2-Component Waterbased Polyurethane Coatings

2021 Waterborne and High Solids Symposium Preconference Tutorial

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Agenda

• History of Polyurethanes
• Applications of 2K Waterborne Polyurethanes
• Chemical Reactions
• Polyol Component Considerations
• Polyisocyanate Types
• Mixing & Potlife Effects
• Film Properties
• Guide Formulas
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Polyurethanes were discovered in 1937 by Otto Bayer

**Reaction of diisocyanates with polyols or amines to form polyurethanes or polyureas**

\[
\begin{align*}
R-N=C=O + R'-OH &\rightarrow R-N-O-R' \\
\text{ISOCYANATE} &\quad \text{ALCOHOL} &\quad \text{URETHANE} \\
R-N=C=O + R'-NH_2 &\rightarrow R-N-N-R' \\
\text{ISOCYANATE} &\quad \text{AMINE} &\quad \text{UREA}
\end{align*}
\]

Otto Bayer
DR Patent 11.11.1937
**Segmentation and hydrogen bonding** are key features of 2K PU coatings

- Fast drying at low baking temperatures
- Very low VOC possible
- Stability towards UV exposure
- High chemical and water resistance
- Pleasing optical properties, high gloss
- Hardness, toughness and elasticity due to urethane and urea structure
- Hydrogen bonds dissipate external energy
## History of Polyurethane Dispersions Resins

<table>
<thead>
<tr>
<th>Decade</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1920s</td>
<td>Bayer starts production of first alkyd resins that cure via auto-oxidation</td>
</tr>
<tr>
<td>1930s</td>
<td>Otto Bayer invents polyurethane foams from aromatic isocyanates and polyols – described as “Swiss cheese”</td>
</tr>
<tr>
<td>1960s</td>
<td>Aliphatic isocyanates commercialized and first PUD research at Bayer AG on cationic PUDs</td>
</tr>
<tr>
<td>1970s</td>
<td>Anionic PUDs made with NMP commercialized</td>
</tr>
<tr>
<td>1980s</td>
<td>PUDs for glass fiber sizing developed</td>
</tr>
<tr>
<td>1990s</td>
<td>PUD adhesives, UV-PUDs and water-dispersible isocyanates commercialized; NMP-free PUDs</td>
</tr>
<tr>
<td>2000s</td>
<td>Auto-oxidatively cured PUDs and acrylic / PUD hybrids commercialized</td>
</tr>
<tr>
<td>2010s</td>
<td>Waterborne textiles coatings and printing inks increased adoption</td>
</tr>
<tr>
<td>2020s</td>
<td>PUDs synthesized from &gt;50% renewable monomers</td>
</tr>
</tbody>
</table>
Waterbased polyurethane is a very versatile chemistry.
Why would a formulator want to use 2K Waterborne Polyurethane?

**Need for Waterborne**
- VOC legislation
- desire for "green"
- low odor

**High Performance Required**
- chemical, abrasion or heat resistance
- UV weatherability

**Curing Favoring 2K**
- field applications
- substrates too large
- temperature sensitivity
- UV cure equipment costs
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2-component waterborne polyurethanes are being used in high performance applications

**Concrete coatings:** high abrasion resistance, chemical resistance and easy graffiti cleaning

**Wood coatings:** high abrasion resistance and resistance to household liquids

**Automotive interior:** soft feel and resistance to suntan lotion and DEET

**Exterior metal:** good weathering and easy graffiti cleaning

- Reduce the amount of volatile HAPS in the range of 70-99%
- Reduce the amount of VOC in the range of 70-99%
- Offer coatings systems that meet performance requirements for many industrial finishes and maintenance markets
- Offers a technology that has the ability to be: Hand mixed when necessary
2K Waterborne PU allows for hard coating with low co-solvent demands.

- Resins are insoluble in water - discrete particles
- For “hard” resins a co-solvent is added to aid coalescence
- Low Tg oligomers react on the substrate
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General Polyurethanes Literature


Isocyanate react with active hydrogen containing compounds

\[
R\text{N}C=O + R'ZH \rightarrow R\text{N}C(O)ZR'
\]

The Isocyanate group is a very reactive species

\[
\begin{align*}
R - N - C &= O \\
R - N &= C = O \\
R - N &= C - O
\end{align*}
\]

Active H-Compounds (H-X) react with isocyanates

1. \(R - NH_2\)
2. \(R - OH\)
3. \(R - NH - R'\)
4. \(H - OH\)
5. \(RC(O) - OH\)
Basic Isocyanate Reactions

\[
R-N=\overset{\cdot}{\text{C}}=O + R'-\overset{-}{\text{OH}} \rightarrow R-N\overset{-}{\text{O}}-R'
\]

**ISOCYANATE**  **ALCOHOL**  **URETHANE**

\[
R-N=\overset{\cdot}{\text{C}}=O + R'-\overset{-}{\text{NH}_2} \rightarrow R-N\overset{-}{\text{N}}-N-R'
\]

**ISOCYANATE**  **AMINE**  **UREA**
Each equivalent of isocyanate generates 22.4 liters of CO$_2$ at 25 °C.
Reaction Scheme of 2K Polyurethane Systems

Polyol (Component A)
Polyisocyanate (Component B, PIC Crosslinker)

Polyaddition
(Crosslinking, Curing)

Chemical linkage

reactive Hydroxy group (...ol)
reactive Isocyanate group

... NH – C O – ...

Polyurethane Polymer
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• **Polyol Component Considerations**
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Basic chemistries of 2K water based polyols are the similar.

**OH Functional**
- Acrylcs
- Urethanes
- Esters
- Alkyds
- Ethers

**Use of COOH salt as dispersants**
- Dispersability must compensate for isocyanate
- Hydrophilically modified polyisocyanates doesn’t affect polyol too much
- Hydrophobic polyisocyanates require greater dispersion stability (surfactant character) from the polyol.
Hydroxy Functional Polyacrylate
Hydroxy Functional Polyurethanes

R = diisocyanate –polyol-diisocyanate
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Combinations of Isocyanate and Polyol in Water

- **Heterogeneous Dispersion**
  - Polyol
  - Iso

- **Homogeneous Dispersion**
  - iso + OH
  - iso + OH
  - iso + OH

- **Reverse Emulsion**
  - Water
  - Water
  - Water
  - Polyol + Iso
Hydrophobic Polyisocyanates

**Advantages**
- Higher %NCO
- Less water sensitivity

**Disadvantages**
- Poor emulsion stability
- Poor compatibility
- Higher shear dependence
- Require organic solvent or 3rd component
Hydrophilic Polyisocyanate

**Advantages**
- Better compatibility
- Easier to emulsify
- Smaller particle size

**Disadvantages**
- Increased water sensitivity
- Over-indexing often required
Methods for the Preparation of Hydrophilic Polyisocyanates

External Emulsifier – Not linked to the polyisocyanate
- ionic or non-ionic surfactants may migrate out of the coating leading to:
  - blistering,
  - decreased water resistance and
  - gloss reduction

Internal Emulsifier – Linked to the polyisocyanate
- ionic or non-ionic internal emulsifier is permanently incorporated into the paint film, which will avoid the above-mentioned disadvantages
Applicability of isocyanate types in 2K waterborne polyurethane

**Aromatic Polyisocyanates**
- Too reactive with water
- Little if any usage in reactive systems

**HDI based Polyisocyanates**
- Greatest research at present
- High Reactivity with water and polyol
- Lower viscosity
- Over indexing often required

**IPDI based Polyisocyanates**
- Moderate Reactivity with water
- Moderate Reactivity with coreactants
- Requires use of organic solvents

**TMXDI/HMDI based Polyisocyanates**
- Low Reactivity with water
- Requires use of organic solvents
Nonionic Urethane Polyisocyanate

Features and benefits

- Hydrophilic standard hardener
- Good property level
- Easy to emulsify
- Stable emulsion
### Generation I product characteristics

<table>
<thead>
<tr>
<th>Product</th>
<th>%NCO</th>
<th>Viscosity cps @ 25°C</th>
<th>Application</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen 1A</td>
<td>17.3</td>
<td>2300</td>
<td>General use, plastics, industrial</td>
<td>Weatherable, non-yellowing</td>
</tr>
<tr>
<td>Gen 1B</td>
<td>19.3</td>
<td>2400</td>
<td>Plastics, industrial, adhesives</td>
<td>Chemical resistance, weather stable</td>
</tr>
<tr>
<td>Gen 1C*</td>
<td>9.4</td>
<td>500</td>
<td>Auto refinish</td>
<td>Hard, fast drying</td>
</tr>
<tr>
<td>Gen 1D</td>
<td>18.3</td>
<td>1000</td>
<td>Refinish, plastics, industrial</td>
<td>Low viscosity</td>
</tr>
<tr>
<td>Gen 1E</td>
<td>20.0</td>
<td>3400</td>
<td>Adhesives</td>
<td>High Functionality, water resistance</td>
</tr>
<tr>
<td>Gen 1F</td>
<td>21.8</td>
<td>1250</td>
<td>Adhesives</td>
<td>Low viscosity, easy dispersibility</td>
</tr>
</tbody>
</table>

* 70% solids
Nonionic Allophanate Polyisocyanate

Features and benefits

- Improved dispersibility
- Lower hydrophilicity in film
- Higher functionality/NCO
  - Hardness
  - Chemical resistance
Generation II product characteristics

<table>
<thead>
<tr>
<th>Product</th>
<th>%NCO</th>
<th>Viscosity cps @ 25C</th>
<th>Application</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen 2A</td>
<td>18.0</td>
<td>4500</td>
<td>Auto refinish, plastics,</td>
<td>High functionality, chemical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>industrial</td>
<td>resistance, good dispersibility</td>
</tr>
<tr>
<td>Gen 2B</td>
<td>16.2</td>
<td>6800</td>
<td>Wood/furniture, industrial</td>
<td>Easy to disperse, weather stable, flexible</td>
</tr>
</tbody>
</table>
Ionically Modified Polyisocyanate

Features and benefits

- Improved dispersibility
- Higher hardness
- No polyether in film
- Comparable hardness and chemical resistance to allophanate
### Generation III product characteristics

<table>
<thead>
<tr>
<th>Product</th>
<th>%NCO</th>
<th>Viscosity cps @ 25C</th>
<th>Application</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen 3A</td>
<td>20.6</td>
<td>5400</td>
<td>Plastics, industrial coatings</td>
<td>Weatherable, non-yellowing</td>
</tr>
<tr>
<td>Gen 3B</td>
<td>23.0</td>
<td>600</td>
<td>Flooring, anti-graffiti</td>
<td>Low viscosity, easy dispersibility, weatherable</td>
</tr>
<tr>
<td>Gen 3C</td>
<td>21.2</td>
<td>3500</td>
<td>Flooring, wood, plastics</td>
<td>Chemical resistance, easy mixing</td>
</tr>
</tbody>
</table>
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Typical mixing and application scheme for a 2K waterborne PU

Challenge is to disperse a reactive system in water and obtain high performance properties of a 2K Urethane.
Mixing a 2K waterborne polyurethane coating is critically important

Need to have a Heterogeneous Dispersal of Reactants

- Coreactants predispersed in water
- Hydrophilically modified polyisocyanate stirred into the coreactant dispersion
- Coreactant helps stabilize the overall dispersion
  - Poor mixing of components leads to poor properties
  - Potlife determined by reaction of isocyanate with water
- Property degradation
  - Reaction rates determined by physical and chemical effects
Hydrophobic polyisocyanates *don’t like water*

Proper amount of shear while mixing is critical.
Many methods are used to create these emulsions

- Hand dispersion
- Mechanical mixer
- Plural component spray
- Jet disperser
Plural Component Spray
Jet stream disperser in automotive OEM applications

Polyol Dispersion

Fine Nozzle (0.2–0.5 mm)

Polyisoisocyanate

Preliminary Emulsion

Nozzle

Jet Stream Disperser

Stable Emulsion
Shear affects the dispersal of particles
Physical and chemical factors affect the potlife of a 2K waterbased polyurethane

**Physical Effects**
- Surface area/particle size
- Shear history
- Coalescence and diffusion

**Chemical Effects**
- Chemical composition
- Emulsion stabilization
- Catalysis and neutralization
- CO₂ generation/pH
Potlife can be difficult to determine

- Viscosity is not an indicator of potlife
- Reactions taking place in the disperse phase have little effect on the continuous phase viscosity
Chemical changes begin occurring after mixing

- Reaction of water with isocyanate results in increasing levels of urea in the product
- Released carbon dioxide acidifies the product
Several physical properties are affected by potlife.

- Properties of the coatings may change depending on how long after mixing the coating is applied.
- Changes are related to reaction of part of the isocyanate.
Viscosity can change within the Isophase after mixing

- Water penetrates and reacts
- Viscosity increases rapidly through MW and H-Bonding
- High reaction at the surface leads to gel formation
- Polarity of isocyanate particle increase with urea
Temperature of the emulsion will also effect potlife and properties

- Temperature of the paint formulation after mixing can affect the application window
- Temperature not only increases rate of reaction but also increases rate of water diffusion into isocyanate particles
Choice of additives will also affect the coating

**Catalysts**
- Typically catalyze isocyanate water reaction (potlife)
- Tin Mercaptides have better hydrolytic stability

**Neutralizing agents**
- Ammonia, 1° and 2° amines will react with iso
- 3° Amines catalyze isocyanate moisture reaction
  - Excess amine can cause problems
  - Type of amine affects potlife

**Co-Solvents**
- OH functional react with isocyanate
- Hydrophilic solvents can decrease potlife
- Hydrophobic solvents are often effective
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Development of Film Properties

Film Hardness as a Function of NCO/OH Ratio

![Graph showing the development of film properties with time for different NCO/OH ratios. The graph includes two lines, one for NCO/OH=1 and another for NCO/OH=2, both showing an increase in hardness with time from 1 to 7 days.]
Development of Film Properties

7 Day Hardness as a Function of Polyether Content of Polyisocyanate
Coalescence and Reaction Caused Viscosity

- The physical phenomenon of drying and the chemical reaction of isocyanate and polyol happen at the same time.
- If the material dries too quickly it will leave urea rich regions and unreacted polyol regions.
- If the chemical reaction occurs too quickly it will cause the film to skin over, trapping water that will lead to bubbles in the film.
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## High Gloss 2K Waterborne Polyurethane Clearcoat

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Weight (lbs)</th>
<th>Volume (gal)</th>
<th>Weight Solids (lbs)</th>
<th>Volume Solids (gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayhydrol XP 2542 OH functional polyacrylate</td>
<td>50</td>
<td>5.64</td>
<td>25</td>
<td>2.64</td>
</tr>
<tr>
<td>Baysilone VP Al 3468 Flow and leveling aid</td>
<td>0.34</td>
<td>0.03</td>
<td>0.34</td>
<td>0.03</td>
</tr>
<tr>
<td>Tego Foamex 822 Defoamer</td>
<td>0.14</td>
<td>0.02</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>BYK 349 Silicone Surfactant</td>
<td>0.54</td>
<td>0.06</td>
<td>0.54</td>
<td>0.06</td>
</tr>
<tr>
<td>Water, DI Solvent</td>
<td>10.25</td>
<td>1.23</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dowanol DPnB Solvent</td>
<td>3.4</td>
<td>0.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water, DI Solvent</td>
<td>5.31</td>
<td>0.64</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td><strong>69.98</strong></td>
<td><strong>8.07</strong></td>
<td><strong>25.92</strong></td>
<td><strong>2.74</strong></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Component 2</th>
<th>Weight (lbs)</th>
<th>Volume (gal)</th>
<th>Weight Solids (lbs)</th>
<th>Volume Solids (gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayhydur XP 2547 Polyisocyanate</td>
<td>42.73</td>
<td>4.41</td>
<td>42.73</td>
<td>4.41</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td><strong>42.73</strong></td>
<td><strong>4.41</strong></td>
<td><strong>42.73</strong></td>
<td><strong>4.41</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>112.72</strong></td>
<td><strong>12.47</strong></td>
<td><strong>68.65</strong></td>
<td><strong>7.14</strong></td>
</tr>
</tbody>
</table>

| Solids (%) | 60.91 |
| Volume Solids (%) | 57.28 |
| Wt/Gal (lbs/gal) | 9.04 |
| Mix Ratio (volume) | 1.83 : 1 |
| NCO:OH | 3 |
| Theoretical VOC (lbs/gal) | 0.5 |

NB# 964566-A
Low Gloss 2K Waterborne Polyurethane Clearcoat

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (lbs)</th>
<th>Volume (gal)</th>
<th>Weight Solids (lbs)</th>
<th>Volume Solids (gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bayhydrol XP 2542 OH functional polyacrylate</td>
<td>238.19</td>
<td>26.88</td>
<td>119.09</td>
<td>12.58</td>
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<tr>
<td>Bayhydrol XP 2546 OH functional polyacrylate</td>
<td>555.67</td>
<td>60.53</td>
<td>227.83</td>
<td>21.27</td>
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<tr>
<td>Baysilone VP Al 3468 Flow and leveling aid</td>
<td>4.99</td>
<td>0.48</td>
<td>4.99</td>
<td>0.48</td>
</tr>
<tr>
<td>Reovis PU 1214 (DSX 1514) (8%) Rheology Modifier</td>
<td>35.59</td>
<td>4.24</td>
<td>1.71</td>
<td>0.18</td>
</tr>
<tr>
<td>Tego Foamex 822 Defoamer</td>
<td>2.19</td>
<td>0.26</td>
<td>0.58</td>
<td>0.07</td>
</tr>
<tr>
<td>Water, DI</td>
<td>150</td>
<td>17.96</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Subtotal</td>
<td>986.63</td>
<td>110.36</td>
<td>354.2</td>
<td>34.58</td>
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<tr>
<td><strong>Component 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bayhydur XP 2547 Polyisocyanate</td>
<td>574.25</td>
<td>59.2</td>
<td>574.25</td>
<td>59.2</td>
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<tr>
<td>Subtotal</td>
<td>574.25</td>
<td>59.2</td>
<td>574.25</td>
<td>59.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1,560.87</td>
<td>169.56</td>
<td>928.45</td>
<td>93.78</td>
</tr>
</tbody>
</table>

| Weight Solids (%) | 59.48 |
| Volume Solids (%) | 55.31 |
| Wt/Gal (lbs/gal) | 9.21 |
| Mix Ratio (volume) | 1.86 : 1 |
| NCO:OH | 3 |
| Theoretical VOC (lbs/gal) | 0.03 |

NB# 934637-H
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This presentation may contain forward-looking statements based on current assumptions and forecasts made by Covestro AG.

Various known and unknown risks, uncertainties and other factors could lead to material differences between the actual future results, financial situation, development or performance of the company and the estimates given here. These factors include those discussed in Covestro’s public reports, which are available on the Covestro website at www.covestro.com.

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Questions?

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