# Development of an Efficient Alternative Manufacturing Process for DNAN Production

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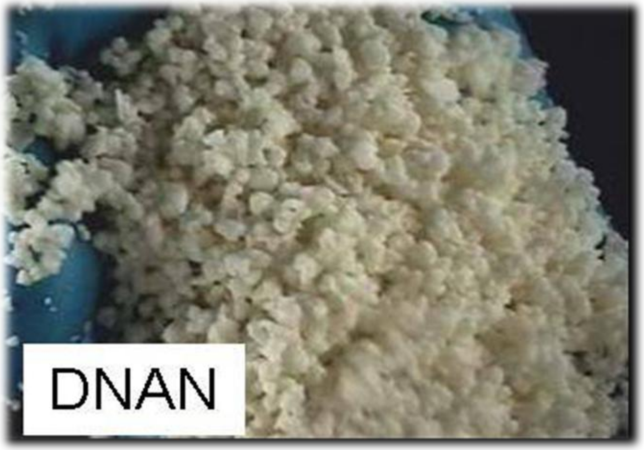
# Background

- 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

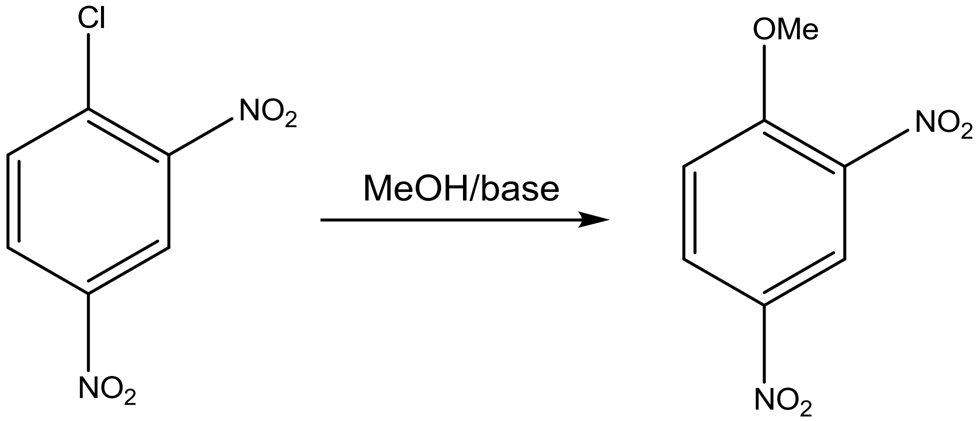
# Project Overview

- 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

Holston Army Ammunition Plant

# 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

*_The Chemistry and Technology of Explosives;_ Pergamon Press: New York, 1964; pp 547.

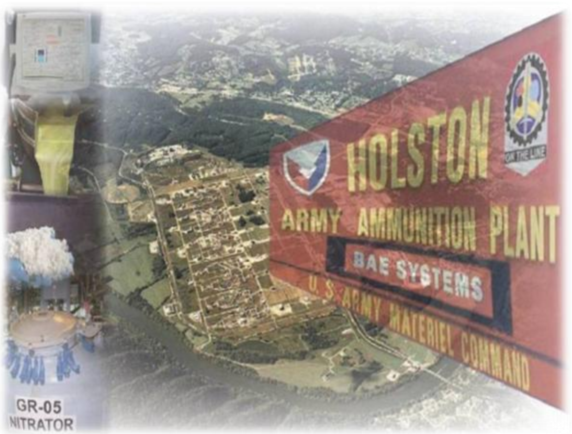
** Heck, D., Heise, H., Hintzmann, M., Process for the Preparation of 2,4-Dinitrophenyl Ethers. US Patent 4,847,426, July 11, 1989.

# 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




*Heck, D., Heise, H., Hintzmann, M., Process for the Preparation of 2,4-Dinitrophenyl Ethers. US Patent 4,847,426, July 11, 1989.

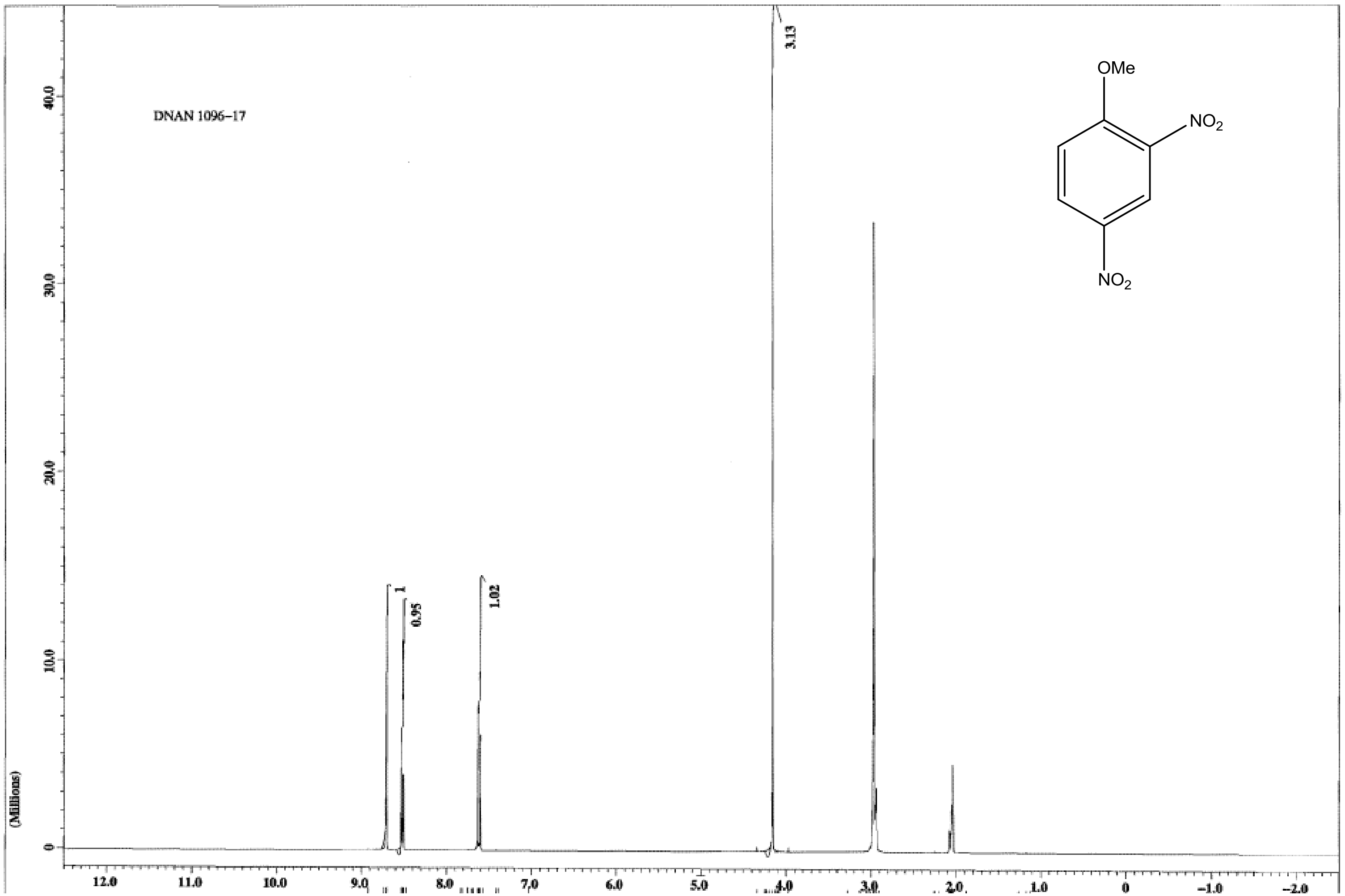
# Potassium Carbonate DNAN Synthesis

- 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

*Heck, D., Heise, H., Hintzmann, M., Process for the Preparation of 2,4-Dinitrophenyl Ethers. US Patent 4,847,426, July 11, 1989.

BAE SYSTEMS

# NMR Characterization of DNAN from $K_2CO_3$ Reaction



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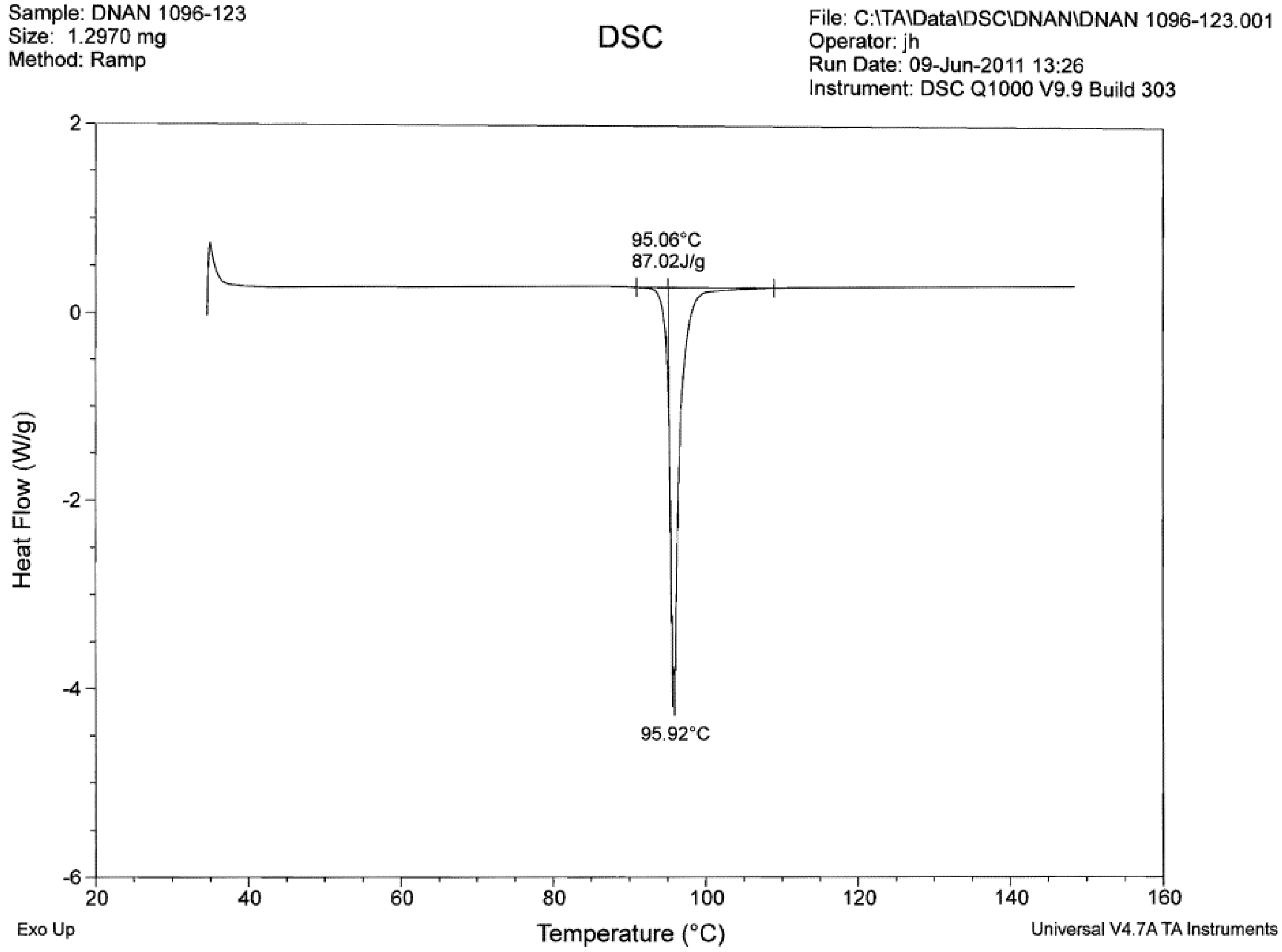
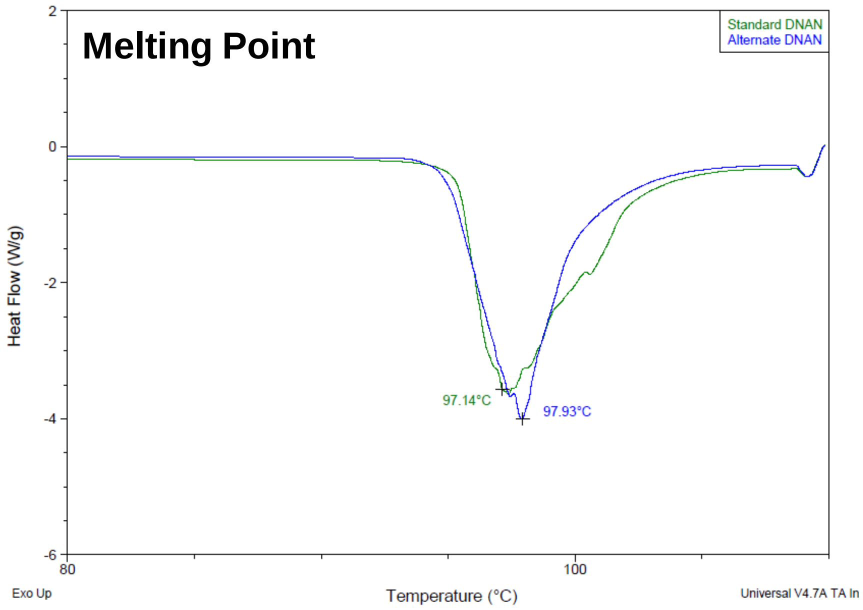
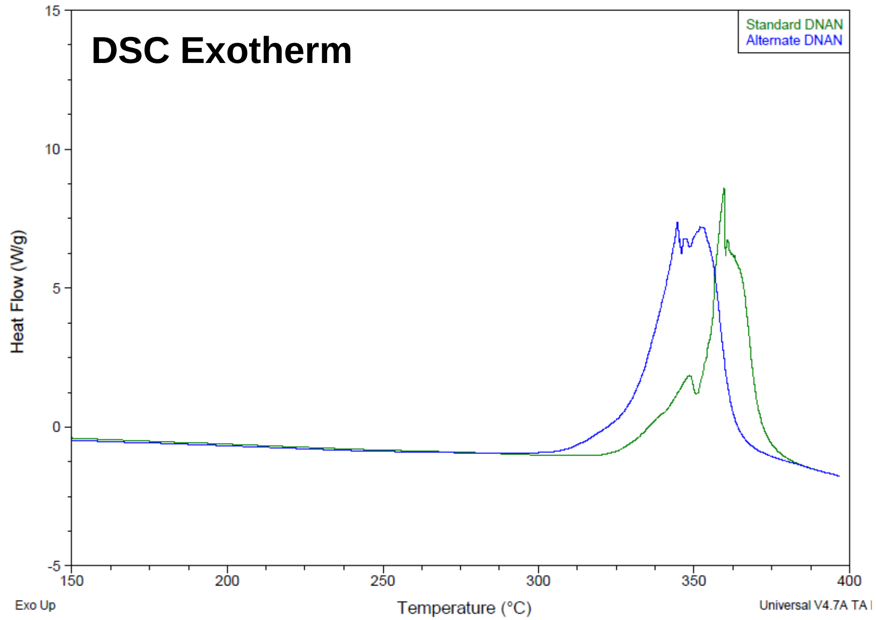
# DSC Characterization of DNAN from $K_2CO_3$ Reaction

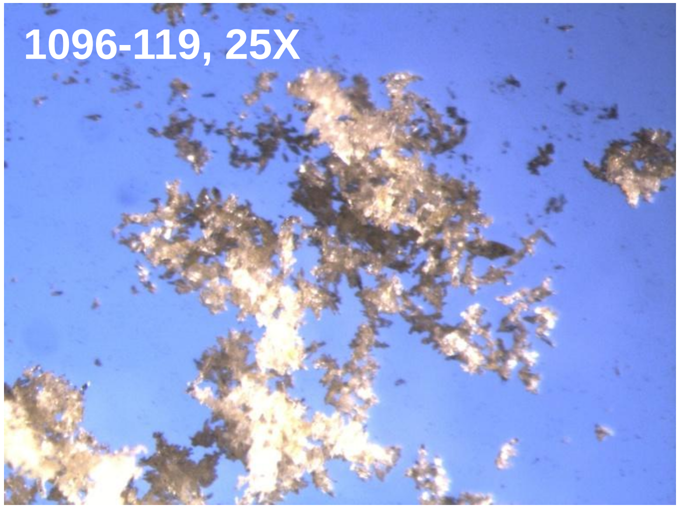


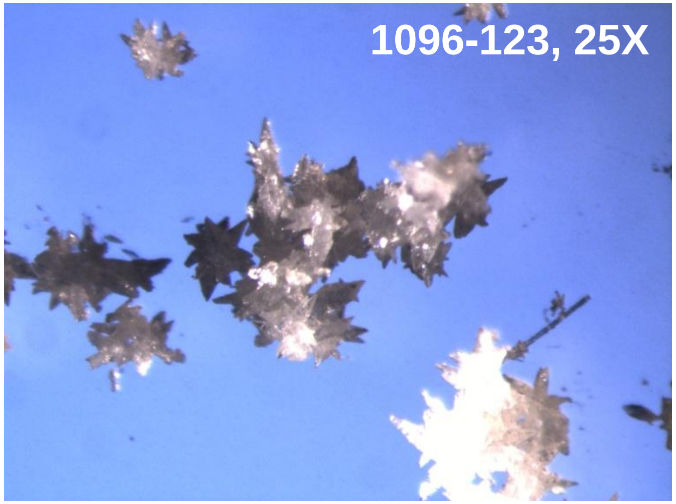
# Thermal Comparison of Nitration and $K_2CO_3$ DNANs



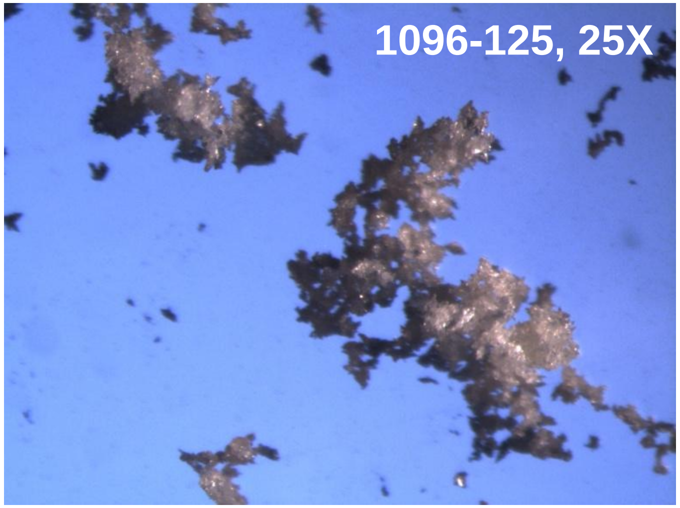



# DNAN Morphology from Various $K_2CO_3$ Reactions







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# Results of 200 g Scale Potassium Carbonate Reaction

| Test Parameter | Met Specification? |
|---|---|
| DNAN Purity | Yes |
| 2,4-Dinitrophenol | Yes |
| 2,5-Dinitroanisole | Not tested |
| Melting Point | Yes |
| Undissolved Solids | Yes |
| Trace Metals Content | No |
| Physical Form | Yes |
| Workmanship | Yes |

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

# 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