Development of Improved Composites and Adhesives for Aircraft Structures and Interiors

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Agenda

- Henkel Background

- Development of Improved Products
  - New Approach to development of FST products

- Specific Examples:
  - Structural Paste adhesive for Aircraft Interiors
  - Composites for structural applications

- Summary
Henkel Areas of Competence

Laundry & Home Care

Cosmetics/Toiletries

Adhesive Technologies

Quality with Brands & Technologies

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Structural Adhesive Products

Hysol® Aerospace Products
   Paste, Films, Primers, Wet Peel Ply

SynCore® Syntactic Films
   Lightweight stiffening replacement

SynSpand® Expanding Syntactic Films
   Lightweight core fill & potting
   Jet engine abradable seal applications

SynSkin® Composite Surfacing Films
   Superior surface for painting & lightning strike
   foil/screen protection

Frekote® Composite Release Polymers
   World’s standard semi-permanent mold release system
Henkel leverages R&D and PD laboratories over the world to serve the Aerospace market.

Henkel Aerospace covers the product range from pretreatment to the final bonding process.

Locations:
- Rocky Hill, CT, USA
- Madison Heights, MI, USA
- Bay Point, CA, USA
- Amersfoort, Netherlands
- Dusseldorf, Headquarters, Germany
Development of Improved Products:
Industry Needs
Industry Needs

- Improved Flame, Smoke and Toxicity
- Performance criteria: mechanical, damage, temperature, ageing.....
- Meet current and future environmental standards
  - Workplace exposure resins/flame retardants
  - In service exposure
  - End of life
- Cost:
  - Acquisition: material and fabrication
  - Total life cost
- Ease of use:
  - Storage, processability, working life, cure etc
Our Strategy for Sustainability: Five Focal Areas

- Energy and climate
- Water and wastewater
- Materials and waste
- Health and safety
- Social progress

Vision and Values
Industrial Applications/Markets of Flame Resistant Materials

Aerospace Industry
- Interior (adhesives, core materials, acoustic materials, laminates)
- Composite structures

Railway and road transportation market
- Interiors (adhesives, foams, laminates)
- Composite structures

Naval Structures
- Interiors (adhesives, foams, laminates)
- Composite structures

Electronics, PCB, battery markets
- Low ignition materials, dielectrics

Offshore Oil & Gas Production Platform

Building & Construction Industry
## Technical Analysis – Flame Resistance

<table>
<thead>
<tr>
<th>Resins</th>
<th>Curatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolics</td>
<td>Phenolics</td>
</tr>
<tr>
<td>Benzoxazines</td>
<td>Cresol Novolacs</td>
</tr>
<tr>
<td>Cyanate Esters</td>
<td>Amines + High Crosslink Density</td>
</tr>
<tr>
<td>Polyimides</td>
<td>Melamines</td>
</tr>
<tr>
<td>Specialty Epoxies</td>
<td>DICY</td>
</tr>
<tr>
<td>Bismaleimide Resins (BMI)</td>
<td>Acids</td>
</tr>
<tr>
<td></td>
<td>Anhydrides</td>
</tr>
<tr>
<td></td>
<td>Amines + Low Crosslink Density</td>
</tr>
</tbody>
</table>

| | | Resins |
| | | Curatives |
| Standard Epoxies | DICY | DICY |
| Polyurethanes | Acids | Acids |
| Acrylcs | Anhydrides | Anhydrides |
| Vinylesters | | |
| Vulcanized Rubbers | | |

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"The thermal stability of epoxy resins, as well as their flammability, depends on the structure of the monomer, the structure of the curing agent and the crosslink density."

"Thermal decomposition, combustion and flame-retardancy of epoxy resins – a review of the recent literature"

**General Trends**

Higher Crosslink Density >> Lower Crosslink Density

→ 1-Part Heat Cure & High Tg >> 2-Part RT Cure & Low/Med Tg

Higher Charring Tendency >> Lower Charring Tendency

→ Phenolic Systems, Highly filled Systems better
Paths to Improved Flammability Resistance

- New Resin Chemistry
- New Flame Retardants
- Formulation Design

Use these approaches individually or in combination
Structural Paste Adhesive: Aircraft Interior Applications
Flame Resistant Structural Paste Adhesive

- Flame retardant paste adhesive designed for interior applications
- White, two-part paste
- High dispensability
- High Mechanical properties
- Meets FST requirements
Flame Resistant Structural Paste Adhesive
LP31007.0

<table>
<thead>
<tr>
<th>Components</th>
<th>Part A</th>
<th>Part B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White</td>
<td>Straw</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.43</td>
<td>1.35</td>
</tr>
<tr>
<td>Characteristic</td>
<td>Moderate Viscosity Liquid</td>
<td>Thixotropic Paste</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixed Adhesive</th>
<th>Units</th>
<th>Temperature</th>
<th>LP31007.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix Ratio A/B</td>
<td>volume/volume</td>
<td>---</td>
<td>2/1</td>
</tr>
<tr>
<td></td>
<td>weight/weight</td>
<td>2.12/1</td>
<td></td>
</tr>
<tr>
<td>Dispensability¹</td>
<td>gpm</td>
<td>23°C (75°F)</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37°C (99°F)</td>
<td>300</td>
</tr>
<tr>
<td>Flow</td>
<td>inches / 10 min cm / 10 min</td>
<td>23°C (75°F)</td>
<td>0.85 2.2</td>
</tr>
</tbody>
</table>

¹ Dispensability determined using 200 ml side-by-side cartridges
### Typical Flammability Results

<table>
<thead>
<tr>
<th>Extinguishing Time (seconds)</th>
<th>Burn length (cm / in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~1</td>
<td>2.5 – 3.8cm (1 – 1.5inch)</td>
</tr>
</tbody>
</table>

- Corner exposed to flame for 60 Seconds
- Extinguish time is time to extinguish after ignition source is removed
- Burn Length is the distance the surface skin was eroded from the edge of specimen
# Flame Resistant Structural Paste Adhesive

## Mechanical Performance

<table>
<thead>
<tr>
<th>Cured Properties</th>
<th>Units</th>
<th>Test Temperature</th>
<th>LP31007.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lap Shear Strength</td>
<td>MPa</td>
<td>23°C (75°F)</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>71°C (160°F)</td>
<td>19.1</td>
</tr>
<tr>
<td>Working Life after 1 hour at 23°C (75°F)</td>
<td>MPa</td>
<td>23°C (75°F)</td>
<td>23.6</td>
</tr>
<tr>
<td>Working Life after 1 hour at 37°C (99°F) (300 gpm)</td>
<td>MPa</td>
<td>23°C (75°F)</td>
<td>21.8</td>
</tr>
<tr>
<td>Modified Bell Peel</td>
<td>N/cm</td>
<td>23°C (75°F)</td>
<td>34.7</td>
</tr>
<tr>
<td>'Ditch and Pot' Mechanical Strength</td>
<td>N</td>
<td>23°C (75°F)</td>
<td>133</td>
</tr>
<tr>
<td>'Ditch and Pot' Burn (extinguish time)</td>
<td>sec</td>
<td>NA</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Using new Technology Approach Henkel has develop a new Structural Paste Adhesive which:

- Exceeds flammability requirements
- Has improved mechanical performance
- Meets dispensability requirements
- Long working life
- Self colored white
Structural Composites: Benzoxazine Matrix Resins
Structural Composites
Industry Needs

- **Structural Composites used for many years:**
  - Commercial Aircraft – secondary structures
  - Military Aircraft – primary structures

- **Main Resin Systems:**
  - Epoxy
  - Bismaleimide

- **Increasing use of composites in commercial aircraft**
  - Structure:
    - Fuselage, Wings
  - Engines and nacelles
  - High temperature areas:
    - APU
    - Engine pylons
    - Wheel wells
    - Leading edges (de-icing)
Henkel Benzoxazine Resin

- Ambient shipping and storage
- Material costs comparable to Epoxy
- Process equivalent to Epoxy
- Excellent FST performance

Compared to epoxy resins
- Lower cure shrinkage and heat release
- Higher hot/wet performance
- Inherent FST characteristics

Compared to phenolics
- No microcracks
- No water generated

Compared to BMI
- Lower cure temp and shorter cure time
- Lower cost
- Higher toughness
Epsilon Benzoxazine Prepreg Resins

- High retention of hot/wet properties
- Damage tolerance equivalent to toughened epoxy prepregs
- Meets flammability and burn-through requirements
- Extended room temperature storage

![Graph showing storage time vs. strength for different conditions](image)

CAI, 30J impact
OHC, Room Temperature, As molded
OHC, 82°C, after 14-days water @ 71°C

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## Epsilon Benzoxazine Prepreg Composite: Flame, Smoke and Toxicity

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Limit</th>
<th>Epsilon Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vertical Burn: 60secs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After burn length</td>
<td>inch</td>
<td>6</td>
<td>0.91</td>
</tr>
<tr>
<td>After flame time</td>
<td>secs</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>After flame time of drips</td>
<td>secs</td>
<td>3</td>
<td>No Drips</td>
</tr>
<tr>
<td><strong>Smoke Density</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Optical Density</td>
<td>N/A</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td></td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>ppm</td>
<td>1000</td>
<td>2</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>ppm</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>SO₂/H₂S</td>
<td>ppm</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>HF</td>
<td>ppm</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>HCl</td>
<td>ppm</td>
<td>150</td>
<td>1</td>
</tr>
</tbody>
</table>

4-ply Carbon Fiber Composite Unidirectional Tape: 1mm thick
Structural Composite: Smoke Test Results

Carbon Fiber Unidirectional tape
Fiber areal weight: 190g/m²
Resin content 35%

Specific Optical Densi

Non-flaming Mode

Flaming Mode

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Carbon Fiber Unidirectional tape
Fiber areal weight: 190g/m²
Resin content 35%
Structural Composite Application

- **A380 APU Housing & Duct:**
  - Carbon fiber, Glass Fiber Prepreg and Film Adhesive
  - Meets Structural Performance requirement
  - Meets standard FST requirements: OSU, Vertical Burn, Smoke, Toxicity
  - Meets oil burner 15min, 1100°C burn-through requirement
Summary

➢ Requirements becoming more demanding:
  Flame, smoke and toxicity requirements
  Health, safety and environmental requirements
  Service performance
  Processability
  Cost: Acquisition and total life cycle

➢ New approach needed to materials development:
  Resin chemistry
  Flame retardants
  Formulation design

➢ Initial Product Developments
  Flame retarded paste adhesive for structural bonding
  Structural composites using Benzoxazine matrix resin