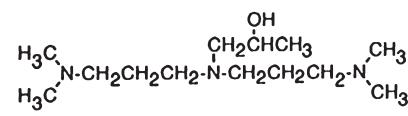
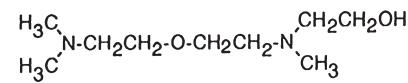


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| FOMREZ SUL-4 | Dibutyltin dilaurate. See DABCO T-12, KOSMOS 19, TOYOCAT TEDA-T411. Used in polyurethane and silicone applications. | |
| FOMREZ SUL-11A | Dibutyl tin oxide/liquid composite. | |
| FOMREZ UL-1 | Dibutyltin dimercaptide. See DABCO 120. Has about the same reactivity as DBTDL but better hydrolysis resistance. Used in rigid, HR and microcellular RIM. | |
| FOMREZ UL-2 | Dibutyltin dicarboxylate. For rigid foams. Does not undergo gross phase separation like dibutyltin dilaurate. Water and acid resistant. See UL-8. Same reactivity as dibutyltin dilaurate. | |
| FOMREZ UL-6 | Dimethyltin dimercaptide. Sensitive to acids and water. Delayed action used in high density, water-blown rigid foam and microcellular elastomers. | |
| FOMREZ UL-8 | Dibutyltin dicarboxylate. Water and acid resistant, more active analogue of UL-2 and can be used at half the level. For rigid spray foams. Also recommended as co-catalyst in isocyanurates. See UL-2. | |
| FOMREZ UL-19 | Metalic carboxylate for use in carpet. A solid. | |
| FOMREZ UL-22 | Dibutyltin dimercaptide. A more active analogue of UL-1 for polyurethane applications with equivalent resistance to moisture. Use about half compared to UL-1. | |
| FOMREZ UL-24 | Dimethyltin diisooctylmercapto-acetate. Sensitive to acids and water. A more active analogue of UL-6, with equivalent delayed action. Use about half compared to UL-6. | |
| FOMREZ UL-28 | Proprietary dimethyltin dicarboxylate. Fastest tin catalyst available for polyurethanes. Use approximately half of DBTDL, about equivalent to dibutyltin diacetate. | |
| FOMREZ UL-29 | Dimethyltin dimercaptide. Sensitive to acids and water, 10% slower than UL-6. Delayed action. Used primarily in microcellular RIM. | |
| FOMREZ UL-32 | Dimethyltin dimercaptide. More delayed-action catalyst than UL-1 but slower reactions. Outstanding resistance to hydrolysis. Used in microcellular RIM, HR foam and rigid boardstock. | |
| FOMREZ UL-38 | Diocetyltin analog of UL-28. | |

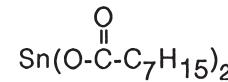
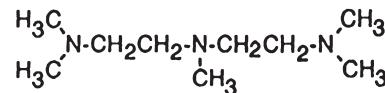
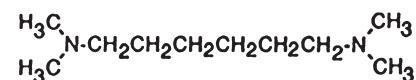
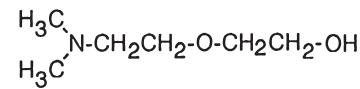
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| JEFFCAT DM-70 | 70% JEFFCAT DMDEE and 30% JEFFCAT DMP. Catalyst for polyester slab and to promote green strength in HR-molded foam. Also promotes top-skin curing in low-density slabstock foams. |
| JEFFCAT DMCHA | N,N-dimethylcyclohexyl amine. Widely used for all types of rigid and semirigid foams. |
| JEFFCAT DMDEE | N,N'-dimorpholinodiethyl ether. Used with stronger catalysts in molding operations for good flowability and cure. A strong blowing catalyst. |
| JEFFCAT DMEA | N,N-dimethylethanolamine. Strong blowing catalyst used in flexible foam and as an acid scavenger in rigid systems based on polymeric MDI. See NIAX DMEA, DABCO DMEA. |
| JEFFCAT DMP | N,N'-dimethylpiperazine. Latent cure catalyst for flexible foams. Balanced blow/gel in semiflex systems. |
| JEFFCAT DPA | N,N-dimethyl-N',N'-2 hydroxy (propyl)-1,3-propylene diamine. Amine catalyst that also has hydroxyl functionality for reaction into the final polymer. Reported to reduce residual amine odor. |
| JEFFCAT DPA-50 | 50% of JEFFCAT DPA and 50% of JEFFCAT DMEA. |
| JEFFCAT E-40 | Low odor, highly effective amine for polyester-based flexible foams. |
| JEFFCAT M-75 | Relatively low odor formulated catalyst that gives excellent processing for polyester-based flexible foams. |
| JEFFCAT MM-70 | A blend of 70% N-methoxyethylmorpholine and 30% JEFFCAT DMP. Low-odor catalyst for use in flexible polyester slab with no discoloration. |
| JEFFCAT NEM | N-ethylmorpholine. Catalyst for flexible polyester slab and surface cure catalyst in flexible foams. See DABCO NEM, TOYOCAT NEM. |
| JEFFCAT NMM | N-methylmorpholine. Catalyst for high-rise, rigid foam panels. See DABCO NMM. |
| JEFFCAT PM | Relatively low odor formulated catalyst that gives excellent processing for polyester-based flexible foams. |
| JEFFCAT PMDETA | Pentamethyldiethylene triamine. Useful in rigid and semirigid foams. |



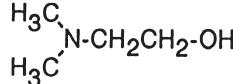
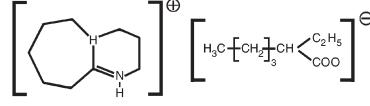
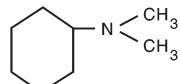
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| JEFFCAT T-9 | Stannous octoate. |
| JEFFCAT T-10 | 50% stannous octoate in dioctylphthalate. |
| JEFFCAT T-12 | Dibutyltin dilaurate. |
| JEFFCAT T-13 | 50% stannous octoate in diisonylphthalate. |
| JEFFCAT T-21 | Dibutyltin dimercaptide. Approximate reactivity of DBTDL but with better hydrolysis resistance. |
| JEFFCAT TD-20 | 20% solution of triethylenediamine in JEFFCAT DMEA. General-purpose catalyst for rigids and continuous laminate boardstock. Also useful in flexible foams. |
| JEFFCAT TD-33A | 33.3% triethylene diamine in dipropylene glycol. See DABCO 33-LV. |
| JEFFCAT TD-100 | Triethylene diamine. See DABCO CRYSTALLINE. |
| JEFFCAT TR | A catalyst designed for rigid isocyanurate foam board stock. |
| JEFFCAT Z-65 | An amine blend useful for faster cure. Improves early compression set. |
| JEFFCAT ZF-10 | N,N,N'trimethyl-N'hydroxyethyl-bis(amino ethyl) ether. Reactive amine catalyst which also provides good blowing catalysis. Low odor. Useful in semiflex and packaging foam. Used in foams molded against vinyl skins. |
| JEFFCAT ZF-20 | Bis(dimethylaminoethyl) ether. See NIAX A-99. |
| JEFFCAT ZF-22 | 70% Bis(dimethylaminoethyl) ether in dipropylene glycol. See DABCO BL-11, NIAX A-1. |
| JEFFCAT ZF-23 | A blend of amines designed for foams run on Maxfoam machines. |
| JEFFCAT ZF-24 | 23% of bis(dimethylaminoethyl) ether in dipropylene glycol. |
| JEFFCAT ZF-26 | 11% of JEFFCAT ZF-20 in dipropylene glycol. |
| JEFFCAT ZF-50 | N,N-bis(3-dimethylamino-propyl) N-isopropanolamine Amine catalyst that reacts into the final polymer. Low odor with good gelation. |
| JEFFCAT ZF-51 | Specialty blend of TD-33A, ZF-20 and DMEA in dipropylene glycol. Offers ease of blow-off point control. |



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| JEFFCAT ZF-52 | Specialty blend of ZF-20, DMEA and DPG, partially blocked with formic acid. Excellent for trough type machines. |
| JEFFCAT ZF-53 | A blend of triethylene diamine and bis-(2-dimethylaminoethyl) ether in dipropylene glycol. Offers a well-balanced blow/gel ratio in most grades of flexible slabstock foam. |
| JEFFCAT ZF-54 | JEFFCAT ZF-22 partially blocked with formic acid. |
| JEFFCAT ZF-57 | Catalyst formulated from TD-33A, ZF-22, DMEA and dipropylene glycol. Designed for flexible slabstock foams. |
| JEFFCAT ZF-62 | Delayed action catalyst made from ZF-2, DMEA and dipropylene glycol. Partially neutralized with formic acid. |
| JEFFCAT ZF-70 | (N,N-dimethylaminoethoxy) ethanol. Amine catalyst that reacts into the final polymer. Useful in foams molded against vinyl and in packaging foams. |
| KAO LIZER #1 | N , N , N ' , N ' - t e t r a m e t h y l - hexamethylene diamine. |
| KAO LIZER #3 | N,N,N',N',N "pentamethyl-diethylenetriamine. |
| KAO LIZER #10 | Dimethylcyclohexylamine. See POLYCAT 8. |
| KOSMOS 10 | 33% stannous octoate in 67% dioctylphthalate. See DABCO T95. |
| KOSMOS 10N | 33% stannous octoate in 67% diisononyl phthalate. |
| KOSMOS 15 | 50% stannous octoate in 50% dioctylphthalate. See, DABCO T-10, FOMREZ C-4. |
| KOSMOS 15N | 50% stannous octoate in 50% diisononyl phthalate. |
| KOSMOS 19 | Dibutyltin dilaurate. See DABCO T-12, FOMREZ SUL-4, TOYOCAT TEDA-T411. |
| KOSMOS 29 | Stannous octoate, stabilized. See DABCO T-9, FOMREZ C-2, TOYOCAT TEDA-D007. |
| METASOL 57 | Phenylmercuric propionate. |
| NIAX A-1 | 70% bis (dimethylaminoethyl)ether and 30% dipropylene glycol. A strong blowing catalyst. See DABCO BL-11, TOYOCAT ET, TEGOAMIN BDE. |

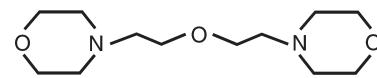


- NIAX A-4** Low-odor catalyst blend that promotes water/iso reaction. A replacement for NEM in HR and hot-molded foam. (0.3 php A-4 = 1.0 NEM). Useful as a surface cure catalyst.
- NIAX A-31** General purpose, low odor, low fogging catalyst for polyester foams.
- NIAX A-33** 33% solution of triethylene diamine in dipropylene glycol. A very efficient gelation catalyst. See DABCO 33-LV, TOYOCAT TEDA-L33.
- NIAX A-99** Pure bis(dimethylaminoethyl) ether.
- $$\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{N}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{N} \\ | \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$$
- NIAX A-107** Formic-acid-blocked version of NIAX A-1. Delayed action blowing catalyst. See DABCO BL-17, TOYOCAT ETF.
- NIAX A-127** Amine mixture. Delayed action catalyst for trough-style slab. Good for high-water formulations on conventional equipment. Useful in filled foams.
- NIAX A-133** 33% solution of NIAX A-1 in dipropylene glycol. Useful when accurate metering of the catalyst is a problem.
- NIAX A-200** Tertiary amine mixture. Well balanced for use as sole amine catalyst.
- NIAX A-230** Tertiary amine mixture. Well balanced blow/gel and can be used as sole amine catalyst.
- NIAX A-300** Delayed action gel catalyst; cell-opening and noncorrosive. Contains water.
- NIAX A-305** Delayed action gel catalyst; cell-opening and noncorrosive. More delayed and more cell-opening than A-300.
- NIAX A-400** Delayed action blow catalyst; cell-opening and minimal corrosion relative to A-107. Contains water.
- NIAX A-405** Delayed action blow catalyst; cell-opening and minimal corrosion relative to A-107. More delayed and more cell-opening than A-400.
- NIAX B-26** Delayed action, low vinyl staining catalyst.
- NIAX C-5** N,N,N',N'',N''' Pentamethyldiethylenetriamine. Balanced blow, gel catalyst.
- NIAX C-6** N,N,N',N' Tetramethylhexanediamine. Strong gel catalyst with good flow properties.
- NIAX C-8** N,N' Dimethylcyclohexylamine. Rapid initiation, moderate blow and gel.
- NIAX C-41** Balanced urethane/isocyanurate catalysis.

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| NIAX C-124 | A diluted version of NIAX A-1 in dipropylene glycol. Useful when accurate metering is needed. | |
| NIAX C-131 | General purpose, low odor, low-fogging catalyst with NEM equivalent reactivity for polyester foams. | |
| NIAX C-174 | Used in semiflex and other polymeric MDI-based foams. Promotes flow, especially for instrument panels. Low vinyl-staining catalyst. | |
| NIAX C-175 | A mixture containing an aromatic amine that builds hardness in foams. Acts as a cross-linker in molded foams. | |
| NIAX C-177 | Delayed action but strong end cure catalyst for RIM, SRIM and EA/EM applications. | |
| NIAX C-183 | Tertiary amine mixture. Well balanced blow/gel and can be used as sole amine catalyst. | |
| NIAX C-225 | A blend of acid-blocked NIAX A-33 and acid blocked NIAX A-1. Delayed action balanced blow/gel catalyst. | |
| NIAX DMEA | N,N dimethylethanolamine. See DABCO DMEA and JEFFCAT DME. |  |
| NIAX LC-5615 | Delayed action, organometallic catalyst for froth foam for carpet applications. | |
| NIAX U-1000 | General purpose, balanced blow/gel catalyst for HR foams. | |
| NIAX U-3000 | General purpose, balanced blow/gel catalyst for HR foams. | |
| PC CAT DBU | 1,8-Diazabicyclo-5,4,0-undecene-7. Very active gelling catalyst. | |
| PC CAT DBU TA 1 | PC CAT DBU blocked with 2 ethylhexanoic acid. Heat activated final cure catalyst. Faster than PC CAT DBU TA3. See POLYCAT SA 102. |  |
| PC CAT DBU TA 2 | PC CAT DBU blocked with phenolic acid. See POLYCAT SA 1. | |
| PC CAT DBU TA 3 | PC CAT DBU blocked with formic acid in 50% DPG. | |
| PC CAT DD 70 | Tertiary amine catalyst blend. Catalyst for moisture cured systems. More reactive than PC CAT DMDEE but reduced shelf life time of the prepolymer. Also used for polyester slabstock. See JEFFCAT DM 70. | |
| PC CAT DMCHA | Dimethylcyclohexylamine. Standard catalyst for rigid foam. See POLYCAT 8. |  |

PC CAT DMDEE

N,N-Dimorpholinodiethylether. Catalyst for moisture cured systems. PC CAT DMDEE secures a long shelf life of the prepolymer. Also used in adhesives and elastomers. Less active than PC CAT T 12 but with reduced depolymerisation effect. See JEFFCAT DMDEE.

**PC CAT DMP**

N,N-Dimethylpiperazine. Balanced blow/gel catalyst for flexible and semiflexible foams. Improves skin formation.

PC CAT K1

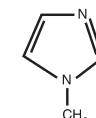
Blend of alkali metal carboxylates. Balanced trimerization catalyst.

PC CAT NEM

N-Ethylmorpholine. See DABCO NEM.

PC CAT NMI

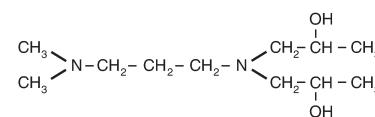
N-Methylimidazole. Strong gelling slow blowing catalyst.

**PC CAT NMM**

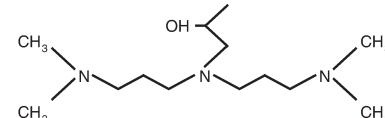
N-Methylmorpholine. See DABCO NMM.

PC CAT NP 10

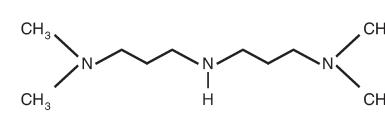
Dimethylaminopropyldipropanolamine. Low odor gelling catalyst with excellent flowability and a good final cure.

**PC CAT NP 15**

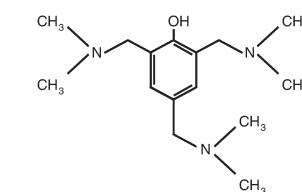
Bis-(dimethylaminopropyl)amino-2-propanol. Excellent rigid foam catalyst for 141b as well as Pentane blown foams.

**PC CAT NP 20**

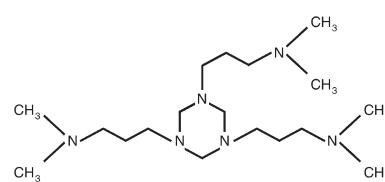
Tetramethylaminobispropylamine. Low fogging catalyst especially for automotive interior application. See POLYCATE 15.

**PC CAT NP 30**

2,4,6-Tris(dimethylaminomethyl)phenol. Weak trimerization catalyst. See DABCO TMR 30, DMP 30.

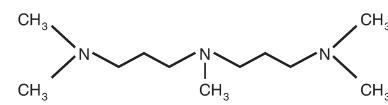
**PC CAT NP 40**

1,3,5-Tris(dimethylaminopropyl)-hexahydrotriazine. Catalyst for trimer and urethane reaction for microcellular and lamination PIR. See POLYCATE 41.



PC CAT NP 50

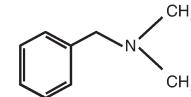
Pentamethyldipropylenetriamine. Basic balanced blowing/gelling catalyst with delayed gelling activity for a very wide range of applications. See POLYCAT 77.

**PC CAT NP 51**

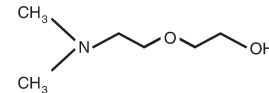
PC CAT NP 50 based catalyst blend. For molded and slab foams. Comparable reactivity with PC CAT TD 33 but improved flowability and better final cure.

PC CAT NP 60

N,N-Dimethylbenzylamine. Standard catalyst for ester flex-foam. Catalyst for appliance application for small cell size and good adhesion.

**PC CAT NP 70**

Dimethyl 2-(2-Aminoethoxy) ethanol. Low fogging blowing catalyst.

**PC CAT NP 72 NT**

Amine catalyst blend. Special blend for packaging foams and rigid spray application. Reduced odor of the final product.

PC CAT NP 73

Acid blocked PC CAT NP 70. Delayed action blowing catalyst for cell opening in semi flexible molded foams. Reduced corrosion.

PC CAT NP 75

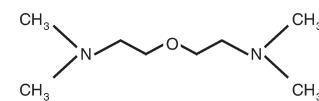
Tertiary amine catalyst blend. Balanced catalyst for HR molded and slab foam.

PC CAT NP 89

(Dimethyl(aminoethoxyethyl))((dimethylamino)ethyl)ether. Good blowing catalyst for ether and blowing/gelling catalyst for ester slab foams. See JEFFCAT E 40.

PC CAT NP 90

70% Bis(2-Dimethylaminoethyl) ether in dipropylene glycol. Standard strong blowing catalyst. See NIAX A1, DABCO BL 11.

**PC CAT NP 97**

Tertiary amine catalyst blend. Very active blowing catalyst. Stronger than PC CAT NP 90.

PC CAT NP 109

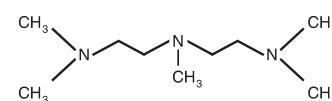
Tris(dimethylaminopropyl)amine. Balanced blowing/gelling catalyst. Lower activity than PC CAT NP 50. See POLYCAT 9.

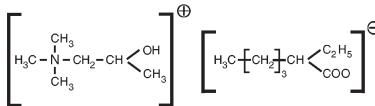
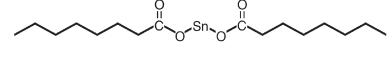
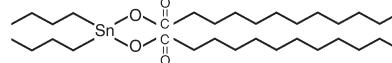
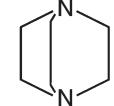
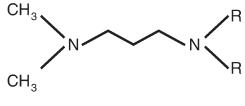
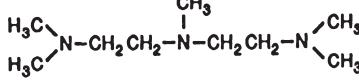
PC CAT NP 112

Dicyclohexylmethylamine. Co-Catalyst with long cream time and improved final cure. See POLYCAT 12.

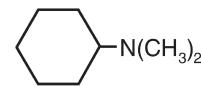
PC CAT PMDETA

Pentamethyldiethylenetriamine. Standard blowing catalyst for rigid and flexible foam. See TOYOCAT DT and POLYCAT 5.

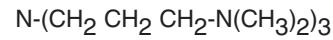


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| PC CAT Q1 | Quaternary ammonium salt in ethylene glycol. Trimerization and delayed action PUR catalyst. See DABCO TMR. |  |
| PC CAT R 94 DV | Catalyst blend. Specially designed for rigid lamination. | |
| PC CAT RL 42 | Special formulated catalyst blend for pentane blown PIR rigid foams. | |
| PC CAT RL 43 | Catalyst blend containing a trimerization catalyst and a polyurethane co-catalyst. Especially used for polyester polyol based 141 b blown PIR rigid lamination. Faster than PC CAT RL 44. | |
| PC CAT RL 44 | Catalyst blend for the trimerization and polyurethane reaction for PIR rigid lamination. Slower than PC CAT RL 43. | |
| PC CAT T 9 | Stabilized Stannous octoate. DABCO T 9, KOSMOS 29. |  |
| PC CAT T 12 | Dibutyltindilaurate. See DABCO 12, KOSMOS 19. |  |
| PC CAT TD 33 | 33.3% Triethylenediamine in dipropylene glycol. See TOYOCAT TEDA L-33, DABCO 33 LV. | |
| PC CAT TD 39 | 75% PC CAT TD 33 and 25% PC CAT NP 90. Standard catalyst. See DABCO BLV. | |
| PC CAT TD 82 | 20% Triethylenediamine in 80% Dimethylethanolamine mainly for rigid foam. See DABCO R 8020. | |
| PC CAT TD 100 | Triethylenediamine(solid crystals). Standard gelation catalyst. See TOYOCAT TEDA, DABCO CRYSTALLINE. |  |
| PC CAT TKA | 38% Potassiumacetate in MEG. Trimerization catalyst. See POLYCATE 46. | |
| PC CAT TKO | 70% Potassiumoctoate in DEG. Trimerization catalyst. | |
| PC CAT TMEDA | Tetramethylethanediamine. See TOYOCAT TE. | |
| PC CAT TMG | Tetramethylguanidine. Very active gelling catalyst for water free formulations. | |
| PC CAT TMHDA | Tetramethylhexanediamine. See TOYOCAT MR, POLYCATE 6. | |
| PC TOPA | N-(Dimethylaminopropyl)tall oil amide, catalyst flow improver. |  |
| POLYCATE 5 | Pentamethyl-diethylene triamine. Catalyst for rigid and flexible foam applications. See TOYOCAT DT. |  |

POLYCAT 8 N,N-dimethyl cyclohexylamine. For rigid spray, slabstock, board laminate and refrigeration foam.

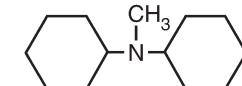


POLYCAT 9 Tris (dimethyl aminopropyl) amine. Low odor blowing and gelling catalyst in medium and low-water systems. For elastomeric foams such as shoe soles. Co-catalyst in semiflex automotive foams.

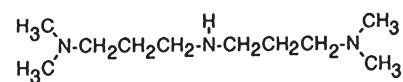


POLYCAT 11 Broad range rigid foam catalyst. Used in insulation board, laminate, refrigeration, and spray. Similar to POLYCAT 8, but faster cure.

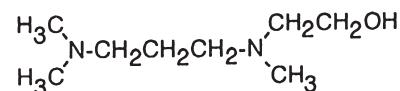
POLYCAT 12 N, methyl dicyclohexylamine. A skin cure catalyst; used as co-catalyst in slabstock, especially where methylene chloride is used. Exhibits delayed cream time with an overall fast cure.



POLYCAT 15 Bis (N,N-dimethyl-3-amino-propyl) amine. Has one active hydrogen. Packaging foam catalyst.

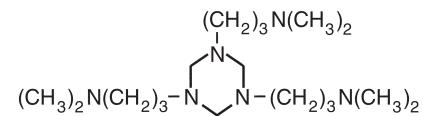


POLYCAT 17 N, N, N' Trimethylaminopropyl ethanolamine. Rigid foam catalyst for packaging. Good blend stability. 25% less reactive than DABCO T, not as specific to water reaction as DABCO T or DABCO BL-11.



POLYCAT 33 Same as POLYCAT 8, but with an agent added to modify the amine odor. Used in insulation (spray, board laminate and refrigeration) and rigid formulations for furniture frame and decorative parts.

POLYCAT 41 1,3,5-tris (3-(dimethylamino)propyl) hexahydro-s-triazine. Rigid foam catalyst, used with POLYCAT 43 in lamination PIR, microcellular and HR slab. Catalyzes urethane and isocyanurate reactions. Stronger urethane than trimer catalyst.

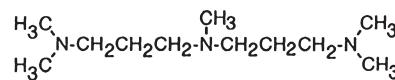


POLYCAT 43 Blended rigid foam catalyst used in PIR lamination and systems. Has a fast cream and final cure.

POLYCAT 46 Potassium acetate in glycol. A trimerization catalyst, also useful as a surface cure catalyst in rigid foams.

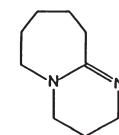
POLYCAT 58 A reactive amine of proprietary composition useful for skin cure and cold-collapse prevention in HR-molded foams.

POLYCAT 77 Pentamethyl, dipropylene triamine. Balanced blow/gel catalyst. For HR-molded foam and slabstock where amines are masterbatched with water, silicone or other ingredients.

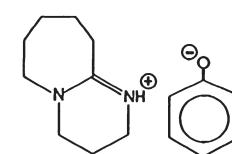


POLYCAT 79 An acid-blocked version of POLYCAT 77.

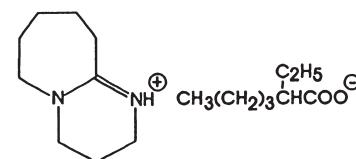
POLYCAT DBU 1,8 diaza bicyclo 5,4,0 undecene 7. Heat-activated, but hydrolyzes in water.



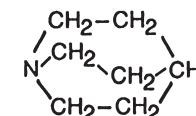
POLYCAT SA-1 62% by weight POLYCAT DBU blocked with phenolic acid (38%). Broad range delayed action catalyst, faster than POLYCAT SA-102.



POLYCAT SA-102 53% POLYCAT DBU blocked with 2-ethylhexanoic acid. Used in rigid foams, promotes final cure. Slower than POLYCAT SA-1.



QUINCAT Quinuclidine (1,4-ethylene piperidine). Double the catalytic activity of DABCO crystalline. Recommended for all types of polyurethane foam.



SPI-30 2,4,6 Tris (Dimethylaminomethyl) Phenol. Polyisocyanurate catalyst for rigid foams that is also used in HR foams. Relatively weak catalyst that provides smooth rise profile.

SPI-41 Hexa Hydro-1,3,5 Tris (3-Dimethylaminopropyl) Triazine. Catalyzes both the polyurethane and polyisocyanurate reactions. Provides excellent processability and physical properties in rigid, flexible and microcellular formulations. Stronger polyurethane than trimerization catalyst.

SPI-43 Polyisocyanurate catalyst to be used as a co-catalyst with SPI-41 to improve the final cure in rigid systems.

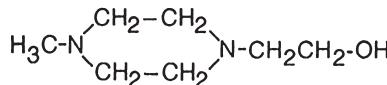
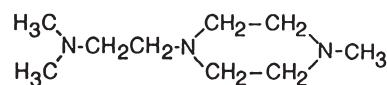
SPI-122 Polyurethane catalyst for use in rigid lamination to prevent winter edge collapse. Allows laminators to run at lower densities during winter months.

SPI-125 Co-catalyst for use in rigid lamination to prevent winter edge collapse. Allows laminators to run at lower densities during winter months.

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| SPI-130 | Provides excellent processability in rigid and flexible foams. Improves flow and stability, especially around corners, under vents and seals and with mold temperature gradients. It also offers a delayed cream time. Can be used alone or as a co-catalyst. |
| SPI-133 | Used in all types of polyurethanes. A strong gelling catalyst that also catalyzes the blowing reaction. Improves flow and produces a more open, stable and forgiving flexible foam, versus foams catalyzed with 33-LV/A-1 blends. Can also be used to fully or partially replace 33-LV and also reduce the level of A-1. Has a lower effect on fogging and staining as compared to 33-LV. |
| SPI-DA1 | A delayed-action catalyst for use in all types of polyurethanes. It is designed for use in formulations requiring a delayed initiation time or where high amounts of traditional catalysts are required to achieve a complete foam cure. Due to its structure, after the delayed initiation, provides a smooth reaction profile. |
| SPI-DA2 | A delayed-action catalyst for use in all types of polyurethanes. Provides a normal initiation time with good flow and an extremely fast cure. |
| SPI-DA3 | A delayed-action catalyst for all types of polyurethanes. Gives extended cream time with short cure times. |
| SPI-KAc | Potassium acetate in ethylene glycol. Strong polyisocyanurate catalyst. |
| SPI-KOc | Potassium octoate in diethylene glycol. Strong polyisocyanurate catalyst. |
| SPI-TC1 | Thermally activated, delayed-action catalyst for use in all types of polyurethanes. Due to its thermal activation, SPI-TC1 is an excellent catalyst to be used as a co-catalyst or with catalytic polyols. |
| SPI-TC2 | Thermally activated, delayed-action catalyst for use in all types of polyurethanes. Provides delayed initiation with strong final cure. |
| SPI-TR1 | Polyisocyanurate catalyst for rigid foams. Typically used in combination with a polyurethane catalyst. Can also be used in combination with other members of the SPI-TR catalyst family. Strongest isocyanurate catalyst in the TR family. The reactivity decreases moving from TR1 to TR5. |
| SPI-TR2 | Suitable for all types of polyisocyanurate foam systems. Gives a slower reaction profile than SPI-TR1. |
| SPI-TR3 | Suitable for all types of polyisocyanurate foam systems. Provides a considerable delay in comparison to SPI-TR1 and SPI-TR2 and yields a uniform, slow and controlled rise profile. |
| SPI-TR4 | Designed for all types of polyisocyanurate foam systems. It provides excellent flowability and high conversion rates in isocyanurate foams. Because of the increased flowability, SPI-TR4 is useful in pour-in-place systems. |

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| SPI-TR5 | Suitable for all types of polyisocyanurate foams. Provides a slower, more even rate of trimerization than most other catalysts. It is useful in modifying the rate of trimer formation. |
| SPI-TR6 | Suitable for all types of polyisocyanurate formulations. Provides a modified rate of trimer formation. Yields a higher trimer conversion than SPI-TR5. |
| TEGOAMIN 33 | 33% solution of TEGOAMIN 100 in dipropylene glycol. |
| TEGOAMIN 100 | Pure triethylene diamine. See DABCO crystalline. |
| TEGOAMIN BDE | 70% Bis(dimethylaminoethyl) ether in dipropylene glycol. |
| TEGOAMIN CPE | Tertiary amine for polyester foams, similar to dimethylbenzylamine, but the cream is retarded. A low odor product. |
| TEGOAMIN DMCHA | Dimethylcyclohexyl amine. A tertiary amine for rigid foam. See POLYCATE 8. |
| TEGOAMIN DMEA | Dimethylethanolamine. Tertiary amine for the production of a wide range of foams. Primarily effects the blowing reaction. See DABCO DMEA, JEFFCAT DMEA. |
| TEGOAMIN EPS | A tertiary amine normally used in the manufacture of polyester type foams. A low odor replacement for the morpholine based catalysts. Exhibits strong effect on the blowing reaction and little impact to the gelling reaction. |
| TEGOAMIN PDD | A tertiary amine for flexible slabstock foam. Offers balanced blowing and gelling and can be used as a sole catalyst. |
| TEGOAMIN PMD | A tertiary amine for flexible molded and slabstock foams. Balanced activity allows it to be used as the sole amine catalyst. Extends tin range and improves porosity in some difficult formulations. |
| TEGOAMIN PTA | A tertiary amine for the manufacture of HR and conventional slabstock foam. Acts as a catalyst for both blowing and gelling. Well suited for use on square block machines. |
| TEGOAMIN SMP | Tertiary amine for flexible and molded foams. Gives a delayed cream reaction but accelerates the curing reaction. Noted to produce harder foam than TEGOAMIN 33. |
| TOYOCAT TEDA | Triethylene diamine. See DABCO crystalline. |
| TOYOCAT TEDA-L25B | Liquid TEDA in 1,4 butanediol. For RIM and microcellular foam applications. See DABCO S-25. |
| TOYOCAT TEDA-L33 | 33% solution of triethylene diamine in dipropylene glycol. See DABCO 33-LV, NIAX A-33. |

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| TOYOCAT TEDA-L33E | TEDA in ethylene glycol. For use in RIM and hard elastomers. See DABCO EG. |
| TOYOCAT - B2 | Proprietary amine blend for use in polyether slab and all rigids. |
| TOYOCAT - B3 | Proprietary amine blend for use in polyether slab and all rigids except spray. |
| TOYOCAT - B4 | Proprietary amine blend for use in polyether slab, hot- and cold-molded and all rigids except refrigerators. |
| TOYOCAT - B5 | Proprietary blend of delayed-action amines. |
| TOYOCAT - B6 | Proprietary amine for use in polyether slab and all rigids. |
| TOYOCAT - B20 | Proprietary blend of amines for use in rigid foams made with HCFCs. |
| TOYOCAT B41 | A delayed action curing catalyst. Strong gelling catalyst useful as co-catalyst for improving cure in thin sections of molded foams. |
| TOYOCAT - B54 | Proprietary blend of amines for use in rigid foams made with HCFCs. |
| TOYOCAT - C1 | Proprietary amine blend for use in all rigid applications except spray. |
| TOYOCAT - C2 | Proprietary amine for use in all rigid applications except spray. |
| TOYOCAT - C3 | Proprietary amine for use in all rigid applications except spray. |
| TOYOCAT - DA | Proprietary amine for use in polyether slab, hot and cold molded and all rigids except spray. |
| TOYOCAT - DT | N,N,N',N'',N''-Pentamethylene diamine. For use in molded foam and all rigids except spray. See POLYCATE 5. |
| TOYOCAT - ET | 70% bis(dimethylaminoethyl) ether in dipropylene glycol. See NIAX A-1, DABCO BL-11. |
| TOYOCAT - ETF | Formic-acid-blocked, bis(dimethylaminoethyl) ether in dipropylene glycol. See NIAX A-107, DABCO BL-17. |
| TOYOCAT - ETS | Pure bis(dimethylaminoethyl) ether. |
| TOYOCAT - F2 | Proprietary amine catalyst useful in all-water-blown MDI-based HR foam. |
| TOYOCAT - F3 | Proprietary amine catalyst useful in all-water-blown MDI-based HR foam. |
| TOYOCAT - F83 | Proprietary amine catalyst for rigid foams. |
| TOYOCAT - F94 | Proprietary blend of amine catalysts offering improved friability and K factor in rigid foams. |

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| TOYOCAT - HP | 90% methyl-hydroxy-ethyl--piperazine and 10% dipropylene glycol. Weak catalyst similar to ethylmorpholine. No residual amine odor. Improves permeability in flexible and semirigid foam. |  |
| TOYOCAT - HX4 | Similar in catalysis to triethylamine. | |
| TOYOCAT - HX4W | Proprietary amine used in polyester slab and semiflex foams. Nonstaining to PVC. Reactivity is comparable to that of triethylamine. A low freeze grade of TOYOCAT - HX4. | |
| TOYOCAT - HX35W | Proprietary amine used in all semiflex applications, nonstaining to PVC. Exhibits strong blowing catalysis. | |
| TOYOCAT-HX75 | Proprietary amine. | |
| TOYOCAT - L20M | Proprietary amine used in all rigid applications. | |
| TOYOCAT - LE | Proprietary amine used in polyether slab, hot and cold-molded, semiflex headrests and rigid spray. | |
| TOYOCAT - M50 | Proprietary amine used in hot and cold-molded and in all semiflex areas. | |
| TOYOCAT - MR | N,N,N',N'-tetramethyl-hexamethylene diamine, used in hot and cold-molded HR and all rigids except spray. See POLYCAT 6. | |
| TOYOCAT - N31 | A functional equivalent to POLYCAT 77. For use in polyether slab, hot and cold-molded and rigid refrigerator foams. | |
| TOYOCAT - N81 | Proprietary amine blend used in polyether slabstock, hot and cold-molded and rigid refrigerator foam. | |
| TOYOCAT - NEM | N-ethylmorpholine. Used in slab polyester, hot and cold-molded, semiflex armrests. See DABCO NEM and JEFFCAT NEM. | |
| TOYOCAT - NP | N-methyl-N'-(2-dimethylamino)ethyl-piperazine). High thermosensitive catalyst, delayed cream time, faster cure. |  |
| TOYOCAT - SPF | Proprietary blocked-amine catalyst blend used in hot and cold-molded and semiflex headrests. | |
| TOYOCAT - SPF2 | Proprietary blocked-amine catalyst used in hot and cold-molded and semiflex headrests. | |
| TOYOCAT - SPF3 | Proprietary blocked-amine catalyst used in hot and HR-molded and semiflex headrests. | |

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| TOYOCAT - TE | N,N,N',N'-tetramethylethylene diamine. Used in hot and cold-molded, semiflex and most rigid applications except spray. |
| TOYOCAT - TEDA-D007 | Stannous octoate. See KOSMOS 29, FOMREZ C-2, DABCO T-9. |
| TOYOCAT - TEDA-T411 | Believed to be dibutyltin dilaurate. See DABCO T-12, FOMREZ SUL-4, KOSMOS 19. |
| TOYOCAT - TEDA-T400 | Believed to be dibutyltin diacetate. See FOMREZ SUL-3, DABCO T-1, COTIN 227. |
| TOYOCAT - TEDA-T401 | Believed to be dibutyltin oxide. $[(C_4H_9)_2SnO]_x$ |
| TOYOCAT - TEDA-T811 | Proprietary tin catalyst. |
| TOYOCAT - TF | Acid-blocked triethylene diamine. Delayed-action amine containing mostly triethylenediamine. A functional equivalent to DABCO 8154. |
| TOYOCAT - TFN | Believed to be similar to NIAX C-225 fast-demold catalyst. Used in fast curing HR flexible and rigids, promotes flow. |
| TOYOCAT - THN | Delayed action version of TOYOCAT TEDA. |

Appendix E

Surfactants

R. Herrington, F. Casati, J.P. Treboux

The following is a descriptive list of the most common surfactants used in manufacturing flexible polyurethane foam. The list is by no means complete, but instead is an attempt to expose the reader to the more common, commercially available surfactants from various vendors. The companies represented in this appendix and their surfactant trademarks are as follows:

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| Air Products and Chemicals Inc. | DABCO |
| OSI Specialties/Witco Corp. | NIAX |
| Th. Goldschmidt Chemical Corp. | TEGOSTAB |

The descriptions below have been gathered from various sources and are intended to serve as a starting point only. More detailed information is readily available in the original vendor publications. In all cases, a thorough understanding of the toxicology and safety information available through the vendor material safety data sheets is required before utilizing these surfactants in foam experiments. Contact the vendors for the latest information on surfactant use and availability.

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| DABCO DC198 | A high-efficiency general purpose surfactant for polyether slabstock foam applications. |
| DABCO DC2585 | A low-efficiency, general purpose surfactant designed for MDI based cold cure type HR molded foam systems. Offers low fogging potential. |
| DABCO DC5043 | A standard, general purpose surfactant for HR slabstock and molded foams based on TDI. Offers a broad processing latitude. |
| DABCO DC5125 | A wide-processing latitude type surfactant for use in conventional and flame resistant grades of polyether slabstock foam. |
| DABCO DC5160 | A medium-potency, wide processing latitude, multipurpose surfactant for use in polyether slabstock foams. Reduces pin holes in both slabstock and integral skin foam applications. |
| DABCO DC5164 | High-efficiency surfactant for use in TDI based HR molded foams. |
| DABCO DC5169 | Surfactant for use in HR molded foams based on TDI or on TDI/polymeric MDI blends. Useful in improving foam molded surface appearance. |
| DABCO DC5180 | Standard surfactant for HR slabstock foam. |
| DABCO DC5188 | High-efficiency surfactant for polyether slabstock foam. Offers excellent emulsification capability in systems containing high levels of water. Specially designed for discontinuous applications. |
| DABCO DC5258 | A low-efficiency surfactant for polymeric MDI based HR molded foams. |
| DABCO DC5526 | A surfactant for use in flexible polyester type slabstock foam. Provides excellent foam stability, with fine, regular and open cells without the need for additional emulsifiers. |
| NIAX L-580 | Nonhydrolyzable surfactant for very low density conventional foams. |
| NIAX L-5770 | Medium-efficiency surfactant for conventional slabstock foams giving wide processing latitude and wide foam grade range. |
| NIAX L-603 | High-efficiency surfactant for conventional slabstock foams giving wide processing latitude and wide foam grade range. |
| NIAX L-618 | High-efficiency surfactant for conventional slabstock foams giving wide processing latitude and wide foam grade range. |
| NIAX L-620 | Highest efficiency nonhydrolyzable surfactant for conventional slabstock foams giving wide processing latitude and wide foam grade range. |
| NIAX L-640 | High-efficiency surfactant for conventional slabstock and hot molded foam. |
| NIAX L-680 | Medium-efficiency surfactant for conventional slabstock foam and hot molding. |

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| NIAX L-700 | For injected carbon dioxide slabstock foam technology. The surfactant gives wide processing latitude, wide foam grade range and fine cell structure. |
| NIAX L-701 | For injected carbon dioxide slabstock foam technology. The surfactant gives wide processing latitude, wide foam grade range and fine cell structure. |
| NIAX U-2000 | General purpose surfactant for HR slabstock foams. |
| NIAX L-2100 | Surfactant for use in HR slabstock foams based on TDI or TDI/polymeric MDI blends. Useful in formulations containing copolymer polyols. Offers a balance of stabilizing and cell regulating effects. |
| NIAX L-3001 | General purpose surfactant for use in molded HR foams based on polymeric MDI. |
| NIAX L-3002 | More stabilizing than NIAX L-3001. For use in lower density molded HR foams based on polymeric MDI or polymeric MDI/TDI blends. |
| NIAX L-3003 | More stabilizing than NIAX L-3002. For use in lower density molded HR foams based on polymeric MDI, polymeric MDI/TDI blends or modified TDI. |
| NIAX L-3100 | A low-activity surfactant for HR molded foams based on TDI or TDI/polymeric MDI blends. Also useful in molded foams based on polymeric MDI. Designed to be blended with NIAX L-3200 to provide a broad continuum of cell-openness and shear stability performance. |
| NIAX L-3200 | For HR molded foams based on TDI or TDI/polymeric MDI blends. Designed to be blended with NIAX L-3100 to provide a broad continuum of cell-openness and shear stability performance. |
| NIAX L-3150 | For use with HR molded foams based on TDI or TDI/polymeric MDI blends. High efficiency while providing a good balance of cell-openness and shear stability. |
| NIAX L-3350 | For HR molded foams based on TDI. Provides a high degree of stabilization with an excellent balance of cell-openness and shear stability. |
| NIAX L-3410 | For HR molded foams based on TDI or TDI/polymeric MDI. Provides improved foam stability under vent holes. |
| NIAX L-3801 | A nonhydrolyzable surfactant for use in energy absorbing/energy managing type foams. Good cell-opening. |
| NIAX L-3802 | A nonhydrolyzable surfactant for use in energy absorbing/energy managing type foams. More cell-opening than NIAX L-3801. |
| NIAX L-5300 | A nonhydrolyzable surfactant for use in hot molded type foams. |

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| NIAX L-5614 | Surfactant giving excellent froth stability in microcellular foams. |
| NIAX Y-10366 | A high-efficiency surfactant for HR molded foams based on TDI or TDI/polymeric MDI blends. Offers a broad processing latitude. |
| NIAX Y-10515 | For TDI based HR molded foams requiring a high degree of stabilization. |
| NIAX Y-10754 | For use in microcellular integral skin formulations. |
| NIAX SC-154 | Surfactant for conventional slabstock and hot molded foam. |
| NIAX RS-171 | General purpose surfactant for HR molded foams based on TDI or TDI/polymeric MDI. |
| NIAX SC-240 | General purpose surfactant for conventional and hot molding foam. |
| TEGOSTAB BF 2270 | A high-activity, conventional surfactant offering a wide processing latitude and high stabilizing potency for polyether slabstock foam formulations with high water content. |
| TEGOSTAB BF 2370 | Conventional, medium activity nonhydrolyzable surfactant for polyether slabstock and hot molded foam. Also found to be useful in systems using liquid carbon dioxide. |
| TEGOSTAB B 3640 | A low-efficiency surfactant designed especially for the manufacture of flame retarded grades of polyether slabstock foam. Used for medium density grade foams. |
| TEGOSTAB B 4113 | A low-efficiency cell regulating type surfactant used mostly in self-supporting HR molded foams based on TDI, polymeric MDI or polymeric MDI/TDI blends. |
| TEGOSTAB B 4351 | A stabilizing and cell regulating surfactant for HR foams. |
| TEGOSTAB B 4380 | A cell regulating and stabilizing surfactant used in HR slabstock or molded foams which are not completely self-supporting. Aids in obtaining good blow-off characteristics and is useful to prevent coarse cell structure near the foam surface. |
| TEGOSTAB B 4690 | A cell-regulating type of surfactant for all self-supporting HR molded foams. Slightly stronger than TEGOSTAB B 4113. Useful to overcome coarse cells directly beneath the foam skin. |
| TEGOSTAB B 4900 | A medium-potency conventional surfactant offering very broad processing latitude in polyether slabstock foams using higher molecular weight polyols. Also useful in hot molded foams. |
| TEGOSTAB B 5055 | High-efficiency surfactant for use in making polyester slabstock foam. Useful in making low density foams and in formulations containing water insoluble amines and/or flame retarding additives. |

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| TEGOSTAB B 8002 | A low-efficiency surfactant for polyether slabstock foam offering a broad processing latitude in formulations containing highly reactive polyols and copolymer polyols. Allows the use of higher tin levels. |
| TEGOSTAB B 8017 | Surfactant for conventional slabstock foam that offers a high-stabilization effect. |
| TEGOSTAB B 8021 | A medium to high-activity surfactant for low-density polyether slabstock foams based on low reactivity polyols and containing high levels of water and/or auxiliary blowing agents. |
| TEGOSTAB B 8110 | A high-efficiency, nonhydrolyzable surfactant especially useful for very low-density polyether slabstock foams requiring a high degree of stabilization. Also noted to enhance the effect of flame retarding additives. |
| TEGOSTAB B 8123 | Recommended for the production of box foams with densities down to < 10 kg/m ³ . |
| TEGOSTAB B 8125 | A high potency surfactant for hot molded foams. |
| TEGOSTAB B 8200 | High-activity surfactant for low density, conventional slabstock foams containing flame retarding additives. |
| TEGOSTAB B 8202 | A medium to high-efficiency polyether slabstock foam surfactant that offers a wide processing latitude while enhancing the effect of flame retardant additives. |
| TEGOSTAB B 8220 | High-efficiency surfactant specifically designed to promote nucleation. Useful in slabstock foams blown with liquid carbon dioxide or other auxiliary blowing agents. |
| TEGOSTAB B 8222 | High-efficiency surfactant that offers a wide processing latitude while enhancing the effect of flame retarding additives in polyether slabstock foams. |
| TEGOSTAB B 8228 | A high-efficiency surfactant for use in a wide range of polyether slabstock foam formulations where operating conditions require a very broad processing latitude. |
| TEGOSTAB B 8234 | Surfactant designed for CME type slabstock foams. |
| TEGOSTAB B 8300 | A universal stabilizer for the production of all kinds of standard polyester slabstock foams. Can be used in formulations containing die cutability additives. |
| TEGOSTAB B 8301 | Specially designed stabilizer for very fine, very open cell polyester type slabstock foams. Allows the production of high density foams with good airflow and little shrinkage. |

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| TEGOSTAB B 8302 | A universal stabilizer with high-potency and broad processing latitude for all grades of polyester slabstock foam. |
| TEGOSTAB B 8305 | A universal stabilizer with high-potency and broad processing latitude for use in polyester slabstock foams. |
| TEGOSTAB B 8312 | A strong emulsifying and stabilizing surfactant useful in making all grades of polyester slabstock foam. Particularly useful in formulations using TDI 65 and high hydroxyl number polyols. |
| TEGOSTAB B 8320 | A stabilizer used for the production of low density, extremely fine cell polyester slabstock foam. |
| TEGOSTAB B 8324 | Designed for use in polyester foams needing a high degree of physical stabilization. |
| TEGOSTAB B 8406 | Surfactant used in integral skin foam for cell size control. |
| TEGOSTAB B 8629 | Surfactant with high cell regulating and some stabilizing characteristics for use in HR molded foams. |
| TEGOSTAB B 8631 | A cell-regulating surfactant used in self-supporting HR foams based on polymeric MDI or polymeric MDI/TDI blends. Useful when additional emulsification is needed to enhance mixing of formulation components. |
| TEGOSTAB B 8636 | A high-efficiency surfactant for HR slabstock foam. Especially useful for the production of combustion modified HR slabstock foam. |
| TEGOSTAB B 8680 | For use in making HR molded foams based on PHD or polymer polyols. Useful in overcoming foam collapse caused by mold leakage or vent holes. |
| TEGOSTAB B 8681 | Surfactant for use in making HR slabstock and molded foams based on TDI or TDI/polymeric MDI blends. Used extensively in formulations containing PHD or polymer polyols. Offers a balance of cell regulating and stabilizing effects. |
| TEGOSTAB B 8694 | A silicone surfactant with cell opening properties for HR molded foams based on polymeric MDI. |
| TEGOSTAB B 8701 | A silicone surfactant for integral skin and HR molded foams based on TDI. Offers a wide processing latitude in formulations containing PHD, polymer or PIPA polyols. |
| TEGOSTAB B 8707 | Surfactant for the production of HR slabstock foams containing polymer polyols. A more efficient stabilizer than TEGOSTAB B 8708 but still provides good open cell characteristics. |
| TEGOSTAB B 8708 | A high-activity cell stabilizing surfactant for use in HR molded foams based on TDI or TDI/polymeric MDI blends. Provides good stabilization and cell opening in formulations using all type of polymer polyols. |

- TEGOSTAB B 8715** For HR foams. Provides mild stabilizing and strong cell regulating effects. A low fogging alternative to TEGOSTAB B 4113.
- TEGOSTAB B 8719** A low fogging version of TEGOSTAB B 8708
- TEGOSTAB B 8720** A high-efficiency stabilizer for HR molded foams based mainly on TDI and polymer polyols. Useful for control of basal cells and vent hole instability. A low fogging alternative to TEGOSTAB B 8708.
- TEGOSTAB B 8724** Surfactant for HR molded foams offering high cell regulating and high stabilizing properties.

Appendix F

Trademark Listing

The following list gives company references for all the known trademarks used in this book.

| Trademark | Company |
|---------------------|--|
| AEROTHENE | The Dow Chemical Company |
| BAIRCAT | The Lonza Chemical Company |
| BICAT | Shepherd Chemical Company |
| CARDIO | Cannon-Viking Ltd |
| COCURE | Cosan Chemical Corporation |
| COSCAT | Cosan Chemical Corporation |
| COTIN | Cosan Chemical Corporation |
| DABCO | Air Products and Chemicals, Inc. |
| DMP | Rohm and Haas Company |
| ENVIRO-CURE | Cannon-Viking Ltd |
| FOMREZ | Witco Chemical Company |
| FREON | E. I. DuPont DeNemours and Company |
| FYROL | Stauffer Chemical Company |
| IMCO-BAR | International Minerals and Chemicals Corp. |
| ISONATE | The Dow Chemical Company |
| ISONOL | The Dow Chemical Company |
| JEFFCAT | The Huntsman Corporation |
| KAO-LIZER | Kao Corporation |
| KOPR-KOTE | Jet-Lube, Inc |
| KOSMOS | Th. Goldschmidt Company |
| LOCTITE | Loctite Corporation |
| NIAX | Osi Specialties-Witco |
| MARBLE WHITE | Mineral Technologies, Inc. |
| METASOL | Merck and Company |
| PAPI | The Dow Chemical Company |
| PC CAT | Nitroil Europe Handels GmbH |
| POLYCAT | Air Products and Chemicals, Inc. |
| PYREX | Corning, Inc. |
| QUADROL | The BASF Corporation |
| QUINCAT | Enterprise Chemical Corporation |
| RAPID CURE | General Foam Corporation |
| SPECFLEX | The Dow Chemical Company |
| SPI | Specialty Products International |
| STATURE | The Dow Chemical Company |
| TEGO | Th. Goldschmidt Company |
| TEGOAMIN | Th. Goldschmidt Company |
| TEGOSTAB | Th. Goldschmidt Company |
| THE ENHANCER | The Dow Chemical Company |
| TAC-FAST | TAC-FAST Systems, Inc. |
| TOYOCAT | Toyo Soda, USA, Inc. |
| VORALUX | The Dow Chemical Company |
| VORANATE | The Dow Chemical Company |
| VORANOL | The Dow Chemical Company |

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