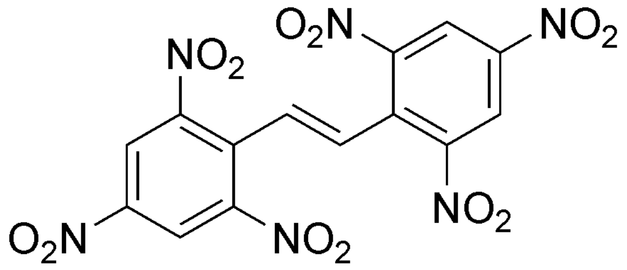
Process Improvement Studies for Scale-Up of HNS at Holston Army Ammunition Plant

Dr. Jacob Morris*, Gary Clark, Dr. David Price

BAE SYSTEMS OSI, Holston Army Ammunition Plant

Background - HNS

- Thermally stable energetic material
- Moderate sensitivity
- Broad range of uses:
  - Military, aviation, space applications
  - Oil and gas well perforating
  - Detonating cords
  - Exploding foil initiators
  - Crystal modifying additive in TNT



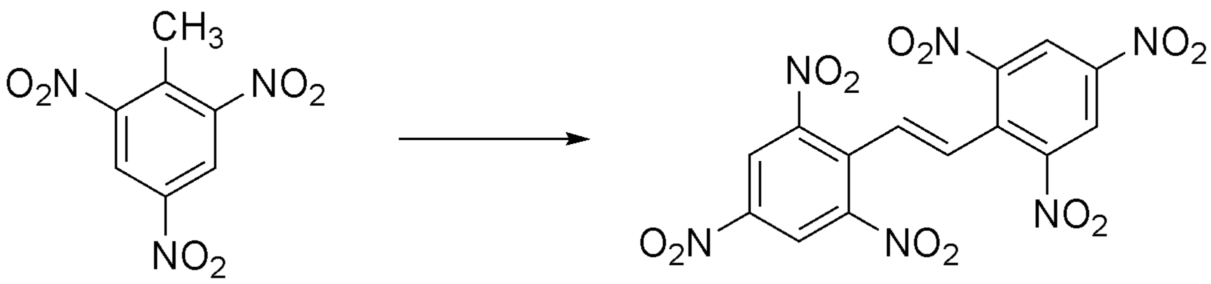
<u>2,2’,4,4’,6,6’-Hexanitrostilbene (**HNS**)</u>

- m.p. = 316 – 318 °C
- Detonation Velocity: 7120 m/s
- Oxygen Balance: -67.6% m/m
- Heat of explosion: 4393 kJ/kg
- ERL Impact Sensitivity: 63 cm

Program Objectives

- Viable Process for Manufacture of HNS at HSAAP
- Use Existing HSAAP Infrastructure
- Competitive Cost
- Meet Requirements of Military and the Oil & Gas Industries
  - Thermal Stability-Deeper Wells, Higher Temperatures
  - Formulation-amenable

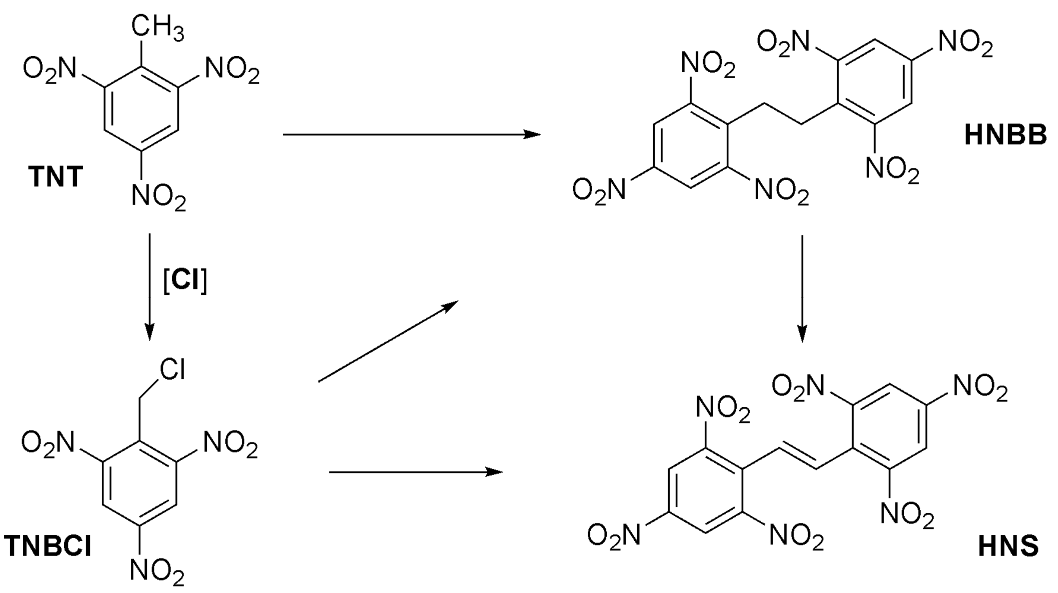
Known Routes: 1-Step Reactions



TNT **HNS**

- Shipp (1964): NaOCl, THF, MeOH
- Kompolthy (1976):, Co/Cu complex, O_2, Base, Polar Aprotic Solvent (PAS)
- Duffin & Golding (1984): Carboxylate base, O_2, PAS
- Duffin & Golding (1987): $CuCl_2$, Carboxylate base, PAS

Known Routes: Multi-Step Reactions



- Kompolthy (1976): HNBB, O_2, Copper complex, Base, PAS
- Gilbert (1980): HNBB, O_2, Copper complex, Base, PAS
- Sollott (1981): TNBCl, THF, Methanol, Base
- Duffin & Golding (1984): HNBB, Carboxylate base, O_2, PAS

BAE SYSTEMS

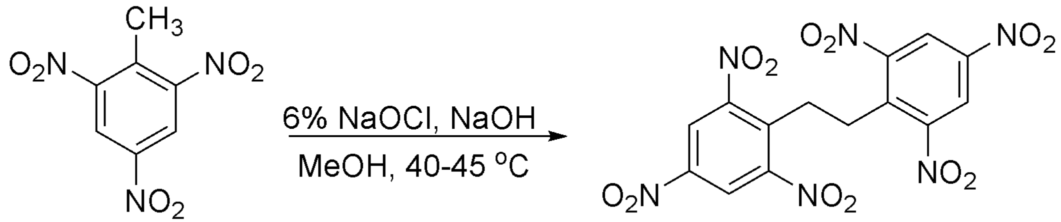
Challenges

- Shipp process: sub-ambient, requires binary solvent system (THF/MeOH)
  - THF-expensive, toxic, flammable, peroxides
  - Recovery and make-up of THF/MeOH
- Other processes require polar aprotic solvents; i.e., DMSO, DMF, HMPA
  - PAS are expensive and not recoverable in-house
  - PAS are not recoverable externally with explosive residue
- High production cost associated with previous processes
  - Large excess of solvent, base, PAS, and/or metal complex
- *Need a 1- or 2-step process with low complexity & cost, and robust purification*

HSAAP Development Work

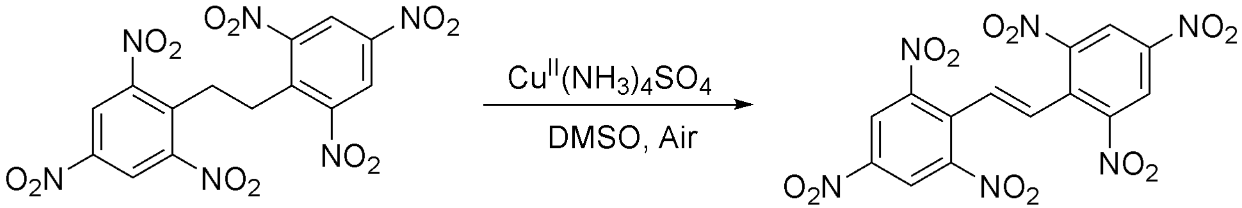
Two Step Process

1. Vary Shipp conditions to maximize HNBB
   - No THF, higher temperature, added base



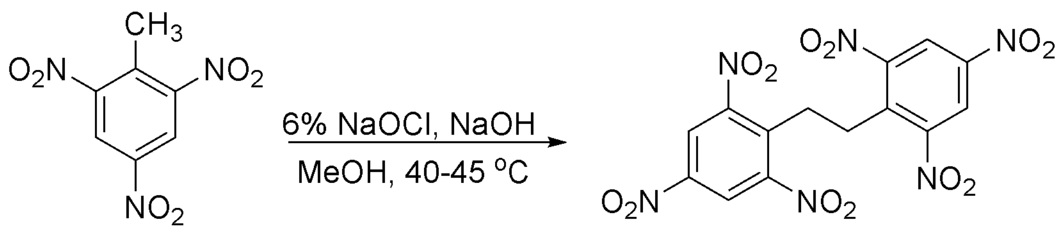
TNT **HNBB**

2. Use Gilbert process to convert HNBB to HNS
   - DMSO, copper amine complex, air



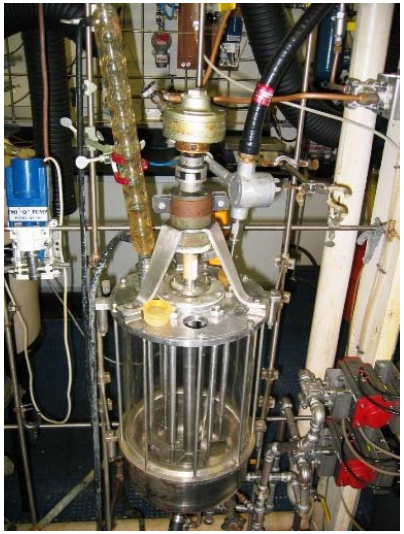
HNBB **HNS**

Optimization - HNBB Synthesis



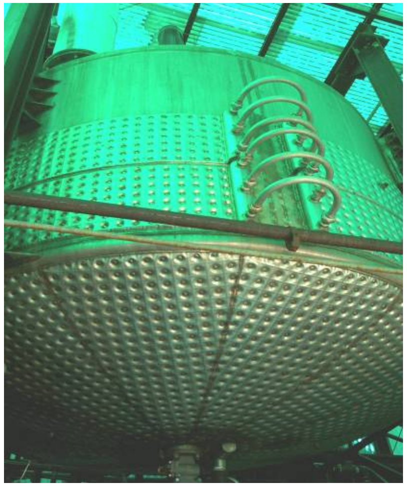
TNT **HNBB**

65-70% crude yield
>90% HNBB, <7% TNT



TNT to HNBB Optimization:

- NaOCl:base ratio (pH control)
- Reaction temperature
- Bleach addition rate
- HNBB Drying
  - Methanol wash removes water without need for drying
- Crude vs. Purified HNBB
  - No purification - saves time and money



BAE SYSTEMS

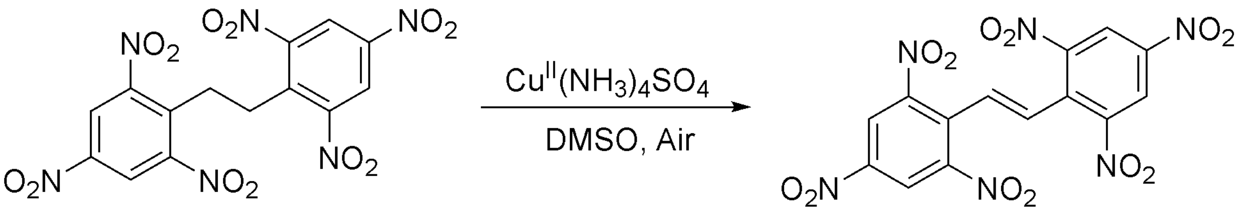
Optimization - HNBB Synthesis

Bleach Addition Rate Study

Bleach Addition Rate	**Yield** Wt. %	**HPLC Area %** HNBB	TNT	**Assay Yield** %HNBB
R_1 (Fastest)	73	96.4	3.7	70.4
R_2	69	94.3	4.9	65.1
R_3	68	89.1	9.7	60.6
R_4 (Slowest)	66	78.6	20.4	47.2

- Faster addition affords more HNBB at a higher purity

Optimization - HNS Synthesis



HNBB **HNS**

HNBB to HNS Optimization:

- Amount of Copper catalyst
- Reaction Time
- Amount of DMSO and number of recycles
  - Optimized to 1 virgin and 3 recycles

BAE SYSTEMS

Optimization - HNS Synthesis

Reaction Time (Hours)	DMSO Ratio (mL:HNBB)	Catalyst Ratio (Cat:HNBB)	HNS Yield Wt. % (From TNT)
>20	High	High	28.5
<10	High	High	29.1
<10	Low	High	39.2
<10	Low	Low	41.5

- Reduction in reaction time gives similar yields (lower overall cost)
- Reduction in solvent leads to increase in yield (and lower cost)
- Reduction in catalyst leads to slight increase in yield (and lower cost)

Optimization – HNS Purification

- Crude HNS-I has dark brown color, contains 8-10% HNBB
- Product failed Thermal Stability Testing
- HNS has poor solubility in common solvents
- Recrystallization from PAS/anti-solvent adds significant cost
- Two purification routes developed:
    - HNO_3 Digestion
    - HNO_3 Recrystallization

BAE SYSTEMS

Optimization – HNS Purification

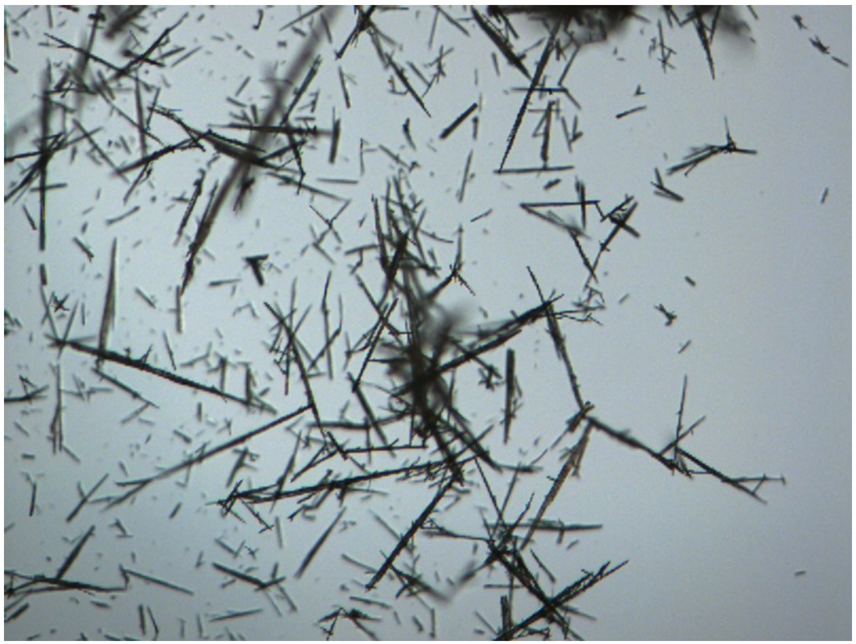
HNO_3 Digestion

Conditions	Wt. % HNO_3	VTS (260ºC) mL/g/mLghr	Bulk Density g/mL	Wt.% Recovery
Targeted Parameters	–	*<0.6/<0.6*	*0.8*	–
Slow Cool	70	0.7/0.2	0.5	85
Fast Cool	80	0.6/0.1	0.3	91
Fast Cool	90	0.3/0.2	0.4	87
Slow Cool	90	0.6/0.1	0.7	74
10x Scale-up of Above	90	0.2/0.1	0.6	83
21x Scale-up of Above	90	0.2/0.1	0.6	86

- Higher concentration of nitric acid affords good recovery, reasonable density, and acceptable thermal stability.

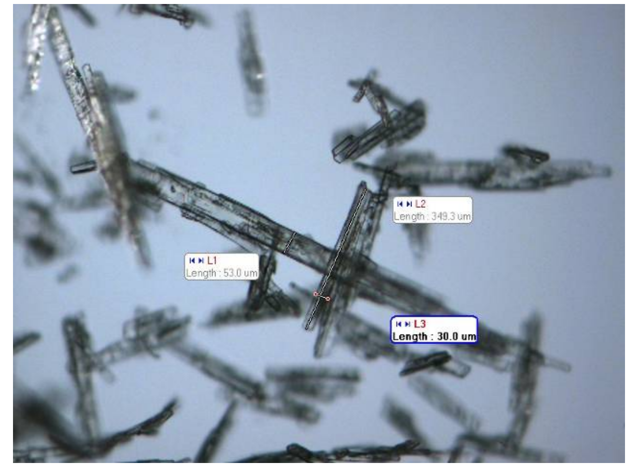
HNS Purification – HNO_3 Digestion

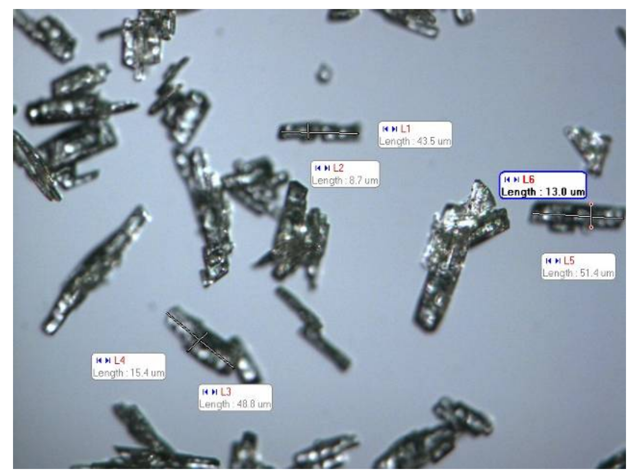
Crude HNS: d=0.25 g/mL



Length: 400 – 800 micron
Width: 12 – 20 micron

Fast cool: d=0.4 g/mL



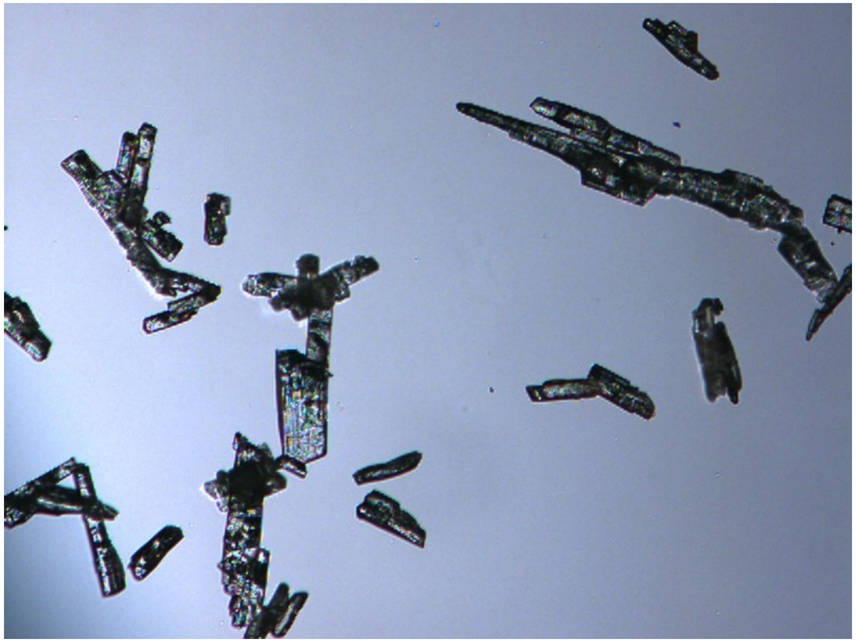


Slow Cool: d=0.7 g/mL

HNS Purification – HNO_3 Digestion

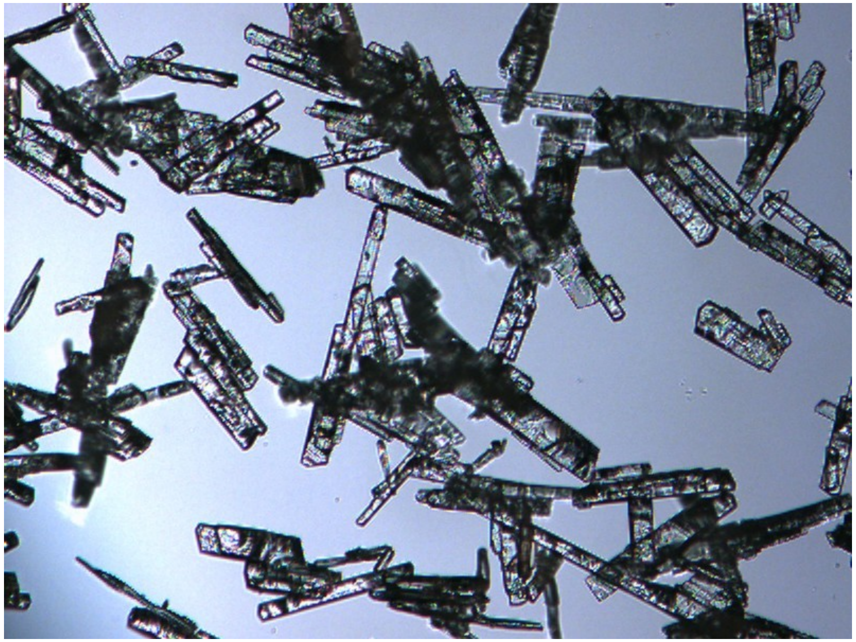
90% HNO_3 Digestion

Small Scale: d=0.7 g/ml



VTS: 0.6/0.1

Lab Scale-Up: d=0.6 g/ml



VTS: 0.2/0.1

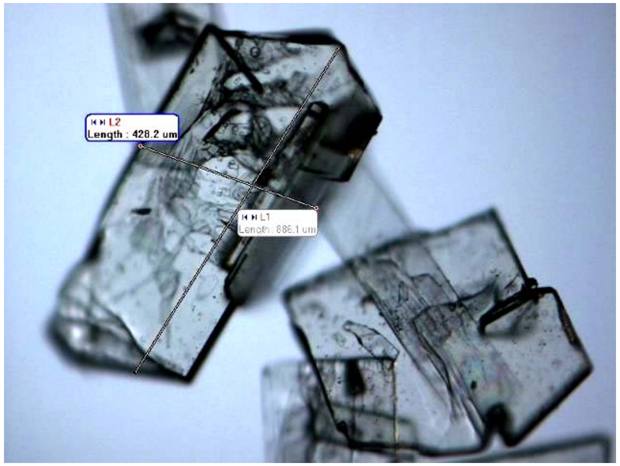
HNS Purification - Recrystallization

90% HNO_3 Recrystallization

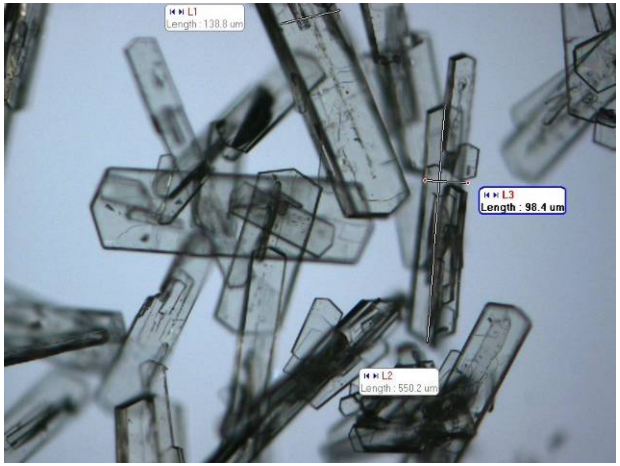
Conditions during cooling	VTS ml/g/ml/ghr	Bulk Density g/ml	% Recovery
Targeted Parameters	*<0.6/<0.6*	*>0.8*	–
No Stirring	0.7/0.2	0.6	64
Normal Stirring	0.4/0.1	0.6	70
Slow Stirring	0.3/0.1	0.8	68
Slow Cooling and Stirring	0.5/0.4	1.0	68
Scale-up of above to ~1 lb scale	0.6/0.3	0.85	70

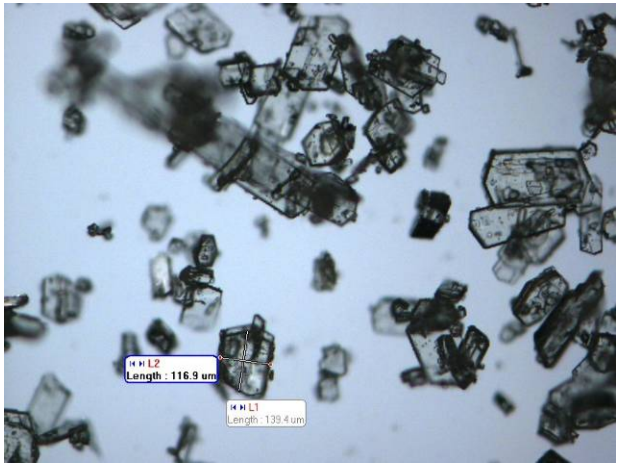
HNS Purification - Recrystallization

No Stir: d=0.6 g/mL

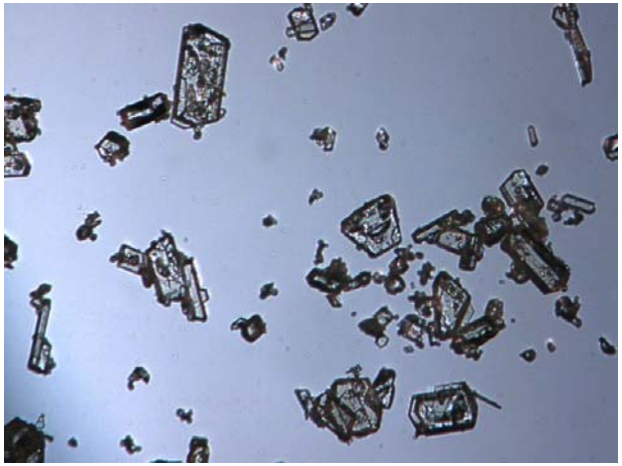


Normal Stir: d=0.6 g/mL





½ Normal Stir: d=0.8 g/mL

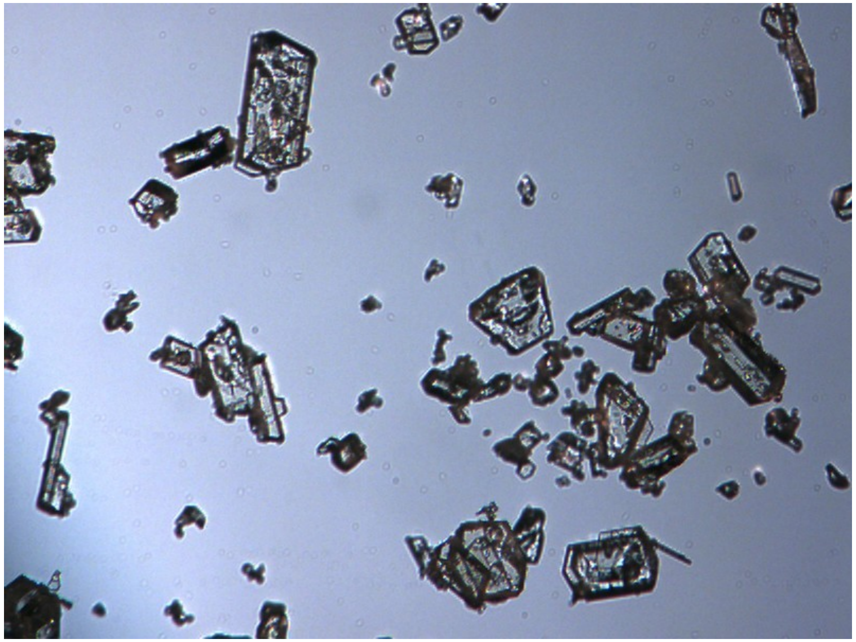


Slow Cool & Stir: d=1.0 g/mL

BAE SYSTEMS

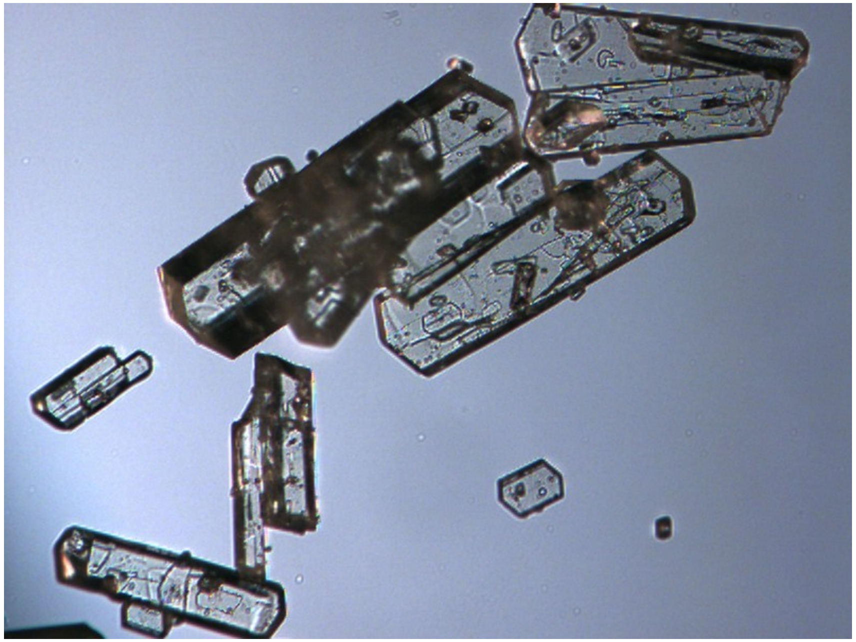
HNS Purification - Recrystallization

Small Scale
d = 1.0g/mL



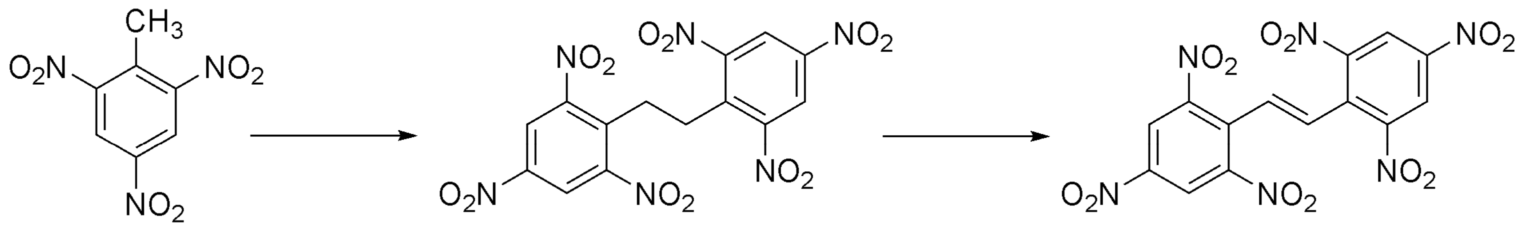
VTS: 0.5/0.4

Lab Scale-up (~1 lb scale)
d = 0.85 g/mL



VTS: 0.6/0.4

HNS Process Optimization



TNT HNBB HNS

- HNS Reaction conditions have been optimized
- Two viable HNO_3 purification routes:
  - Digestion:
    - VTS: 0.2/0.1 mL/g/mL/ghr
    - Bulk Density: 0.6 g/mL
  - Recrystallization:
    - VTS: 0.6/0.4 mL/g/mL/ghr
    - Bulk Density: 0.85 g/mL

Conclusions and Future Work

- Viable 2 step process for HNS identified
- Robust purification process identified
- All material processed passes thermal stability test
- Process is highly cost-competitive
- Further optimize weight yield of crude HNS
- Optimize scale-up cooling and agitation rates for maximum densities of purified HNS

Holston Army Ammunition Plant

HNS manufacture at HSAAP by FY 2010

Acknowledgements

- Mr. Jim Owens
- Ms. Kelly Guntrum
- Mrs. Lisa Hale
- Mrs. Roberta Tabor
- Mr. Jim Haynes
- Mr. Ed LeClaire