DYHARD®

New liquid latent hardener for Automotive RTM applications
New liquid latent hardener for Automotive RTM


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   1. Processing properties
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AlzChem Group

History

1908
Founding of the Bayerische Stickstoff-Werke AG in Munich

1978
Change of company name to SKW Trostberg AG

1995
Listing of SKW Trostberg AG as a public company

2001
Merger of Degussa-Hüls AG with SKW Trostberg AG to form the new Degussa AG

2006
Founding of the AlzChem Group

2009
bluO Fonds becomes new shareholder

2013
The shares are taken over by the bluO partners

2014
Acquisition of SKW Metallurgy Sweden AB, renamed Nordic Carbide AB

2014
AlzChem is investing in the segment feed additives and are building a dedicated CreAMINO® production facility
AlzChem Group
Facts & figures

- Sales: approx. **320 m. euros**
- Employees: **1,400**
- Main areas: **NCN chemistry** (products with a nitrogen-carbon-nitrogen bond)
- Product applications: **nutrition, renewable energies, fine chemicals, agriculture, metallurgy**
- Services: **toll synthesis, industrial toll milling and filling**
- Production sites: **Trostberg, Hart, Schalchen, Waldkraiburg, Sundsvall**
New liquid latent hardener for Automotive RTM

Background

• In recent years we have seen a high interest in carbon fiber reinforced automotive parts. All major OEM’s and carbon fiber manufacturers have their own strategic development projects.

• One of the manufacturing processes in focus has been Resin Transfer Molding (RTM).

• In this paper we will focus on recent developments in liquid latent curing agents, which can be processed at low pressures with low cost equipment.
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Current situation

• Currently epoxy RTM systems are based on amine curing systems.

• To accommodate these fast curing systems new RTM machinery and processes had to be developed. This resulted in the High-Pressure-RTM system in which the high reactive resin system is injected in an as short as possible time with a very high injection pressure.

• Despite all recent developments, HP-RTM is still considered to be a very expensive and critical process.
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Our offering

To overcome the critical process step of injecting the resin in a very short time we have developed a new curing system based on a different chemistry, which gives a much longer latency and therefore longer injection time.

This latent liquid curing agent package for Automotive RTM processes consists of:

- **RF1000**: A low viscos modified BPA epoxy resin.
- **F151**: A novel latent liquid curing agent.
- **AC11**: A special accelerator, with which the injection- and cure time can be adjusted.
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Characteristics of this system

1. Processing properties:
   1. Rheology; viscosity increase in time
   2. Cycle time; cure time
   3. Laminate Tg after different molding times

2. Cured resin properties:
   1. Mechanical properties: tensile- + flexural strength
   2. Laminate properties: flexural strength + ILSS
   3. Shrinkage
   4. Color stability
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Viscosity increase at 120 °C (250 F)
New latent hardener compared with Isophoronediamine (IPDA)

IPDA (red line) reacts immediately, as can be seen by the fast viscosity increase directly upon injection.

The Fluid system has a long, stable low viscosity, giving flow times up to 3 minutes, allowing injection of large, complex, high fiber content parts.

Injection can be done at low pressures.

The flow time can be easily adjusted through varying the accelerator content.
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Isothermal DSC at 120 °C (250 F)
New latent hardener compared with Isophoronediamine (IPDA)

With the amount of the accelerator (AC11) the cure time can be controlled.

Medium cure times of 20 min and fast cure <10 min at 120 °C are possible.
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**Laminate Tg at 120 °C (250 F)**
Development of laminate Tg after different cure times

<table>
<thead>
<tr>
<th></th>
<th>RF1000</th>
<th>F151</th>
<th>AC11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Cure condition</td>
<td>15 Min @ 120 °C</td>
<td>10 Min @ 120 °C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dynamic mechanical analysis</th>
<th>Tg from Peak tan δ</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
</tr>
<tr>
<td>RF1000</td>
<td>118</td>
</tr>
<tr>
<td>F151</td>
<td>125</td>
</tr>
</tbody>
</table>

These cure times of 20 min and fast cure <10 min at 120 °C can be achieved in the RTM process as well.
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Characteristics of this system

1. Processing properties:
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2. Cured resin properties:
   1. Mechanical properties: tensile- + flexural strength
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Mechanical properties
4 mm thick unreinforced cast resin.

<table>
<thead>
<tr>
<th></th>
<th>RF1000</th>
<th>F151</th>
<th>AC11</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 hr. @ 100 ºC +</td>
<td>1 hr. @ 100 ºC +</td>
<td>1 hr. @ 100 ºC +</td>
</tr>
<tr>
<td>Cure condition</td>
<td>100</td>
<td>6</td>
<td>3</td>
<td>1 hr. @ 130 ºC</td>
<td>1 hr. @ 130 ºC</td>
<td>1 hr. @ 130 ºC</td>
</tr>
<tr>
<td>Tensile properties (ISO 527-2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>MPa 2970</td>
<td>64</td>
<td>3</td>
<td>3.1</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Max. tensile strength</td>
<td>MPa 3050</td>
<td>68</td>
<td>4</td>
<td>3.2</td>
<td>3.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Elongation at tensile strength</td>
<td>% 3030</td>
<td>73</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural properties (ISO 178)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>MPa 2940</td>
<td>93</td>
<td></td>
<td>3.4</td>
<td>3.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Max. flexural strength</td>
<td>MPa 3010</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elongation at flexural strength</td>
<td>% 3010</td>
<td>113</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The accelerator content, and thus the cure time, does not have an influence on the mechanical properties.

Automotive parts of different sizes can be made with appropriate processing conditions and equal mechanical performance.
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**Laminate properties**
- UD-Carbon Fabric: Saertex S32 CU 980-00860-00470-264000
- Carbon fiber: Zoltek Panex 35

<table>
<thead>
<tr>
<th>Cure condition</th>
<th>1 hr. @ 120 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Fiber content</td>
<td>Vol%</td>
</tr>
</tbody>
</table>

**Flexural properties (ISO 14125)**
- Flexural modulus: GPa 83
- Flexural strength: MPa 1330
- Elongation at break: % 1.6

**ILSS (ISO 14130)**
- Inter Laminar Shear Strength: MPa 72

The adhesion on carbon fibers is excellent.
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**Volume shrinkage during cure at 120 °C (250 F)**
Total shrinkage measured by volume dilatometry.

<table>
<thead>
<tr>
<th>Resin system</th>
<th>Volume shrinkage</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine RTM system</td>
<td>3.6 %</td>
<td>-</td>
</tr>
<tr>
<td>RF1000 + F151 + AC11 100 + 8 + 2</td>
<td>3.0 %</td>
<td>-17 %</td>
</tr>
<tr>
<td>RF1000 + F151 + AC11 100 + 8 + 4</td>
<td>2.7 %</td>
<td>-25 %</td>
</tr>
</tbody>
</table>

A lower shrinkage leads to:
- Better surface quality.
- Lower internal stress in the cured part.
- Reduced warpage, improved dimensional stability.
- Improved fatigue resistance.
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**Color stability**
Thermal yellowing at 80 °C (175 F) and 120 °C (250 F).

<table>
<thead>
<tr>
<th></th>
<th>Original</th>
<th>Storage at 80 °C</th>
<th>Storage at 120 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Week</td>
<td>3 Weeks</td>
<td>1 Week</td>
</tr>
<tr>
<td>RF1000 : F151 : AC11 100 : 6 : 2</td>
<td><img src="image1.png" alt="Picture" /></td>
<td><img src="image2.png" alt="Picture" /></td>
<td><img src="image3.png" alt="Picture" /></td>
</tr>
<tr>
<td>RF1000 : F151 : AC11 100 : 6 : 4</td>
<td><img src="image5.png" alt="Picture" /></td>
<td><img src="image6.png" alt="Picture" /></td>
<td><img src="image7.png" alt="Picture" /></td>
</tr>
<tr>
<td>BPA-Epoxy : IPDA 100 : 24</td>
<td><img src="image9.png" alt="Picture" /></td>
<td><img src="image10.png" alt="Picture" /></td>
<td><img src="image11.png" alt="Picture" /></td>
</tr>
</tbody>
</table>
The advantages of this new liquid latent RTM system are:

1. Adjustable processing times in terms of flow-, injection time and total cycle time.

2. Long injection times for complete mold filling, excellent and homogeneous fiber wetting, which results in reduced scrap rates.

3. Lower investment costs in injection equipment. No need for expensive HP-RTM equipment. One injection unit can accommodate multiple molds to produce the desired units per day.

4. One cure-package for different processing conditions with equal final cured product properties, irrespective of cure conditions.

5. Low shrinkage resulting in excellent surface quality.

6. Low thermal yellowing for long lasting optical clarity.

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Thank you for your attention!