A New Preformed Polyurea Thickener for Grease

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Seek Together™
Grease Market Overview

- Grease = **Thickener** + Base Stock + Additives

- Total grease production was about **2.57 BM lbs** in 2016 (1.4% increase from 2015)
  - Polyurea thickened greases account for approximately **158 MM lbs** with a market share of **6%**
Polyurea Greases

- **Primary Applications for Polyurea Greases:** high temperature, anti-oxidative and fill-for-life applications (e.g., CVJ, electric motor bearings, etc.)
  - Market demands high performance grease
  - Less availability and increasing price of LiOH
  - Limited by the toxicity of the raw materials and handling complexity

- **Predominant *in situ* technology (isocyanate + amine reacted *in situ* in the base stock)**

\[
\begin{align*}
\text{Diisocyanate} & \quad \text{Diamine} & \quad \text{Monoamine} & \quad \text{Polyurea} \\
(\text{R}) \quad \text{H}_2\text{N}^\text{R}^\prime \text{NH}_2 & \quad 2 \quad \text{R}'' \text{NH}_2 & \quad \text{base oil} & \quad \text{R}'' \text{NH-NH-NH-NH-R} \\
\end{align*}
\]
Polyurea Chemistry Overview

- Reaction takes place in the base stock
- Isocyanate + (diamine linkage) + alkyl / alicyclic / aromatic amine tail $\rightarrow$ often are diureas and tetraureas
- Thickener microstructure is very important (H-bonding, dispersibility and mechanical stability, etc.)
### Structure vs. Property

Chemical structure of thickener has a significant impact on grease properties.

<table>
<thead>
<tr>
<th>Structure Selection v.s. Grease Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine end group</td>
</tr>
<tr>
<td>Thickening efficiency</td>
</tr>
<tr>
<td>Thermal stability</td>
</tr>
<tr>
<td>Shear stability</td>
</tr>
<tr>
<td>Pumpability</td>
</tr>
</tbody>
</table>

- TDI and MDI are most commonly used isocyanates
- More variations provided by choice of amines
- Usually a combination of amine/isocyanates used in formulation to achieve structure complexity
In situ Manufacturing Process

- Mixing and dispersion process is important to achieve desired consistency and completion of reaction
- Manufacturing can be difficult due to health hazards of raw materials
- Specially designed facilities are required to effectively handle the reaction of toxic raw materials
Preformed Thickener Technology

- Less hazardous raw material handling for grease manufacturers
- May not require special equipment to handle toxic raw materials
- Standard Li grease kettle may be used to formulate polyurea grease
- Reduce batch to batch variation from *in situ* production
- Tailor the thickener structure according to specific needs

This *preformed polyurea thickener* will provide an alternative for polyurea grease production with competitive lubricating properties, and enhanced safety & handling benefits.
Preformed Thickener Structure

Model compound used for this study

Straightforward chemistry but difficult to operate:
- Hazardous raw materials
- Exothermic – urea bond formation generates ~ 40 kcal/mol
- Fast kinetics – hard to achieve stoichiometric reaction

R = aliphatic alkyl group
Other urea structures were also made
Dow Process Technology*

*Patent pending
Batch Process v.s. Continuous Process

- **Batch Process**
  - A Isocyanate solution
  - B Amine solution
  - Filtration
  - Vacuum
  - Packaging

- **Continuous Process**
  - Tanks
    - Amine
    - Solvent
    - Isocyanate
  - Continuous Reactor
  - Dryer
  - Packaging

- Flexible process to give various thickener structures
- Highly reliable process
- Controllable reaction
- Uniform particle size
# Preformed Polyurea Thickener Overview

<table>
<thead>
<tr>
<th>Spec</th>
<th>Target</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unreacted raw materials</strong></td>
<td>&lt;0.1 wt% free isocyanate; &lt;1 wt% free amine</td>
<td>Pass</td>
</tr>
<tr>
<td><strong>Residual Solvent</strong></td>
<td>&lt;0.5 wt%</td>
<td>Pass</td>
</tr>
<tr>
<td><strong>Particle size distribution</strong></td>
<td>Narrow distribution, agglomerates &lt;500 µm</td>
<td>Pass</td>
</tr>
<tr>
<td><strong>Shear stability</strong></td>
<td>NLGI grade 2 with 12.5% thickener loading; Penetration increase &lt;15% after 100k strokes</td>
<td>Exceed - NLGI grade 3 with 12.5% thickener loading; &lt;9% penetration loss after 100k strokes</td>
</tr>
<tr>
<td><strong>Dropping point</strong></td>
<td>240 ºC</td>
<td>&gt; 260 ºC (exceed instrument detection capability)</td>
</tr>
</tbody>
</table>

- ✓ Dow proprietary process technology
- ✓ Enhanced thickening efficiency and shear stability v.s. batch process
- ✓ High process flexibility → Enable tuning of thickener structure according to needs

Grease application guide
ASTM D217 - Standard Test Methods for Cone Penetration of Lubricating Grease
ASTM D2265 - Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range
Material Characterization – FTIR

No residual isocyanate
Material Characterization – SEM
Narrow particle size distribution
XRD of Preformed Thickener and Grease

- XRD shows difference in both preformed thickener powder and grease
- Slightly higher average spacing and narrower distribution for the high level structure observed in Dow urea
- Grease made by Dow urea presents slightly higher crystallinity
- Higher level structure gives different spacing in the grease made by Preformed urea A and Dow urea
Grease Shear Stability

Preformed ureas at 12.5 wt% loading v.s. In situ made greases

- Higher thickening efficiency
- Superior shear stability
- Excellent reproducibility
- Competitive property

![Graph showing penetration values for different greases and their comparisons](image)
### Roll Stability Test

<table>
<thead>
<tr>
<th></th>
<th>ASTM D1831</th>
<th></th>
<th>ASTM D1831 Modified</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM D1403 Original Worked Penetration</td>
<td>ASTM D1403 Worked Penetration After Rolling</td>
<td>Δ</td>
<td>ASTM D1403 Original Worked Penetration</td>
</tr>
<tr>
<td>Dow urea *</td>
<td>211</td>
<td>206</td>
<td>-5</td>
<td>211</td>
</tr>
<tr>
<td>Preformed urea A *</td>
<td>315</td>
<td>355</td>
<td>40</td>
<td>315</td>
</tr>
<tr>
<td>Commercial grease B</td>
<td>268</td>
<td>292</td>
<td>24</td>
<td>268</td>
</tr>
<tr>
<td>Commercial grease C</td>
<td>266</td>
<td>300</td>
<td>34</td>
<td>266</td>
</tr>
</tbody>
</table>

* Greases made by Dow urea and Preformed urea A are unformulated with 12.5% thickener loading in Group II mineral oil. Made through the same procedure.
Thickener Structure Variations
Flexible process can produce customized thickener structures

R and R' = aliphatic alkyl, alicyclic, or aromatic group
Flexible Process Enables Tailored Products
to meet registration requirements

<table>
<thead>
<tr>
<th>Polyurea Thickener</th>
<th>Structure</th>
<th>Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preformed thickener 1</td>
<td>MDI based diurea, asymmetric</td>
<td>US, Canada, Australia, Taiwan</td>
</tr>
<tr>
<td>Preformed thickener 2</td>
<td>MDI based diurea, asymmetric</td>
<td>US, EU, China, South Korea, Philippines, Taiwan</td>
</tr>
<tr>
<td>Preformed thickener 3</td>
<td>MDI based diurea, symmetric</td>
<td>US, Canada, South Korea, Taiwan</td>
</tr>
<tr>
<td>Preformed thickener 4</td>
<td>MDI based diurea, symmetric</td>
<td>US, EU, China, South Korea, Philippines, Taiwan</td>
</tr>
</tbody>
</table>
Conclusions

This work reports the development of a multi-component polyurea mixture designated for lubricating grease application. It is produced through a novel continuous synthesis of isocyanates and amines, and can be offered as a preformed thickener for the manufacture of polyurea grease.

This novel process presents high flexibility and enables tailored product. NLGI Grade 3 grease can be made with 12.5% thickener loading. The resulted grease also shows enhanced thickening efficiency and shear stability.

This preformed polyurea thickener will provide global lubricating grease market an alternative for polyurea grease production with competitive lubricating properties, and enhanced safety & handling benefits.
Thank you!

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