TMXDI® (META)
Aliphatic Isocyanate
About allnex

Facts & Figures

- Global company with over €2.1 billion in sales
- Broad Technology portfolio: liquid coating resins, energy curable resins, powder coating resins, crosslinkers and additives, composites and construction materials
- Approximately 4000 employees
- Customers in more than 100 countries

With manufacturing, R&D and technical facilities located throughout Europe, North America, Asia Pacific and Latin America, allnex offers global and reliable supply of resins and additives combined with local, responsive customer support.

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Isocyanate Determination
**TMXDI® (META) Aliphatic Isocyanate**

**Goal**
Provide information on the performance benefits, chemistry, and processing advantages of TMXDI monomer for water-based coating technology as it applies to polyurethane dispersions.

**Opportunities**
- Provide a coating technology that allows for the preparation of solvent-free waterborne polyurethane dispersions
- Develop TMXDI monomer based polyurethane coatings with a broad range of hardness and performance properties

**Application Areas for Technology**

<table>
<thead>
<tr>
<th>Aqueous Dispersions</th>
<th>Two-Component</th>
<th>UV Curable</th>
<th>Moisture Cure</th>
<th>Lacquers</th>
<th>One Shot</th>
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<tbody>
<tr>
<td>Adhesives</td>
<td>Adhesives</td>
<td>Floor Coatings</td>
<td>Roof Coatings</td>
<td>Flexible Coatings</td>
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<tr>
<td>Specialty Coatings</td>
<td>Specialty Coatings</td>
<td>Flexible Coatings</td>
<td>Floor Coatings</td>
<td>Plastic Coatings</td>
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</tr>
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<td>Roof Coatings</td>
<td>Roof Coatings</td>
<td>Plastic Coatings</td>
<td>Specialty Coatings</td>
<td>Sealants</td>
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</tr>
<tr>
<td>Floor Coatings</td>
<td>Floor Coatings</td>
<td>Sealants</td>
<td>Sealants</td>
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<tr>
<td>Flexible Coatings</td>
<td>Flexible Coatings</td>
<td>RIM</td>
<td>Potting/Encapsulation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plastic Coatings</td>
<td>Plastic Coatings</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Why use TMXDI monomer over other isocyanates?**
- TMXDI is uniquely suited for waterborne application
- Manufacturing advantages
  - Processing ease due to low prepolymer viscosity
  - Solvent free, no acetone or NMP
  - Higher through-puts
- Performance advantages
  - Broad range of properties obtainable
  - Flexible coatings with superior adhesion
  - Exceptional toughness
  - Improved aluminum flake orientation
- FDA Sanction for use in food packaging adhesives under 21CFR 175.105, Non Food Contact

**Physical Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C14H16N2O2</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>244.3</td>
</tr>
<tr>
<td>NCO Content, % By Weight</td>
<td>34.4</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>122.1</td>
</tr>
<tr>
<td>Boiling Point, °C mmHg</td>
<td>150 (3 mmHg)</td>
</tr>
<tr>
<td>Melting Point, °C</td>
<td>10</td>
</tr>
<tr>
<td>Vapor Pressure, mmHg @ 25°C</td>
<td>0.003</td>
</tr>
<tr>
<td>Flash Point, °C (Setaflash Closed Cup)</td>
<td>153</td>
</tr>
<tr>
<td>Autoignition Point, °C</td>
<td>450</td>
</tr>
<tr>
<td>Solubility</td>
<td>Inert organic solvents</td>
</tr>
</tbody>
</table>

1 Data obtained from sponsored research program at the Emulsion Polymers Institute, Lehigh University.
TMXDI® (META) Aliphatic Isocyanate

Chemistry Characteristics
- TMXDI is an aliphatic isocyanate because the NCO is not conjugated to the aromatic ring
- Excellent light stability and exterior durability
- Steric hindrance by dimethyl groups provides lower reactivity and reduces hydrogen bonding
- Lower reactivity with water
- Controlled reactivity by use of catalysts
- No self-condensation reactions leading to branching, e.g., allophanate, biuret, isocyanurate
- Minimal reactivity with carboxyl groups
- Significantly lower prepolymer viscosity
- Equal isocyanate reactivity
- Higher reaction temperatures possible for prepolymer formation
- 100°C-120°C not a problem
- Stable viscosity in absence of water

Polyurethanes Intermediates (Prepolymers)
- Almost all polyurethane polyureas are prepared via NCO prepolymer intermediates
- The possibility to tailor-make any desirable intermediate by the polyaddition reaction is an important attribute

NCO-Terminated Prepolymers
- These are prepared by the reaction of di- or polyhydroxyl compounds with an excess of diisocyanates
- Typical molecular weight 7,000 - 12,000
- Further reaction with difunctional chain extenders gives rise to the fully reacted high molecular weight polyurethane-polyurea network

Advantages in Prepolymer Formation
- Effects of reduced hydrogen bonding
- Low prepolymer viscosity
- Higher ionic containing prepolymer can be processed
- Trifunctional polyols should be added to maintain film properties when replacing other isocyanates with TMXDI
- Processing advantages
- Hot prepolymer can be pumped with ease (no viscosity build-up)
- Higher prepolymer temperature (120°C) may be used to reduce viscosity
- No solvent needed to reduce viscosity
- Solvent removal step eliminated
- Slower reaction rate allows heated prepolymer to be added into water below 40°C with minimal hydrolysis

Prepolymer Viscosities Formulated to Equal NCO Equivalents

<table>
<thead>
<tr>
<th>Polyl</th>
<th>Prepolymer % Solids</th>
<th>TMXDI®</th>
<th>H_MDI</th>
<th>IPDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tone 230/305</td>
<td>65 (Toluene)</td>
<td>220</td>
<td>970</td>
<td>340</td>
</tr>
<tr>
<td>Tone 240</td>
<td>100</td>
<td>1,255</td>
<td>1,965</td>
<td>1,540</td>
</tr>
<tr>
<td>HD-AA</td>
<td>100</td>
<td>2,300</td>
<td>100,000</td>
<td>100,000</td>
</tr>
<tr>
<td>HD-AA</td>
<td>85 (NMP)</td>
<td>400</td>
<td>1,300</td>
<td>780</td>
</tr>
<tr>
<td>BD-11</td>
<td>85 (NMP)</td>
<td>600</td>
<td>4,050</td>
<td>1,500</td>
</tr>
<tr>
<td>HD-AA-IPA</td>
<td>100</td>
<td>2,700</td>
<td>200,000</td>
<td>4,500</td>
</tr>
</tbody>
</table>

Physical Property Characteristics of Urethanes Made From Aliphatic Disocyanate Monomers

<table>
<thead>
<tr>
<th>Property</th>
<th>TMXDI</th>
<th>IPDI</th>
<th>H_MDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Softer</td>
<td>Harder</td>
<td>Harder</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Lower</td>
<td>Higher</td>
<td>Higher</td>
</tr>
<tr>
<td>Elongation</td>
<td>Higher</td>
<td>Lower</td>
<td>Lower</td>
</tr>
<tr>
<td>Hydrolytic Stability</td>
<td>Better</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Clarity</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>Prepolymer Viscosity</td>
<td>Low</td>
<td>Midd</td>
<td>High</td>
</tr>
</tbody>
</table>

- TMXDI cannot be directly substituted due to:
  - NCO content
  - Reduced hydrogen bonding
Dispersion Structure / Property Relations

Formulation Variables

<table>
<thead>
<tr>
<th>Category</th>
<th>Effect</th>
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</thead>
<tbody>
<tr>
<td><strong>Polyls</strong></td>
<td></td>
</tr>
<tr>
<td>Trifunctional Caprolactones, TMP</td>
<td>Toughness</td>
</tr>
<tr>
<td></td>
<td>Hardness</td>
</tr>
<tr>
<td></td>
<td>Chemical/Solvent resistance</td>
</tr>
<tr>
<td></td>
<td>Humidity resistance</td>
</tr>
<tr>
<td><strong>Polyethers</strong></td>
<td>Softness</td>
</tr>
<tr>
<td></td>
<td>Flexibility</td>
</tr>
<tr>
<td></td>
<td>Adhesion</td>
</tr>
<tr>
<td><strong>Chain Extenders</strong></td>
<td></td>
</tr>
<tr>
<td>2-Methyl Pentamethylene Diamine (Dytek A)</td>
<td>Toughness with elongation</td>
</tr>
<tr>
<td>Diethylene Triamine (DETA)</td>
<td>Hardness</td>
</tr>
<tr>
<td>Hydrazine Hydrate (HH)</td>
<td>Soft-Feel</td>
</tr>
<tr>
<td>Ethylene Diamine (EDA)</td>
<td>Toughness with elongation</td>
</tr>
</tbody>
</table>

Dispersion Process

**TMXDI® Monomer**

```
NCO
\( + \text{HO} \quad \text{OH}^+ \)
\( \text{CH}_2\text{OH} \quad \text{CH}_3\text{CO}_2\text{H} \)
```

**NCO-Terminated Prepolymers**

```
\( \text{NCO} \quad \text{CO}_2\text{H} \)
\( \text{NHCO}_2\text{CH}_2\text{CH}_2\text{O}_2\text{CHN} \)
```

**Hydrophilic Modified NCO-Terminated Prepolymer**

Prepolymer 85˚C - 115˚C

\( \text{H}_2\text{O} 20˚C - 40˚C \)

```
\( \text{HN(CH}_2\text{CH}_3)_3 \quad + \)
```

**Aqueous Polyurethane-Polyurea Dispersion**

\( \text{NCO: NH}_2\text{ ratio 1:1} \)

```
\( \text{H}_2\text{N-R-NH}_2 \quad + \)
```

---

1 Temperature to achieve 200 MEK double rubs without marring coating with 20 minutes bake cycle.
### Formulation Parameters

#### NCO:OH
- 1.4 to 1.7:1 to control molecular weight of isocyanate terminated prepolymer (7,000 - 12,000 MW typical)

#### Trimethylol Propane (TMP)
- Trifunctional polyol is added for controlled branching which improves strength and resistance properties

#### Dimethylol Propionic Acid (DMPA)
- The ionic content is a major factor for controlling the particle size of the dispersion
- Low ionic content (acid number 16) dispersion must be neutralized to 120% to achieve a stable dispersion during production
- Increasing acid number to 20 (4.78 wt% DMPA) widens the processing window, allows lower neutralizing amine level, and allows lower pH of the dispersion

### Processing Parameters

#### Prepolymer (Intermediate)
- Dry nitrogen blanket must be maintained to keep out moisture
- Agitation must be sufficient to ensure proper bulk mixing with high viscosity prepolymer
- Higher processing temperature may be used (120°C) to speed-up reaction time and lower viscosity
- Prepolymer temperature must be lowered to 80°C - 85°C when using TEA for pre-neutralized systems
- Reaction is complete when NCO value is at or below theoretical (constant value)
- Prepolymer may be held at reaction temperatures until the dispersion step

#### Dispersion Equipment, High Speed
- Use pitched turbine or Cowles blades agitators
- Size blades so that the ratio of the dispersing vessel diameter to blade is 2
- Position blade at least one blade diameter off the bottom
- Adjust agitator speed to optimize dispersion step
- Use a closed system (not airtight) dispersing vessel to keep in amine
- Jacket vessel with sufficient cooling capacity to remove latent heat of prepolymer and reaction exotherm
- Do not exceed a water temperature of 40°C during dispersion and chain extension steps to avoid NCO reaction with water

### Dispersing Parameters

#### Water Neutralization Process
- Tertiary amine is charged to the water. The hot prepolymer is added into the water with agitation while simultaneously neutralizing and dispersing the prepolymer
- Particle size of the dispersion is usually larger
- Amine volatility can be a problem
- Accurate prepolymer transfer can be a problem causing uncertainty in % neutralization and chain extension
  - for low ionic content dispersions at 120% neutralization, pH should be 9.3 - 9.5 during dispersion
  - for high ionic content dispersions at 80% neutralization, pH should be 7 - 8 during dispersion
- Higher prepolymer temperature can be used to reduce viscosity

#### Pre-neutralization Process
- Tertiary amine is added to the prepolymer prior to dispersing it in water
- Particle size of the dispersion is smaller
- No uncertainty in determining the prepolymer’s % neutralization
- Use lower prepolymer temperatures (80°C - 85°C) to allow the amine to be mixed into prepolymer without volatilizing the amine

### Formulation Parameters

#### Neutralizing Amine
- Tertiary amines are required
- Triethylamine (TEA) is used for its base strength and low boiling point
- DMAMP-80 can be an alternate for TEA
- The level (%) of neutralization has an effect on pH, particle size and appearance for a given ionic content
- TEA can be used for water neutralized or pre-neutralized processes. DMAMP-80 used only for water neutralized process (OH group will react)
- The % neutralization has an effect on the final viscosity of the dispersion for a given ionic content
Chain Extension Parameters

- The amount of chain extending amine should be calculated to give a stoichiometric addition based on the amount of NCO titrated, and the amount of prepolymer added.
- IPDI & H12MDI systems are typically under chain extended (~85%).
- Under chain extension of TMXDI® prepolymers can lead to grit formation.
- Expect an exotherm. Dilution of the chain extending amine will reduce the exotherm and also prevent shocking the system.
- The final pH of the dispersion is normally close to the initial pH of the neutralized dispersed prepolymer. This will happen as the chain extending amine reacts with the isocyanate forming high MW polymer in water.

Aqueous Polyurethane Dispersions

Dispersion Characteristics

- Prepared without solvents
- No added surfactants
- Low VOC
- Low viscosity
- Shelf stability > 1 Year
- Can be formulated for freeze-thaw stability

Urethane Characteristics

- Superior toughness
- Combination of high tensile strength / elongation
- High elongation
- Attained for soft and hard systems
- Excellent abrasion resistance

Polyols Used In Starting Point Formulations

<table>
<thead>
<tr>
<th>Polyls</th>
<th>Type</th>
<th>Eq. Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Hexanediol adipate polyester</td>
<td>500</td>
</tr>
<tr>
<td>B1</td>
<td>Neopentyl glycol adipate polyester</td>
<td>500</td>
</tr>
<tr>
<td>B2</td>
<td>Neopentyl glycol adipate polyester</td>
<td>250</td>
</tr>
<tr>
<td>C</td>
<td>Polytetramethylene ether glycol diol</td>
<td>500</td>
</tr>
<tr>
<td>D1</td>
<td>Poly (propylene glycol) diol</td>
<td>500</td>
</tr>
<tr>
<td>D2</td>
<td>Poly (propylene glycol) diol</td>
<td>1000</td>
</tr>
<tr>
<td>D3</td>
<td>Poly (propylene glycol) diol</td>
<td>240</td>
</tr>
</tbody>
</table>

Polyols Used In Starting Point Formulations

Abbreviations Used In Formulations

- DMPA: Dimethylol propionic acid
- TEA: Triethylamine
- DMAMP-B0: Dimethylamino methyl propanol
- Dytek A: Methylpentamethylene diamine
- DBTDL: Dibutyl tin dilaurate (catalyst)
- NPG: Neopentyl glycol
- TMP: Trimethylol propane

Starting Point Polyester Formulations

<table>
<thead>
<tr>
<th>Component</th>
<th>Dispersion I</th>
<th>Dispersion II</th>
<th>Dispersion III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol A</td>
<td>57.50 Wt%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polyol B1</td>
<td>-</td>
<td>27.25 Wt%</td>
<td>31.82 Wt%</td>
</tr>
<tr>
<td>Polyol B2</td>
<td>-</td>
<td>22.49 Wt%</td>
<td>7.08 Wt%</td>
</tr>
<tr>
<td>TMXDI monomer</td>
<td>38.10</td>
<td>45.00 Wt%</td>
<td>52.11 Wt%</td>
</tr>
<tr>
<td>DMPA</td>
<td>3.82 Wt%</td>
<td>4.50 Wt%</td>
<td>4.49 Wt%</td>
</tr>
<tr>
<td>TMP</td>
<td>0.57 Wt%</td>
<td>0.75 Wt%</td>
<td>0.50 Wt%</td>
</tr>
<tr>
<td>NPG</td>
<td>-</td>
<td>-</td>
<td>3.99 Wt%</td>
</tr>
<tr>
<td>DBTDL</td>
<td>0.01 Wt%</td>
<td>0.01 Wt%</td>
<td>0.01 Wt%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>% NCO</td>
<td>5.38</td>
<td>5.86</td>
<td>7.49</td>
</tr>
<tr>
<td>NCO:OH</td>
<td>1.70</td>
<td>1.91</td>
<td>1.72</td>
</tr>
<tr>
<td>Acid Number</td>
<td>16.0</td>
<td>18.8</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Free Film Properties

- Tensile strength, MPa: 46.6, 37.7, 41.8
- % Elongation @ Break: 400, 260, 30
- 100% modulus, MPa: 6.5, 23.3, -
- Gloss 20° / 60°: 89/109, 87/106, 91/109
- Glass Transition Tg (°C): -31.25, -15.34, -26.42
Key Benefits Offered by Dispersions Based on TMXDI®

- Very low VOC
- 36 g/L (0.3 lb/gal) from neutralizing amine
- Either zero or limited amount of organic solvent required in formulating
- Formulator has choice of solvent
- Coating toughness
- Combination of high tensile strength with high elongation and tear strength
- Excellent abrasion resistance
- Coating flexibility
- Particularly suited for coating flexible substrates
- Harder coatings maintain a good degree of flexibility
- Coating appearance
- High gloss, 20° gloss >88
- Excellent gloss retention
- Excellent coating adhesion
- Adheres well to most metallic and non-metallic surfaces

Appendix - Example Lab Scale Preparation & Calculations

<table>
<thead>
<tr>
<th>Components</th>
<th>Wt%</th>
<th>Wt</th>
<th>Eq. Wt.</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6 Hexane Diol Adipate Polyester (OH #114)</td>
<td>57.57</td>
<td>252.29</td>
<td>492.1</td>
<td>0.513</td>
</tr>
<tr>
<td>TMXDI® monomer Mw 244/2</td>
<td>37.96</td>
<td>166.36</td>
<td>122.0</td>
<td>1.364</td>
</tr>
<tr>
<td>Trimethylol Propane (TMP) Mw 135/3</td>
<td>0.54</td>
<td>2.36</td>
<td>45.0</td>
<td>0.052</td>
</tr>
<tr>
<td>Dimethyl Propionic Acid (DMPA) Mw 134/2</td>
<td>3.83</td>
<td>16.77</td>
<td>67.0</td>
<td>0.250</td>
</tr>
<tr>
<td>Dibutyl Tin Dilaurate (T-12) (10% Soln. in NMP)</td>
<td>0.10</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.00</td>
<td>438.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Prepolymer Formula & Preparation*

* 2 - 4 Hrs @ 120°C

Viscosity @ 80°C = 5500 mPa•s, Brookfield Cone-plate Sp.52, 10 RPM

Dispersion Preparation

<table>
<thead>
<tr>
<th>Components</th>
<th>Wt%</th>
<th>Wt</th>
<th>Eq. Wt.</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>779.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylamine (TEA)</td>
<td>13.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prepolymer from above</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chain extender: Dytek</td>
<td>26.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A Diamine (1-Methyl Pentaethylene Diamine)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculations

Theoretical % NCO = 5.26
Actual % NCO Titrated = 4.87

\[
\text{Example:} \quad \% \text{ NCO} = \frac{(\text{NCO EQ.} - \text{Total OH EQ.}) \times 42 \times 100}{\text{total formula} \times \text{MW TEA}}
\]

Neutralizing Amine

Amount added is determined by calculating the carboxyl eq. of the prepolymer.

\[
\text{Example:} \quad \text{Prepolymer Wt.} = \frac{\text{DMAPA Wt.}}{\text{MW DMAPA}} \times \text{MW TEA}
\]

Chain Extension Amine

Calculating the NCO equivalent of the prepolymer and adding stoichiometric amount of amine. Exact % NCO is determined from titration methods.

\[
\text{Example:} \quad \% \text{ NCO} = \frac{\text{NCO MW}}{\text{Chain Extension Amine Wt.}} \times \frac{\text{DYTEK A MW} = 116/2}{0.116 \times 58 \times \text{Eq. Wt.}} = \frac{6.73 \text{gms/100 gms Prepolymer}}{400 \text{ gms Prepolymer} \times 26.92 \text{ gms Dytek A diamine}}
\]
Key Benefits Offered by Dispersions Based on TMXDI®

**Reagents**
- n-Dibutylamine/Toluene solution: 1080 ml dry n-dibutylamine diluted to 4000 ml with dry toluene
- 1N HCl
- 0.04% Aqueous Bromophenol Indicator

**Procedure**
1. Accurately weigh sample* into a clean, dry 500 ml Erlenmeyer flask.
2. Add 100 ml (graduate) dry toluene.
3. Pipette 25 ml n-dibutylamine/toluene solution into flask containing sample.
4. Heat solution while stirring to dissolve.
5. Cool solution to ambient temperature.
6. Prepare a blank using 100 ml toluene and 25 cc n-dibutylamine/toluene solution.
7. Add 200 cc dry isopropanol and approximately 0.5 ml n-bromophenol indicator to blank.
8. Titrage blank with 1N HCl to a yellow color which persists for at least 1 minute. Call this Solution A.
9. Add 200 cc of isopropanol and approximately 0.5 ml of n-bromophenol indicator to flask containing sample.
   Titrage to a yellow color as in Step #8. Call this Solution B.

**Calculation:**
\[
\% \text{ NCO} = \frac{(\text{Solution A} - \text{Solution B}) \times 4.2}{g \ \text{sample}}
\]

*For samples of TMXDI® (META) aliphatic isocyanate prepolymers, use 6-10 g sample.*