Imuthathane
Product family overview
The Chemistry of Polyurethane Elastomers
DEFINITION

• Chemically, Polyurethanes are polymeric materials formed by the reaction of Isocyanates and Hydroxyl groups.
A. RAW MATERIALS

POLYOLS: \( \text{HO} \quad \text{---------} \quad \text{OH} \)

DIISOCYANATES: \( \text{OCN} \quad - \quad \text{X} \quad - \quad \text{NCO} \)

CURATIVES:
- (Diols) \( \text{HO} \quad \text{-----} \quad \text{OH} \)
- (Triols) \( \text{HO} \quad \text{-----} \quad \text{OH} \)
- \( \text{H}_2\text{N} \quad - \quad \text{Y} \quad - \quad \text{NH}_2 \) (Diamines)
PREPOLYMER/ELASTOMER FORMATION
DIISOCYANANATES USED

• TDI – Most Common
• MDI- Next Most Common
• H_{12}DI- Aliphatic – Special purposes
• HDI- New Aliphatic – High Performance
Toluene Diisocyanates

80/20 2,4/2,6 TDI
65/35 2,4/2,6 TDI
2,4 - TDI
TDI POLYURETHANES

• GENERALLY CURED WITH AMINE BASED CURATIVES.
• CURING WITH POLYOLS WILL GIVE SOFTER DUROMETERS.
• LESS SENSITIVE TO WATER THAN MDI.
• SHORTER DEMOLD.
• LONGER POT LIFE.
• Milder CURE REQUIREMENTS.
MDI

Diphenylmethane -4,4 diisocyanate
Forms: Pure – Crude - Polymeric
MDI POLYURETHANES

- GENERALLY CURED WITH DIOL CURATIVES.
- HAVE LOWER ISOCYANATE ODOUR COMPARED TO SIMILAR TDI TYPES (THIS HAS CHANGED WITH LF’S).
- HIGHER RESILIENCE.
- SUPERIOR HYDROLYTIC STABILITY.
## OVERALL COMPARISON

### MDI / DIOL V TDI MBCA

<table>
<thead>
<tr>
<th></th>
<th>MDI</th>
<th>TDI</th>
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<tbody>
<tr>
<td><strong>Processing:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio Control</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Mixing</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Moisture</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Demold Time</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Cure Temperatures</td>
<td>-</td>
<td>+</td>
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<tr>
<td><strong>Health Considerations:</strong></td>
<td></td>
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<tr>
<td>Curative Concerns</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Isocyanate Exposure</td>
<td>+ (-)*</td>
<td>- (+)**</td>
</tr>
<tr>
<td><strong>Physical Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rebound</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Modulus, Tensile, Tear</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>High Temp. (Dry)</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Hydrolytic Stability</td>
<td>+***</td>
<td>-</td>
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<tr>
<td><strong>Formulation:</strong></td>
<td></td>
<td></td>
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<tr>
<td>Flexibility</td>
<td>+</td>
<td>-</td>
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<tr>
<td>Food Use</td>
<td>+</td>
<td>-</td>
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</table>

* = Dermal Exposure  ** = Low Free TDI Types  *** = Polyethers
APPLICATIONS FOR MDI’ S

- Virtually all Known Applications for TDI / MBCA Systems Can be Successfully Handled by MDI Systems

- MDI Polyethers Have Distinct Advantages in Hydrolysis Resistance & Rebound

- Some MDI Polyesters and Polyethers are Approved for Wet and Dry Food Use
H$_{12}$MDI

Methylene – bis –(4 cyclohexylisocyanate)
HDI

Hexamethylene Diisocyanate
POLYOLS USED

• POLYETHERS.
• POLYESTERS.
• POLYCAPROLACTONE.
POLYOLS - POLYETHERS

Propylene Oxide

Polypropylene Glycol (PPG) (Medium Performance)

Poly(oxytetramethylene) glycol (PTMG) (High Performance)
• ADVANTAGES IN RESILIENCE.
• LOW TEMPERATURE PERFORMANCE IS IMPROVED.
• HYDROLYTIC STABILITY.
• LOW HEAT BUILD UP.
• LOW VISCOSITY.
WHERE ARE PPG’s USED

• Where the Application is Not VeryDemanding
• Static Applications
• Over-Engineered Applications
  — *Examples:*
• After-Market Auto Suspension Components
• Dunnage and Cradles for Shipping Engines,
  Transmissions, etc.
• Lower-End Wheels & Tires
• Pipe “V” Rollers
WHAT’S GOOD ABOUT PPG’s

- Liquid at Room Temperature
- Low Viscosity
- Low Cost
- Recent Improvements in Quality
- No Melting, Low Temp. Processing
- Easy Processing
- Economy
- Wider Application
WHAT’S NOT GOOD ABOUT PPG’s

- Physicals Lower
- Environmental Resistance Lower (Oxidation)
- Lower Performance
- Long-Term Stability in Field Applications
POLYOLS - POLYESTERS

Ethylene Glycol

Adipic Acid

Polyethylene Adipate Glycol
POLYESTER BACKBONES

• All Based on Adipic Acid*
• Diols are Ethylene Glycol, Propylene Glycol and Butylene Glycol
• All kinds of Mixtures Made.
• Various Molecular Weights
• Terminology is PEAG, PBAG, PEBAG, etc.
• Used With all Isocyanates

*Except for Succinates
GENERAL CHARACTERISTICS OF POLYESTER BACKBONES

• Ethylene – High Tensile, Tear – *But* Hard to Melt
• Butylene – Good Dynamics, FDA
• Ethylene/Butylene - Liquid
POLYESTER POLYURETHANES

• CUT RESISTANCE
• TEAR RESISTANCE.
• ABRASION RESISTANCE.
• IMPACT RESISTANCE.
• OIL & SOLVENT RESISTANCE.
• HEAT AGEING RESISTANCE.
• OXYGEN RESISTANCE.
WHAT ARE THE MAJOR BENEFITS OF ESTER POLYURETHANES?

Feature | Benefit
--- | ---
High Tear, Tensile | Toughest Applications
Oil/Solvent resistance | Printing, Petroleum Apps.
Cheaper than PTMEG | Cost-effectiveness
Low Resilience (some) | Impact Absorption
Versatile microstructure | Tailor to Application
**WHAT ARE THE MAJOR LIMITATIONS OF POLYESTERS?**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Limitation</th>
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<tbody>
<tr>
<td>Ester Linkages</td>
<td>Hydrolysis</td>
</tr>
<tr>
<td>Poorer Dynamics*</td>
<td>Heat Build-up</td>
</tr>
<tr>
<td>Higher S.G. than PTMEG (~10%)</td>
<td>Cost-effectiveness</td>
</tr>
<tr>
<td>Low Resilience (some)</td>
<td>Impingement Abrasion, Rolling Resistance</td>
</tr>
<tr>
<td>Higher Tg</td>
<td>Low Temp. Properties</td>
</tr>
<tr>
<td>Higher Viscosity</td>
<td>Processing Effects</td>
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</tbody>
</table>

* *This picture has Improved with LFTDI*
POLYCAPROLACTONE

\[
\text{(CH}_2\text{)}_5\text{C=C=O } + \text{HO.(CH}_2\text{)}_2\text{.OH } + \text{O=O(C(CH}_2\text{)}_5\text{)}_n \quad \downarrow \quad \text{(CH}_2\text{)}_5\text{O-C-C=O(n mols)} \\
\text{HO-[\text{(CH}_2\text{)}_5\text{CO.C-OC(CH}_2\text{)}_5\text{]}_n \quad \text{poly(caprolactone)}
\]

POLYCARBONATE

\[
\text{HO-\left[(CH}_2\text{)}_6\text{O-C-C-O\right]_n(CH}_2\text{)}_6\text{-OH} \\
\text{Poly(1,6-hexamethylene carbonate)}
\]
POLYCAPROLACTONE POLYURETHANES

• BALANCE OF PROPERTIES BETWEEN ESTER AND ETHERS.

• OFFER IMPROVED UV RESISTANCE, RADIATION RESISTANCE, ACID BASE RESISTANCE.

• FLEX FATIGUE.
SOME COMMON CURATIVES

**MBCA (4,4'-Methylene bis (2-chloroaniline)**

**GR133**

**1,4 -Butanediol**

**GR45**

**Hydroquinone bis (beta hydroxyethyl) ether (HQEE, XA)**

**HQEE**

**Trimethylolpropane (TMP)**

**GR44**
CURATIVES

3,3’-Dichloro-4,4’-diamino Diphenylmethane (GR133)

4,4’-methylene dianiline

4,4’-methylene bis(3-chloro-2,6’-diethylaniline (GR189)
CURATIVES

Diethyl toluene diamine (DETDA)
80:20 mixture of 2,4: 2,6 Isomers

3,5-dimethylthio-2,4-toluenediamine;
3,5-dimethylthio-2,6-toluenediamine
Trimethyleneglycol p-amino benzoate

Unilink
CURATIVES

- Ethylene Glycol
- 2-Methyl-1,3-propanediol
- Tripropylene Glycol (TPG)
- Trimethylol propane
- 1,4-Butanediol (1,4-BD)
- Diethylene glycol
- Dipropylene Glycol
- Glycerin
- Hydroquinone-bis(2-hydroxyethyl) ether (HQEE)
PRODUCT NOMENCLATURE

- 12 & 13 Series = Polyester TDI.
- 17 & 18 Series = Polyester MDI.
- 22 & 23 Series = PTMEG TDI.
- 27 & 28 Series = PTMEG MDI.
- 32 & 33 Series = PPG TDI.
- 37 & 38 Series = PPG MDI.
- 42 & 43 Series = PCL TDI.
- 47 & 48 Series = PCL MDI.
- 51 Series = Aliphatics.
- 52 Series = Ester TDI.
- 57 Series = Ester MDI.
PRODUCT NOMENCLATURE I

- AP = Low Free IPDI PTMEG.
- PCM = Compression Molding TDI PTMEG.
- PET = Low Free TDI PTMEG.
- PHP = Low Free TDI PTMEG.
- PPT = Low Free TDI PPG.
- PST = Low Free TDI Polyester

*The last two numbers of all products relate to their hardness scale.