A new Cycloaliphatic Amine for Coatings and Composites Applications

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Presentation Contents

• New Cycloaliphatic Amine and Regulatory Status
• Commercial Cycloaliphatic Amines
• Mechanism and Rate Constants
  • Reactivity comparison
• Performance Evaluation of the amine and amine adduct
  • Material Properties
  • Composites Application
  • Coatings Application
• Commercial Status
• Conclusions

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New Cycloaliphatic Amine

Structure

Mixture of cis and trans 1,3-bis(aminomethyl)cyclohexane (CAS 2579-20-6) and 1,4-bis(aminomethyl)cyclohexane (CAS 2549-93-1)

Applications

As a amine hardener and as amine-adduct hardener in coatings and composites applications.
Regulatory Listings

**CAS 2579-20-6**
Current Regulatory Listings: ASIA-PACIFIC: ASIA-PAC; AUSTRALIA: AICS; CANADA: DSL, NDSL; EEC: EINECS; JAPAN: ENCS; KOREA: ECL; PHILIPPINES: PICCS; USA: TSCA

**CAS 2549-93-1**
Current Regulatory Listings: CANADA: NDSL, WHMIS; EEC: EINECS; USA: TSCA

For the rest of the presentation the mixture of cis and trans 1,3-bis(aminomethyl)cyclohexane (CAS 2579-20-6) and 1,4-bis(aminomethyl)cyclohexane (CAS 2549-93-1) will be referred as 1,3/1,4-BMAC
## Major Commercial Cycloaliphatic Amines

<table>
<thead>
<tr>
<th>Cycloaliphatic Amines</th>
<th>Suppliers</th>
<th>Molecular Weight</th>
<th>Amine Equivalent Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-BAC</td>
<td>Mitsubishi</td>
<td>142.2</td>
<td>35.6</td>
</tr>
<tr>
<td>IPDA</td>
<td>Degussa</td>
<td>170.3</td>
<td>42.6</td>
</tr>
<tr>
<td>NBDA</td>
<td>Mitsui</td>
<td>154.3</td>
<td>38.6</td>
</tr>
<tr>
<td>CHDA+/Amicure® PACM</td>
<td>BASF/Air Products</td>
<td>210.3</td>
<td>52.6</td>
</tr>
<tr>
<td>1,2 DACH</td>
<td>Multiple</td>
<td>114</td>
<td>28.5</td>
</tr>
</tbody>
</table>

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Some of these commercial products may have multiple suppliers
Commercial Cycloaliphatic Amines

Consumption of Cycloaliphatic Amine Hardeners by Type (Unformulated)
Total Size 105 MM lb

- IPDA: 51%
- DACH: 7%
- PACM: 14%
- Polycycloaliphatic: 25%
- 1,3 BAC: 2%
- MACM: 1%

Source: unknown

2005 Data
Mechanism of the curing of epoxy by amines

- The lone pair of the primary amine attacks the CH2-epoxy group via a SN2 mechanism.
- The amine exclusively attacks the methylene group.
- The addition reaction forms a hydroxyl group and a secondary amine.
- The lone pair of the secondary amine attacks the CH2-epoxy group via a SN2 mechanism.
- The addition reaction forms a hydroxyl group and a tertiary amine.
Structure Details and Comparison with IPDA

1,3/1,4-BMAC

IPDA

- Primary amine on a primary carbon atom
- Primary amine on a secondary carbon atom (ring carbon)
Rate Constants Comparison (Computational Method)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Primary Amine $k_1N$</th>
<th>Primary Amine $k_2N$</th>
<th>Secondary Amine $k_1N$</th>
<th>Secondary Amine $k_2N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>170°C</td>
<td>2.10X10^{-15}</td>
<td>2.09X10^{-15}</td>
<td>0.69X10^{-15}</td>
<td>-</td>
</tr>
<tr>
<td>200°C</td>
<td>3.57X10^{-14}</td>
<td>3.44X10^{-14}</td>
<td>1.28X10^{-14}</td>
<td>0.077X10^{-14}</td>
</tr>
<tr>
<td>240°C</td>
<td>9.54X10^{-13}</td>
<td>8.68X10^{-13}</td>
<td>3.73X10^{-13}</td>
<td>0.22X10^{-13}</td>
</tr>
</tbody>
</table>

* The rate constant is for the primary amine directly to the cyclohexyl ring and the secondary amine is the one formed from the reaction of primary amine.

Courtesy of M. Marks and N. Rondan, Dow Chemical Company

Spartan® MO program package
• The primary amino group directly to the ring in IPDA is 3X times slower than the 1,3/1,4-BMAC primary amino group
• The secondary amino group formed from the reaction of the primary amine connected directly to the ring in IPDA is 50X times slower than the similar secondary amino group in 1,3/1,4-BMAC
Amine Reactivity Comparison

Liquid Epoxy Resin/Cycloaliphatic amines – DSC Analysis

1,3/1,4-BMAC is more reactive than IPDA
Amine Reactivity Comparison

Liquid Epoxy Resin/Cycloaliphatic amines – DSC Analysis

Reactivity of cycloaliphatic amine hardeners with LER
Ambient Cure Condition

Reactivity in first 100 hours
Amine Reactivity Comparison

Liquid Epoxy Resin/Cycloaliphatic amines – DSC Analysis

Reactivity of cycloaliphatic amine hardeners with LER
Ambient Cure Condition

1,3/1,4-BMAC is slightly faster than 1,3-BAC
Rheokinetic Modeling

Rate Constant $K_1$

![Graph showing the rate constant $K_1$ as a function of temperature for different materials (LER_1,3/1,4-BMAC, LER_IPDA, LER_PACM).]
Rheokinetic Modeling

Rate Constant $K_2$

![Graph showing the rate constant $K_2$ versus temperature (°C). The graph compares different materials, including LER_1,3/1,4-BMAC, LER_IPDA, LER_PACM, and 383_AEP.](image)
Rheokinetic Modeling

Conversion

![Conversion Graph]

- LER_1,3/1,4-BMAC
- LER_IPDA
- LER_PACM

Degree of Cure vs Time (Min)
Epoxy - Amine Formulations

Epoxy-Amine Formulations and Clear Castings

<table>
<thead>
<tr>
<th>Cycloaliphatic Amines</th>
<th>Amine HEW</th>
<th>LER EEW</th>
<th>Amine Wt. %</th>
<th>LER Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-1,4/BMAC</td>
<td>35.6</td>
<td>188.4</td>
<td>15.9</td>
<td>84.1</td>
</tr>
<tr>
<td>IPDA</td>
<td>42.6</td>
<td>188.4</td>
<td>18.4</td>
<td>81.6</td>
</tr>
</tbody>
</table>

- Made 1/8” clear castings
- Curing Condition: 150ºC / 3h
## Material Properties Comparison

<table>
<thead>
<tr>
<th>Cycloaliphatic Amines</th>
<th>Tg* (°C)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>% Strain @ Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3/1,4/BMAC</td>
<td>145</td>
<td>84</td>
<td>2.6</td>
<td>7.30 ± 0.61</td>
</tr>
<tr>
<td>IPDA</td>
<td>160</td>
<td>90</td>
<td>2.8</td>
<td>7.31 ± 0.18</td>
</tr>
</tbody>
</table>

* DMTA

IPDA has a high final Tg for a fully cured system

Comparable Material Properties

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**Note:** ASTM D638
Evaluation of fully cured clear castings

Fracture Toughness Comparison

Improved Fracture Toughness for 1,3/1,4-BMAC

IPDA

Fracture Toughness, K\textsubscript{IC} (MPa.m\textsuperscript{1/2})

1,3/1,4-BMAC

0.5961

0.8264

ASTM D5045
# Amine Adduct Preparation and Properties

<table>
<thead>
<tr>
<th>Cycloaliphatic Amines</th>
<th>Weight % Amine</th>
<th>Weight % LER</th>
<th>Adduct AEW</th>
<th>Viscosity mPa.s @ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-BAC</td>
<td>75.2</td>
<td>24.8</td>
<td>50.2</td>
<td>440</td>
</tr>
<tr>
<td>IPDA</td>
<td>78.5</td>
<td>21.6</td>
<td>57.8</td>
<td>2846</td>
</tr>
<tr>
<td>NBDA</td>
<td>76.7</td>
<td>23.3</td>
<td>53.2</td>
<td>1406</td>
</tr>
<tr>
<td>CHDA</td>
<td>81.8</td>
<td>18.2</td>
<td>68.1</td>
<td>20,259</td>
</tr>
<tr>
<td>1,3-1,4/BMAC</td>
<td>75.2</td>
<td>24.8</td>
<td>50.4</td>
<td>554</td>
</tr>
</tbody>
</table>

- Synthesis Ratio: Amine:LER:: 8:1 (molar ratio)
- Synthesis condition: 80°C/2h
## Epoxy-Amine Adduct Formulations and Clear Castings

<table>
<thead>
<tr>
<th>Cycloaliphatic Amine Adducts</th>
<th>Adduct HEW</th>
<th>LER EEW</th>
<th>Amine Wt. %</th>
<th>LER Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-BAC</td>
<td>50.2</td>
<td>188.4</td>
<td>21.1</td>
<td>78.9</td>
</tr>
<tr>
<td>IPDA</td>
<td>57.8</td>
<td>188.4</td>
<td>23.5</td>
<td>76.5</td>
</tr>
<tr>
<td>NBDA</td>
<td>53.2</td>
<td>188.4</td>
<td>22.0</td>
<td>78.0</td>
</tr>
<tr>
<td>CHDA</td>
<td>68.1</td>
<td>188.4</td>
<td>26.6</td>
<td>73.4</td>
</tr>
<tr>
<td>1,3-1,4/BMAC</td>
<td>50.4</td>
<td>188.4</td>
<td>21.1</td>
<td>78.9</td>
</tr>
</tbody>
</table>

- Made 1/8” clear castings
- Curing Condition: 150°C / 3h
**Material Properties Comparison**

<table>
<thead>
<tr>
<th>Cycloaliphatic Amines</th>
<th>Tg* (°C)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>% Strain @ Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-BAC</td>
<td>142</td>
<td>85</td>
<td>2.5</td>
<td>7.48±0.73</td>
</tr>
<tr>
<td>IPDA</td>
<td>158</td>
<td>87</td>
<td>2.3</td>
<td>7.51±0.43</td>
</tr>
<tr>
<td>NBDA</td>
<td>145</td>
<td>84</td>
<td>2.6</td>
<td>7.64±0.14</td>
</tr>
<tr>
<td>CHDA</td>
<td>165</td>
<td>84</td>
<td>2.3</td>
<td>7.00±0.78</td>
</tr>
<tr>
<td>1,3-1,4/BMAC</td>
<td>142</td>
<td>83</td>
<td>2.5</td>
<td>7.21±0.64</td>
</tr>
</tbody>
</table>

Some variation in Tg
Comparable Material Properties
Epoxy – Amine Adduct Formulations

Evaluation of fully cured clear castings

Fracture Toughness Comparison

Improved Fracture Toughness for NBDA and 1,3/1,4-BMAC
Wind Blade Application
Infusion System

Rheokinetic Modeling
Reactivity

Rate Constant $K_1$
Tg Development
Viscosity Development

- Experimental 1
- Experimental 2
- Experimental 3
- Experimental 4
- Control
- Temp
# Amine Adduct Formulations

Comparison of a epoxy thermoset formulation with a commercial curing agent

## Formulation Details

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Amine AHEW</th>
<th>LER EEW</th>
<th>Amine %</th>
<th>LER %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancamine* 1618</td>
<td>113.00</td>
<td>188.4</td>
<td>37.5</td>
<td>62.5</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 20% Benzyl Alcohol</td>
<td>63.05</td>
<td>188.4</td>
<td>25.1</td>
<td>74.9</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 40% Benzyl Alcohol</td>
<td>84.07</td>
<td>188.4</td>
<td>30.9</td>
<td>69.1</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 60% Benzyl Alcohol</td>
<td>126.10</td>
<td>188.4</td>
<td>40.1</td>
<td>59.9</td>
</tr>
</tbody>
</table>

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## Physical Properties Development

### Epoxy-Amine Adduct Systems

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Pencil Hardness</th>
<th>Konig Pendulum Hardness (osc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>3 days</td>
</tr>
<tr>
<td>Ancamine* 1618</td>
<td>HB</td>
<td>F</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 20% Benzyl Alcohol</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 40% Benzyl Alcohol</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 60% Benzyl Alcohol</td>
<td>2B</td>
<td>2B</td>
</tr>
</tbody>
</table>

Softest 4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H Hardest

### Thin Film Dry Times

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Dust Free</th>
<th>Dry Through</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(hr)</td>
<td>(hr)</td>
</tr>
<tr>
<td>Ancamine* 1618</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 20% Benzyl Alcohol</td>
<td>3.5</td>
<td>5.5</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 40% Benzyl Alcohol</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 60% Benzyl Alcohol</td>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>

19.5º C and 25% humidity

Faster dust free and dry through times and faster hardness development over 7 days for 1,3/1,4-BMAC systems
## Coating Properties

### Epoxy-Amine Adduct Systems
7 day ambient cure

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Gloss</th>
<th>Impact (in-lb)</th>
<th>Appearance</th>
<th>Tg °C</th>
<th>Cross Hatch Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20º</td>
<td>60º</td>
<td>85º</td>
<td>Forward</td>
<td>Reverse</td>
</tr>
<tr>
<td>Ancamine* 1618</td>
<td>113</td>
<td>124</td>
<td>101</td>
<td>20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 20% Benzyl Alcohol</td>
<td>113</td>
<td>126</td>
<td>100</td>
<td>20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 40% Benzyl Alcohol</td>
<td>114</td>
<td>124</td>
<td>98</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>1,3/1,4-BMAC Adduct w/ 60% Benzyl Alcohol</td>
<td>118</td>
<td>127</td>
<td>98</td>
<td>160</td>
<td>160</td>
</tr>
</tbody>
</table>

5B = No loss  
0B = >65% loss

- Improved or comparable properties for 1,3/1,4-BMAC systems
External Evaluation

- Better adhesion (lap shear)
- Better hydrolytic stability
- Less Yellowing
- Better reactivity

- Blush
- Solt Fog
- UV
Commercial Availability

1,3/1,4-BMAC

- We have produced in drum quantities for internal testing
- We are working internally and with external toll manufacturers to produce the amine on a commercial level
- Like other cycloaliphatic amines, 1,3/1,4-BMAC requires specialized high pressure amination equipment in the manufacturing process
Conclusions

• We have a new cycloaliphatic amine hardener
• It has a high reactivity with liquid epoxy resin
• 1,3/1,4-BMAC is on TSCA and EINECS
• We have successfully evaluated in coatings and composites (wind blade) applications
• Commercial availability of 1,3/1,4-BMAC is planned for 2008