Polyurethane Elastomers
One-Component Bonding Technology
PMA Las Vegas 7 May 2013
Agenda

A fast Drying bonding agent for PU

Results of comparative test between 1 and 2 K PU BA

Discipline of making a Good bond
PU Wheels, Castors and Rollers Bonded using Cilbond 49SF
PU Bonding

- Diamond tipped Granite cutting wires
- PU to steel wire
  Cilbond used
- 49SF
- Possible future use for CB48
ROTATIONAL PU CASTING

A MOULDLESS METHOD OF COATING ROLLERS AND PIPE

THE ROLL STOCK IS ROTATED

THE MACHINE MIXED PU IS “INJECTED” ONTO THE ROLL STOCK, WHILST MOVING THE APPLICATION NOZZLE ALONG THE ROLL

HEAT IS A LUXURY

COLD CASTING IS THE NORM

PU gel time 5-20 seconds
Hot Cast Polyurethanes

Reaction triggered by heat

Cilbond 49SF
Cold Cast Polyurethanhes

Reaction triggered by chemical Bonding

Cilbond 41
Hot/Cold Cast Polyurethanes

Heat/Fluid & Environmental Resistance

Need of second component

Add Cilcure B
Hot/Cold Cast Polyurethane

Heat/Fluid & Environmental Resistance

Development of One component

CILBOND 48
In terms of environmental resistance, Cilbond 48 exhibits excellent heat resistance, salt spray resistance, boiling water resistance and resistance to oils, fuels and brake fluids. Series of tests have demonstrated the resistance of this new PU bonding agent to heat, boiling water and salt spray. The following paper presents these results and provides useful comparative data for processors of PU cast elastomers.
## Physical Properties Cilbond 48

<table>
<thead>
<tr>
<th>Property</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td>Viscosity no 3 Zahn Cup @ 26 C</td>
<td>13-17 seconds</td>
</tr>
<tr>
<td>Viscosity Din 4 @ 26 C</td>
<td>25 seconds</td>
</tr>
<tr>
<td>Non –volatile solids</td>
<td>21.5% by weight</td>
</tr>
<tr>
<td>Specific gravity@ 26C</td>
<td>0.88-0.92</td>
</tr>
<tr>
<td>Flash Point ( Abel Pensky)</td>
<td>-2C</td>
</tr>
<tr>
<td>Moulding Temperature Range</td>
<td>20-135C ( cast elastomers) 150-230C (TPUs)</td>
</tr>
<tr>
<td>Optimium Dry Coating Thickness</td>
<td>25micron for max adhesion &amp; corrosion resistance</td>
</tr>
<tr>
<td>Typical coverage at 25 micron dry coating thickness</td>
<td>15 sq m/l</td>
</tr>
<tr>
<td>Shelf life</td>
<td>12 months from date of manufacture</td>
</tr>
</tbody>
</table>
Metal Surface Preparation

To be most effective, Cilbond 48 must be applied to carefully prepared surfaces, which have been grit blasted with clean, filtered (200-400micron) sharp alumina or sharp chilled iron grit and degreased with a solvent. Good metal preparation is vital if the environment is to be continually wet, such as for sub-sea applications. Most engineering plastics can be grit blasted, but it may be necessary to used finer grit and a lower air pressure to prevent plastic flow and fibrilation.
Mild steel ASTM D429 test pieces were prepared according to CIL test method 32a by MEK (methyl ethyl ketone) degreasing, 200-400 micron sharp chilled iron grit blasting and then MEK degreasing. To compare the performance of Cilbond 48 with existing bonding agents that are specifically formulated for use with either hot or cold cure elastomers, the following bonding agent systems were spatula/knife coated onto the steel test pieces to give a recommended dried thickness of ca. 25 microns. Each coat was left to dry for at least 90 minutes.
Bonding Systems Tested

Bonding systems tested:

- Cilbond 41
- Cilbond 41+Cilcure B at 100:5 mix ratio
- Cilbond 45SF
- Cilbond 48
- Cilbond 49SF
- Cilbond 49SF + Cilcure B at 100:10 mix ratio
### Typical Pre-Bake Resistance

<table>
<thead>
<tr>
<th>Product</th>
<th>Amine Cured TDI pre-polymer (polyether)</th>
<th>Vulkollan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cilbond 48</td>
<td>16 hours @ 130°C (266°F)</td>
<td>16 hours @ 130°C (266°F)</td>
</tr>
<tr>
<td>Cilbond 49SF</td>
<td>16 hours @ 130°C (266°F)</td>
<td>16 hours @ 130°C (266°F)</td>
</tr>
<tr>
<td>Cilbond 49SF + Cilcure B (100:10)</td>
<td>30 minutes @ 105°C (221°F)</td>
<td>16 hours @ 130°C (266°F)</td>
</tr>
<tr>
<td>Cilbond 49SF + Cilcure B (100:5)</td>
<td>16 hours @ 130°C (266°F)</td>
<td>16 hours @ 130°C (266°F)</td>
</tr>
</tbody>
</table>

- Pre-bake resistance of Cilbonds can be dependent on the polyurethane type
- Longer/higher temperature pre-bakes can be possible but must be fully validated
- If the pre-bake is too excessive then PU to cement failure is usually seen rather than a visual deterioration of the coating
When casting with hot cure TDI prepolymer /Ethacure 300 systems or with hot cure quasi MDI systems, all coated bars were dried and then pre-baked for 1hr @ 105°C except CB49SF + Cilcure B which was given 30 minutes @ 105°C. All PU’s were cast using standard mix ratio and conditions, and left for 24 hours at room temperature.
Environmental Testing

Salt spray testing consisted of placing both unstressed and stressed pieces into the salt spray cabinet. Each bar was checked every 24 hours for signs of failure. The test conditions were set to meet those of DIN EN ISO 9227:2006/10, 35°C with 5% salt solution. The test was run for 700 hours.

Boiling water testing was conducted by placing both unstressed and stressed pieces into a hot water bath set at 99°C. Each piece was fully submerged at all times and checked every 24 hours for signs of failure. The test was run for 500 hours.

Heat resistance tests were conducted by checking at which temperature, moulded peel test specimens showed signs of bond failure, either CM (cement to metal) or RC (rubber (PU) to cement) fail.
Table 2. Properties of the CIL PU bonding systems.

Note: Very little difference was observed between stressed and unstressed parts using the above procedures, so the results apply to both.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cilbond 41</td>
<td>20 - 90°C</td>
<td>400 hours</td>
<td>2 hours @ 95°C</td>
<td>300 hours</td>
<td>Good</td>
<td>Good</td>
<td>120°C</td>
<td>Cold cast PU, quasi prepolymers, sprayable systems, foams generally.</td>
<td></td>
</tr>
<tr>
<td>Cilbond 41 + Cilcure B (mixed at 100:5)</td>
<td>15-90°C (plus limited use up to 180°C)</td>
<td>≥700 hours</td>
<td>1 hour @ 105°C</td>
<td>&gt;&gt;400 hours (9)</td>
<td>Excellent</td>
<td>Fair</td>
<td>140°C</td>
<td>Cold cast PU, quasi prepolymers, sprayable systems, foams generally. Improved adhesion to FBE, etc. Excellent for rotational casting of large rollers, where there is no heat input.</td>
<td>Limited open time. Bonds fast-cure amines. Bonds PVC, CR, CSM &amp; some NBR compounds.</td>
</tr>
<tr>
<td>Cilbond 45SF</td>
<td>80 - 180°C</td>
<td>400 hours</td>
<td>48 hours @ 100°C</td>
<td>300 hours</td>
<td>Good</td>
<td>Excellent</td>
<td>130°C</td>
<td>High temperature bonding of all hot cast PU types and TPU.</td>
<td>For best performance Cilbond 45SF must be pre-baked.</td>
</tr>
<tr>
<td>Cilbond 48</td>
<td>20 - 180°C</td>
<td>700 hours</td>
<td>24 hours @ 110°C or 16 hours @ 130°C</td>
<td>400 hours</td>
<td>Excellent</td>
<td>Very Good</td>
<td>150°C</td>
<td>Cold cast, all quasi prepolymers, Vulkollan, all hot-cure prepolymer types.</td>
<td>The most versatile one-component system. Fast-drying and works with or without pre-bakes.</td>
</tr>
<tr>
<td>Cilbond 49SF</td>
<td>70 - 180°C</td>
<td>500 hours</td>
<td>350 hours</td>
<td>Very Good</td>
<td>Excellent</td>
<td>130°C</td>
<td>High temperature bonding to hot cast PU types such as Adiprene, Vibrathane and Vulkollan and TPU where hydrolysis resistance is required.</td>
<td>For best performance Cilbond 49SF must be pre-baked.</td>
<td></td>
</tr>
<tr>
<td>Cilbond 49SF + Cilcure B (mixed at 100:10)</td>
<td>40 - 140°C</td>
<td>≥700 hours</td>
<td>30 minutes @ 105°C</td>
<td>≥500 hours</td>
<td>Excellent</td>
<td>Very Good</td>
<td>180°C</td>
<td>High temperature resistance and good solvent resistance. Best system for rotational casting of small to medium sized rollers.</td>
<td>For better pre-bake resistance and longer storage of coated metals, use a cover-coat of Cilbond 49SF.</td>
</tr>
</tbody>
</table>

(9) The cold cast PU’s fail before the Cilbond 41+Cilcure B.

Adiprene® and Vibrathane® are registered trademark of Chemtura Corp.  Vulkollan® is a registered trademark of Bayer AG.
Conclusions.

1. Cilbond 48 proved to be the most versatile one-component bonding system, bonding all types of PU’s, from cold cure to hot cast prepolymers and TPU’s.
2. Cilbond 49SF + Cilcure B gave the best salt spray and boiling water resistance on high performance polyether prepolymers cured with likes of Ethacure 300.
3. Both Cilbond 41 + Cilcure B and Cilbond 48 gave excellent salt spray and boiling water resistance with Cilcast 100 + Cilcure B, though Cilbond 48 showed slightly less cement-metal failure after the salt spray test.
Think Differently?
What can WE do?
Discipline of a Good bond

How can YOU do things differently?

Clean and Calm Environment

Tidy & Organized workshop

Brighter Lighter
Discipline of a Good bond

How can WE help you do things differently?

Train your people to
  Mix it
  Apply it
  Dry it
  Bond it

Cilbond: Its secret is in its name
What are we Bonding?

Metal Substrates
Substrates

- Steel, Cast Iron
- S/S, Case Hardened Steel
- Chromium, Nickel.
- Aluminium and Alloys
- Zinc, Brass, Bronze
- Engineering Plastics, incl. FRP/GRP, PPO, POM, PPS, PEEK, PET, PBT, Polyamides (Nylon)
- Other Plastics; Glass, Ceramics
Holistic View

Polyurethane Elastomer

Metal or Plastic

BONDING AGENT

PRIMER & TOP COAT
ONE COAT
WATER BASED
Mechanisms of Adhesion between the Primer and Metal

In preparing metals for bonding, steel in particular, the idea is to produce a surface free of contamination, is easy to wet, has a “sharp” irregular surface to promote a mechanical key and controlled oxidation:

We are fortunate that for the commonly used metals this ‘controlled’ oxidation occurs naturally after grit blasting or acid etching. In the case of plastics, no such convenient oxidation process takes place.
Mechanisms of Adhesion between bonding agent and metal

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**Diagram:**
- Bonding agent
- Metal Surface
- Van de Waals Forces
- Polar Forces
- Hydrogen Bonding
- Site for Chemical Bonding
One-Coat Bonding

Good Wetting of the one-coat by the elastomer in the moulding process is important.

- **Van De Waals Forces**
- **Hydrogen bonds**
- **Inter-mixing**
- **Polar attraction**
- **Chemical reaction/covalent bonds**

**ELASTOMER**

**ONE-COAT**

**METAL**

- Oxide Layer
- Interlocking Shapes/mechanical key at metal surface

Melding applies only to speciality one-coats.
## Typical Bond Forces

<table>
<thead>
<tr>
<th>Type of Bond</th>
<th>Bond Strength, kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals forces</td>
<td>8</td>
</tr>
<tr>
<td>Polar bonds</td>
<td>10-20</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>12-30</td>
</tr>
<tr>
<td>C-H</td>
<td>412</td>
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<td>C-O</td>
<td>360</td>
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<td>C-N</td>
<td>305</td>
</tr>
<tr>
<td>C=C</td>
<td>612</td>
</tr>
<tr>
<td>Intermixing/melding</td>
<td>???? High</td>
</tr>
<tr>
<td>Mechanical “key”</td>
<td>???? Variable</td>
</tr>
</tbody>
</table>
Demands on the bonds can be very severe:

- High temperatures
- Static and/or dynamic fatigue
- High impact stresses
- Hot water/high and low pH’s
- Aggressive fluids
One-Coat Bonding Agent Attributes

- Low viscosity and wet metals
- Dry to tough durable coatings
- The designed polar resins bond to metals and some elastomers
- The designed polymers are aliphatic chlorine free and are multifunctional
- The designed polymers bond elastomers
- The curing agents cross-link the resins, the polymers and they also co-cure
Benefits of One-Component CILBOND

- Reduced process duplication
- Reduced inventory levels
- Reduced health & safety hazards
- Reduced Risk of mis-identification on parts
- No risk of C-C bond failure
- Reduced overall cost (production, storage, etc.)
CIL Technology

- One component Cilbond:
  - Water-Based
  - Solvent-Based
  - Lead-Free

- Produce own Polymers

- Quality control at all levels

- Continuous Improvement
One component bonding agent technology outperforms traditional two component bonding agents
Thank you for Listening
What is the mode of Failure?

- Cement failure (C)
  - Poor drying
  - Blistering of bonding agent
  - Bonding agent contaminated
  - Inadequate cure
  - Bonding agent out of date
  - Bonding agent not homogenised

- PU Tear (RT or R)
  - Poor drying
  - Blistering of bonding agent
  - Bonding agent contaminated
  - Inadequate cure
  - Bonding agent out of date
  - Bonding agent not homogenised

- Cement Cement (CC)
  - Surface Contaminated
  - Bonding Agent contaminated
  - Bonding Agent out of date
  - Inadequate cure (heat)

- Cement Metal (CM or M)
  - Layer of Bonding Agent too thin
  - Bonding Agent not Dried
  - Poor Metal/surface Preparation
  - Compound’s adhesive ingredients
  - Environmental attack
  + see CC

- PU Cement (RC)
  - Incorrect Bonding Agent
  - Compound out of date
  - Compound bloom
  - Bonding Agent pre-cured
  - Bonding agent not dried
  - Incorrect pressure/cure
  + see CC

…..or a mixture of failure modes
BASIC REACTIONS IN URETHANE CHEMISTRY

1. R - NCO + R' - OH → R - N - C - O - R' → URETHANE
   ISOCYANATE  ALCOHOL
   Slow, but catalysable

2. R - NCO + R' - NH2 → R - N - C - N - R' → UREA
   ISOCYANATE  AMINE
   V fast

3. 2R - NCO + H - O - H → R - N - C - N - R' + CO2↑ → UREA
   ISOCYANATE  WATER
   Slow
The main types of polyurethane elastomers, which are bonded

- TPU’s
- TDI prepolymer
- MDI prepolymer
- NDI systems
- MDI quasi’s
- MDI quasi’s
- Millable PU’s
  - Sulphur cured
  - Peroxide cured
  - NCO cured
- Injection moulded
- Hot cast 90-110°C
- Hot cast 90-110°C
- Hot cast 100-120°C
- Hot cast 70-100°C
- Cold cast 20-50°C
- Injection, transfer or compression moulded as for a typical rubber
Possible Mechanisms for Chemical Bonding of Adhesives to PU’s

<table>
<thead>
<tr>
<th>ADHESIVE</th>
<th>PU DURING CURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>- O – H</td>
<td>O = C – N –</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td></td>
</tr>
<tr>
<td>- N = C = O</td>
<td>H – N – C – O –</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>O</td>
</tr>
<tr>
<td>- C – O – CH₂</td>
<td>H – N – C – O –</td>
</tr>
<tr>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>- N = C = O</td>
<td>H – N – C – N –</td>
</tr>
<tr>
<td>Isocyanate</td>
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</tr>
<tr>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>- O – H</td>
<td>O = C – N –</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td></td>
</tr>
<tr>
<td>- N = C = O</td>
<td>H – N – C – O –</td>
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<td>Epoxy</td>
<td></td>
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Net: Urethane, Allophanate, Branched Urethane, Branched Urea.
# Recommendations

## Table 3. Summary of PU bonding recommendations.

<table>
<thead>
<tr>
<th>Bonding System</th>
<th>PU types bonded</th>
<th>Maximum Boiling Water Resistance (Hours)</th>
<th>Maximum Salt Spray Resistance (Hours)</th>
<th>Maximum heat resistance of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB48</td>
<td>All PU system types and processes, except on-site cold cast PU’s at &lt;&lt;20º C</td>
<td>400</td>
<td>700</td>
<td>150 ºC</td>
</tr>
<tr>
<td>CB49SF or CB45SF</td>
<td>Hot prepolymer systems&lt;br&gt;Hot quasi systems&lt;br&gt;Vulkollan TPU</td>
<td>350</td>
<td>500</td>
<td>130 ºC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>CB49SF + B (100:10)</td>
<td>All systems used with 49SF plus warm rotational cast systems</td>
<td>≥2500</td>
<td>≥700</td>
<td>180 ºC</td>
</tr>
<tr>
<td>CB41</td>
<td>All cold cast systems</td>
<td>≥300 (RTV PU)</td>
<td>≥400 (RTV PU)</td>
<td>120ºC</td>
</tr>
<tr>
<td>CB41 + B (100:5)</td>
<td>All cold cast systems and especially large rotational cast rollers and pipes, etc</td>
<td>&gt;400 (RTV PU)</td>
<td>≥700 + (RTV PU)</td>
<td>140 ºC</td>
</tr>
</tbody>
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