Update and Overview of Polyurea Spray Technology and New Amine Chain Extenders Useful in Polyurethane Systems

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The History and Background of Polyurea Spray Elastomers
Key Developments Along the Polyurea Spray Elastomer Timeline

1980’s: Texaco Chemical’s Austin Research Laboratories develop polyurea reaction-injection-molding (RIM) for automotive exterior body panel applications.

1989: Texaco Chemical’s Austin Research Laboratories develop and introduce 100% solids polyurea spray elastomer coatings.

1990’s: Numerous equipment advances by industry leaders.

1990’s: Huntsman Corporation and ICI Polyurethanes co-develop and commercialize isocyanate prepolymers for polyurea spray.


Key Developments Along the Polyurea Spray Elastomer Timeline-cont.

**2000:** Formation of the Polyurea Development Association

**2002:** Huntsman commercializes JEFFLINK® 754 chain extender for polyurea and other polymer markets.

**2002:** UOP suddenly exits chain extender market in December.

**2003:** UOP sells rights to UNILINK® 4200 and CLEARLINK® 1000 chain extenders to Dorf Ketal in India.

**2004:** Nissan is first company to offer OEM truck-bed liner.

**2005:** Huntsman commercializes Secondary Polyetheramines.
## THE POLYUREA SPRAY ELASTOMER MARKET AT A GLANCE*

**ESTIMATED 2001 SYSTEM SOLD:** 20-25MM LBS

**ESTIMATED MARKET VALUE:** $60-75MM

**GEOGRAPHIC BREAKDOWN:**

<table>
<thead>
<tr>
<th>Region</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORTH AMERICA</td>
<td>85%</td>
</tr>
<tr>
<td>APAC</td>
<td>10%</td>
</tr>
<tr>
<td>EUROPE</td>
<td>4%</td>
</tr>
<tr>
<td>SOUTH AMERICA</td>
<td>1%</td>
</tr>
</tbody>
</table>

*-2001 Industry Report Conducted by the Polyurea Development Association*
POLYUREA SPRAY ELASTOMER APPLICATION AREAS*

- 60% Concrete
- 15% Bedliners
- 10% Steel
- 10% Roofing
- 5% Other

*-2001 Industry Report Conducted by the Polyurea Development Association
CHEMICAL REACTIONS:
POLYURETHANE AND POLYUREA

\[
\text{Isocyanate} + \text{Polyol} = \text{Urethane}
\]

\[
\text{Isocyanate} + \text{Polyamine} = \text{Urea}
\]
NOTE:
A myriad of other additives can be incorporated into any of these systems. Examples include pigments, adhesion promoters, UV-absorbers, anti-oxidants, and texturing agents.
BENEFITS OF POLYUREA SPRAY ELASTOMERS

- Sprayable coating application.
- Two component, 100% solids systems, Zero VOC.
- 1:1 volume mix ratio, wide formulation latitude.
- Fast reactivity and cure without a catalyst, lack of catalyst leads to better long term stability.
- Relatively moisture and temperature insensitive during application.
- Excellent physical properties.
- High thermal stability (up to 175° C).
- Excellent abrasion resistance.
TYPICAL PHYSICAL PROPERTIES FOR POLYUREA ELASTOMERS

- **Tensile Strength** up to 28 MPa (4000 psi)
- **Shore Hardness** A30 to D75
- **Elongation** up to 1200 %
- **Tear Strength** up to 127000 N/m (725 pli)
- **100% Modulus** (Stress@100%) up to 14 MPa (2000 psi)
- **300% Modulus** (Stress@300%) up to 17 MPa (2500 psi)
Common Raw Materials for Polyurea Spray Elastomers

“New” Amines for Possible Use in Polyurethanes
ISOCYANATE SYSTEMS FOR POLYUREA ELASTOMER COATINGS

Aromatic-Based Systems

\[
\begin{align*}
4,4{'}-\text{MDI} & \quad \text{OCN} \quad \text{NCO} \\
2,4{'}-\text{MDI} \quad \text{OCN} & \quad \text{NCO}
\end{align*}
\]

Aliphatic-Based Systems

\[
\begin{align*}
\text{IPDI} & \quad \text{OCN} \quad \text{NCO} \\
\text{H12MDI} & \quad \text{OCN} \quad \text{NCO} \\
\text{HDI Trimer} & \quad \text{OCN} \quad \text{NCO}
\end{align*}
\]
ISOCYANATE PREPOLYMERS FOR ELASTOMER COATINGS

**Aromatic-Based Systems**

MDI-PPG-2000 Prepolymer

**Aliphatic-Based Systems**

IPDI - D-2000 Prepolymer
AROMATIC CHAIN EXTENDERS FOR POLYUREA ELASTOMER COATINGS

ETHACURE® 100 curing agent

ETHACURE® 300 curing agent

UNILINK® 4200 chain extender

ETHACURE is a trademark of Albemarle. UNILINK is a trademark of Dorf Ketal.
CYCLOALIPHATIC CHAIN EXTENDERS

JEFFLINK® 754 curing agent

CLEARLINK® 1000 curing agent

CLEARLINK is a trademark of Dorf Ketal.
JEFFLINK is a trademark of Huntsman LLC or an affiliate thereof in one or more, but not all countries.
Secondary Aspartic Ester Amines

DESMOPHEN® NH1420 curing agent
JEFFAMINE® POLYETHERAMINES
FOR POLYUREA ELASTOMER COATINGS

Product | x
--- | ---
JEFFAMINE® D-400 amine | 5-6
JEFFAMINE® D-2000 amine | 32-34

JEFFAMINE(R) T-403 amine \( x + y + z = \sim 5.3 \)
\( R = C_3H_5 \quad n = 1 \)

JEFFAMINE(R) T-3000 amine \( x + y + z = \sim 50 \)
\( R = H \quad n = 0 \)

JEFFAMINE(R) T-5000 amine \( x + y + z = \sim 85 \)
\( R = H \quad n = 0 \)

JEFFAMINE is a trademark of Huntsman LLC or an affiliate thereof in one or more, but not all countries.
New Secondary Polyetheramines

- Proprietary Huntsman catalyst technology allows high secondary amine formation with little primary or tertiary.

- Intrinsic reactivity drops roughly a factor of 20 for secondary compared to primary amines.
  - Steric hindrance plays an additional role
- Cure speed (gel time) of a formulation is dependent on concentrations and intrinsic reactivity.
- Products are stable, so there is no off-gassing of reversible blocking agents.
Huntsman’s New Secondary Polyetheramines

<table>
<thead>
<tr>
<th>Product Name</th>
<th>XTJ-584</th>
<th>XTJ-585</th>
<th>XTJ-576</th>
<th>XTJ-586</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary Version of</td>
<td>D-230</td>
<td>D-400</td>
<td>D-2000</td>
<td>T-403</td>
</tr>
<tr>
<td>Approximate Functionality</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Density, 25°C, g/cm³</td>
<td>0.885</td>
<td>0.921</td>
<td>0.978</td>
<td>0.923</td>
</tr>
<tr>
<td>Kinematic Viscosity, 25°C, cSt</td>
<td>7</td>
<td>18</td>
<td>209</td>
<td>46</td>
</tr>
<tr>
<td>Total Amine, meq/gram</td>
<td>5.3-6.3</td>
<td>3.5-4.0</td>
<td>0.9-1.0</td>
<td>4.5-5.5</td>
</tr>
<tr>
<td>Target Equivalent weight, grams/eq</td>
<td>172</td>
<td>270</td>
<td>1042</td>
<td>204</td>
</tr>
</tbody>
</table>
COMMON ADDITIVES:

- Pigment, such as TiO$_2$
- Adhesion Promoter
- UV-Stabilizers/Antioxidants
- Thixotrope
- “Defoamer”/”Dispersant”
- Solvent
- Plasticizer
- “Filler”
Processing Polyurea Spray Elastomers
Static-Mix Dispensing Equipment
Gusmer H-2000
Proportioning Unit
HIGH TEMPERATURE/ HIGH PRESSURE IMPINGEMENT-MIX SPRAY APPLICATION
STANDARD SPRAY PROCESSING PARAMETERS

• **Component Viscosity:** <2000 cPs (at RT)
  – **If too high:** pump cavitation may occur
  – **If mismatched:** large pressure differential may exist
  – along with poor mixing

• **Operating Pressure:** >138 bar (2000 psi)
  – **If too low:** poor mixing and loss of spray
  – pattern may occur.

• **System Temperature:** 60-80°C (150-170°F)
  – **If too low:** poor mixing and loss of spray
  – pattern may occur.
Formulating Polyurea Spray Elastomers
KEY FORMULATION PARAMETERS AFFECTING ELASTOMER PROPERTIES

SYSTEM TYPE: aromatic or aliphatic (cost vs. UV-color stability)

PREPOLYMER TYPE: isocyanate type, isomer distribution, and polyol (polyetheramine) composition can greatly affect elastomer properties

INDEX: can be used to help overcome brittleness and extend working time (INDEX = Free Eq’ s Isocyanate/ Free Eq’ s Amine)

CROSSLINK DENSITY: can affect brittleness/flexibility, permeability, and chemical resistance

SECONDARY AMINE CONTENT: modulates system speed
THE EFFECT OF %NCO VALUE ON ELASTOMER HARDNESS

![Graph showing the relationship between NCO Value (%) and Hardness (Shore D). The data points are plotted on a line graph, indicating a positive correlation between the two variables.](image-url)
FINDING THE OPTIMAL SYSTEM INDEX
THE DECELERATING EFFECTS OF SECONDARY AMINES

Time (s)

Secondary Amine Content (% Resin Side)

0% 8.1% 18.6% 29.9%

Gel Time
Tack-Free Time
## THE TYPICAL POLYUREA SPRAY ELASTOMER FORMULATION PROFILE

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ISOCYANATE COMPONENT</strong></td>
<td></td>
</tr>
<tr>
<td>Adduct, Prepolymer, or Quasi-Prepolymer</td>
<td>100%</td>
</tr>
<tr>
<td><strong>RESIN COMPONENT</strong></td>
<td></td>
</tr>
<tr>
<td>Polyetheramine</td>
<td>40-70%</td>
</tr>
<tr>
<td>Chain Extender</td>
<td>10-50%</td>
</tr>
<tr>
<td>Additives</td>
<td>0-10%</td>
</tr>
</tbody>
</table>

**VOLUME RATIO: 1:1**
STARTING-POINT FORMULATION FOR AN AROMATIC POLYUREA COATING

**ISOCYANATE COMPONENT**

15.4% NCO MDI-Based Quasi-Prepolymer 100%

**RESIN COMPONENT**

JEFFAMINE® D-2000 amine 57.7%
JEFFAMINE® T-5000 amine 5.3%
ETHACURE® 100 curing agent 18.6%
UNILINK® 4200 curing agent 18.6%

Index: 1.05   Volume Ratio: 1:1

Gel Time: 7.0 s  Tack-Free Time: 12.5 s
Hardness: D51
Tensile Strength: 2128 psi
Elongation: 529 %
Modulus, 100%: 1027 psi
Modulus, 300%: 1471 psi
Tear Strength: 456 pli
# STARTING-POINT FORMULATION FOR AN ALIPHATIC POLYUREA COATING

## ISOCYANATE COMPONENT

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPDI / D-2000 or PPG-2000</td>
<td></td>
<td>100%</td>
</tr>
<tr>
<td>Pre-polymer: 16.8% NCO</td>
<td></td>
<td>100%</td>
</tr>
</tbody>
</table>

| Lot Number: | 8276-59 |
| Gel Time:   | 5.0 s   |
| Tack-Free Time: | 22.0 s |

## RESIN COMPONENT

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEFFAMINE® D-2000 amine</td>
<td>39.0%</td>
<td></td>
</tr>
<tr>
<td>JEFFAMINE® T-5000 amine</td>
<td>10.0%</td>
<td></td>
</tr>
<tr>
<td>JEFFLINK® 754 curing agent</td>
<td>44.0%</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.0%</td>
<td></td>
</tr>
</tbody>
</table>

| Index: | 1.06 |
| Volume Ratio: | 1:1 |

| Hardness:    | D55   |
| Tensile Strength: | 2670 psi |
| Elongation:  | 875 % |
| Modulus, 100%: | 1003 psi |
| Modulus, 300%: | 1120 psi |
| Tear Strength: | 526 pli |
Application Examples of Polyurea Spray Elastomers
Polyurea Applications

• Steel coating - automotive, bridges, tanks, etc.
• Concrete coating - roads, parking structures, water-proofing, explosion mitigation, etc.
• Naval vessels - corrosion protection, non-skid, anti-fouling, explosion mitigation.
• Water/waste-water tanks and piping
• Other substrates - polystyrene, plastic, ....
SLOW-SET POLYUREA ELASTOMER TANK LININGS
POLYUREA ELASTOMERS AS PROTECTIVE COATINGS
Truck Bed Liner
Forms of Polyurea and Hybrids

- Caulk for concrete joints (low strength, high elongation)
- Adhesive for a variety of substrates.
- Polyurea Spray Foam.
- Polyetheramines and amine chain extenders can be added to PU foam formulations to make hybrid PU foams.
- Reaction-Injection Molding (RIM) and other molded polyurea parts.
- Roll-on polyurea with hours of work time
- Sprayed-on elastomers with seconds to hours dry time.
Polyurethane Uses of Amines

• Isocyanate Prepolymers
• Chain extenders for quicker viscosity build
• Cast Polyurea parts
• Polyurethane Dispersions
• 1K coatings (especially secondary amines)
• Polyurethane/Polyurea Hybrids
Conclusions

• The lines between polyurethane and polyurea are becoming blurred.
• There are many new amines available, especially secondaries, that can be used in PU formulations.
• The ability to use both polyols and amines greatly increases formulating flexibility.
• Formulators and applicators with knowledge of both chemistries will increase their breadth of projects and profits.
More Information

- JEFFAMINE.com
- Huntsmanchainextenders.com
- Polyurea Development Association (PDA) www.pda-online.org
- mark_posey@huntsman.com

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