Studies of the Crystallization of CL-20

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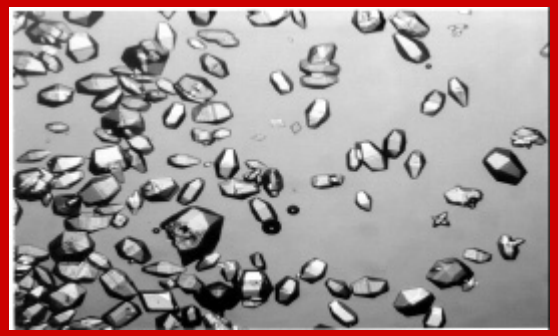
Karen Burrows, Naval Surface Warfare Center – Indian Head Division

Background

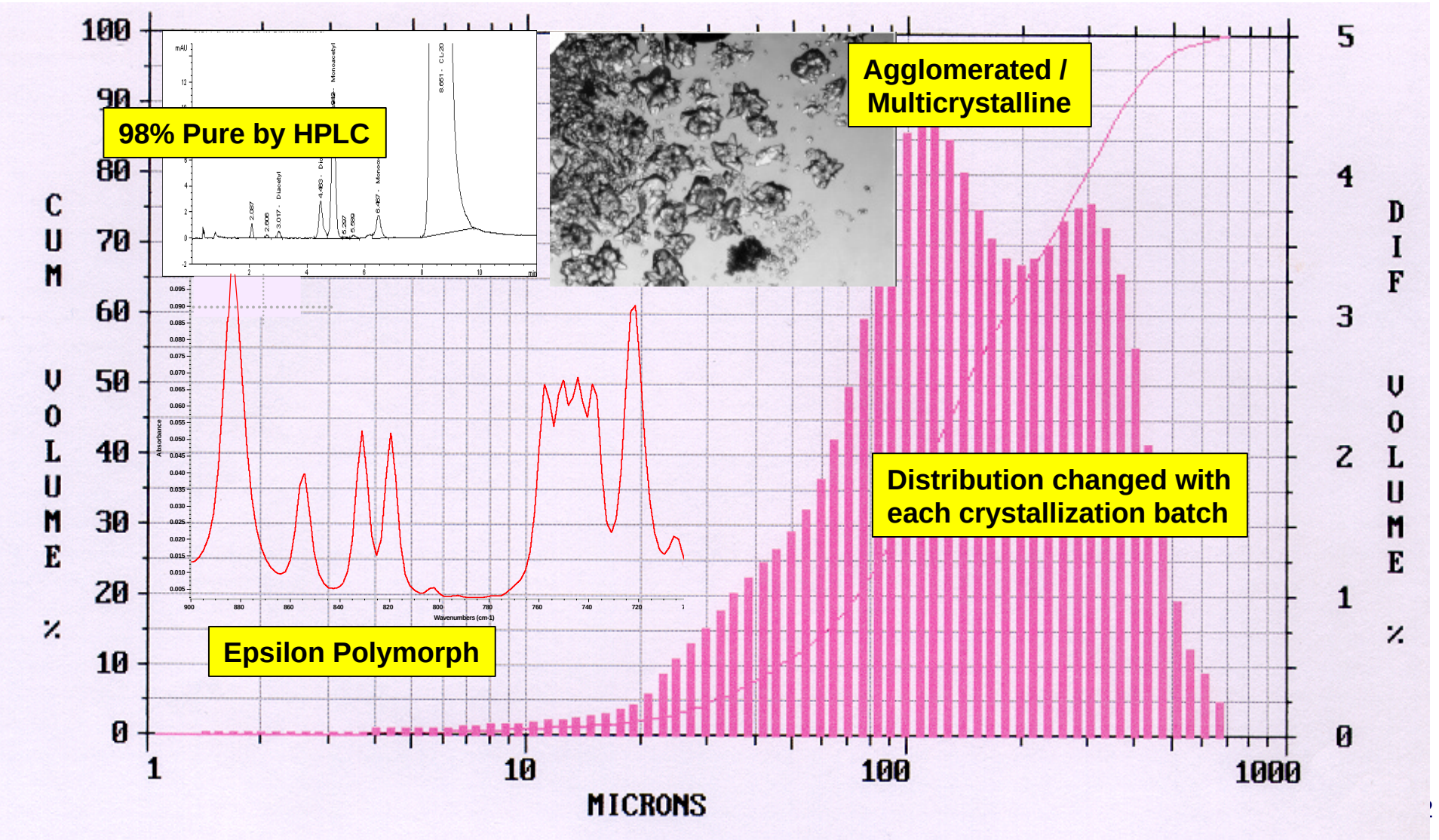


- **CL-20 is the most energetic conventional explosive available for military use in Explosives, Rocket, and Gun Propellants.**

- **Variability in production scale batches and the cost of CL-20 limit wide acceptance of CL-20 based energetic materials.**
  - **-Crystal agglomerates**
  - **-Particle size distributions inconsistent**
  - **-Lot-to-lot variability in sensitivity**
  - **-TADF precursor expense**

- **CL-20 MANTECH Program implemented to positively impact:**
  - **- CL-20 Reproducibility/Consistency**
  - **- Crystal Quality and Sensitivity**
  - **- Cost**

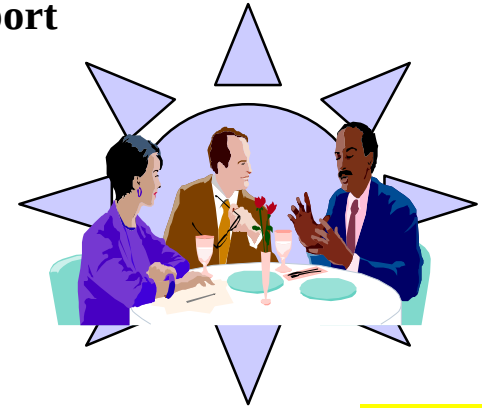
CL-20 Prior to Mantech



CL-20 MANTECH Government/Industry Team

NSWC/Indian Head Division

Project Management for Navy efforts
Crystal Sensitivity Evaluation
Crystallization Analytical Support



TACOM-ARDEC

Project Management for Army Efforts
Nitration & Crystallization Modeling
CL-20 Coating Studies

NAWC-WD/China Lake

Crystallization Technology

ATK-Thiokol Propulsion

Nitration/Crystallization Technology
Crystallization Process Control
Scale-up & Transition to Production

SRI, Intl.
GeoCenters, Inc.
Stevens Inst. Tech

Navy Program Objectives

- **Task 1 – Identify critical physical and chemical characteristics of CL-20**
- **Task 2 – Evaluate alternative crystallization techniques at the laboratory scale**
- **Task 3 – Evaluate crystal reproducibility, down select, and transition process(es) to the pilot plant for full scale production demonstration**

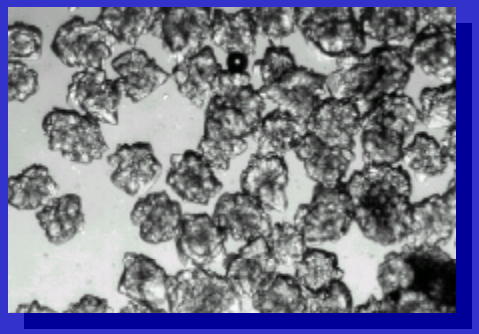
Critical Characteristics of CL-20 and Laboratory Scale Crystallizations

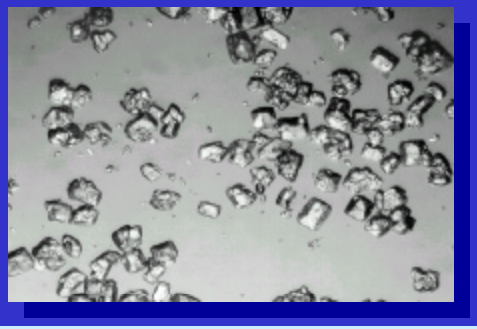
- **Database compiled for correlating CL-20 sensitivity with physical and chemical properties**
- **Round Robin Testing- Many CL-20 samples (>50) submitted for visual assessment, testing and discussion**
  - **Used *controlled* impact and friction testing**
    - **NSWC-IH, NAWC-CL, ATK Thiokol, ARDEC, Aerojet, Bofors, SNPE submitted samples**
    - **Testing at NSWC-IH, NAWC-CL, ARDEC, ATK Thiokol**

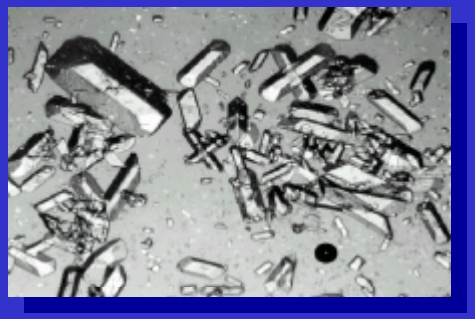
Findings:

- **Impact and friction showed little difference between samples**
- **Neat CL-20 is more sensitive than RDX/HMX standards despite differences in :**
- **Crystallization Method** **- Precursor Type**
- **Impurity Level** **- Visual differences (e.g., shape, crystallinity, etc.)**

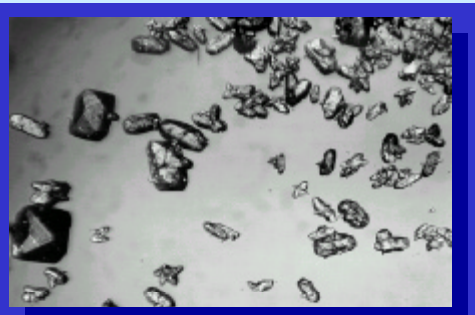
Round Robin Testing Samples

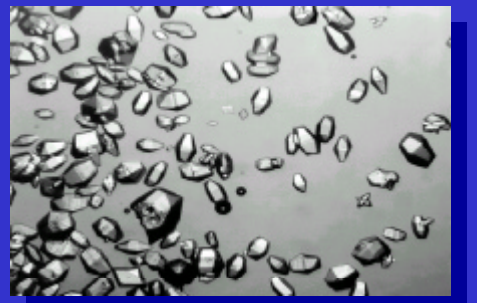




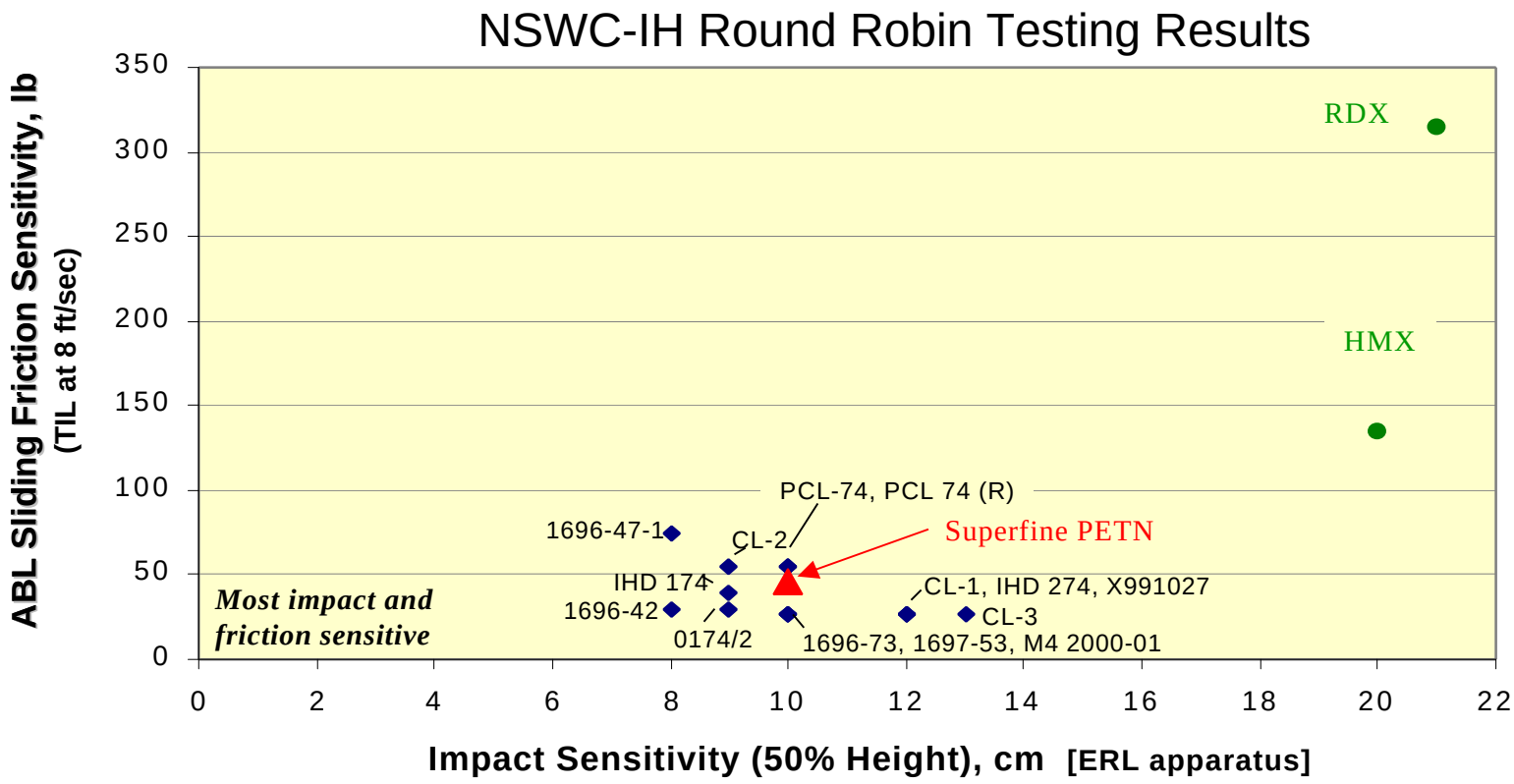


- Highly purified CL-20
- TADF based CL-20
- TADA based CL-20
- Various crystallization techniques





Round Robin Testing Results



Round Robin Testing Quantified the Sensitivity of CL-20

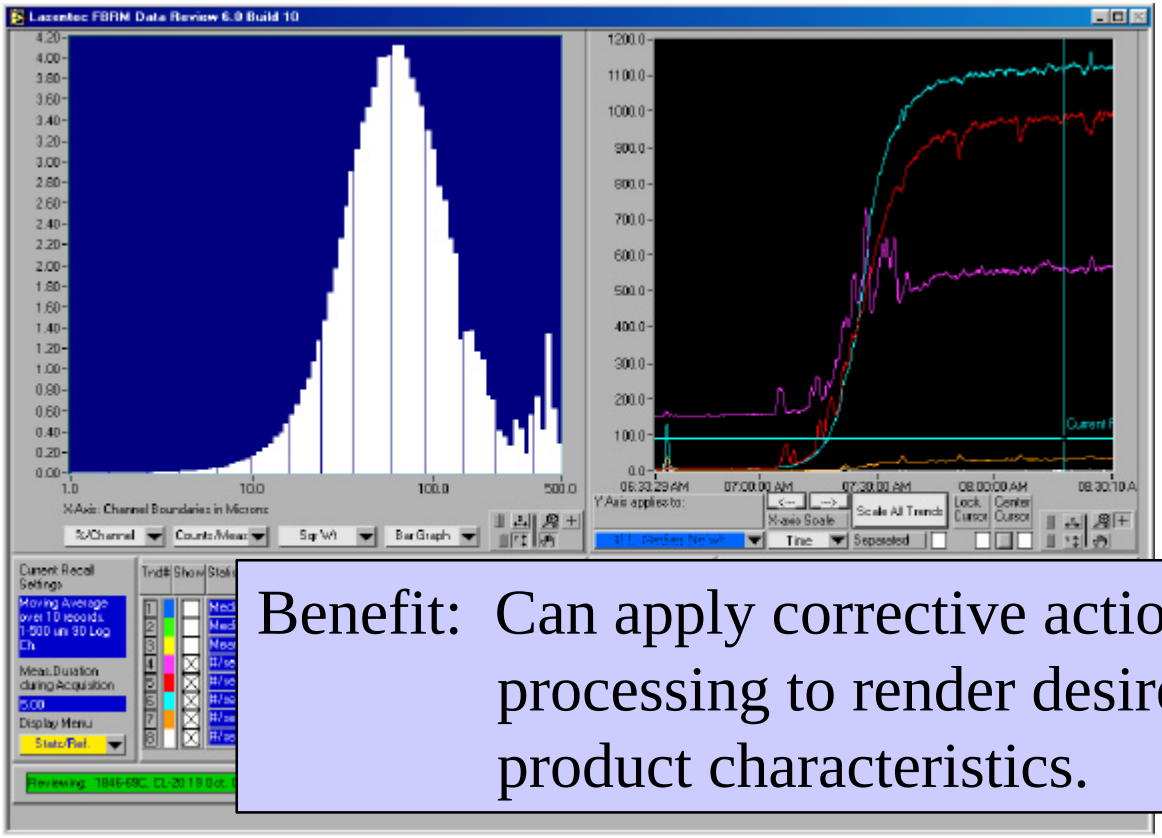
Crystallization Process Development

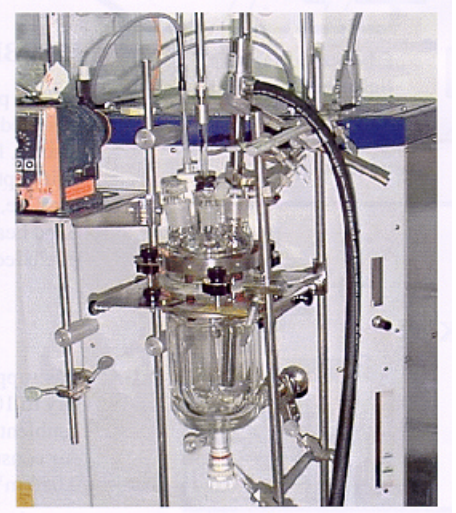
- Applied methods learned on early crystallization processes
- Developed 2 reproducible processes on 100-gram scale
  - Precipitation
  - Evaporation
- Implemented Crystallization Process and Product Monitoring equipment using laser light-scattering technology
  - Determined effects of temperature, stir rate, stirrer type, and seed quality/quantity on crystallization process
  - Evaluated trends so that scale-up would go smoothly

Understanding the effects of crystallization variables is critical to ensure product outcome during processing.

Real Time Crystallization Monitoring

- Able to observe real time particle size distribution
- Able to observe crystal growth characteristics within chosen channel (particle size) groupings
- Watch fine and course particle behavior
- Observe average particle size over time





e Crystallizer
iguration

Benefit: Can apply corrective action during processing to render desired product characteristics.

Scale-up Process

- Developed methods on 100-gram scale
- Demonstrated reproducibility on 200 gram scale
  - Observed crystal growth characteristics with Lasentec Instrument (evaporative method)
- Scaled-up to the 50-gallon reactor
  - Demonstrated that acceptable crystals could be produced by precipitation and evaporative methods
- Scaled-up to the 500-gallon reactor
  - Used processes developed on the lab scale and sub scales
  - Followed crystallization with Lasentec Instrument
  - Demonstrated repeatability from batch-to-batch

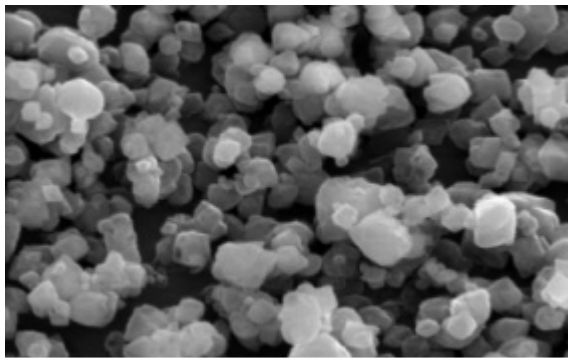
500-Gallon Precipitation Crystallization Matrix

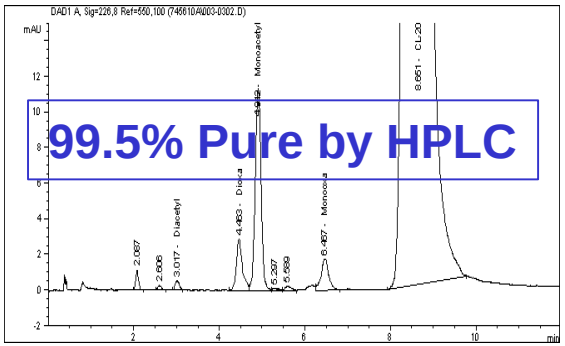
- Reduced original matrix due to time and expense issues
- Showed that process was stable at two different temperatures with virgin materials
- Non-virgin materials produced somewhat smaller particles than the virgin counterparts
- Produced small particles without the need for grinding

Lot Number	Batch Size (lbs)	Stir Rate (rpm)	Temp (deg F)	Seed Quantity (lbs)	Seed Size (lot 2180150)	Starting Materials	Crystal Size (microns)
590N-02-0078	100	125	68	10	2 microns	virgin	30
590N-02-0081	100	125	115	10	2 microns	virgin	31
590N-02-0083	100	125	68	10	2 microns	non-virgin	23

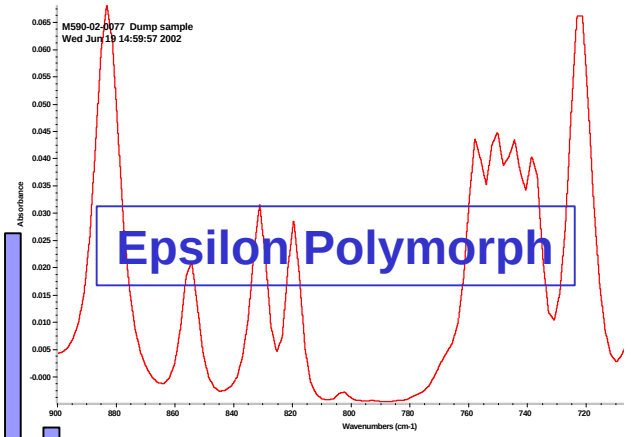
Unground 30 micron CL20

Lot 590N-02-0077





99.5% Pure by HPLC



Epsilon Polymorph

29 Micron

Percent per Channel

18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00

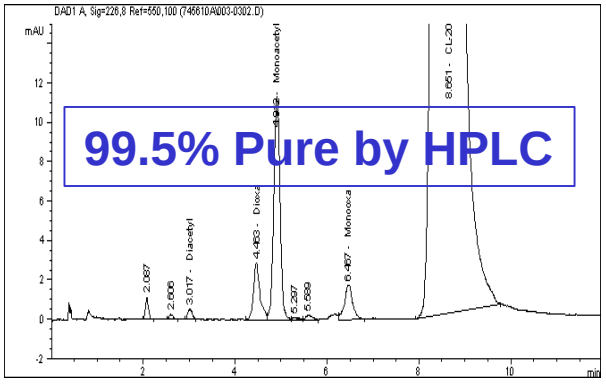
0.69 0.82 0.97 1.16 1.38 1.64 1.95 2.31 2.75 3.27 3.89 4.63 5.50 6.54 7.78 9.25 11.08 13.08 15.56 18.50 22.00 26.16 31.11 37.00 44.00 52.33 62.23 74.00 88.00 104.70 124.50 148.00 176.00 209.30 248.90 296.00 352.00 418.60 497.80 592.00 704.00

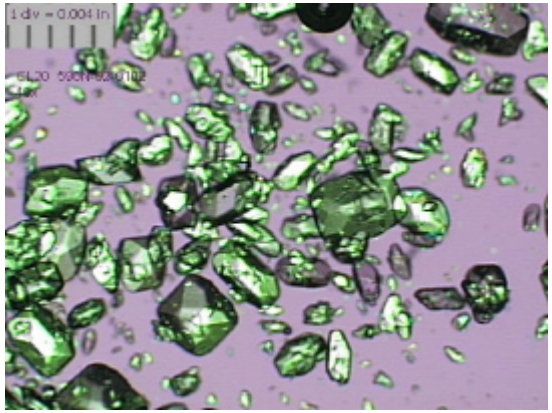
Diameter (microns)

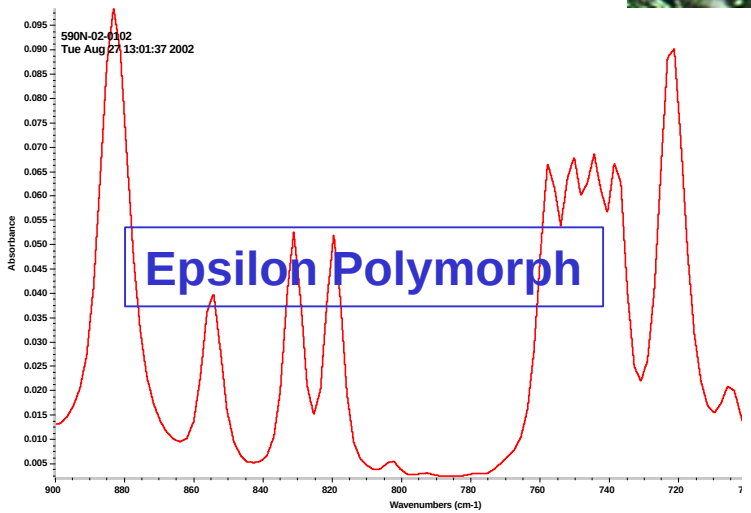
500-Gallon Evaporative Crystallization Matrix

- Monitored process by Rockwell trend software, Lasentec Instrument and NMR.
- Evaluated effects of crystallization variables
  - Stir rate – 95, 110, 125 rpms
  - Temperature – 35, 45, 55 celcius
  - Seed quality – 2 micron
  - Stir time – 3, 10, 14 hours
- Demonstrated reproducibility at two different conditions
  - 110 rpms and 55 deg C,
  - 125 rpms and 60 deg C
  - Recycled and virgin CL-20 was used

CL-20 Lot 590N-02-0102







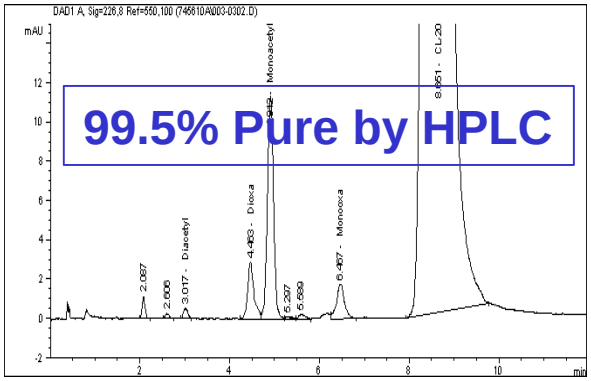
224 micron

Cumulative %

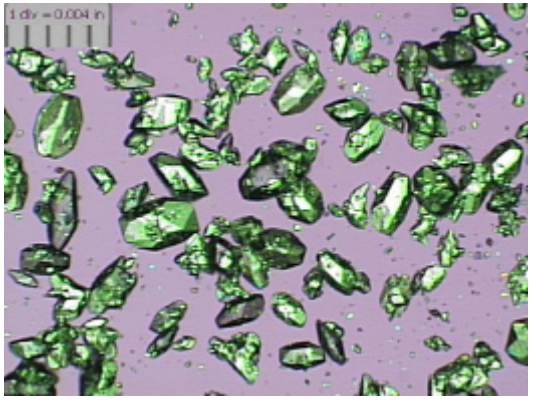
Percent per Channel

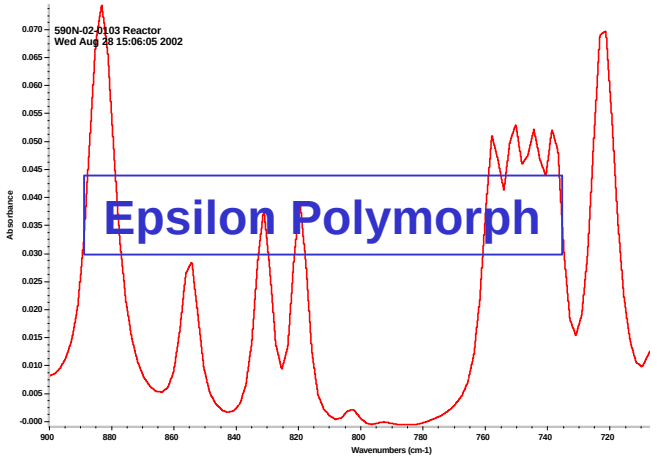
Diameter (microns)

CL-20 Lot 590N-02-0103



99.5% Pure by HPLC





Epsilon Polymorph

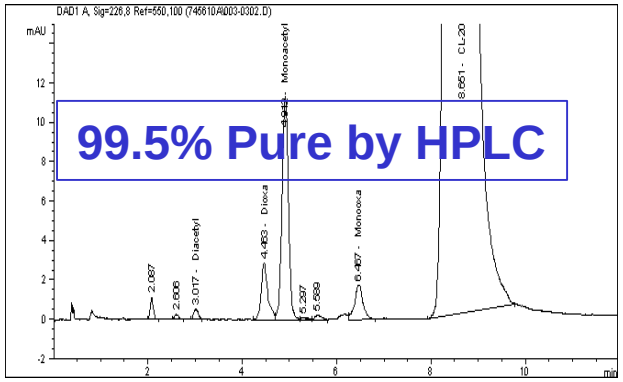
188 micron

Cumulative %

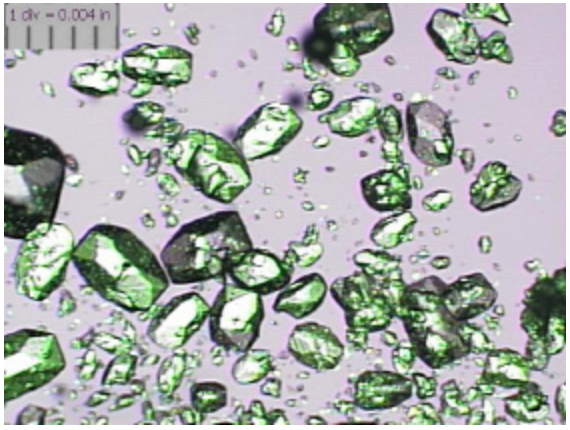
Percent per Channel

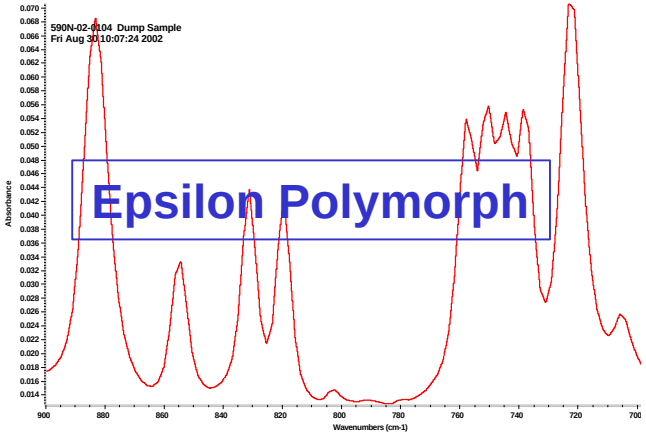
Diameter (microns)

CL20 Lot 590N-02-0104



99.5% Pure by HPLC





Epsilon Polymorph

196 micron

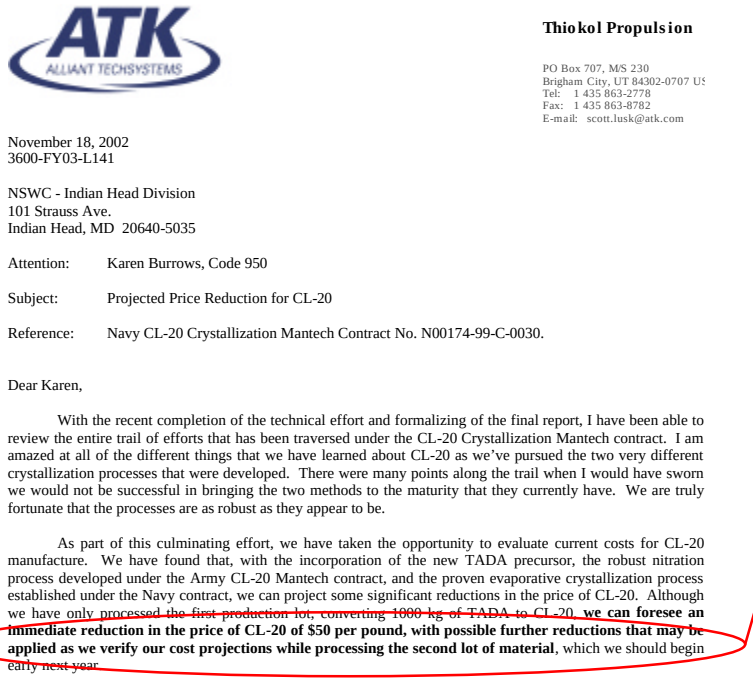
Cumulative %

Percent per Channel

Diameter (microns)

0.69 0.82 0.97 1.16 1.38 1.64 1.95 2.31 2.75 3.27 3.89 4.63 5.50 6.54 7.78 9.25 11.08 13.08 15.56 18.50 22.00 26.16 31.11 37.00 44.00 52.33 62.23 74.00 88.00 104.70 124.50 148.00 176.00 209.30 248.90 296.00 352.00 418.60 497.80 592.00 704.00

CL-20 Cost Reduction



ATK ALLIANT TECHSYSTEMS

Thiokol Propulsion

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November 18, 2002
3600-FY03-L141

NSWC - Indian Head Division
101 Strauss Ave.
Indian Head, MD 20640-5035

Attention: Karen Burrows, Code 950

Subject: Projected Price Reduction for CL-20

Reference: Navy CL-20 Crystallization Mantech Contract No. N00174-99-C-0030.

Dear Karen,

With the recent completion of the technical effort and formalizing of the final report, I have been able to review the entire trail of efforts that has been traversed under the CL-20 Crystallization Mantech contract. I am amazed at all of the different things that we have learned about CL-20 as we've pursued the two very different crystallization processes that were developed. There were many points along the trail when I would have sworn we would not be successful in bringing the two methods to the maturity that they currently have. We are truly fortunate that the processes are as robust as they appear to be.

As part of this culminating effort, we have taken the opportunity to evaluate current costs for CL-20 manufacture. We have found that, with the incorporation of the new TADA precursor, the robust nitration process developed under the Army CL-20 Mantech contract, and the proven evaporative crystallization process established under the Navy contract, we can project some significant reductions in the price of CL-20. Although we have only processed the first production lot, converting 1000 kg of TADA to CL-20, **we can foresee an immediate reduction in the price of CL-20 of $50 per pound, with possible further reductions that may be applied as we verify our cost projections while processing the second lot of material**, which we should begin early next year.

Of course, there are some underlying assumptions upon which this cost reduction projection is dependent. The principle assumptions are that the precursor price remains where it is at or below and that the annual CL-20 sales volume remains where it is at or above. The first assumption is probably dependent mostly on the second, but we are working with our supplier to obtain independent price reductions which we would pass along to our CL-20 customers. Also, with the many organizations currently evaluating CL-20 for defense as well as commercial applications, we do not expect a problem with the sales volume dropping in the near future.

We have also identified other potential opportunities to save on CL-20 processing costs and we will be pursuing these as well. As processing of other materials such as TEX, TATB, DNAN, and MNA reach the pilot plant scale and processing in our M-590 facility we could foresee some processing synergies that could further reduce the price of processing CL-20.

Immediate **$50/lb reduction** in cost attributable to:

- ✓ Lower cost precursor, TADA
- ✓ TADA Nitration process developed under Army Mantech
- ✓ Optimized crystallization process and SOTA process monitoring developed under Navy Mantech

Further cuts to be determined after completion of future production-scale runs to fulfill orders.

Conclusions

- Sensitivity of CL-20 is similar to PETN
- TADA is acceptable for use a CL-20 precursor
- 30 micron CL-20 can be made reproducibly without grinding
- Large (>100 micron) unground CL-20 can be made reproducibly
- Price of CL-20 reduced by $50/lb and further cuts are anticipated

The Way *Forward*

CL-20 Is Ready for Transition and Implementation into DoD Weapons

- ✓ **CL-20 can now be produced on the production scale (500 gallon) that is similar from lot-to-lot.**
- ✓ **Advanced process monitoring technology is now being utilized in the production of CL-20**
  - **A window of acceptable operating conditions has been established to ensure lot-to-lot consistency**