



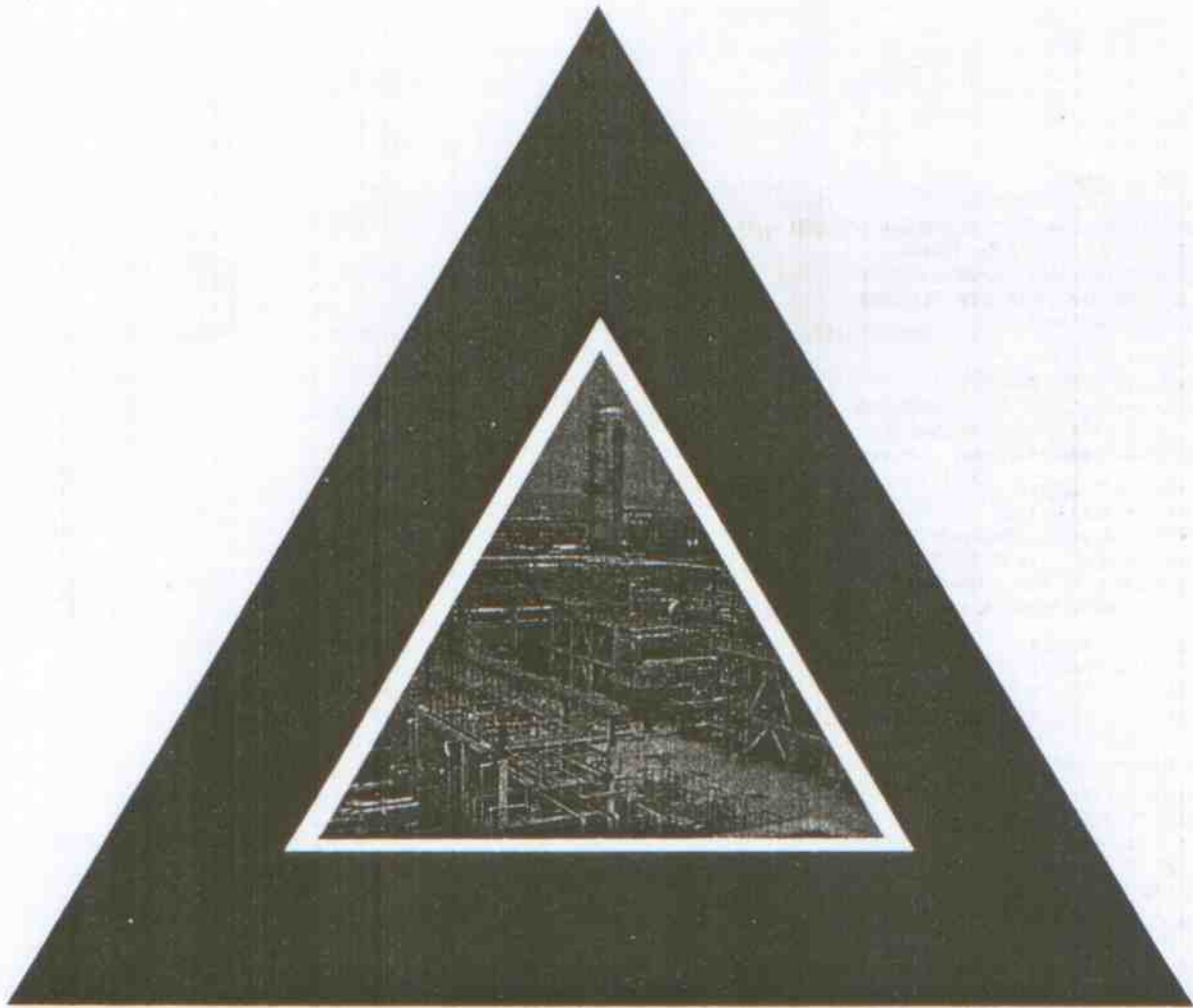
# POLYURETHANES

INDIA

(The official house magazine of Polyurethane Association of India)

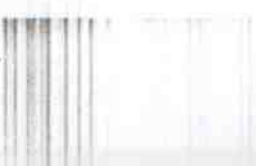
Vol. 23

October – December 2001



**2001 – SAFETY YEAR**

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## FIRE RETARDANT STUDIES ON POLYURETHANE FOAMS

AT

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### INTRODUCTION

Polyurethane was first time described by Prof. Otto Bayer of Germany in 1937. Besides Otto Bayer, A. Hoechtlen, P. Hoppe and E. Meinbrenner had combined the description of the polyurethanes on the scientific basis and their analysis with potential application areas and corresponding market volumes for this new material. Rinke and collaborators were successful to form a low viscosity melt which resulted in what now known as polyurethane. Rinke and associates were awarded the first US Patent on Polyurethanes in 1938.

The basic technology for the commercial production of flexible polyester foams was developed in Leverkusen (Germany) from 1952 to 1954. At that time, all commercial applications of polyurethanes were based almost exclusively on polyester polyols. Polyether polyols were first introduced in 1957. Because of technical and commercial advantages these new polyols rapidly gained the preferred role in polyurethanes. The immense variability in the preparation and structure of polyether polyols was responsible in achieving an invaluable broadening of the property spectrum of polyurethanes at considerably lower cost. From that time the gradually growing interest in polyurethanes gained ground in the world. Thus from these humble beginnings emerged the polyurethanes, one of the most versatile polymers in the modern cellular plastics industry.

### BASIC CONCEPT IN POLYURETHANE FOAM CHEMISTRY

Polyurethanes are extremely large and complex molecules produced by combining a large number of simpler molecules called monomers. But actually polyurethanes are neither derived from polymerizing

a urethane monomer nor they are polymers containing primarily urethane groups. The polyurethanes include those polymers containing a plurality of urethane groups in the molecular backbone regardless of the chemical composition of the rest of the chain. Thus a typical polyurethane foam structure may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, biuret, allophanate, isocyanurate, uretidione and carbodimide groups.

Polyurethane foams are microcellular cross-linked, thermoset duroplastic structure. The chemical formulations of polyurethane foams are based on the following ingredients.

- ❖ Polyol
- ❖ Isocyanate
- ❖ Catalysts
- ❖ Water
- ❖ Blowing agent
- ❖ Surfactant
- ❖ Pigment
- ❖ Additives

The chemistry of polyurethane makes use of the reactions of organic isocyanates with compounds containing at least two active hydrogen atoms. When polyfunctional isocyanates and intermediates containing at least two active hydrogen atoms per mole reacted at proper ratios and under certain conditions of temperatures, catalysts etc., a polymer results that can produce flexible or rigid foams. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkages. The isocyanate and polyol reaction is catalysed by organotin catalyst. The isocyanates also react with water to form carbamic acid which is unstable intermediates and decomposes readily to evolve carbon dioxide and an amine. This carbon dioxide acts as blowing agent during the formation of

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polyurethane foams. The maximum expansion of polyurethane foam i.e. 80% is controlled by the carbon dioxide itself and remaining 20% expansion is controlled by the addition of external foaming agents. This important isocyanate-water reaction is catalysed by tertiary amine compound. The amine formed during the isocyanate-water reaction, reacts with additional isocyanate to form disubstituted urea. In addition, a number of cross-linking side reactions may also take place, depending upon the reaction conditions such as temperature, the presence of catalysts, the structure of the isocyanate, polyols and amines involved. These reactions form linkages of biuret (reaction between substituted urea and isocyanate), allophanate (reaction between urethane-isocyanate). Isocyanate also undergoes self-addition reaction to form isocyanurate (trimerisation of isocyanate group), uretidinedione and carbodimide (dimerisation of isocyanate groups). Isocyanurate and carbodiimide linkages provide improved thermal stability and flammability performance to polyurethane foams to a certain extent. The important chemical reactions take places during polyurethane foam formation have been illustrated in Figure 1.

The types of polyurethane foams are classified as flexible foam, semiflexible foam, reticulated foam, microcellular foam, high resiliency foam, semi rigid foam and rigid foam. The polyurethane foams are generally manufactured in three ways i.e. slab stock foam, moulded foam and sprayed foam by using three basic approaches. In the one shot process, all the components are combined at one time to produce foam and the reaction is completed in one shot. In the quasi-prepolymer approach part of the polyol to be used in the formulation is pre-reacted with all of the isocyanate. The resultant product is isocyanate terminated prepolymer having free isocyanate contents between 16 and 32 percent by weight. Foams are prepared by adding rest of the foam ingredients along with remaining polyol. In the prepolymer foaming process, the hydroxyl compound is reacted with an excess of isocyanate to form an isocyanate-terminated prepolymer with free isocyanate contents of 1 to 15 percent by weight. But out of these three methods, the one shot process is

most important and used maximum today because it provides the fastest, simplest and most economical manufacturing technique. These are the reasons which often favour its use in highly competitive commodity fields such as flexible foam.

#### POLYURETHANE MARKETS AND APPLICATIONS

The worldwide demand for polyurethane foams is estimated about 5% of total world consumption of plastics. Polyurethane foams are considered to be a special product ahead of other commodity plastics in overall volume. The polyurethane foams market is increasing at a rate of close 6% per year. Figure-2 presents the break down of polyurethane usage; as the figure indicates, the majority of polyurethanes are used in the production of flexible foam and followed by rigid foam. The maximum Consumption of polyurethane foams is in North America which is estimated around 32 percent.

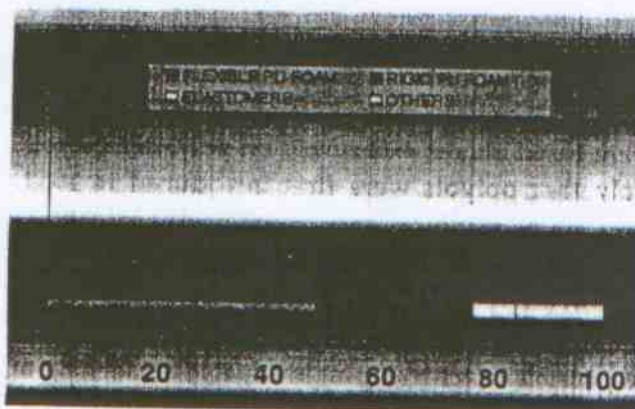


FIGURE 2. WORLDWIDE CONSUMPTION OF POLYURETHANE FOAMS

The wide spectrum of properties, simple fabricating techniques and attractive cost are the important factors which have led to the manifold use of polyurethane foams. Some of the important applications of flexible polyurethane are as under.

**Furniture Cushioning** is one of the large outlets estimated about 40% for flexible polyurethane foam. Lighter weight, greater strength, and ease of fabrication of up holstered furniture as compared to latex foam are some of the deciding factors in its success. Seating furniture in which polyurethane flexible foam is used as the sole cushioning materials

has attained increasing importance over the year. Improved molded techniques of flexible foam are responsible for its acceptance in furniture industry with unusual shapes.

**Mattresses** of polyurethane flexible foam are being produced in large quantities every year. Thus about 25% foam is being consumed in the form of bedding and mattresses. They have found acceptance because of their high air permeability, superior durability, odourless, nonallergenic properties, ease of cleaning, resistant to dry cleaning solvents and the fact that they are only one fourth of the weight of a comparable innerspring and one half to one third the weight of latex foam.

**Transportation** area is the third major consumer of polyurethane flexible foam i.e. 20% of the production is being consumed due to the requirement for improved safety and increased comfort. Because vehicle seats are often occupied for hours at a time it is necessary to provide the seats for adequate air permeability and humidity. Proper contouring of the seating surface is especially important since perspiration occurs primarily on the surface touched. Thus the main use of flexible foam in the automotive industry (automobiles, airplanes and rail cars) for seat cushioning, instrument panel trim, safety pads, arm rests, floor mats, roof insulation, weather stripping and air filters etc. The low weight of foam is of special interest in equipping airplanes.

About 6% of flexible foam is used as a **bonding material for fabric** specially in the fabrication of apparel due to more favorable melting characteristics of foam required for flame lamination technique. Foam lining for the garments makes the fabric dimensionally stable and provide high insulating properties. Other advantages include excellent hand drape and outstanding crease and wrinkle resistance.

Another important area for flexible polyurethane foams is in **carpet underlay**. The interior decoration of rooms in the living areas with carpeting is increasingly leading to the use of carpet underlay where they provide cushioning, non-skiddy surface, heat and sound insulation.. Flexible polyurethane foams in the form of sponges find their use in the household goods of window cleaner, pot scrubbers,

cleaning brushes and are usually combined with other materials.

The second largest foam use in today is **polyurethane rigid foam**. The rigid foam is used as insulation and structural material and some times a combination of both. The insulating efficiency of rigid foam is unsurpassed. A mere 2 inch of rigid polyurethane foam is equivalent in its insulating capacity at ambient temperature to 3 inch of polystyrene foam, 3.5 inch of mineral wool, 4 inch of cork, 6 inch of glass fibre mat, 11 inch of wood or 30 inch of cemented concrete blocks. Due to great insulation and structural capacity this foam find many applications and some of them are as under:

One of the major uses of rigid polyurethane foam is in **Refrigeration Technology and Appliances** such as refrigerators and freezers, commercial display cases, refrigerated trucks (milk trucks, ice-cream trucks and trailers) and container, refrigerated warehouses and walk-in-coolers and water heaters.

Potentially, the biggest market for rigid polyurethane foam is in the **Building Construction and Industry** in the form of insulation boards (flat roofs, ventilated roofs, pitched roofs, ventilated facades, thermowall system, interior walls, floors and ceilings), sandwich elements, specialty elements (sanitary walls, bathrooms and window sills), PU light weight concrete, wall blocks with integrated insulation, curtain wall construction, preformed rigid panels and spray-applied wall construction. The market for these includes residential homes, commercial and industrial buildings such as large refrigerated warehouses. The other important uses of polyurethane rigid foam are **technical insulation** (pipe insulation and insulation of tanks), **automotive industry** (interior liners and cavity foaming), **transportation** (refrigerated vehicles, insulation for transportation of special products and caravans and mobile homes), **shipbuilding** (foaming of cavities, insulation of cold storage holds in fishing boats, boat building), **Packaging** (direct encapsulation, transportation protection in vehicles and sandwich-card board boxes), **horticulture**, **sporting goods**, **furniture**, **solar technology** and **radomes**.

The utility and versatility of polyurethane foams

have resulted in their introduction into a wide variety of Markets, and their widespread acceptance has made them significant materials in many applications in which fire hazard is an important consideration. Because polyurethane foams, like most organic materials, tend to be combustible hence care has to be taken to render them flame retardant. Thus flammability of polyurethane foams has long been a factor limiting their greater use.

#### COMBUSTION OF POLYURETHANE FOAMS

Polyurethane foams have highly cellular structures, which are easily ignitable and highly flammable, flame spread is very fast on the surface of these materials and results in engulfing the entire area in a few minutes. The burning process of polyurethane foams may be considered as occurring in five stages:

- ❖ Heat from external source is applied to foam progressively raising its temperature. The thermal insulation properties of foam promote a rapid temperature rise at the exposed surface because heat can not be easily transmitted to the lower layer of foam.
- ❖ The polyurethane foam reaches its temperature of initial decomposition and begins to form combustible gases, non-combustible gases, entrained solid particles and carbonaceous char. The evolution of gases expand the foam structure and thus combustible and non-combustible gas both cause difficulty by disrupting the chemical and physical structure of foam, exposing new surfaces to destructive temperatures.
- ❖ The resulting combustible gases ignite in the presence of sufficient oxygen and further combustion begins. The condition of ignition depends on the presence of an external source of ignition and the temperature and composition of the gas phase.
- ❖ The heat of combustion raises the temperature of the gaseous products of combustion and of the noncombustible gases results increasing heat transfer by conduction.
- ❖ The heat transferred from the combustion zone to adjacent foam surface produces further

decomposition and ignition, resulting in flame propagation.

#### SMOKE AND TOXICITY OF POLYURETHANE FOAMS

The thermal decomposition products of polyurethane foams vary with polymer composition, temperature level, rate of temperature rise, endotherms, exotherms and rate of volatile evolution. When polyurethane foams involved in fire, there is concern that the nitrogen contents of these foams may be released as toxic and deadly poisonous gases at different temperature stages. At low temperatures (200 - 300°C) there is a rapid and complete loss of the isocyanate unit of each foam as a volatile smoke leaving a polyol residue. The black dense smoke is stable at temperatures up to 750°C. At about 800°C the rapid decomposition of foams takes place with the evolution of hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile. Besides these nitrogenous gases some other gases and gaseous compounds are also evolved such as carbon monoxide, ethylene, ethane, propane, butadiene, propionitrile, acetaldehyde, methylacrylonitrile, benzene, pyrrole, toluene, methyl pyridine, methyl cyanobenzene, naphthalene, quinoline, indene, carbondioxide and water vapours. At 35% weight loss of polyurethane foam, all the nitrogen-containing compounds get evaporated. At 900°C, hydrogen cyanide and benzonitrile are predominant and at 1000°C, hydrogen cyanide is virtually the only product. At 1000°C, approximately 70% of the available nitrogen of the foam has been recovered as hydrogen cyanide.

Among all the above gases evolved during thermal decomposition of polyurethane foam, carbon monoxide and hydrogen cyanide are lethal. Carbon monoxide is colourless, odourless and not detectable at all by the senses. The toxicity of carbon monoxide is mainly due to its affinity towards haemoglobin (Main structural protein of blood). Haemoglobin has 200-300 times more affinity for carbon monoxide than for oxygen. Carbon monoxide, when breathed in along with air, is absorbed by the blood depriving it of its oxygen carrying capacity. Hence, carbon monoxide readily reacts with haemoglobin to form carboxyhaemoglobin a stable compound resulting

