Development of an Efficient Alternative Manufacturing Process for DNAN Production

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Background

• DNAN (2,4-dinitroanisole) commonly used in melt-pour explosive compositions
• DNAN used in IM explosives, IMX-101 and IMX-104
  • Both formulations manufactured at the Holston Army Ammunition Plant
• IMX-101 selected by the US Army for use as TNT replacement
• IMX-104 performance similar to that of Comp B
DNAN Formulation Advantages

- Better IM properties than TNT
- Solidify more quickly than TNT-based formulations
- Shrink less than TNT-based formulations
- DNAN formulations adhere better than TNT-based formulations
  - Better adherence = less voids
Project Overview

- Current OSI DNAN production involves nitration
  - Process yields significant volumes of acidic waste
- Alternative DNAN synthesis process exists
  - Reaction of 1-chloro-2,4-dinitrobenzene (CDNB) with methanol/base
    - Base can be carbonate, hydroxide, or methoxide
    - Methanol could be recycled yielding a more environmentally friendly synthesis
Alternative DNAN Synthesis

- Methoxylation reaction of 1-chloro-2,4-dinitrobenzene (CDNB)
- Base can be carbonate, hydroxide, methoxide
- Main byproducts are chloride salt and 2,4-dinitrophenol (DNP)
- Methanol solvent may be recycled
Sodium Hydroxide DNAN Synthesis

- Employed process described in Urbanski’s “The Chemistry and Technology of Explosives”*
- Completed on laboratory scale
- Significant exotherm noted
- Additional methanol required to maintain stirring
- Low yield compared to nitration
  - Product loss probably due to generation of DNP
  - US Patent 4847426** indicates that hydroxide bases yield more DNP than carbonates

Sodium Methoxide DNAN Synthesis

- Required additional methanol to maintain stirring
  - Probably due to nearly immediate generation of Meisenheimer complex intermediate
- Mass yield = 95%
- Manageable exotherm
- Material 100% pure via GC/MS
- Additional MIL spec testing not completed
  - Sodium methoxide considered inferior to potassium carbonate route and therefore not pursued
Sodium Carbonate DNAN Synthesis

• Sodium carbonate listed as possibility in US Patent 4847426*
  • Slightly less expensive than potassium carbonate

• Sodium carbonate reaction attempted using process described in the patent
  • Incomplete reaction: Reaction time may be slow due to low solubility of sodium carbonate
  • Method abandoned due to slow reaction time when compared to potassium carbonate

Potassium Carbonate DNAN Synthesis

- Process described in US Patent 4847426*
- Exact synthesis in patent attempted
  - Reaction too viscous to maintain stirring
- Concentration of CDNB in methanol reduced
  - Stirring improved to an acceptable level
  - Mass yield of 94%
  - Scaled to the 200 g level
  - Product subjected to MIL spec testing

NMR Characterization of DNAN from K₂CO₃ Reaction
DSC Characterization of DNAN from K$_2$CO$_3$ Reaction

Sample: DNAN 1096-123
Size: 1.2970 mg
Method: Ramp

DSC

File: C:\Data\DSC\DNAN\DNAN 1096-123.001
Operator: jh
Run Date: 09-Jun-2011 13:26
Instrument: DSC Q1000 V9.9 Build 303

95.06°C
87.02 J/g

95.92°C
Thermal Comparison of Nitration and K₂CO₃ DNANs

Melting Point

DSC Exotherm
DNAN Morphology from Various $K_2CO_3$ Reactions
Results of 200 g Scale Potassium Carbonate Reaction

- Residual potassium inhibited passage of trace metals content specification
  - All other specifications met
- After simple purification, all specifications passed

| Test Parameter          | Met Specification?
<table>
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<tr>
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<tbody>
<tr>
<td>DNAN Purity</td>
<td>Yes</td>
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<tr>
<td>2,4-Dinitrophenol</td>
<td>Yes</td>
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<tr>
<td>2,5-Dinitroanisole</td>
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<td>Melting Point</td>
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<tr>
<td>Undissolved Solids</td>
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<td>Physical Form</td>
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<td>Workmanship</td>
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Potassium Carbonate Reaction Optimization

- **Reaction concentration optimization**
  - Patent concentration not suitable for scale up: stirring concerns
  - Concentration lowered to an acceptable level
  - Low concentrations yield product that passes MIL spec without purification

- **Methanol recycle optimization**
  - Water-quenched reactions require more complex distillation equipment
    - Initial studies show that purification is possible
  - Cooling without quench = lower yield but simpler distillation equipment
  - Direct reuse of reaction solution being explored
    - After several iterations, methanol would be distilled
Methanol Recycle Investigation

- **Quenchless reaction**
  - Mixture cooled then filtered
  - Filtrate could be purified with simple distillation and reused
  - Low yielding: 70-80%

- **Quenchless reaction followed by direct reuse of reaction solution**
  - Mixture cooled then filtered
  - Reaction liquid reused several times then distilled
  - Initial yield low but successive yields near quantitative
  - 100% pure via GC/MS up to 2 reuses
  - Investigation on-going
Conclusions and Future Work

- **Potassium carbonate the preferred base for the methoxylation reaction**
  - Less water-sensitive than methoxides and hydroxides
  - Yields milder exotherm than hydroxides
  - Less corrosive than methoxides and hydroxides
- **Methanol recycle is possible**
  - Equipment required depends on the presence of water
  - Will yield much less waste than nitration method
  - Direct recycle is an option
- **Purification step may or may not be required**
  - Pure material can be obtained directly from reaction mixture