This paper will review the following:

- Laminating adhesives and their end uses.
- The growth of waterborne laminating adhesives
- The chemistries of waterborne and solvent adhesives
- Testing of new waterborne acrylic adhesive vs. solvent borne urethane
- Life cycle analysis of waterborne acrylic vs. solvent borne urethane

Laminating adhesives are generally classified by end use from general purpose with typical end uses such snack food and bottle labels, medium performance for hot fill and pasteurized products, and high performance for retort packages. Laminating adhesives are classified as solvent borne, waterborne, and solventless adhesives. Solvent borne adhesives account for the earliest chemistry and are still utilized in approximately two-thirds of applications.

The driver in the growth of waterborne adhesives is fueled by several factors:

- Economics – cost of solvent and favorable cost of waterborne adhesives
- Productivity improvements and ease of handling
- Health and safety – eliminates potential fire hazards
- Government regulations on VOC emissions
- Capital expenditure of moving from solvent to water requires minimal capital expense.

In the last decade, research has been focused on developing water borne laminating adhesives that are comparable to solvent based adhesives. This has lead to the introduction of both acrylic emulsion and polyurethane water dispersion (PUD) adhesives. Waterborne acrylic adhesives have historically been used for general purpose applications. Typical problems which limited the switch from solvent based adhesives to water based adhesives have been:

- Poor adhesion, moisture resistance and heat resistance
- Foaming, short pot life, clogged anilox cells
- Interaction of organic amines with ink and metallized film.

**Two part urethane adhesive**

NCO----polymer----NCO (in Solvent) + HO---R----OH (in solvent)

**Adhesive** **Coreactant**
Drying → Curing
-------→ -------→ -------polymer –NH-CO-O-polymer-------

Polyurethane Adhesive:
- Isocyanate (NCO) terminated polyether or polyester urethane dissolved in solvent
- Molecular weight: 1,000-50,000

Coreactant:
- Hydroxyl (OH) terminated polyester or polyether dissolved in solvent

This chemistry offers high crosslink density which provides the lamination with good product and heat resistance. Waterborne chemistry is an emulsion polymer made through free radical polymerization of acrylic monomers in water. This chemistry allows for the film formation of the adhesive. In comparison this results in the following:

Waterborne acrylic
- high molecular weight
- low viscosity
- high application solids

Solvent borne urethane
- low molecular weight
- high viscosity
- low application solids

A series of tests were run comparing seal strength, interbond adhesion and heat and moisture resistance. In all cases the waterborne chemistry provided similar performance to that of the solvent based adhesive. Another application that requires unique properties is fresh produce packaging. While solvent borne adhesives can effect the critical oxygen transmission rate of the laminate, the oxygen transmission rate is not effected whatsoever when water based technology is utilized.

Life cycle inventory (LCI) is the quantification of energy/material inputs and environmental impacts of a material or operation over its life cycle. An LCI study of waterborne vs. solventborne adhesives was initiated with the following results:

<table>
<thead>
<tr>
<th></th>
<th>MJ/Ream Laminated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solvent-borne</td>
</tr>
<tr>
<td>Feedstocks</td>
<td>70.9</td>
</tr>
<tr>
<td>Transportation</td>
<td>5.7</td>
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<td>Electricity Generation</td>
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</tr>
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<td>Total Energy</td>
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</tr>
</tbody>
</table>
From this study, the overall performance of waterborne adhesives and solvent borne adhesives is very comparable. Life cycle inventory analysis shows that energy use, carbon dioxide emission and water use are much less for waterborne laminating adhesive when compared to solvent borne adhesives.
Medium Performance Acrylic Waterborne Laminating Adhesives

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Technical Service Manager

ROHM & HAAS | Packaging and Building Materials
Agenda

• Laminating Adhesive and its End-use
• Growth of Waterborne Laminating Adhesive
• Chemistry Difference between Solvent Borne Urethane and Water-borne Acrylic
• Test Results of New Waterborne Acrylic vs. Solvent borne Urethane
• Life Cycle Analysis of Waterborne Acrylic vs. Solvent Borne Urethane
Laminating Adhesive Classified by End-Use

• **Medium performance laminating adhesive**
  – Good adhesion on film/film and film/foil
  – Good product resistance and moisture resistance for hot fill and pasteurization
  – Typical end-use:
    • frozen food, fruit juice, meat, detergent packaging, medical packaging
  – Structures:
    • PET/Al/PE,
    • PET/PE,
    • Nylon/PE,
Laminating Adhesive Classified by End-Use

- **High performance laminating adhesive**
  - High heat and moisture resistance for retort applications
  - Typical end-use: MRE, ready-to-eat meal, pet food and medical packaging
  - Structure:
    - PET/Al/CPP,
    - PET/Al/OPA/CPP,
    - PET/CPP
Laminating Adhesive Classified by End-Use

• General purpose dry bond laminating adhesive
  – Good adhesion on plastic and metallized films
  – Typical end-use:
    • Snack food
    • Bottle label
  – Structures:
    • OPP/OPP, OPP/PE,
    • OPP/metOPP, PET/PE,
Laminating Adhesive Classified by Solvent/Carrier

- Laminating adhesive
  - Solvent borne adhesive
  - Solventless adhesive
  - Waterborne adhesive

![Pie chart showing the distribution of laminating adhesives by solvent type: Solvent borne 67%, Solventless 25%, Waterborne 8%](chart.png)
Solvent Borne Adhesive

- Solvent borne adhesive is the most widely used technology for flexible packaging laminating adhesives.
  - Based on urethane technology.
  - Long history of product development.
  - Provides good adhesion and performance to meet requirements from general to high performance food packaging.
  - Offers good adhesion, good product resistance and heat resistance.
Solvent/water-borne Dry based Lamination

- Adhesives
- Storage
- Mixing Unit
- Application Unit
- Drying
- Laminating Unit
- Cutting
- Delivery
- Finished Products Stock
What is Driving the Growth in Waterborne Adhesive?

• **Economics**
  – The cost of solvent is getting more expensive
  – Waterborne adhesive is typically less expensive than solvent borne adhesive for converters

• **Productivity Improvements**
  – Easy to use, no dilution needed
  – High running solids: 45% solids
  – Waterborne adhesive gives higher shear strength, allowing for immediate slitting of the lamination
What is Driving the Growth in Water-Based Adhesive?

- **Health and Safety**
  - Eliminates the potential fire hazard of solvent borne adhesives
  - Healthier food packaging: No risk of aromatic amine and retained solvent

- **Governmental Regulatory**
  - Government regulations on VOC and CO$_2$ emission

- **Capital Expenditure**
  - The transition from solvent to water requires little, if any, capital expense
Waterborne Laminating Adhesive: In the past

- In the last decade, research has been focused on developing waterborne laminating adhesives that are comparable to solvent-based adhesives.
- Both acrylic emulsion and polyurethane water dispersion (PUD) adhesives are available in the market.
- Waterborne acrylic adhesives have historically been used for general purpose applications.
- Polyurethane water dispersions (PUD) have been used to improve the adhesion and product resistance of water-based adhesive.
Waterborne Laminating Adhesive: in the past

• Typical problems which have limited the switch from solvent-based adhesive to water-based adhesive:
  – Poor adhesion, poor moisture resistance and poor heat resistance
  – Foaming, short pot life, clogging anilox cells
  – Interaction of organic amine with ink and metallized film
Medium Performance Acrylic Adhesive: Is it possible?

• Two key questions for developing medium performance water-based acrylic adhesive:
  – Can waterborne acrylic offer the same excellent adhesion, product resistance and heat resistance as solvent borne urethane?
  – Can waterborne acrylic overcome the mechanical stability problems commonly seen in polyurethane water dispersion (PUD)?
Solvent-Based Adhesive and Chemistry

Two part urethane adhesive

\[
\text{NCO----polymer-----NCO (in Solvent)} + \text{HO---R----OH (in solvent)} \\
\text{Adhesive} + \text{Coreactant}
\]

Drying     Curing
-------→ -------→ -------polymer –NH-CO-O-polymer-------

Polyurethane

Adhesive:
- Isocyanate (NCO) terminated polyether or polyester urethane dissolved in solvent
- Molecular weight: 1,000-50,000

Coreactant:
- Hydroxyl (OH) terminated polyester or polyether dissolved in solvent
The performance of medium performance solvent-based adhesive is achieved through urethane chemistry:
- The hydrogen bonding from urethane provides good adhesion on various substrates including foil.
- Urethane chemistry in solvent-based adhesives gives the high crosslink density required for good product and heat resistance.
Chemistry of Water-Based Acrylic Adhesive

• The chemistry of waterborne acrylic is very different from solvent-borne urethane.

• Waterborne acrylic is an emulsion polymer made through free radical polymerization of acrylic monomers in water.
Free Radical Addition Polymerization

Initiation

\[
R-O-O-R \xrightarrow{\Delta} 2 \text{ RO} \cdot
\]

Propagation

\[
\text{RO} \cdot + M \rightarrow \text{RO}M \cdot
\]

\[
\text{RO}M \cdot + nM \rightarrow \text{RO}M-(M)n \cdot
\]

Termination
Emulsion Polymers: What Are They?

- **High molecular weight polymer particles finely dispersed in water**
- **Appearance**
  
  Like milk - translucent to opaque white.
- **Particle Size**
  
  Usual range is 50 to 1000 nanometers. (0.05 to 1.0 microns)
- **Molecular Weight**
  
  500,000 - 1,000,000 is typical.
  
  Molecular weight much higher than solvent-based urethane
Water-based Acrylic vs. Solvent-based Urethane

- **Waterborne Acrylic**
  - The emulsifier serves as a stabilizer for polymer particles suspended in water

- **Solvent borne urethane**
  - The polyurethane network is formed after the adhesive is applied on substrates.
Film Formation of Acrylic Waterborne Adhesive

Adhesive particles dispersed in water

Adhesive particles coated on substrates, dried through oven

Cold flow of adhesive to fill space
Waterborne Acrylic vs. Solvent Borne Urethane

- **Waterborne Acrylic**
  - Very high molecular weight, high shear resistance
  - Low viscosity
  - High application solids

- **Solvent borne urethane**
  - Low molecular weight
  - Viscosity increases dramatically with increasing molecular weight
  - Low application solids
Seal Strength Test

- The seal strength of a laminate is critical to prevent the packaging from falling apart during processing and transportation. This is especially important for large bags with heavy weight.

- Generation 2 waterborne adhesive has the same good seal strength as solvent-based urethane.

- Table 1 shows the results of a heat seal strength test on PET/PE laminates.
### Table 1: Seal Strength

(Heat seal condition: 1.5 second, 380F, 25µPET /38µPE, 40psi)

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Chemistry</th>
<th>Seal Strength (N/15mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane Adhesive A</td>
<td>Solvent-based urethane</td>
<td>32.2±3.7</td>
</tr>
<tr>
<td>Urethane Adhesive B</td>
<td>Solvent-based urethane</td>
<td>37.6±3.9</td>
</tr>
<tr>
<td>Generation 2 waterborne adhesive</td>
<td>Water-based acrylic/urethane hybrid</td>
<td>32.6±2.9</td>
</tr>
</tbody>
</table>
Adhesion Test Results

- Generation 2 waterborne adhesive has good adhesion on various films including foil, nylon, polyethylene, polyester and polypropylene.

  Urethane Adhesive A and Urethane Adhesive B, two widely used solvent borne urethane adhesives, were used as the control in adhesion tests.

- The adhesion of Generation 2 waterborne adhesive is similar to solvent-based products.
Adhesion Comparison  Solvent borne vs. Waterborne

- OPP/OPP
- PET/38µ PE
- Nylon/PE-EVA
- Nylon/80µ PE
- Foil/80µ PE
- Foil/PET
- Foil/LLDPE

Film Destruct

Generation 2
WB adhesive
Urethane Adhesive A
Urethane Adhesive B

T-Peel (N/15mm) @ 100mm/min speed
Heat and Moisture Resistance Test

• Heat and moisture resistance is required for various food packaging, since the package has to be able to withstand processes like pasteurization.

• Three typical structures were used in the “boil-in-bag” test to compare Generation waterborne adhesive with solvent borne products.
  – PET/PE
  – Nylon/PE
  – Foil/PE
Heat and Moisture Resistance Test

- Generation 2 had similar to slightly better adhesion compared to solvent-based urethane after the boiling test in PET/PE and Nylon/PE structures.

- For the foil/PE structure, the adhesion of Generation 2 was better than both solvent borne urethane adhesives after boiling, with the adhesion of one solvent-based urethane dropping after the test.
Adhesion after "Boil-in-Bag" Test
(Pouch filled with water and boiled in water for 30 minutes)

<table>
<thead>
<tr>
<th>Material</th>
<th>Adhesive A before test</th>
<th>Adhesive A after test</th>
<th>Adhesive B before test</th>
<th>Adhesive B after test</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/38µ PE</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
</tr>
<tr>
<td>Nylon/80µ PE</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
</tr>
<tr>
<td>Foil/80µ PE</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
<td>Urethane</td>
</tr>
</tbody>
</table>

Film Destruct
Fresh Produce Packaging

- Fresh-cut vegetable packages are becoming more popular because they are convenient.

- The quality of packaged fresh-cut lettuce and other produce is best maintained by selecting packaging laminates that match the oxygen transmission rate (OTR) to the respiration rate of the product being packaged.

- Typical solvent borne urethane adhesives will provide some gas barrier and affect the oxygen transmission rate of laminates.
Fresh Produce Packaging

- The Generation 2 waterborne acrylic product is oxygen permeable. The oxygen transmission rate of the laminate will not be affected by Generation 2 adhesive.

- There is no solvent used in waterborne acrylic products. This eliminates retained solvent in the packaging due to the adhesive.
Table 3: Oxygen Transmission Rate Test

(\text{cc/100in}^2/24\text{hours}, 23^\circ\text{C}, 0\%\text{RH})

<table>
<thead>
<tr>
<th>Construction</th>
<th>OTR (Without adhesive)</th>
<th>OTR (With Generation2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPP/PE</td>
<td>110</td>
<td>109</td>
</tr>
<tr>
<td>OPP/PE</td>
<td>143</td>
<td>154</td>
</tr>
</tbody>
</table>
Life Cycle Inventory

• Quantification of energy/material inputs and environmental impacts of a material or operation over its life cycle
  – Can range from mineral extraction/crop production (cradle) to ultimate disposal of discarded material (grave)
  – Common metric (megaJoules/kg) used for energy and feedstock inputs
Adhesives LCI Scope

“Cradle-to-gate” LCI, where “gate” is the customer’s shipping gate
Flexible Packaging Adhesives/Co-Reactants for LCI Comparison

Basis: Laminate 1 ream of flexible packaging

Rohm and Haas Products for LCIs:

<table>
<thead>
<tr>
<th>Solvent-borne</th>
<th>Adhesive “A”</th>
<th>Co-Reactant “B”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterborne</td>
<td>“L”</td>
<td>“CR”</td>
</tr>
</tbody>
</table>
# LCI Adhesive Application Data

<table>
<thead>
<tr>
<th>Adhesive System</th>
<th>Application Rate</th>
<th>Product % Solids</th>
<th>Application Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lbs Solids/Ream</td>
<td>Lbs Organics/Ream</td>
<td>CR Adhesive</td>
</tr>
<tr>
<td>Solvent</td>
<td>2.25</td>
<td>3.72</td>
<td>60</td>
</tr>
<tr>
<td>Waterborne</td>
<td>1.5</td>
<td>1.5</td>
<td>45</td>
</tr>
</tbody>
</table>
Flexible Packaging Drying Ovens

- Potentially energy intensive operation
- Needed for solvent-borne and waterborne adhesives, but not for solvent-free
- Energy values based on Boustead data for packaging lamination
  - 20% added for additional energy needed for waterborne adhesives
  - Largest uncertainty of all energy inputs to the LCI
Transportation of RMs and Products

- Petrochemicals/RM transport from US Gulf Coast (or western Canada) to upper-midwest
  - 1760 km by rail or truck, as appropriate

- Product transport to customer
  - 1000 km by truck
# LCI Results – Feedstocks and Energy

<table>
<thead>
<tr>
<th></th>
<th>Solvent-borne</th>
<th>Water-borne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstocks</td>
<td>70.9</td>
<td>36.0</td>
</tr>
<tr>
<td>Transportation</td>
<td>5.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Electricity Generation</td>
<td>45.7</td>
<td>11.6</td>
</tr>
<tr>
<td>Drying Oven</td>
<td>69.1</td>
<td>88.4</td>
</tr>
<tr>
<td>Other Direct Fuel Use</td>
<td>117.1</td>
<td>20.4</td>
</tr>
<tr>
<td><strong>Total Energy</strong></td>
<td><strong>308.4</strong></td>
<td><strong>158.7</strong></td>
</tr>
</tbody>
</table>
Energy LCI for Lamination Adhesives

- **Solvent-borne**
  - Feedstocks
  - Transportation
  - Electricity generation
  - Drying Oven
  - Other Direct Fuel Use

- **Waterborne**
  - Feedstocks
  - Transportation
  - Electricity generation
  - Drying Oven
  - Other Direct Fuel Use
CO2, Water consumption and Raw Material Use SB vs. WB
Energy- and Material-Intensity

- Differences in the energy and resource impacts of the alternate adhesives is caused primarily by:
  1. The amount of organic material applied per ream
  2. The need for drying ovens for the solvent- and water-borne adhesives

<table>
<thead>
<tr>
<th></th>
<th>Solvent</th>
<th>Waterborne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lbs organic/ream</td>
<td>3.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Conclusion

• We reviewed the applications and chemistries of laminating adhesives

• We compared performance of waterborne adhesives and solvent borne adhesives and showed that they are very comparable

• Life cycle inventory analysis shows that energy use, carbon dioxide emission and water use are much less for waterborne laminating adhesives when compared to solvent borne adhesives.
Please remember to turn in your evaluation sheet...