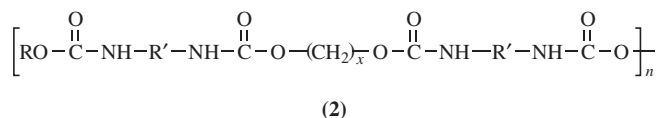
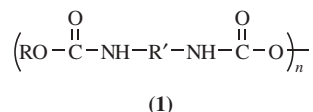


URETHANE POLYMERS

1. Introduction

The addition polymerization of diisocyanates with macroglycols to produce urethane polymers was pioneered in 1937 (1). The rapid formation of high molecular weight urethane polymers from liquid monomers, which occurs even at ambient temperature, is a unique feature of the polyaddition process, yielding products that range from cross-linked networks to linear fibers and elastomers. The enormous versatility of the polyaddition process allowed the manufacture of a myriad of products for a wide variety of applications.

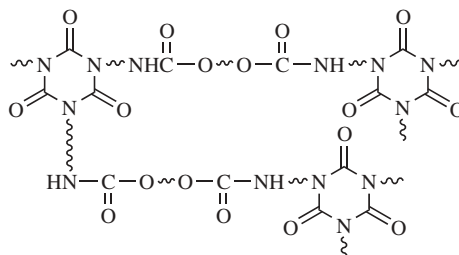
Polyurethanes contain carbamate groups, —NHCOO— , also referred to as urethane groups, in their backbone structure. They are formed in the reaction of a diisocyanate with a macroglycol, a so-called polyol, or with a combination of a macroglycol and a short-chain diol extender. In the latter case, segmented block copolymers are generally produced. The macroglycols are based on polyethers (qv), polyesters, or a combination of both. A linear polyurethane polymer has the structure of (1), whereas a linear segmented copolymer obtained from a diisocyanate, a macroglycol, and a diol extender, $\text{HO(CH}_2)_x\text{OH}$, has the structure of (2).



In addition to the linear thermoplastic polyurethanes obtained from difunctional monomers, branched or cross-linked thermoset polymers are made with higher functional monomers. Linear polymers have good impact strength, good physical properties, and excellent processibility, but, owing to their thermoplasticity, limited thermal stability. Thermoset polymers, on the other hand, have higher thermal stability but sometimes lower impact strength (rigid foams). The higher functionality is obtained with higher functional isocyanates (polymeric isocyanates), or with higher functional polyols (see ISOCYANATES; GLYCOLS; POLYESTERS). Cross-linking is also achieved by secondary reactions. For example, urea groups are generated in the formation of water-blown flexible foams. An isocyanato group reacts with water to form a carbamic acid, which dissociates into an amine and carbon dioxide, with the latter acting as a blowing agent. The amine reacts with another isocyanate to form a urea linkage. Further reaction of the urea group with the isocyanate leads to cross-linking via a biuret group. Water-blown flexible foams contain urethane, urea, and some biuret groups in their network structure (see FOAMED PLASTICS). Urea-modified segmented

polyurethanes are manufactured from diisocyanates, macroglycols, and diamine extenders.

Urethane network polymers are also formed by trimerization of part of the isocyanate groups. This approach is used in the formation of rigid polyurethane-modified isocyanurate (PUIR) foams (3).



(3)

2. History

The early German polyurethane products were based on toluene diisocyanate (TDI) and polyester polyols. In addition, a linear fiber, Perlon U, was produced from the aliphatic 1,6-hexamethylene diisocyanate (HDI) and 1,4-butanediol. Commercial production of flexible polyurethane foam in the United States began in 1953. In Germany a toluene diisocyanate consisting of an isomeric mixture of 65% 2,4-isomer and 35% 2,6-isomer was used in the manufacture of flexible foam, whereas in the United States the less expensive 80:20 isomer mixture was used. In 1956, Du Pont introduced poly(tetramethylene glycol) (PTMG), the first commercial polyether polyol; the less expensive polyalkylene glycols appeared by 1957. The availability of the lower cost polyether polyols based on both ethylene and propylene oxides provided the foam manufacturers with a broad choice of suitable raw materials, which in turn afforded flexible foams with a wide range of physical properties. Polyether polyols provide foams with better hydrolytic stability, whereas polyester polyols give superior tensile and tear strength. The development of new and superior catalysts, such as Dabco (triethylenediamine) and organotin compounds, has led to the so-called one-shot process in 1958, which eliminated the need for an intermediate prepolymer step. Prior to this development, part of the polyol was treated with excess isocyanate to give an isocyanate-terminated prepolymer. Further reaction with water produced a flexible foam.

The late 1950s saw the emergence of cast elastomers, which led to the development of reaction injection molding (RIM) at Bayer AG in Leverkusen, Germany, in 1964 (see PLASTICS PROCESSING). Also, thermoplastic polyurethane elastomers (TPUs) and Spandex fibers (see FIBERS, ELASTOMERIC) were introduced during this time. In addition, urethane-based synthetic leather (see LEATHER-LIKE MATERIALS) was introduced by Du Pont under the trade name Corfam in 1963.

The late 1950s also witnessed the emergence of a new polymeric isocyanate (PMDI) based on the condensation of aniline with formaldehyde. This product was introduced by the Carwin Company (later Upjohn and Dow) in 1960 under the trade name PAPI. Similar products were introduced by Bayer and ICI in Europe in the early 1960s. The superior heat resistance of rigid foams derived from PMDI prompted its exclusive use in rigid polyurethane foams. The large-scale production of PMDI made the coproduct 4,4'-methylenebis(phenyl isocyanate) (MDI) readily available, which has since been used almost exclusively in polyurethane elastomer applications. Liquid derivatives of MDI are used in RIM applications, and work has been done since the 1990s to reinforce polyurethane elastomers with glass, graphite, boron, and aramid fibers, or mica flakes, to increase stiffness and reduce thermal expansion. The higher modulus thermoset elastomers produced by reinforced reaction injection molding (RRIM) are also used in the automotive industry. In 1969 Bayer pioneered an all-plastic car having RIM-molded bumpers and fascia; in 1983 the first plastic-body commercial automobile (Pontiac Fiero) was produced in the United States.

The availability of PMDI also led to the development of polyurethane-modified isocyanurate (PUIR) foams by 1967. The PUIR foams have superior thermal stability and combustibility characteristics, which extend the use temperature of insulation foams well above 150°C. The PUIR foams are used in pipe, vessel, and solar panel insulation; glass-fiber-reinforced PUIR roofing panels having superior dimensional stability have also been developed. More recently, inexpensive polyester polyols based on residues obtained in the production of dimethyl terephthalate (DMT) have been used in the formulation of rigid polyurethane and PUIR foams.

One of the trends in polyurethanes is the gradual replacement of TDI by the less volatile PMDI or MDI in many applications. Elimination of chlorinated fluorocarbon (CFC) blowing agents and the reduction of emission of volatile organic compounds (VOCs) have been ongoing. Flexible foam producers have eliminated auxiliary blowing agents, and the rigid foam producers use water-blown formulations in combination with hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), or hydrocarbons. Adhesives and sealants are reformulated to 100% solid and water-based systems.

3. Formation and Properties

3.1. Polyurethane Formation. The key to the manufacture of polyurethanes is the unique reactivity of the heterocumulene groups in diisocyanates toward nucleophilic additions. The polarization of the isocyanate group enhances the addition across the carbon–nitrogen double bond, which allows rapid formation of addition polymers from diisocyanates and macroglycols.

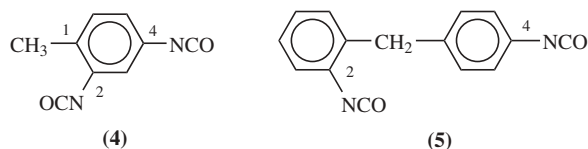


The liquid monomers are suitable for bulk polymerization processes. The reaction can be conducted in a mold (casting, reaction injection molding),

continuously on a conveyor (block and panel foam production), or in an extruder (thermoplastic polyurethane elastomers and engineering thermoplastics). Also, spraying of the monomers onto the surface of suitable substrates provides insulation barriers or cross-linked coatings.

The polyaddition reaction is influenced by the structure and functionality of the monomers, including the location of substituents in proximity to the reactive isocyanate group (steric hindrance) and the nature of the hydroxyl group (primary or secondary). Impurities also influence the reactivity of the system; for example, acid impurities in PMDI require partial neutralization or larger amounts of the basic catalysts. The acidity in PMDI can be reduced by heat or epoxy treatment, which is best conducted in the plant. Addition of small amounts of carboxylic acid chlorides lowers the reactivity of PMDI or stabilizes isocyanate terminated prepolymers.

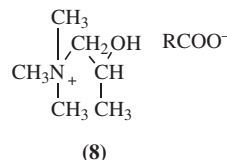
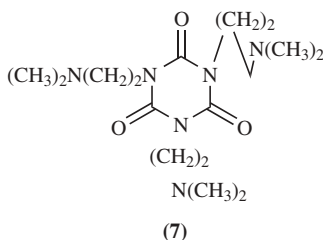
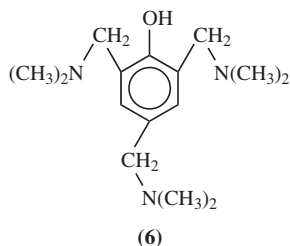
The steric effects in isocyanates are best demonstrated by the formation of flexible foams from TDI. In the 2,4-isomer (4), the initial reaction occurs at the nonhindered isocyanate group in the 4-position. The unsymmetrically substituted ureas formed in the subsequent reaction with water are more soluble in the developing polymer matrix. Low density flexible foams are not readily produced from MDI or PMDI; enrichment of PMDI with the 2,4'-isomer of MDI (5) affords a steric environment similar to the one in TDI, which allows the production of low density flexible foams that have good physical properties. The use of high performance polyols based on a copolymer polyol allows production of high resiliency (HR) slabstock foam from either TDI or MDI (2).



The uncatalyzed reaction of diisocyanates with macroglycols is of no significance in the formation of polyurethanes. Tailoring of performance characteristics to improve processing and properties of polyurethane products requires the selection of efficient catalysts. In flexible foam manufacturing a combination of tin and tertiary amine catalysts are used in order to balance the gelation reaction (urethane formation) and the blowing reaction (urea formation). The tin catalysts used include dibutyltin dilaurate, dibutylbis(laurylthio)stannate, dibutyltinbis(isooctylmercapto acetate), and dibutyltinbis(isooctylmaleate). The principal tertiary amines used are listed in Table 1.

Strong bases, such as potassium acetate, potassium 2-ethylhexoate, or amine-epoxide combinations are the most useful trimerization catalysts. Also, some special tertiary amines, such as 2,4,6-tris(*N,N*-dimethylaminomethyl)phenol (DMT-30) (6), 1,3,5-tris(3-dimethylaminopropyl)hexahydro-*s*-triazine (7), and

ammonium salts (Dabco TMR) (8) are good trimerization catalysts.



Hydroxy group containing tertiary amines are also used because they become incorporated into the polymer structure, which eliminates odor formation in the foam (3). Delayed-action or heat-activated catalysts are of particular interest in molded foam applications. These catalysts show low activity at room temperature but become active when the exotherm builds up. In addition to the phenol salt of DBU (4), benzoic acid salts of Dabco are also used (5).

For the reaction of TDI with a polyether triol, bismuth or lead compounds can also be used. However, tin catalysts are preferred mainly because of their slight odor and the low amounts required to achieve high reaction rates. Carboxylic acid salts of calcium, cobalt, lead, manganese, zinc, and zirconium are employed as cocatalysts with tertiary amines, tin compounds, and tin-amine combinations. Carboxylic acid salts reduce cure time of rigid foam products. Organic mercury compounds are used in cast elastomers and in RIM systems to extend cream time, ie, the time between mixing of all ingredients and the onset of creamy appearance.

The formation of cellular products also requires surfactants to facilitate the formation of small bubbles necessary for a fine-cell structure. The most effective surfactants are polyoxyalkylene-polysiloxane copolymers. The length and ethylene oxide/propylene oxide (EO/PO) ratio of the pendant polyether chains determine the emulsification and stabilizing properties. In view of the complexity of the interaction of surfactant molecules with the growing polymer chains in foam production, it is essential to design optimal surfactants for each application. Flexible polyurethane foams require surfactants that promote improved cell-wall drainage. This allows the cell walls to become more open during the foaming reaction. Also the shift away from TDI to MDI in molded high resiliency foams adds new demands on foam surfactants (6).

The physical properties of polyurethanes are derived from their molecular structure and determined by the choice of building blocks as well as the supra-molecular structures caused by atomic interaction between chains. The ability to crystallize, the flexibility of the chains, and spacing of polar groups are of considerable importance, especially in linear thermoplastic materials. In rigid cross-linked systems, eg, polyurethane foams, other factors such as density determine the final properties.

3.2. Thermoplastic Polyurethanes. The unique properties of polyurethanes are attributed to their long-chain structure. In segmented polyether- and polyesterurethane elastomers, hydrogen bonds form between -NH- groups (proton donor) and the urethane carbonyl, polyether oxygen, or polyester carbo-

nyl groups. The symmetrical MDI is more suitable for the preparation of segmented polyurethane elastomers having excellent physical properties. Segmented polyurethanes are also obtained from 2,6-TDI, but an economically attractive separation process for the TDI isomers has yet to be developed.

The melt viscosity of a thermoplastic polyurethane (TPU) depends on the weight-average molecular weight and is influenced by chain length and branching. TPUs are viscoelastic materials, which behave like a glassy, brittle solid, an elastic rubber, or a viscous liquid, depending on temperature and time scale of measurement. With increasing temperature, the material becomes rubbery because of the onset of molecular motion. At higher temperatures a free-flowing liquid forms.

The melt temperature of a polyurethane is important for processability. Melting should occur well below the decomposition temperature. Below the glass-transition temperature (T_g), the molecular motion is frozen, and the material is only able to undergo small-scale elastic deformations. For amorphous polyurethane elastomers, the T_g of the soft segment is ca -50 to -60°C , whereas for the amorphous hard segment, T_g is in the 20 – 100°C range. The T_g and T_m of the more common macrodiols used in the manufacture of TPU are listed in Table 2.

The choice of macrodiol influences the low temperature performance, whereas the modulus, ie, hardness, stiffness, and load-bearing properties, increases with increasing hard-segment content.

The pseudocross-links, generated by the hard-segment interactions, are reversed by heating or dissolution. Without the domain crystallinity, thermoplastic polyurethanes would lack elastic character and be more gum-like in nature. In view of the outlined morphology, it is not surprising that many products develop their ultimate properties only on curing at elevated temperature, which allows the soft- and hard-phase segments to separate.

Mesogenic diols, such as 4,4'-bis(ω -hydroxyalkoxy)biphenyls, are used with 2,4-TDI or 1,4-diisocyanatobenzene (PPDI) to construct liquid crystalline polyurethanes (7). Partial replacement of the mesogenic diols by PTMG shows that the use of lower molecular weight flexible spacers form polymers that have a more stable mesophase and exhibit higher crystallinity (8). Another approach to liquid crystal polyurethanes involves the attachment of cholesterol to the polyurethane chain utilizing the dual reactivity in 2,4-TDI (9).

Polyurethane ionomers are segmented polymers in which ionic groups are separated by long-chain apolar segments (10). In the presence of water the ionic centers are hydrated. This effect enables ionomers to form stable dispersions in water, and solventless polyurethane coatings are formulated in this manner. The use of *N*-alkyldiethanolamines or dimethylolpropionic acid as extenders allows incorporation of ionic groups into the polymer backbone. Also, reaction of $-\text{NH}-$ group containing polyurethane chains having 1,3-propane sultone affords ionomers. If the ionic centers are located in the hard segment, these then align to form a domain morphology. Anionic dispersions have greater stability than cationic dispersions, but cationic polymers show better adhesion to glass.

3.3. Thermoset Polyurethanes. The physical properties of rigid urethane foams are usually a function of foam density. A change in strength

properties requires a change in density. Rigid polyurethane foams that have densities of $< 0.064 \text{ g/cm}^3$, used primarily for thermal insulation, are expanded with HCFCs, HFCs, or hydrocarbons (see INSULATION, THERMAL). Often water or a carbodiimide catalyst is added to the formulation to generate carbon dioxide as a coblowing agent. High density foams are often water-blown. In addition to density, the strength of a rigid foam is influenced by the catalyst, surfactant, polyol, isocyanate, and the type of mixing. By changing the ingredients, foams can be made that have high modulus, low elongation, and some brittleness (friability), or relative flexibility and low modulus (see FOAMED PLASTICS).

Rigid polyurethane foams generally have an elastic region in which stress is nearly proportional to strain. If a foam is compressed beyond the yield point, the cell structure is crushed. Compressive strength values of 10 to 280 kPa (1–14 psi) can be obtained using rigid polyurethane foams of 0.032 g/cm^3 density. In addition, the elastic modulus, shear strength, flexural strength, and tensile strength all increase with density.

Most low density rigid polyurethane foams have a closed-cell content of $> 90\%$. Above 0.032 g/cm^3 , closed-cell content increases rapidly and is generally $> 99\%$ above 0.192 g/cm^3 . Bun foam, produced under controlled conditions, has a very fine-cell structure, with cell sizes of 150–200 μm .

The properties of thermoset flexible polyurethane foams are also related to density; load-bearing properties are likewise important. Under normal service temperatures, flexible foams exhibit rubber-like elasticity to deformations of short duration, but creep under long-term stress. Maximum tensile strength is obtained at densities of ca $0.024\text{--}0.030 \text{ g/cm}^3$. The densities are controlled by the amount of water in the formulation and may range from 0.045 to 0.020 g/cm^3 by raising the amount of water from 2 to 5%. Auxiliary blowing agents are also used to reduce density and control hardness. The size and uniformity of the cells are controlled by the efficiency of mixing and the nucleation of the foam mix. Flexible foams are anisotropic and the load-bearing properties are best when measured in the direction of foam rise. Some of the polyurethane machine suppliers have developed machinery to use liquid carbon dioxide as coblowing agent in the manufacture of water-blown flexible foams.

Hyperbranched polyurethanes are constructed using phenol-blocked trifunctional monomers in combination with 4-methylbenzyl alcohol for end capping (11). Polyurethane interpenetrating polymer networks (IPNs) are mixtures of two cross-linked polymer networks, prepared by latex blending, sequential polymerization, or simultaneous polymerization. IPNs have improved mechanical properties, as well as thermal stabilities, compared to the single cross-linked polymers. In pseudo-IPNs, only one of the involved polymers is cross-linked. Numerous polymers are involved in the formation of polyurethane-derived IPNs (12).

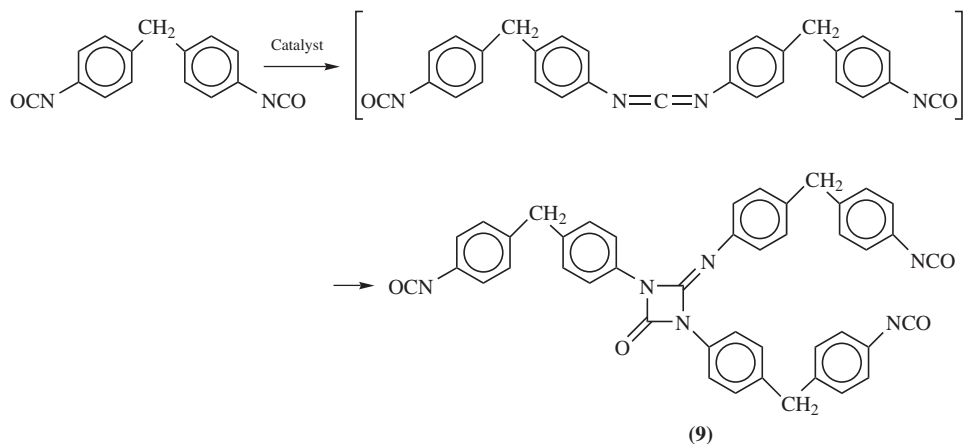
4. Raw Materials

4.1. Isocyanates. The commodity isocyanates TDI and PMDI are most widely used in the manufacture of urethane polymers (see also ISOCYANATES, ORGANIC). The former is an 80:20 mixture of 2,4- and 2,6-isomers, respectively;

the latter a polymeric isocyanate obtained by phosgenation of aniline–formaldehyde-derived polyamines. A coproduct in the manufacture of PMDI is 4,4'-methylenebis(phenylisocyanate) (MDI). A 65:35 mixture of 2,4- and 2,6-TDI, pure 2,4-TDI and MDI enriched in the 2,4'-isomer are also available. The manufacture of TDI involves the dinitration of toluene, catalytic hydrogenation to the diamines, and phosgenation. Separation of the undesired 2,3-isomer is necessary because its presence interferes with polymerization (13).

Polymeric isocyanates or PMDI are crude products that vary in exact composition. The main constituents are 40–60% 4,4'-MDI; the remainder is the other isomers of MDI, trimeric species, and higher molecular weight oligomers. Important product variables are functionality and acidity. Rigid polyurethane foams are mainly manufactured from PMDI. The so-called pure MDI is a low melting solid that is used for high performance polyurethane elastomers and spandex fibers. Liquid MDI products are used in RIM polyurethane elastomers.

The basic raw materials for the manufacture of PMDI and its coproduct MDI is benzene. Nitration and hydrogenation affords aniline (see AMINES, AROMATIC). Reaction of aniline with formaldehyde in the presence of hydrochloric acid gives rise to the formation of a mixture of oligomeric amines, which are phosgenated to yield PMDI. The coproduct, MDI, is obtained by continuous thin-film vacuum distillation. Liquid MDI (Isonate 143-L) is produced by converting some of the isocyanate groups into carbodiimide groups, which react with the excess isocyanate present to form a small amount of the trifunctional four-membered ring cycloadduct (9). The presence of (9) lowers the melting point of MDI to give a liquid product.



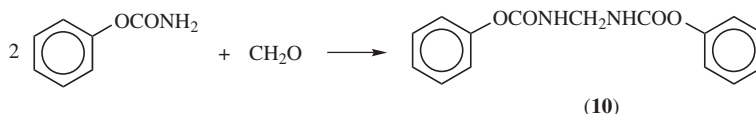
Liquid MDI products are also made by reaction of the diisocyanate with small amounts of glycols. These products are called prepolymers.

Several higher priced specialty aromatic diisocyanates are also available, including 1,5-naphthalene diisocyanate (NDI), *p*-phenylene diisocyanate (PPDI), and bitolyene diisocyanate (TODI). These symmetrical, high melting diisocyanates give high melting hard segments in polyurethane elastomers.

Urethanes obtained from aromatic diisocyanates undergo slow oxidation in the presence of air and light, causing discoloration, which is unacceptable in some applications. Polyurethanes obtained from aliphatic diisocyanates are color-stable, although it is necessary to add antioxidants (qv) and uv-stabilizers to the formulation to maintain the physical properties with time. The least costly aliphatic diisocyanate is hexamethylene diisocyanate (HDI), which is obtained by phosgenating the nylon intermediate hexamethylenediamine. Because of its low boiling point, HDI is mostly used in form of its derivatives, such as biurets, allophanates, dimers, or trimers (14). Isophorone diisocyanate (IPDI) and its derivatives are also used in the formulation of rigid coatings; hydrogenated MDI (HMDI) and cyclohexane diisocyanate (CHDI) are used in the formulation of flexible coatings and polyurethane elastomers.

HMDI was originally produced by Du Pont as a coproduct in the manufacture of Qiana fiber. Du Pont subsequently sold the product to Bayer. In the 1990s MDA was hydrogenated by Air Products for Bayer (see AMINES, AROMATIC-METHYLENEDIANILINE). Commercial HMDI is a mixture of three stereoisomers. Semicommercial aliphatic diisocyanates include *trans*-cyclohexane-1,4-diisocyanate (CHDI) and *m*-tetramethylxylylene diisocyanate (TMXDI). A coproduct in the production of TMXDI is *m*-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI), which can be copolymerized with other olefins to give aliphatic polyisocyanates.

Masked or blocked diisocyanates are used in coatings applications. The blocked diisocyanates are storage-stable, nonvolatile, and easy to use in powder coatings. Blocked isocyanates are produced by reaction of the diisocyanate with blocking agents such as caprolactam, 3,5-dimethylpyrazole, phenols, oximes, acetoacetates, or malonates. Upon heating at 120–60°C, the blocked isocyanates dissociate and the generated free isocyanate reacts with hydroxyl groups available in the formulation to give high molecular weight polyurethanes. In the case of acetoacetates and malonates, the free isocyanates are not regenerated, but the adducts undergo transesterification reactions with the present polyol upon heating (15). A phenol-blocked methylene diisocyanate (**10**) is obtained in the reaction of phenyl carbamate with formaldehyde (16).



Since the early 1970s, attempts have been made by the principal global producers of isocyanates to avoid use of the toxic phosgene (qv) in the manufacture of isocyanates. Attempts to produce TDI and PMDI by nonphosgene processes have failed, but several aliphatic diisocyanates, eg, CHDI and TMXDI, have been manufactured using nonphosgene processes. Plans to use nonphosgene processes for the manufacture of IPDI in their new plants are under construction. In nonphosgene chemistry, isocyanic acid, generated by thermolysis of urea, reacts with diamines to give a bis-urea derivative. Subsequent reaction with diethylamine affords tri-substituted urea derivatives, which are thermolyzed in an inert solvent in the presence of an acidic catalyst to give the diisocyanate (17). Gaseous

ammonia is the only by-product in this process. Also, reaction of aliphatic diamines with carbon dioxide, in the presence of triethylamine, affords bis-carbamate salts, which can be dehydrated with phosphoryl chloride to give the diisocyanate (18). Sterically hindered aromatic diamines can be converted in high yield into diisocyanates at room temperature using di-*t*-butyl dicarbonate in the presence of dimethylaminopyridine (19).

The properties and manufacturers of the commercial isocyanates are presented in Table 3.

4.2. Polyether Polyols. Polyether polyols are addition products derived from cyclic ethers (Table 4). The alkylene oxide polymerization is usually initiated by alkali hydroxides, especially potassium hydroxide. In the base-catalyzed polymerization of propylene oxide, some rearrangement occurs to give allyl alcohol. Further reaction of allyl alcohol with propylene oxide produces a mono-functional alcohol. Therefore, polyether polyols derived from propylene oxide are not truly difunctional. By using zinc hexacyano cobaltate as catalyst, a more difunctional polyol is obtained (20). Trichlorobutylene oxide-derived polyether polyols are useful as reactive fire retardants. Poly(tetramethylene glycol) (PTMG) is produced in the acid-catalyzed homopolymerization of tetrahydrofuran. Copolymers derived from tetrahydrofuran and ethylene oxide are also produced.

Polyether polyols are high molecular weight polymers that range from viscous liquids to waxy solids, depending on structure and molecular weight. Most commercial polyether polyols are based on the less expensive ethylene or propylene oxide or on a combination of the two. Block copolymers are manufactured first by the reaction of propylene glycol with propylene oxide to form a homopolymer. This polymer upon further reaction with ethylene oxide affords the block copolymer. Because primary hydroxyl groups, resulting from the polymerization of ethylene oxide, are more reactive than secondary hydroxyl groups, the polyols produced in this manner are more reactive. Random copolymers are obtained by polymerizing mixtures of propylene oxide and ethylene oxide. The viscosity of polyether polyols increases with hydroxyl equivalent weight. The higher molecular weight polyether polyols are soluble in organic solvents. Poly(propylene oxide) is soluble in water up to a molecular weight of 760, and copolymerization with ethylene oxide expands the range of water solubility.

With amine initiators the so-called self-catalyzed polyols are obtained, which are used in the formulation of rigid spray foam systems. The rigidity or stiffness of a foam is increased by aromatic initiators, such as Mannich bases derived from phenol, phenolic resins, toluenediamine, or methylenedianiline (MDA).

In the manufacture of highly resilient flexible foams and thermoset RIM elastomers, graft or polymer polyols are used. Graft polyols are dispersions of free-radical-polymerized mixtures of acrylonitrile and styrene partially grafted to a polyol. *In situ* polyaddition reaction of isocyanates with amines in a polyol substrate produces PHD (polyharnstoff dispersion) polyols (21). In addition, blending of polyether polyols with diethanolamine, followed by reaction with TDI, also affords a urethane/urea dispersion. The polymer or PHD-type polyols increase the load bearing properties and stiffness of flexible foams. Interreactive dispersion polyols are also used in RIM applications where elastomers of high modulus, low thermal coefficient of expansion, and improved paintability are needed.

4.3. Polyester Polyols. Initially polyester polyols were the preferred raw materials for polyurethanes, but in the 1990s the less expensive polyether polyols dominated the polyurethane market. Inexpensive aromatic polyester polyols have been introduced for rigid foam applications. These are obtained from residues of terephthalic acid production or by transesterification of dimethyl terephthalate (DMT) or poly(ethylene terephthalate) (PET) scrap with glycols.

Polyester polyols are based on saturated aliphatic or aromatic carboxylic acids and diols or mixtures of diols. The carboxylic acid of choice is adipic acid (qv) because of its favorable cost/performance ratio. For elastomers, linear polyester polyols of ca 2000 mol wt are preferred. Branched polyester polyols, formulated from higher functional glycols, are used for foam and coatings applications. Phthalates and terephthalates are also used.

In addition, polyester polyols are made by the reaction of caprolactone with diols. Poly(caprolactone diols) are used in the manufacture of thermoplastic polyurethane elastomers with improved hydrolytic stability (22). The hydrolytic stability of the poly(caprolactone diol)-derived TPUs is comparable to TPUs based on the more expensive long-chain diol adipates (23). Polyether/polyester polyol hybrids are synthesized from low molecular weight polyester diols, which are extended with propylene oxide.

5. Processing

5.1. Flexible Foam. Flexible slab or bun foam is poured by multicomponent machines at rates of >45 kg/min. One-shot pouring from traversing mixing heads is generally used. A typical formulation for furniture-grade foam having a density of 0.024 g/cm³ includes a polyether triol, mol wt 3000; TDI; water; catalysts, ie, stannous octoate in combination with a tertiary amine; and surfactant. Cblowing agents are often used to lower the density of the foam and to achieve a softer hand. Cblowing agents are methylene chloride, methyl chloroform, acetone, and CFC 11, but the last has been eliminated because of its ozone-depletion potential. HCFC blowing agents are replacing CFC 11. Additive systems (24) and new polyols (25) are being developed to achieve softer low density foams. Higher density (0.045 g/cm³) slab or bun foam, also called high resiliency (HR) foam, is similarly produced, using polyether triols having molecular weight of 6000. The use of polymer polyols improves the load-bearing properties.

Flexible foams are three-dimensional agglomerations of gas bubbles separated from each other by thin sections of polyurethanes and polyureas. The microstructures observed in TDI- and MDI-based flexible foams are different. In TDI foams monodentate urea segments form after 40% conversion, followed by a bidentate urea phase, which is insoluble in the soft segment. As the foam cures, annealing of the precipitated discontinuous urea phase occurs to optimize alignment through hydrogen bonding (26).

Flame retardants (qv) are incorporated into the formulations in amounts necessary to satisfy existing requirements. Reactive-type diols, such as *N,N*-bis(2-hydroxyethyl)aminomethyl phosphonate are preferred, but nonreactive phosphates are also used. Often, the necessary results are achieved using mineral fillers, such as alumina trihydrate or melamine. Melamine melts away from the

flame and forms both a nonflammable gaseous environment and a molten barrier that helps to isolate the combustible polyurethane foam from the flame. Alumina trihydrate releases water of hydration to cool the flame, forming a noncombustible inorganic protective char at the flame front. Flame-resistant upholstery fabric or liners are also used (27).

There are four main types of flexible slabstock foam: conventional, high resiliency, filled, and high load-bearing foam. Filled slabstock foams contain inorganic fillers to increase the foam density and improve the load-bearing characteristics. High load-bearing formulations incorporate a polymer polyol. Slabstock flexible foam is produced on continuous bun lines. The bun forms while the material moves down a long conveyor. In flat-top bun lines, the liquid chemicals are dispensed from a stationary mixing head to a manifold at the bottom of a trough. More rectangular foams are produced by several newer processes. However, the most popular rectangular block foam process is the Maxfoam process. The high outputs require faster and longer conveyors. An exception is the Vertifoam process, in which the reaction mixture is introduced at the bottom of an enclosed expansion chamber. The chamber is lined with paper or polyethylene film, which is drawn upward at a controlled rate. Because the Vertifoam machine is much smaller than the horizontal machines, operational savings can be achieved (28). Two newer slabstock foam manufacturing processes have been developed.

A high rate of block foam production (150–220 kg/min) is required in order to obtain large slabs to minimize cutting waste. Bun widths range from ca 1.43 to 2.2 m, and typical bun heights are 0.77–1.25 m. In a flexible foam plant, scrap can amount to as much as 20%. Most of it is used as carpet underlay and in pillows and packaging (see PACKAGING MATERIALS). The finished foam blocks are stored in a cooling area for at least 12 h before being passed to a storage area or to slitters where the blocks are cut into sheets. In the production plant the fire risk must be minimized. Temperatures of up to 150°C can be reached in the interior of the foam blocks. Blowing of ambient air through the porous foam allows dissipation of the heat generated in the exothermic reaction (29).

Most flexible foams produced are based on polyether polyols. Flexible polyether foams have excellent cushioning properties, are flexible over a wide range of temperatures, and can resist fatigue, aging, chemicals, and mold growth. Polyester-based foams are superior in resistance to dry cleaning and can be flame-bonded to textiles.

In more recent years, molded flexible foam products are becoming more popular. The bulk of the molded flexible urethane foam is employed in the transportation industry, where it is highly suitable for the manufacture of seat cushions, back cushions, and bucket-seat padding. TDI prepolymers were used in flexible foam molding in conjunction with polyether polyols. The introduction of organotin catalysts and efficient silicone surfactants facilitates one-shot foam molding, which is the most economical production method.

The need for heat curing has been eliminated by the development of cold-molded or high resiliency foams. These molded HR foams are produced from highly reactive polyols and are cured under ambient conditions. The polyether triols used are 4500–6500 mol wt and are high in ethylene oxide (usually > 50% primary hydroxyl content). Reactivity is further enhanced by triethanolamine,

liquid aromatic diamines, and aromatic diols. Generally, PMDI, TDI, or blends of PMDI–TDI are used. Load-bearing characteristics are improved by using polymer polyol. High resiliency foams exhibit relatively high SAC (support) factors, ie, load ratio; excellent resiliency (ball rebound > 60%); and improved flammability properties.

Semiflexible molded polyurethane foams are used in other automotive applications, such as instrument panels, dashboards, arm rests, head rests, door liners, and vibrational control devices. An important property of semiflexible foam is low resiliency and low elasticity, which results in a slow rate of recovery after deflection. The isocyanate used in the manufacture of semiflexible foams is PMDI, sometimes used in combination with TDI or TDI prepolymers. Both polyester as well as polyether polyols are used in the production of these water-blown foams. Sometimes integral skin molded foams are produced.

Semirigid foams are also manufactured. These foams do not fully recover after deformation; they are used in the construction of energy-absorbing automobile bumpers. Integral skin molded foams have an attached densified water skin, which is produced during manufacture. The preferred isocyanate for integral skin foams is carbodiimide-modified liquid MDI, which is used with ethylene oxide-capped polyols or polymer polyols. Thicker skins are obtained by lowering mold temperatures and increasing the percentage of overpack.

5.2. Rigid Foams. Rigid polyurethane foam is mainly used for insulation (qv). The configuration of the product determines the method of production. Rigid polyurethane foam is produced in slab or bun form on continuous lines (Fig. 1), or it is continuously laminated between either asphalt or tar paper, or aluminum, steel, and fiberboard, or gypsum facings (Fig. 2). Rigid polyurethane products, for the most part, are self-supporting, which makes them useful as construction insulation panels and as structural elements in construction applications. Polyurethane can also be poured or frothed into suitable cavities, ie, pour-in-place applications, or be sprayed on suitable surfaces. Spray-applied polyurethane foams are produced in densities ranging from 0.021 to 0.048 g/cm³. The lower density foams are used primarily in nonload-bearing applications, eg, cavity walls and residential stud-wall insulation, whereas the higher density foams are used in roofing applications. Applicators can buy formulated systems consisting of the isocyanate component, as well as the polyol side containing the catalysts, surfactants, and blowing agent.

Almost all rigid polyurethanes are produced from PMDI. Some formulations, particularly those for refrigerator and freezer insulation, are based on modified TDI (golden TDI) or TDI prepolymers, but these are being replaced by PMDI formulations. The polyols used include propylene oxide adducts of polyfunctional hydroxy compounds or amines (see Table 4). The amine-derived polyols are used in spray foam formulations where high reaction rates are required. Crude aromatic polyester diols are often used in combination with the multifunctional polyether polyols. Blending of polyols of different functionality, molecular weight, and reactivity is used to tailor a polyol for a specific application. Polyether–polyester polyol hybrids are also synthesized from low mol wt polyesters, which are subsequently propoxylated. The high functionality of the polyether polyols combined with the higher functionality of PMDI contributes to the rapid network formation required for rigid polyurethane foams.

Reactive or nonreactive fire retardants, containing halogen and phosphorous, are often added to meet the existing building code requirements. The most commonly used reactive fire retardants are Fyrol 6, chlorendic anhydride-derived diols, and tetrabromophthalate ester diols (PHT 4-Diol). There is a synergistic effect of nitrogen and phosphorus observed in P–N compounds. Phosphonates, such as Fyrol 6, are effective in char formation, whereas phosphine oxide-derived fire retardants are reactive in the gas phase. Because the reactive fire retardants are combined with the polyol component, storage stability is important. Nonreactive fire retardants include halogenated phosphate esters, such as tris(chloroisopropyl) phosphate (TMCP) and tris(chloroethyl) phosphate (TCEP), and phosphonates, such as dimethyl methylphosphonate (DMMP). Highly halogenated aromatic compounds, borax, and melamine are also used as fire retardants in rigid foams.

Insulation foams are halocarbon-blown. Chlorofluorocarbons, eg, CFC-11 (bp 23.8°C) and CFC-12 (bp –30°C), were used extensively as blowing agents in the manufacture of rigid insulation foam. Because of the mandatory phaseout of CFCs, it had become necessary to develop blowing agents that have a minimal effect on the ozone layer. The new HCFC blowing agents for foam blowing applications include HCFC-141b ($\text{C}_2\text{H}_3\text{FCl}_2$), HCFC-142b ($\text{C}_2\text{H}_3\text{F}_2\text{Cl}$), HCFC-22 (CHF_2Cl), HFC-134a ($\text{C}_2\text{H}_2\text{F}_4$) and HFC-152a ($\text{C}_2\text{H}_4\text{F}_2$), but these also faced a phaseout period in 2003 (for “developed” countries) or 2020 (depending on the specific region and/or product). However, a combination of new blowing agents (HFC-134a, HCFC-245fa, HFC-365mfc, blends and hydrocarbons, CO_2 and water-blown systems), machinery and foaming technologies will be developed to ensure a supply of quality polyurethane foams (30). Addition of water or carbodiimide catalysts to the formulation generates carbon dioxide as a coblowing agent. Longer-range environmental considerations have prompted the use of hydrocarbons such as pentanes and cyclopentane as blowing agents. Pentane blown foams have already been used in the appliance industry in Europe. Pentane-based formulations are typically used in conjunction with water. Because rigid foams blown with alternative blowing agents have λ -values ($\text{m}\cdot\text{W}/\text{m}\cdot\text{K}$) of about 19.5, as compared to 18.0 for CFC-11-blown foams, they are thus less efficient in their insulation performance. In addition, because rigid polyurethane foams at a density of $0.032\text{ g}/\text{cm}^3$ are ca 97% gas, the blowing agents determine the k -factor (insulation value).

From the onset of creaming to the end of the rise during the expansion process, the gas must be retained completely in the form of bubbles, which ultimately result in the closed-cell structure. Addition of surfactants facilitates the production of very small uniform bubbles necessary for a fine-cell structure.

The catalysts used in the manufacture of rigid polyurethane foams include tin and tertiary amine catalysts. Combinations of catalysts are often used to achieve the necessary balance of reaction rates. This is especially necessary if part of the blowing agent is carbon dioxide, generated in the reaction of the isocyanate with added water. New surfactants are required for the emerging water-coblown formulations, using pentanes as the main blowing agent (31). A typical water-coblown rigid polyurethane formulation is shown in Table 5.

During the molding of high density rigid foam parts, the dispensed chemicals have to flow a considerable distance to fill the cavities of the mold. In the

filling period, the viscosity of the reacting mixture increases markedly from the initial low value of the liquid mixture to the high value of the polymerized foam. If the viscosity increases rapidly, incomplete filling results. Chemical factors that influence flow properties are differential reactivity in the polyol components and the addition of water to the formulation. Because venting holes allow the escape of air displaced by the rising foam, a moderate degree of overpacking is often advantageous. Newer high pressure RIM machines have simplified the mold-filling procedure, so filling of intricate molds is no longer a problem.

Many of the rigid insulation foams are urethane-modified isocyanurate (PUIR) foams. In the formulation of poly(urethane isocyanurate) foams an excess of PMDI is used. The isocyanate index can range from 105 to 300 and higher. PUIR foams have a better thermal stability than polyurethane foams (33). The cyclotrimerization of the excess isocyanate groups produces heterocyclic triisocyanurate groups, which do not revert to the starting materials, but rather decompose at much higher temperatures. In the decomposition of the PUIR foams a char is formed, which protects the foam underneath the char.

The formation of isocyanurates in the presence of polyols occurs via intermediate allophanate formation, ie, the urethane group acts as a cocatalyst in the trimerization reaction. By combining cyclotrimerization with polyurethane formation, processibility is improved, and the friability of the derived foams is reduced. The trimerization reaction proceeds best at 90–100°C. These temperatures can be achieved using a heated conveyor or a RIM machine. The key to the formation of PUIR foams is catalysis. Strong bases, such as potassium acetate, potassium 2-ethylhexoate, and tertiary amine combinations, are the most useful trimerization catalyst. A review on the trimerization of isocyanates is available (34).

Modification of cellular polymers by incorporating amide, imide, oxazolidinone, or carbodiimide groups has been attempted but only the urethane-modified isocyanurate foams are produced. PUIR foams often do not require added fire retardants to meet most regulatory requirements (35).

5.3. CASE Polyurethanes. CASE is the acronym for coatings, adhesives, sealants, and elastomers. Polyurethane coatings are mainly based on aliphatic isocyanates and acrylic or polyester polyols because of their outstanding weatherability. For flexible elastomeric coatings, HMDI and IPDI are used with polyester polyols, whereas higher functional derivatives of HDI and IPDI with acrylic polyols are mainly used in the formulation of rigid coatings. Plastics coatings, textile coatings, and artificial leather are based on either aliphatic or aromatic isocyanates. For light-stable textile coatings, combinations of IPDI and IPDA (as chain extender) are used. The poly(urethane urea) coatings are applied either directly to the fabric or using transfer coating techniques. The direct-coating method is applied for rainwear because the microporous coating is permeable to air and water vapor, but not to liquid water. Microporous polyurethane sheets (poromerics) are used for shoe and textile applications. An artificial velour leather is used in the fabrication of fashion wear. Polyurethane binder resins are also used to upgrade natural leather.

Blocked aliphatic isocyanates or their derivatives are used for one-component coating systems. Masked polyols are also used for this application. For example, polyols capped with vinyl or isopropenyl ethers produce polyace-

tals, which do not react with isocyanates. Hydrolysis of the acetals with moist air regenerate the hydroxyl groups, which undergo polyurethane reaction with isocyanate-terminated prepolymers. In addition, substituted oxazolines are used as masked cross-linkers (36). Ketimine cross-linkers are also utilized in the formulation of one-component coating systems (37). Hydrolysis of ketimines produces diamines, which undergo a very fast reaction with isocyanate-terminated prepolymers. Blocked isocyanates are also used in the cross-linking of acrylic resins for automotive coatings. Incorporation of masked diisocyanates into epoxy resins lowers the moisture absorption in the derived coatings (38).

Powder coatings are formulated from the reaction product of trimethylolpropane and IPDI, blocked with caprolactam, and polyester polyols. The saturated polyester polyols are based on aromatic acid diols, neopentyl glycol, and trimellitic anhydride for further branching. To avoid the release of caprolactam in the curing reaction, systems based on IPDI dimer diols are used.

Water-borne polyurethane coatings are formulated by incorporating ionic groups into the polymer backbone. These ionomers are dispersed in water through neutralization. The experimental 1,12-dodecane diisocyanate (C12DI; Du Pont) is especially well suited for the formation of water-borne polyurethanes because of its hydrophobicity (39). Cationomers are formed from IPDI, *N*-methyldiethanolamine, and poly(tetramethylene adipate diol) (40); anionic dispersions are obtained from IPDI, PTMG, poly(propylene glycol) (PPG), and dimethylol propionic acid (41). The ionic groups can also be introduced in the polyol segment. For example, reaction of diesterdiol, obtained from maleic anhydride and 1,4-butanediol, with sodium bisulfite produces the ionic building block, which on reaction with HDI gives a polyurethane ionomer (42). The weatherability of aliphatic polyurethane coatings is related to their structures. Polyester polyol-based polyurethanes are more uv-resistant than polyether polyol-based polyurethanes, but the latter offer better hydrolytic stability.

Ionic polymers are also formulated from TDI and MDI (43). Poly(urethane urea) and polyurea ionomers are obtained from divalent metal salts of *p*-aminobenzoic acid, MDA, dialkylene glycol, and 2,4-TDI (44). In the case of polyureas, the glycol extender is omitted. If TDI is used in coatings applications, it is usually converted to a derivative to lower the vapor pressure. A typical TDI prepolymer is the adduct of TDI with trimethylolpropane. Carbodiimide-modified MDI offers advantages in polyester-based systems because of improved hydrolytic stability (45). Moisture cure systems based on aromatic isocyanates are also available.

Polyurethane adhesives are known for excellent adhesion, flexibility, toughness, high cohesive strength, and fast cure rates. Polyurethane adhesives rely on the curing of multifunctional isocyanate-terminated prepolymers with moisture or on the reaction with the substrate, eg, wood and cellulosic fibers. Two-component adhesives consist of an isocyanate prepolymer, which is cured with low equivalent weight diols, polyols, diamines, or polyamines. Such systems can be used neat or as solution. The two components are kept separately before application. Two-component polyurethane systems are also used as hot-melt adhesives.

Water-borne adhesives are preferred because of restrictions on the use of solvents. Low viscosity prepolymers are emulsified in water, followed by chain extension with water-soluble glycols or diamines. As cross-linker PMDI can be

used, which has a shelf life of 5 to 6 h in water. Water-borne polyurethane coatings are used for vacuum forming of PVC sheeting to ABS shells in automotive interior door panels, for the lamination of ABS/PVC film to treated polypropylene foam for use in automotive instrument panels, as metal primers for steering wheels, in flexible packaging lamination, as shoe sole adhesive, and as tie coats for polyurethane-coated fabrics. PMDI is also used as a binder for reconstituted wood products and as a foundry core binder.

Polyurethane sealant formulations use TDI or MDI prepolymers made from polyether polyols. The sealants contain 30–50% of the prepolymer; the remainder consists of pigments, fillers, plasticizers, adhesion promoters, and other additives. The curing of the sealant is conducted with atmospheric moisture. One-component windshield sealants utilize diethyl malonate-blocked MDI prepolymers (46). Several polyurethane hybrid systems, containing epoxies, silicones, or polysulfide, are also used.

The largest segment of the CASE family of polyurethanes are elastomers. Cast polyurethane elastomers reached a new dimension when high pressure impingement mixing led to reaction injection molding (RIM). This technology is used widely in the automotive industry, and reinforced versions (RRIM) and structural molded parts (SRIM) have been added in more recent years.

Polyurethane elastomers are either thermoplastic or thermoset polymers, depending on the functionality of the monomers used. Thermoplastic polyurethane elastomers are segmented block copolymers, comprising of hard- and soft-segment blocks. The soft-segment blocks are formed from long-chain polyester or polyether polyols and MDI; the hard segments are formed from short-chain diols, mainly 1,4-butanediol, and MDI. Under ambient conditions the higher melting hard segments are incompatible with the soft segments, and microphase separation occurs. The hard segments aggregate into crystalline domains, in which hydrogen bonding of the -NH- groups of the urethane chain bond to neighboring carbonyl groups. Upon melting, the crystalline domains are disrupted and the polymer can be processed.

Polyester and polyether diols are used with MDI in the manufacture of thermoplastic polyurethane elastomers (TPU). The polyester diols are obtained from adipic acid and diols, such as ethylene glycol, 1,4-butanediol, or 1,6-hexanediol. The preferred molecular weights are 1,000 to 2,000, and low acid numbers are essential to ensure optimal hydrolytic stability. Also, caprolactone-derived diols and polycarbonate diols are used. Polyether diols are mainly poly(tetramethylene glycol) (PTMG), but polyalkylene oxide-derived diols are also used. TPUs contain wax to aid in mold release and diatomaceous silica for added slip and as antiblocking agents in films. Antioxidants (hindered phenols or hindered amines) and uv-stabilizers (benzotriazoles) are also added to improve the environmental resistance.

Thermoset polyurethanes are cross-linked polymers, which are produced by casting or reaction injection molding (RIM). For cast elastomers, TDI in combination with 3,3'-dichloro-4,4'-diphenylmethanediamine (MOCA) are often used. In the RIM technology, aromatic diamine chain extenders, such as diethyltoluenediamine (DETDA), are used to produce poly(urethane ureas) (47), and replacement of the polyether polyols with amine-terminated polyols produces polyureas (48). The aromatic diamines are soluble in the polyol and provide fast reaction

rates. In 1985, internal mold release agents based on zinc stearate compatibilized with primary amines were introduced to the RIM process to minimize mold preparation and scrap from parts torn at demold. Some physical properties of RIM systems are listed in Table 6.

Polyurethane engineering thermoplastics are also manufactured from MDI and short-chain glycols (49). These polymers were introduced by Upjohn/Dow under the trade name Isoplast. The glycols used are 1,6-hexanediol and cyclohexanedimethanol. 1,4-Butanediol is too volatile at the high processing temperatures used in the reaction extrusion process. Blends of engineering thermoplastics with TPU are also finding uses in many applications (50).

Segmented elastomeric polyurethane fibers (Spandex fibers) based on MDI have also been developed. Du Pont introduced Lycra in 1962. The generic name Spandex fibers designates elastomeric fibers, in which the fiber-forming substance is a long-chain polymer consisting of > 85% of polyurethane (see FIBERS, ELASTOMERIC). Extenders used in Spandex fibers include hydrazine and ethylenediamine. Du Pont uses a dry-spinning process, in which the polymer solution in dimethylformamide (DMF) is extruded through a spinnerette into a column of circulating hot air. Wet-spinning processes are also used, in which isocyanate-terminated prepolymers are extruded into a nonaqueous diamine bath.

6. Economic Aspects

6.1. Elastomers. The United States, Western Europe, and Japan are currently the major producers and consumers of polyurethane elastomers. In 2001, an estimated 581×10^3 t were consumed in these areas (51).

Western Europe accounted for 60% of consumption in 2002. The United States is the next largest regional consumer. The largest percentage of its consumption is for cast elastomers. Japan's consumption is dominated by thermoset polyurethanes (TPUs).

The polyurethane elastomer market is dominated by the major suppliers of raw materials and prepolymers. Bayer is the recognized leader and produces or supplies all product types except millable gums.

Growth is expected to rise 2.7% through the year 2006 for the three regions.

Highest growth is expected for the United States (4%), modest growth for Europe (2.3%) and slight growth is expected in Japan (0.9%). TPU growth is expected to range from 2.8% to 5% per year with an average of 4.2% per year. Cast PU elastomer consumption is projected to grow at GDP levels, while microcellular products will show annual growth of 3.1%, 1.5% and -4.2% in the United States, Western Europe and Japan, respectively, through 2006.

6.2. Foams. On a regional basis, polyurethane foam demand is relatively close to production because trade is comparatively small. Approximately 60% of world consumption is for flexible foam (30).

Several thousand producers in the world manufacture PU foam. Most producers concentrate on flexible or rigid foam because the market and technologies are quite different. In recent years, there has been a consolidation process, primarily in the United States and Western Europe. Production capacity for both flexible and rigid foams seems to be adequate to meet demands.

Flexible foam is used primarily as a cushioning material in furniture, transportation and bedding applications. Rigid foam is utilized mainly as an insulation material in construction and refrigeration applications. Automotive seating is produced in several regions of the world.

For most of the regions of the world, demand for flexible foam is expected to grow at the rate of 2–5% from 2004 to 2009. Demand for rigid foams will grow faster than for flexible foams.

6.3. Surface Coatings. Urethane coatings have been one of the fastest-growing sectors of the worldwide paint and coatings industry. Despite high costs, their excellent durability, resistance to corrosion and abrasion, make urethane coatings suitable for a range of high performance applications. Formulations with lower organic solvents are also possible. Total world consumption in 2003 was 1.6×10^6 t. Urethane coatings account for 8% of total coatings volume, but 15% of total sales by the manufacturers (52).

Global consumption of urethane coating resins (includes only film formers made from polyols, isocyanates and/or fatty acids/oils) in 2003 was as follows: Western Europe, 34%; United States, 30.5%; Japan, 10.5%; rest of the world, 25% (52).

Certain markets are dominant in all three industrialized regions, including automotive refinishes, wood finishes and high-performance anticorrosion coatings. The fastest-growing market for urethanes in the 1990s was automotive OEM clear coat finishes. In 2003 about 10×10^6 vehicles received urethane clear coats. However, there are major differences among the regions. Urethane clear coats now account for 30% of the topcoat market in Europe and 20% in North America. In Japan, only small amounts of urethane formulations are now used for topcoats. In addition to the high cost of urethanes, environmental and regulatory pressures in Japan have not forced a switch away from the conventional solventborne low-solids acrylics. Also, in Europe, wood finishing is much more important than in the United States. Urethane powder coatings are more significant in the United States. On a global basis, consumption of urethane coating resins is forecast to grow at an average annual rate of 3%.

7. Recycling

The methods proposed for the recycling of polyurethanes include pyrolysis, hydrolysis, and glycolysis. For example, introducing pyrolysis products obtained from a mixture of plastic products into a refinery could be a viable method for the recycling of mixtures of plastics. Energy recovery from scrap polyurethanes or mixed plastic waste products by incineration is another useful recycling method. Polyurethane regrind is used extensively as fillers in a variety of polyurethane applications. For example, flexible foam powder can be used as filler (15–25%) in the molding of automotive car seats, and up to 20% of reground flexible foam can be added to virgin polyol in the manufacture of slabstock foam. Regrind from polyurethane RIM elastomers is used as filler in some RIM as well as compression molding applications. The RIM chips are also used in combination with rubber chips in the construction of athletic fields, tennis courts, and pavement of working roads of golf courses.

The use of rebound flexible foam for carpet underlay and for high load-bearing padding for furniture or for gymnasium mats is already a reality. Rebound flexible foam can also be used for sound dampening in cars. Rebounding of rigid foam particles with PMDI produces polyurethane particle boards. These boards are unaffected by water and are therefore used in furniture aboard ships. Rigid foam scrap is also used as filler in the manufacture of building products.

The most convenient chemical recycling process, pioneered by Upjohn in the 1970s, consists of glycolysis of solid polyurethane products (53). Heating of polyurethane scrap in a mixture of glycols and diethanolamine converts the cross-linked polymers into linear soluble oligomers via a transesterification process. Replacement of 10–30% of virgin polyol by glycolysate has been achieved in rigid foam production. In RIM applications only 10–15% of recycled polyol can be used (54).

8. Health and Safety Factors

Fully cured polyurethanes present no health hazard; they are chemically inert and insoluble in water and most organic solvents. However, dust can be generated in fabrication, and inhalation of the dust should be avoided. Polyether-based polyurethanes are not degraded in the human body, and are therefore used in biomedical applications.

Some of the chemicals used in the production of polyurethanes, such as the highly reactive isocyanates and tertiary amine catalysts, must be handled with caution. The other polyurethane ingredients, polyols and surfactants, are relatively inert materials having low toxicity.

8.1. Isocyanates. Isocyanates in general are toxic chemicals and require great care in handling. Oral ingestion of substantial quantities of isocyanates can be tolerated by the human body, but acute symptoms may develop from the inhalation of much smaller amounts. The inhalation of isocyanates presents a hazard for the people who work with them as well as the people who live in the proximity of an isocyanate plant. Adequate control of exposure is necessary to achieve a safe working environment. The suppliers Material Safety Data Sheets (MSDS) have to be consulted for the most current information on the safe handling of isocyanates.

Respiratory effects are the primary toxicological manifestations of repeated overexposure to diisocyanates (55). Once a person is sensitized to isocyanates, lower concentrations can trigger a response (56). Most of the industrial diisocyanates are also eye and skin irritants. Controlling dermal exposure is good industrial hygiene practice. The 1997 American Conference of Governmental Industrial Hygienists (ACGIH) exposure guideline for TDI is 0.005 ppm as a TWA-TLV (an eight-hour time-weighted average concentration); the 1997 TLV for TDI in Japan is 20 ppb.

Overexposure to TDI can cause chemical bronchitis (isocyanate asthma) in sensitized individuals. Transient acute asymptomatic changes in respiratory function and deterioration of lung function following long-term repeated exposure have also been encountered. Allergic sensitization may occur within months or after years of exposure to isocyanates. Animal studies using TDI showed no

teratologic response at exposure concentrations up to 0.5 ppm. A chronic gavage study indicated tumor formation in the animals, but the study was found to be of doubtful toxicological relevance because of the method used and the excessively high dose levels. Vapor exposure to MDI is limited by the low vapor pressure, corresponding to a saturated atmosphere of 0.1 mg/m^3 at 25°C . An acute aerosol inhalation study on PMDI using rats indicated that the 4-h LC_{50} is 490 mg/m^3 (57). The current ACGIH TLV for MDI is 0.051 mg/m^3 (0.005 ppm) as a TWA. The OSHA PEL is 0.02 ppm as a ceiling limit.

The toxicity of aliphatic diisocyanates also warrants monitoring exposure to its vapors. HDI has a moderate potential for acute systemic dermal toxicity; rabbit dermal LD_{50} is 570 mL/kg (58). However, HDI is severely irritating to the skin and eyes. Irritation, lacrimation, rhinitis, burning sensation to throat and chest, and coughing have all been reported in humans following acute inhalation exposure to HDI. HMDI has a low eye and dermal irritation potential, as well as a low potential for acute toxicity. Exposure to HMDI aerosol can cause dermal sensitization of laboratory animals. IPDI can cause skin sensitization reactions as well as eye irritation.

There are a multitude of governmental requirements for the manufacture and handling of isocyanates. The U.S. Environmental Protection Agency (EPA) mandates testing and risk management for TDI and MDI under Toxic Substance Control Administration (TSCA). Annual reports on emissions of both isocyanates are required by the EPA under SARA 313.

Thermal degradation of isocyanates occurs on heating above $100\text{--}120^\circ\text{C}$. This reaction is exothermic, and a runaway reaction can occur at temperatures $>175^\circ\text{C}$. In view of the heat sensitivity of isocyanates, it is necessary to melt MDI with caution and to follow suppliers' recommendation. Disposal of empty containers, isocyanate waste materials, and decontamination of spilled isocyanates are best conducted using water or alcohols containing small amounts of ammonia or detergent. For example, a mixture of 50% ethanol, 2-propanol, or butanol; 45% water, and 5% ammonia can be used to neutralize isocyanate waste and spills. Spills and leaks of isocyanates should be contained immediately, ie, by dyking with an absorbent material, such as saw dust.

The total U.S. airborne emission of volatile TDI is estimated by the International Isocyanate Institute (III) to be $<25 \text{ t}$, or less than 0.005% of the annual U.S. production. Published data show that TDI has a $1/3$ life of 8 s in air at 25°C and 50% rh, and a 0.5 s to 3 d half-life in water, depending on pH and agitation. Without agitation, isocyanates sink to the bottom of the water and react slowly at the interface. Because of this reactivity, there is no chance of bioaccumulation.

8.2. Tertiary Amine Catalysts. The liquid tertiary aliphatic amines used as catalysts in the manufacture of polyurethanes can cause contact dermatitis and severe damage to the eye. Inhalation can produce moderate to severe irritation of the upper respiratory tracts and the lungs. Ventilation, protective clothing, and safety glasses are mandatory when handling these chemicals.

8.3. Polyurethanes. These polymers can be considered safe for human use. However, exposure to dust, generated in finishing operations, should be avoided. Ventilation, dust masks, and eye protection are recommended in foam fabrication operations. Polyurethane or polyisocyanurate dust may present an explosion risk under certain conditions. Airborne concentrations of $25\text{--}30 \text{ g/m}^3$

are required before an explosion occurs. Inhalation of thermal decomposition products of polyurethanes should be avoided because carbon monoxide and hydrogen cyanide are among the many products present. When the foam is heated to decomposition, it emits acrid, toxic fumes of CN^- and NO_x (59).

The polyurethane industry has made significant contributions towards environmental improvements by reducing VOCs and using new blowing agents (60).

Because polyurethanes are combustible, they have to be applied in a safe and responsible manner. At no time should exposed foam be used in building construction. An approved fire-resistive thermal barrier must be applied over foam insulation on interior walls and ceilings. Model U.S. building codes specify that foam plastic used on interior walls and ceilings must have a flame-spread rating, determined by ASTM E84, of < 75 , and smoke generation of < 450 . The foam plastic must be covered with a fire-resistive thermal barrier either having a finish rating of not less than 15 min or equivalent to 12.7-mm gypsum board, or having a flame-spread rating of < 25 , smoke generation of < 450 (if covered with approved metal facing), and protection by automatic sprinklers. Under no circumstances should direct flame or excessive heat be allowed to contact polyurethane or polyisocyanurate foam. The ASTM numerical flame-spread rating is not intended to reflect hazards presented under actual fire conditions.

9. Uses

9.1. Flexible Foam. The largest markets for flexible polyurethane foam are in the furniture, transportation, bedding, carpet underlay and packaging industries. Most furniture cushioning is made of polyurethane foam, predominantly cut from slabs or buns having a density of $0.0192\text{--}0.0288\text{ g/cm}^3$. Polyurethane viscoelastic foam is used increasingly in bedding. High resiliency flexible foam having a density of 0.040 g/cm^3 is used for seat cushions in higher priced furniture. Molded flexible polyurethane foam is used in the automotive industry for seating, instrument panels, head rests, and arm rests applications. Semiflexible molded polyurethane foams are used in dashboards and door liners. Semiflexible foams are also formulated for sound and vibrational control in automotive applications (61). Other foam uses include textile laminates and interior padding. Specialty applications include reticulated foams for filtration and foams for such consumer products as sponges, scrubbers, squeegees, and paint applicators. Foams that provide radiation protection (62) and flame retardant foam that can be obtained using a general-purpose polyol (63) have been reported.

9.2. Rigid Foam. The bulk of rigid polyurethane and polyisocyanate foam is used in insulation. There has been a major demand for spray foams in the construction industry (60). The use of rigid foam continues to improve energy efficiency (60). Laminates are used for residential sheathing and board for flat-deck commercial roofing. Commercial buildings are often covered with polyurethane spray foam. Pour-in-place foam is typically integrated in large-scale assembly operations, such as aircraft carriers. Insulation of trucks, railroad freight cars and cargo containers is performed by either spray or pour-in-place techniques. Tank and pipe insulation is either sprayed or cut from bun stock.

Ships transporting liquid natural gas (LNG) are usually insulated with rigid PUIR foam laminates, which provide temperature stabilities from -180 to 150°C . The main fuel tank of the National Aeronautics and Space Administration (NASA) space shuttles is also insulated with PUIR foam. Rigid polyurethane foam is used in engineered foamed-in-place packaging of industrial or scientific equipment and in the molding of furniture, simulated-wood ceiling beams, and a variety of decorative and structural furniture components. Rigid foam is also used in movie props, for the repair of river barges, and in boat flotation applications.

9.3. CASE. The CASE marketplace covers polyurethane coatings, adhesives, sealants, and elastomers (64).

Coatings. Urethane coatings have been one of the fastest growing sectors of the worldwide paint and coatings industries (52). Polyurethane coatings are used wherever applications require abrasion resistance, skin flexibility, fast curing, good adhesion, and chemical resistance. The polyaddition process allows formulation of solvent-based or solventless liquid two-component systems, water-borne (aqueous) dispersions, or powder coatings. Polyurethane coatings are applied to products to improve their appearance and lifespan. Polyurethane coatings are used on automobile exteriors, in construction where building floors, steel trusses, and concrete supports are sprayed-coated to make them more durable and easier to clean. Coatings are used in the aerospace industry to protect external parts of aircraft from extreme temperatures, and help protect the skin from rust and pitting.

Synthetic leather products are also produced using a urethane binder. These leather-type products are used for shoes, handbags, luggage, and apparel. Leather-like sheet materials with excellent water resistance have been reported (65). Polyurethane films having oxygen and water permeability are applied in bandages and wound dressings and as artificial skin for burn victims.

Adhesives and Sealants. Polyurethane adhesives and sealants provide strong bonding and tight seals in a variety of applications. Polyurethane adhesives provide the rapid development of green strength, where the adhesive provides an initial bond before fully curing. This reduces the need for clamping and holding materials, thereby reducing costs and increasing manufacturing flexibility. Custom adhesives and sealants can be manufactured.

Adhesives are used in the assembly of shoes, automotive interiors, windshield bonding, and as textile laminates. Conveyor belts are usually closed with polyurethane adhesives. Polyurethane binders are mixed with wood chips or sawdust to form fiberboard. Sealants are used in road repair, plumbing, and construction. Polyurethane sealants provide excellent stress recovery to retain shape after being pulled or bent, are fast curing, and adhere to non-primed concrete. These sealants and adhesives can be painted to match surrounding surfaces.

Elastomers. Polyurethane elastomers are rubber-like materials that can be created with a wide variety of properties and molded into almost any shape. They can provide resistance to abrasion, impact and shock, temperature, cuts and tears, oils and solvents, aging, mold, mildew, and fungus, and most chemicals. Polyurethane elastomers are used almost everywhere. Snowplow blades are made of the elastomers to reduce road damage caused by scraping, wheels for

shopping carts, skateboards, roller coasters, and heavy trash containers made with polyurethane elastomers provide for high-load bearing capacity and abrasion resistance. Tubing and injection molded parts are used in the medical sector. Cast and RIM elastomers are used in auto fascia, bumper and fender extensions, printing and industrial rolls, industrial tires, and agricultural parts, such as oil well plugs and grain buckets. Elastomeric spandex fibers are a large market and these fibers are used in all types of hosiery, undergarments, swim wear and other sports clothing. Elastomers with improved antistatic behavior for these fibers uses have been reported (66).

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HENRI ULRICH
Consultant
Updated by Staff

Table 1. Tertiary Amine Catalysts for Flexible Foams

Name	CAS Registry Number	Structure	Activity	Application
Dabco			gelation catalysts	flexible foams
pentamethyl- dipropylene- triamine		$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2 \end{array}$	balanced blow and gelation catalyst	cold-cure HR foams
bis(dimethyl- amino ethyl ether)		$(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$	blowing catalyst	slabstock foam
pentamethyl- diethylene- triamine		$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{N}-(\text{CH}_2)_2-\text{N}-(\text{CH}_2)_2 \end{array}$	blowing catalyst	semi- flexible foam
DBU ^a			heat- activated catalyst	molded foam
dimethylcy- clohexyla- mine	[98-96-2]		balanced gelation and blowing catalyst	slabstock foam

^aPhenol salt.

Table 2. Macrodiols for Thermoplastic Polymethane^a

Polyol	T_g , °C	T_m , °C
poly(propylene glycol) (PPG)	-73	
poly(tetramethylene glycol) (PTMG)	-100	32
poly(1,4-butanediol adipate)	-71	56
poly(ethanediol-1,4-butanediol adipate)	-60	17(37)
polycaprolactone	-72	59
poly(1,6-hexanediol carbonate)	-62	49

^aMol wt = 2000.

Table 3. Properties of Commercial Diisocyanates


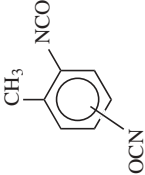
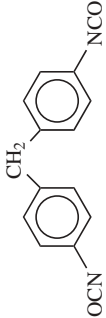
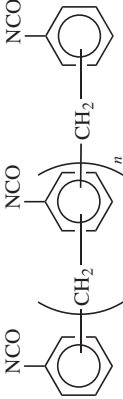
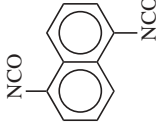
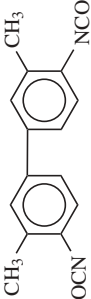
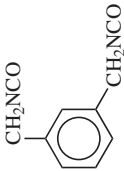
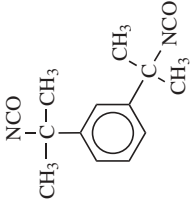
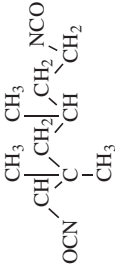
Name	Acronym	CAS Registry Number	Structure	Bp, °C _{kPa} ^a	Mp, °C	Producer
<i>p</i> -phenylene diisocyanate	PPDI	[104-49-4]		110–112 _{1,6}	94–96	Akzo, Du Pont
toluene diisocyanate	TDI	[1321-38-6]		121 _{1,33}	14 ^b	BASF, Bayer, Eni-chem, Dow, Olin, Rhone-Poulenc, Mitsui
4,4'-methylenebis-(phenylisocyanate)	MDI	[101-68-8]		171 _{0,13}	39.5	BASF, Bayer, Dow, Eni-chem, ICI, Mitsui
polymethylene polyphenylisocyanate	PMDI	[9016-87-9]				BASF, Bayer, Dow, Eni-chem, ICI, Mitsui
1,5-naphthalene diisocyanate	NDI	[3173-72-6]		244 _{0,017}	130–132	Bayer, Mitsui

Table 3. (Continued)

Name	Acronym	CAS Registry Number	Structure	Bp, °C _P ^a	Mp, °C	Producer
bitolylene diisocyanate	TODI	[91-97-4]		160–170 _{0.066}	71–72	Nippon-Soda
<i>m</i> -xylylene diisocyanate	XDI	[3634-83-1]		159–162 _{1.6}		Takeda
<i>m</i> -tetramethylxylylene	TMXDI	[58067-42-8]		150 _{0.4}		American Cyanamid
hexamethylene diisocyanate	HDI	[822-06-0]	OCN(CH ₂) ₆ NCO	130 _{1.73}		Bayer, Olin
1,6-diisocyanato-2,2,4,4-tetramethylhexane	TMDI	[83748-30-5]		149 _{1.33}		Rhône Poulenc, Mitsui, Hüls

1,6-diisocyanato-2,4,4-trimethylhexane	TMDI	[15646-96-5]			
<i>trans</i> -cyclohexane-1,4-diisocyanate	CHDI	[2556-36-7]		122–124 _{1,6}	Akzo
1,3-bis(isocyanatomethyl)cyclohexane	HXDI ^c	[38661-72-2]		98 _{0,053}	Takeda
3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate	IPDI	[4098-71-9]		153 _{1,33}	BASF, Bayer, Hüls, Olin
dicyclohexylmethane diisocyanate	HMDI ^c	[5124-30-1]		179 _{0,12}	Bayer

^aTo convert kPa to mm Hg, multiply by 7.5.

^bMixture of 80% 2,4-isomer [584-84-9] and 20% 2,6-isomer [91-08-7].

^cMixture of stereoisomers.

Table 4. Commercial Polyether Polyols

Product	Nominal functionality	Initiator ^a	Cyclic ether ^b
poly(ethylene glycol) (PEG)	2	water or EG	EO
poly(propyleneglycol) (PPG)	2	water or PG	PO
PPG/PEG ^c	2	water or PG	PO/EO
poly(tetramethylene glycol)	2	water	THF
glycerol adduct	3	glycerol	PO
trimethylolpropane adduct	3	TMP	PO
pentaerythritol adduct	4	pentaerythritol	PO
ethylenediamine adduct	4	ethylenediamine	PO
phenolic resin adduct	4	phenolic resin	PO
diethylenetriamine adduct	5	diethylenetriamine	PO
sorbitol adduct	6	sorbitol	PO/EO
sucrose adduct	8	sucrose	PO

^aEG = ethylene glycol; PG = propylene glycol.^bEO = ethylene oxide; PO = propylene oxide; THF = tetrahydrofuran.^cRandom or block copolymer.

Table 5. **Typical Rigid Polyurethane Panel Formulation^a**

Ingredients	Parts
PMDI	135.0
polyol	98.0
water	1.9
catalyst	2.0
surfactant	2.0
HFC 134a	17.0

^aRef. 32.

Table 6. Properties of RIM Systems

Properties	Flexural modulus, MPa ^a		
	0.137–0.517	0.517–1.03	1.37–2.75
elongation at break, %	100–300	50–200	< 50
Izod impact, J/m ^b	534–801	267–801	< 267
impact strength	high	medium high	low
material description	elastomer	pseudo-plastic	plastic
automotive application	fascia	fender	hood or deck lid

^aTo convert MPa to psi, multiply by 145.^bTo convert J/m to ft·lb/in., divide by 53.38.

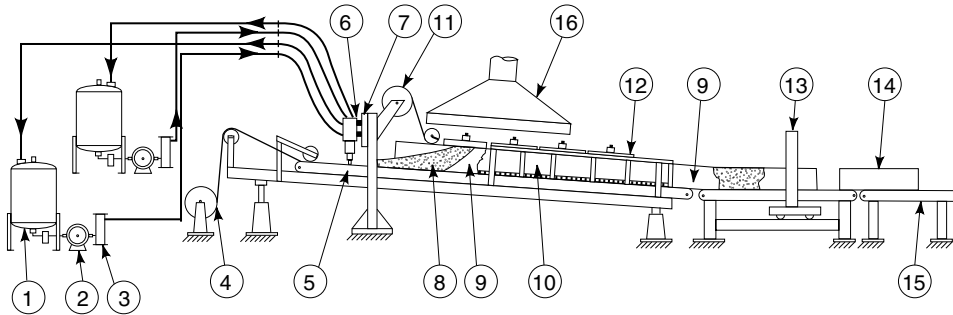


Fig. 1. Rigid bun foam line: 1, material tank with agitators; 2, metering pump; 3, heat exchanger; 4, bottom paper roll; 5, conveyor; 6, mixing head; 7, traverse assembly; 8, rising foam; 9, side paper; 10, adjustable side panels; 11, top paper roll; 12, top panels with adjustable height; 13, cutoff saw (traversing); 14, cut foam bun; 15, roller conveyor; 16, exhaust hood.

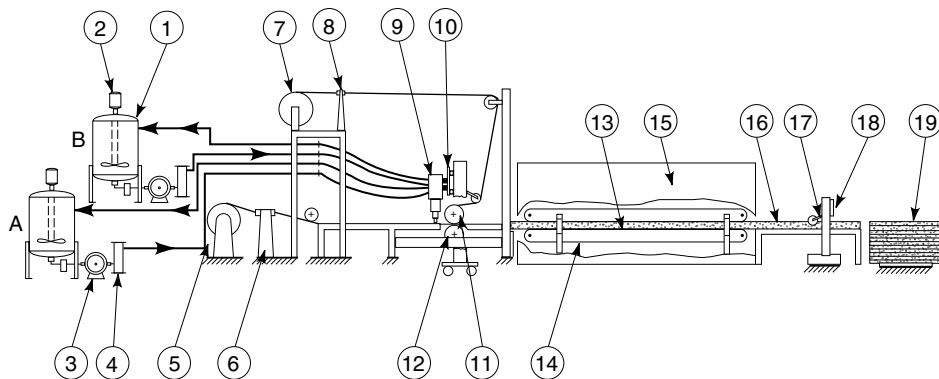


Fig. 2. Rigid foam laminating line: 1, material tank; 2, agitator; 3, metering pump; 4, heat exchanger; 5, bottom facer roll; 6, bottom facer alignment device; 7, top facer roll; 8, top facer alignment device; 9, mixing head; 10, traverse assembly; 11, top nip roll; 12, bottom nip roll; 13, take-up conveyor top belt with adjustable height; 14, take-up conveyor bottom belt; 15, curing oven; 16, laminate; 17, side-trim saws; 18, cutoff saw (traversing); 19, laminated-panel stack and packaging.