New Fast Curing Aliphatic Laminating Adhesives Reduce Waste and Energy Consumption

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Why Flexible Packaging Adhesives?

Flexible packaging adhesives are used to protect graphics and add utility to a package by bonding two or more films together.

- Laminated packages can have explosive graphics and unique mixes of aggressive ingredient resistance.
- Laminated labels are scuff and scratch resistant and very glossy.

Example lamination for packaging:

- 0.7 mil clear OPP
- Printing Ink
- Adhesive
- 1 mil white OPP
How Do They Work?

**Bond Strength**
Tested by pulling apart one inch strips of laminated films

**Heat Resistance**
Tested by folding a one inch strip of laminate, heat sealing the inner film surface to itself, and then pull apart

**Coefficient Of Friction (COF)**
Tested by dragging a weighted piece of film across another piece of film and measuring the resulting force

**Aggressive Ingredients**
Tested by making & filling small pouches with product. Accelerated aging done in ovens. Inspect and test for deteriorated appearance or bonds.
Flexible Packaging Converting Process

1. Film, foil and/or paper substrate
2. Substrate is printed
3. Web substrates are laminated together
4. Wide web laminated rolls are slit
5. Rolls converted to bags or pouches and filled
6. Finished product
Historical Background for Solventless Laminating Adhesives in Flexible Packaging

- R&D: 1960s
- Final developments in 1970s
- Market introduction in late 1970s
- First 5 roller coating unit in early 1980s
- Market success:
  - Europe in mid-1980s
  - North America mid-1990s
Solventless Laminator

Photo courtesy of Nordmeccanica® Solventless Laminators
Typical Properties of the Adhesive

- Two components:
  1. Polyisocyanate (usually MDI-based)
  2. Curative (polyol)
- Low initial mixed viscosity (1,000 – 3,000 cps); reaction begins immediately after mixing the two components.
- Slightly over-indexed with isocyanate
- Low-to-zero green bond off-line; requires high tension control coater.
- Cure rate is typically 1-3 days.
Advantages in Solventless Laminating

• Smaller capital investment (i.e., lower cost laminator, no ovens, no incinerator)
• Less energy (no ovens or incinerator)
• Lower coat weight
• Higher production speed
• No solvent costs or VOCs
• Smaller floor space requirement
• Aromatic solventless adhesives are typically less expensive on a dry pound compared to solvent-based adhesives
Disadvantages of Solventless Adhesives

- Low-to-zero green bond; unable to laminate and slit films in-line
- Poor balance of long pot-life and fast full cure; especially for aliphatic urethane adhesives
  - 3 – 10 days to cure is typical
  - Hot rooms typically used to force cure adhesive in shorter time. Hot room can cause heat sensitive films to curl in laminate
Pot Life of Typical Aliphatic Laminating Adhesives

- Pot-life too short; Full cure acceptable
- Pot-life good; Full cure slow.
DSC Cure Rate of Typical Aliphatic Laminating Adhesives

Control 1 (4 days)

Control 2 (> 4 days)
Develop aliphatic urethane adhesive technology that provides flexible packaging converters an adhesive with good balance of long pot-life with faster full cure.
Background:
Trigger Cure Aliphatic Urethane Coatings

aliphatic isocyanate monomer / prepolymer in solvent

+ curative polyol with blocked catalyst in solvent

mix → extended pot-life → aliphatic polyurethane coating

excess R”-SH

faded catalyst

NR₃

Initial Attempt at Implementing Blocked Catalyst into Solventless Laminating Adhesives

aliphatic isocyanate monomer / prepolymer + curative polyol with blocked catalyst (30 : 1) → mix → unacceptable pot-life (< 2hrs)

Viscosity Cure profile @ 35 C

- Short pot-life
- Shift longer
Variables Effecting Blocked Catalyst Reactivity

1. Ratio of catalyst to blocking agent
2. Type of catalyst and blocking agent
3. Time
4. Temperature
5. Formulation
1. Effect of Ratio of Catalyst to Blocking Agent

Viscosity Cure Profile @ 35°C

- TMPTMP / T-12 (30 : 1)
- TMPTMP / T-12 (45 : 1)
- TMPTMP / T-12 (60 : 1)
2. Effect of Type of Blocking Agent

Viscosity Cure Profile @ 35°C

- mercapto-silane / T-12 (30:1)
- TMPTMP / T-12 (30:1)
3. Effect of Time

Sample 11 - TMPTMP / T-12 Ratio 60 : 1
Curative stored at @ 40°C

Viscosity (Poise)

Time (minutes)
4. Temperature

**Viscosity Cure Profile**

Heat Treated Curative with mercapto-silane / T-12 (30 : 1)

- Initial
- 75°C for 1hr
- 100°C for 5hr
- 125°C for 3hr

- Time (minutes)
- Viscosity (Poise)
5. Formulation Effect

- **Sample 1** – tested immediately (time zero)
- **Sample 2** – curative from Sample 1 stored at 60°C for 4 weeks before testing – pot-life increased substantially
- **Sample 3** – same curative, but only blocked catalyst mixture stored at 60°C for 4 weeks – formulated into curative and ran immediately – no change in reactivity

### Viscosity Cure Profile

Curatives with mercapto-silane / T-12 (30 : 1)

![Graph showing viscosity cure profile with three samples: Sample 1, Sample 2, and Sample 3.](image)

- **Sample 1**
- **Sample 2**
- **Sample 3**
How is the Catalyst / Blocking Agent Working?

Proposed blocked structure

active catalyst

excess R''-SH

blocked catalyst
Tin signal becomes severely attenuated and / or dispersed with aging and heat. The electronic environment around the tin has changed significantly.
Even at 10% blocked catalyst loading, the signal is severely attenuated / dispersed with elevated temperature and time.
Results

Viscosity Cure Profile with Time
Comparing Improved Cure Adhesives vs Industry Standards

- **Improved Cure 1**
- **Improved Cure 2**
- **Control 1 - poor potlife**
- **Control 2 - slow full cure**
Temperature Effect on Final Cure Times (DSC)
- Improved Cure Formulation 2

![Graph showing % Conversion vs Time (hrs) for 25C and 35C cure temperatures. The graph indicates faster and more substantial conversion at 35C compared to 25C.](image-url)
Does It Stick?

Bond strengths (gli)

- Improved Cure 2
- Control 2

PET/PE (tear)
OPP/PE (bonds) (tear)
Nylon/cast prop (tear)
Celplast**/PE (adh)
Besela*/PE (tear)
PLA/PLA (adh)
PET(PVDC coated)/PE (tear)

*Besela is a registered trademark of Kureha Corporation
**Celplast is a trademark of Celplast Limited
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**Common Characteristics**

- OPP DISCOLORATION
- SLIGHT DISCOLORATION
- DISCOLORATION ON ALL

+ Indicates film PASSED ingredient test

- Indicates film FAILED ingredient test

WB = Weak bonds after ingredient testing
Summary

- Developed long pot-life with fast full cure for solventless aliphatic urethane technology
  - Blocked catalyst mechanism not well understood
  - Variables influencing blocking / deblocking are well understood and controllable
- New technology has been incorporated into solventless aliphatic urethane adhesives and provides converters the benefit of long pot-life and fast full cure for both food and industrial laminates
- Patent application pending
Acknowledgements

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Ashland Performance Materials
Thank You

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