Polyurethane Chemistry and Products:
Past, Present and Future

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Agenda

- Polyurethane Chemistry Introduction
- Applications – Chemistry and Socioeconomic Impact
- Innovation in PU Chemistry
- Polyurethane (Isocyanate) Emissions and Degradation
- Health and Safety Considerations
- Summary
Introduction

Otto Bayer
DR Patent 11.11.1937

Commercial Isocyanates in the Polyurethane Industry

- Aromatic
  - TDI, MDI Monomers
  - pMDI (polymeric MDI)

- Aliphatic
  - HDI, IPDI, H₁₂MDI Monomers
  - HDI and IPDI homopolymers
Isocyanate Reaction Pathways

Monomeric Diisocyanate Relative Reactivity

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>$k_1$</th>
<th>$k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDI</td>
<td>400</td>
<td>33</td>
</tr>
<tr>
<td>MDI</td>
<td>320</td>
<td>110</td>
</tr>
<tr>
<td>HDI</td>
<td>1</td>
<td>0.50</td>
</tr>
<tr>
<td>H$_2$MDI</td>
<td>0.57</td>
<td>0.40</td>
</tr>
<tr>
<td>IPDI</td>
<td>0.62</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Relative volatility of isocyanate types

- HDI Isocyanurate trimer: 0.00052
- HDI Biuret: 0.93
- Monomeric MDI: 1
- Polymeric MDI: 1
- $\text{H}_2\text{MDI}$ diisocyanate: 1
- IPDI diisocyanate: 48
- HDI diisocyanate: 1,100
- TDI diisocyanate: 2,500
- Water: 1,800,000
- Solvent (methyl ethyl ketone): 9,100,000
- Methyl isocyanate: 34,800,000

Polymeric MDI Composition

Polymeric MDI is a mixture of isomers and oligomers with an average functionality of 2.7 and 31.5% NCO groups.
**Polymeric Aliphatic Isocyanates**

- Biuret
- Trimer Isocyanurate
- HDI
- Asymmetric Trimer Iminoxadiazindione
- Dimer Uretdione
- Allophanate

**Aliphatic Polyisocyanate Oligomers**

**Typical Oligomer Breakdown**

- \( n = 1 \): <0.01%
- \( n = 3 \): ~50%
- \( n = 5 \): ~20%
- \( n = 7 \): ~10%
- \( n = 9 \): ~6%
- \( n > 9 \): ~14%
- \( n = \) oligomer #

*Product contains fractions of trimers, pentamers, heptamers, and higher oligomers.
Chemistry introduction
Unparalleled Versatility and Utility

Segmentation: Chemistry is the key!
• Hard and soft segments
• Polyols to give crystalline or amorphous properties

Hydrogen bonding in Urethane Linkages:
• acts as non-covalent “crosslinking”
• Vital to good elastomeric properties

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Polyurethane Application Versatility

Polyurethane Foam Cell Formation

Bubbles grow but do not touch at this stage; the PU is microcellular.

Carbon dioxide separates from reacting phase and diffuses into nucleation points.

Mixed liquids with nucleating air.

Bubbles touch to form cell windows.

Closed cell foam.

Interconnecting labyrinth.

Open cell foam.
Rigid PU Foam Chemistry

- Polyols
  - Low MW
  - High Functionality
- pMDI – highly branched
- Structure
  - Highly crosslinked
  - Rigid
  - Small closed cell traps gases
  - Thermal insulation

Flexible PU Foam Chemistry

- Polyether Polyols
  - Vary MW and functionality
- TDI diisocyanate
  - Lower crosslink density than rigid
- Water reaction produces Carbon Dioxide as the principle method of expanding the foam
- Additives controls
  - Reactivity
  - Cell size and breathability
  - Flammability
  - Color
- High Resiliency Foam – Memory Foam
  - Hybrid of Rigid and Flexible
Coatings Technology
Wide Variety of application techniques and markets

Solventborne
1 Component
-Moisture cure
-Blocked Iso

2 Component
-Polyol
-Crosslinker

1 Component
-Moisture cure
-Blocked Iso

2 Component
-Polyol/urea
-Crosslinker

2 Component
-Polyurethane Dispersion
-Crosslinker

1 Component
-Polyurethane Dispersion

Crosslinking improves properties
Abrasion
Chemical
Weathering
Strength

Waterborne

Crosslinking improves properties

Thermoplastic Polyurethane (TPU)

Aromatic Isocyanate
Polyether

Hydrolysis Resistance
Fungus & Moisture Resistance
Cold Temperature Flexibility
Resistant to Salt Water Cracking
Ozone Resistance
Better Transparency

Aliphatic Isocyanate
Polyester

Cut & Scratch Resistance
Superior Wear Resistance
Higher Mechanical Properties
Fuel & Oil Resistance
Heat Stability
Better Inherent UV Stability

Non-yellowing
UV resistance
Socioeconomic Impact of Polyurethanes in the US*

- The PU Industry directly generates $19.7 B in output and 37,700 jobs
- Multiplier effect impacts jobs and output in downstream industries:
  - Additionally, the PU industry indirectly supports $40.1 B in output and 165,000 jobs
  - In total: $59.9 B in output and 202,600 jobs
- PU products are used in industries generating $245.5 B in output and employing nearly 1 million workers

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**The Economic Impact of the Polyurethane Industry in 2010**, Economics & Statistics Department of the American Chemistry Council

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**Historical Development: Isocyanates and Polyurethane Technologies**

- **1930’s** Isocyanates/urethanes developed by Otto Bayer
- **1940’s** Addition to alkyds to improve quality/productivity
- **1950’s** Commercialization of Flexible Foam (TDI/Polyester)
- **1960’s** Development of aliphatic polyurethane coatings PMDI for rigid foams
- **1970’s** Aqueous polyurethane dispersions (PUDs) Elastomers, Footwear, High Resilience Flex Foam Urethane acrylate resins
- **1980’s** Two component (2K) urethane coatings Spray foam building insulation Automotive energy absorption for passenger safety
- **1990’s** 2K waterborne coatings Hydrophilic polyisocyanates and functional PUDs Commercialization of visco-elastic memory foam Radiation curable PUDs
- **2000’s** 2K WB PUR with excellent chemical resistance Co-solvent free PUD/acrylic dispersions

**Rigid PUR / PIR Insulation Foams Innovation Drivers**
Innovation Driver in Coatings Applications

1960

Enable Waterborne system

2010

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Polyurethane Application/Use Considerations
- Aerosolizing

• Processes involve spray applications (e.g., foam and coatings) can generate airborne monomeric and polymeric isocyanate aerosols

• Monomeric isocyanate vapor pressures influence potential airborne concentrations:
  - the more volatile isocyanate monomers (e.g., TDI and HDI) have a greater potential to release airborne concentrations than the less volatile isocyanate monomers (e.g., MDI and H_{12}MDI)

Polyurethane Application/Use Considerations
– Thermal Degradation

• Releases of airborne isocyanate can occur when a polyurethane product is thermally degraded
• Polyurethane, like all organic material, will burn when supplied with sufficient heat and air
• When a fire occurs the gases produced depend upon the temperature, the amount of oxygen and some catalytic effects.
• In a fire situation typical off-gases of PUR include:
  – Carbon dioxide, carbon monoxide and carbon (soot)
  – Water
  – Nitrogen oxides (NO_{2}, N_{2}O, N_{2}O_{5}) commonly referred to as NOx
  – Hydrogen cyanide
  – Isocyanates
• Other plastics and wood emit similar gases when burned
Polyurethane Products in Fires: Acute Toxicity of Smoke and Fire Gases*

- Toxic effluents in fires are influenced by multiple factors.
- Combustible materials (synthetic or man-made) generally produce toxic products when burned.
- Carbon monoxide is the most prevalent and abundant toxicant in fires involving natural products and synthetic materials under most combustion conditions.
- The acute toxicity of natural and synthetic materials (including polyurethanes) appears to be more similar than different.


Thermal Degradation of Car Paint in Body Shop Repair*

- Generation of airborne isocyanates was identified during cutting, grinding, and sanding operations in Body Repair Shops.
- Highest levels of airborne isocyanates were seen during the cutting process.

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- HDI diisocyanate 1,100
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- Methyl isocyanate 34,800,000
Health and Safety Considerations

- Exposure Routes
  - Inhalation, Dermal, Eye, Ingestion
- Hazard communication
  - MSDS and Label Review
  - Safe Use & Handling Literature Review
  - Workplace Training
- Best Practices:
  - Routine Air Monitoring
  - Appropriately designed ventilation; particularly local exhaust ventilation
  - Proper use of personal protective equipment (PPE)
  - Effective workplace practices or housekeeping standards
  - Medical Surveillance

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- PUR chemistry offers versatility and unique properties to meet various application requirements
- PUR chemistry contributes to sustainability by directly impacting reduced energy usage and solvent levels, while extending product life
- Similar to other chemicals, isocyanates used in the polyurethanes industry are reactive chemicals that need to be handled in a safe manner. Such that:
  - There is a need for appropriately designed ventilation, proper use of personal protective equipment (PPE), and effective workplace practices/housekeeping standards
  - Safe use and handling of isocyanates should be achieved in accordance with the principals of Product Stewardship and Best Industry Practices.

Backup
Polyurethane Products in Fires: Acute Toxicity of Smoke and Fire Gases

Table 1.
Average LC50 values with 95% confidence limits (g/m³) and sample size in small-scale combustion tests.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Well-ventilated Combustion</th>
<th>Ventilation-limited Combustion</th>
<th>Oxidative Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LC50 (g/m³)</td>
<td>Sample Size</td>
<td>LC50 (g/m³)</td>
</tr>
<tr>
<td>Polyurethane, flexible</td>
<td>35.4 (21.8-38.9)</td>
<td>18</td>
<td>20.4 (16.0-24.9)</td>
</tr>
<tr>
<td>Polyurethane, rigid</td>
<td>13.0 (11.6-14.5)</td>
<td>12</td>
<td>25.9 (15.8-35.2)</td>
</tr>
<tr>
<td>Polyester fabric,</td>
<td>41.0 (30.5-55.9)</td>
<td>1</td>
<td>(no data reported)</td>
</tr>
<tr>
<td>Polyurethane foam</td>
<td>46.2 (34.8-45.1)</td>
<td>14</td>
<td>(no data reported)</td>
</tr>
</tbody>
</table>

Thermoplastic Polyurethane (TPU)

TPU is a multi-phase block-copolymer made from three raw materials:

Raw Materials: \( \text{HO}_{\text{OH}} + \text{OCN} - \text{R} - \text{NCO} + \text{HO}_{\text{OH}} \)

Polyster Block:

\[
\begin{array}{ccc}
\text{O} & \text{II} & \text{O} \\
\text{- CHN} & \text{- R} & \text{- NHC} - \text{O}_{\text{OW}} & \text{O}_{\text{II}} \\
\end{array}
\]

Soft segment

Hard segment

Multiphase Domain Structure:

Hard Segment: Imparts rigidity, hardness, & flexural modulus characteristics and determines the upper use of temperature.

Soft Segment: Imparts elasticity, flexibility & resilience and determines the low temperature performance.
2K Solventborne Coreactants

Coreactants typically make up a majority of the polyurethane resin system strongly influencing modulus, Tg, elasticity, VOC.

- **Acrylics**
  - Fast physical dry
  - Low iso demand
  - UV resistance

- **Polyesters**
  - Chemical Resistance
  - Versatile chemistry
  - UV resistance

- **Polyethers**
  - Low cost
  - Hydrolytic stability
  - High Solids

- **Polyaspartates**
  - Weatherable
  - High Solids
  - High Productivity

- **Polyamines**
  - Rapid cure
  - High Solids
  - Chain extender

2K Solventborne Crosslinkers

- HDI Polyisocyanate
- IPDI Polyisocyanate
- HDI/IPDI Polyisocyanate blend

- Suitable for blending in 2K WB coatings
- Fast Drying Hardness
- Blends

- UV and weather resistance
- Water, chemical, solvent resistance
- Combination of hardness and flexibility
- Variations in structure and MW modify physical properties
2K Waterborne Crosslinkers

- Improved Performance
- Robust Processing
- Low Viscosity, Low VOC
- Higher Functionality
- Improved Chemical Resistance
- Improved Weather Resistance
- Easy mixing
- Isocyanurate Trimer
- Lower MW
- IPDI Polyisocyanate
- HDI Polyisocyanate
- Fast Drying (Tg)
- Chemical resistance