Recent Developments in CL-20 Synthesis and Processing

Dr. Nicholas Straessler
Dr. Melissa Mileham
Dr. Michael Kramer
Paul Braithwaite

Research and Development, ATK Aerospace Group, Brigham City, Utah 84302
Nick.Straessler@ATK.com

Prepared for:
2012 NDIA IM/EM Symposium
Las Vegas, Nevada
14 - 17 May 2012
Abstract 13899
Outline

• Acknowledgements
• Overview
• CL-20 synthesis
  – Process improvements
• Use in formulations
• Summary
Acknowledgements

- Support of CL-20 from many DoD and DOE partners
- Dedicated team at ATK Aerospace
  - PM: Nathan Seidner
  - Scientists: Dr. Mike Killpack, Michael Adams
  - Analytical team: Max Patterson, Brian Rosa, Erin Anderson, Ken Spaulding, Joanne Bingham, Dr. Shawn Parry, Dr. Ping Li
  - Operations: David Schmidt
  - Quality: Kirk Bailey
  - Safety: Arlan Brandt
Overview

• CL-20 is one of the most interesting energetic molecules to be developed since WW II

• Original CL-20 synthesis route developed at NAWC by Dr. Arnold Nielson, 1987

• TADF process pioneered by Thiokol in early 1990s provided access to thousands of pounds of material for development programs
  – Synthesis was not optimal

• TADA, discovered by Dr. Robert Wardle in 1988, was not considered a viable precursor until independent development of a large-scale process for its synthesis was revealed by Asahi in 1997 time frame
  – TADA nitration produces higher yield and purity product and lower, more easily controlled exotherm than the TADF process

• During the past decade regular improvements in the synthesis and crystallization have been made
CL-20 Synthesis Summary

• Four step process from commercially available feed stock:

\[
\begin{align*}
\text{glyoxal} + 6 \text{benzylamine} & \quad \xrightarrow{\text{Formic Acid MeCN}} \quad \text{PhH}_2\text{C} - \text{N} - \text{N} - \text{CH}_2\text{Ph} \\
& \quad \xrightarrow{\text{H}_2, \text{Ac}_2\text{O Pd/C}} \quad 2 \text{ steps} \quad \text{Ac}_1\text{N} - \text{N} - \text{Ac} \\
& \quad \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} \quad \text{O}_2\text{N} - \text{N} - \text{N} - \text{O}_2\text{N} \\
\end{align*}
\]

- Recrystallization is required to obtain the desired \(\varepsilon\) polymorph - crude CL-20 from nitration is a mixture of \(\alpha\) and \(\gamma\)
- Recrystallization is essential to achieving desired particle size, morphology, and purity
  - Therefore any optimization of the recrystallization process is expected to have a positive impact on material cost and product quality
Nitration process is being continually refined and improved
CL-20 Recrystallization Overview

- Process is the result of a 2003 Navy Mantech effort
  - Determined that “evaporative recrystallization” was optimum for reproducibility
    - Scaled to multiple 500-gallon runs
    - Gives reproducible “unground” particle size
    - Consistently \( \varepsilon \) polymorph
    - Good particle morphology (distinct crystals)
Recrystallized (Unground) CL-20

- CL-20 is manufactured to an internal ATK specification
  - Specification is based on the existing STANAG for CL-20
- Improvements to crystallization step produces crystals that are more rounded and easier to process
  - Internal defects have been minimized

Epsilon Polymorph

99.5% Pure by HPLC
Ground CL-20

- Two grades of ground CL-20 are produced on a routine basis
  - FEM ground
    - Nominally 2 micron
  - Jar milled
    - Nominally 11 micron
- FEM facility has been recently refurbished and upgraded
  - Improvements to grounding, smooth walls, collector, etc.
• New formulations and applications involving CL-20 have emerged as a result of:
  – Better CL-20 crystal quality
  – Availability of multiple and useful sizes of CL-20
  – Greater understanding of CL-20 binder filler interaction

• Notable examples include:
  - High solids cast cure explosives with good IM properties
  - Initiator systems that utilize CL-20 based formulations
Approach for CL-20 Cost Reduction

- ATK has invested substantial internal funds during the past three years to decrease CL-20 cost and improve the CL-20 manufacturing process.

- The approach to cost reduction has focused in two key areas which have been attacked vigorously:
  - Process efficiency improvements
  - Precursor (TADA) cost reduction
    - TADA accounts for over 50% of the cost of CL-20

- Early studies were focused on process improvements.

- More recent efforts have concentrated on developing a domestic TADA manufacturer and optimizing the TADA synthesis process.

- Continued long-term objectives are being pursued.
Precursor Improvement Initiative

- Experiments were performed to understand reaction conditions and improve yield

**Synthesis Step 1**
- Reaction rates
- Temperature
- Pressure
- Time
- Wet catalyst vs. dry
- Best catalyst (evaluated 18 catalysts)

**Synthesis Step 2**
- Filtration, H$_2$O, solvent rinse, etc.
- Time
- Temperature
- Catalyst - one addition vs. two additions
- Reuse of catalyst
Experimental Setup and Results

Seven experiments are run at once under identical pressure and temperature conditions

- Work resulted in drastically increased yield and reduced catalyst costs
  - Early improvements focused on Step 1
  - Later efforts refined Step 2
  - Substantial improvements were made in both steps
  - Efforts are continuing on work-up of the TADA
Summary

- CL-20 provides enabling capability for several key areas
- Processing improvements, such as FEM grinding, make CL-20 a more viable ingredient for new state-of-the-art energetic formulations
- Synthesis of CL-20 continues to be refined and improved
  - In recent years activities have focused in two areas:
    - Development of a domestic source for TADA
    - Cost reduction