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IMPROVED PROCESS YIELDS EXTREME TEMPERATURE DETONATORS

IPS-16-05

PACIFIC SCIENTIFIC
ENERGETIC MATERIALS COMPANY

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AUTHORS: Jonathon G. Bragg, John W. Fronabarger, Michael D. Williams, Alex Linville, Neal Kerr

Agenda/Introduction

- Reason For The study?
- Lead Azide Overview
- Silver Azide Overview
  - Costain & Wells Process of Preparation
  - New Process
- Results Comparison
- Industry Benefit
- Acknowledgements
- Questions

Reason For The Study

- Lead azide (LA) supply
  - Type of LA used at PSEMC was no longer commercially available (at that time)
  - Age of existing stock

- Desire to reduce use of lead
  - LA contains lead that is released into the environment during production, use and disposal
    - Detonation generates nitrogen gas and lead vapor
  - Lead is regulated under TSCA (EPA)
  - LA is a candidate "substance of very high concern" under REACH regulations (toxic to reproduction)

- Industry need for higher temperature products
  - Industry approached us to offer products capable of operating at 500°F and higher

Lead Azide Overview

- LA is most widely used primary explosive with extreme sensitivity
  - DLA (dextrin)
  - PVA (polyvinyl alcohol)
  - RD-1333 (CMC – carboxy methyl cellulose)

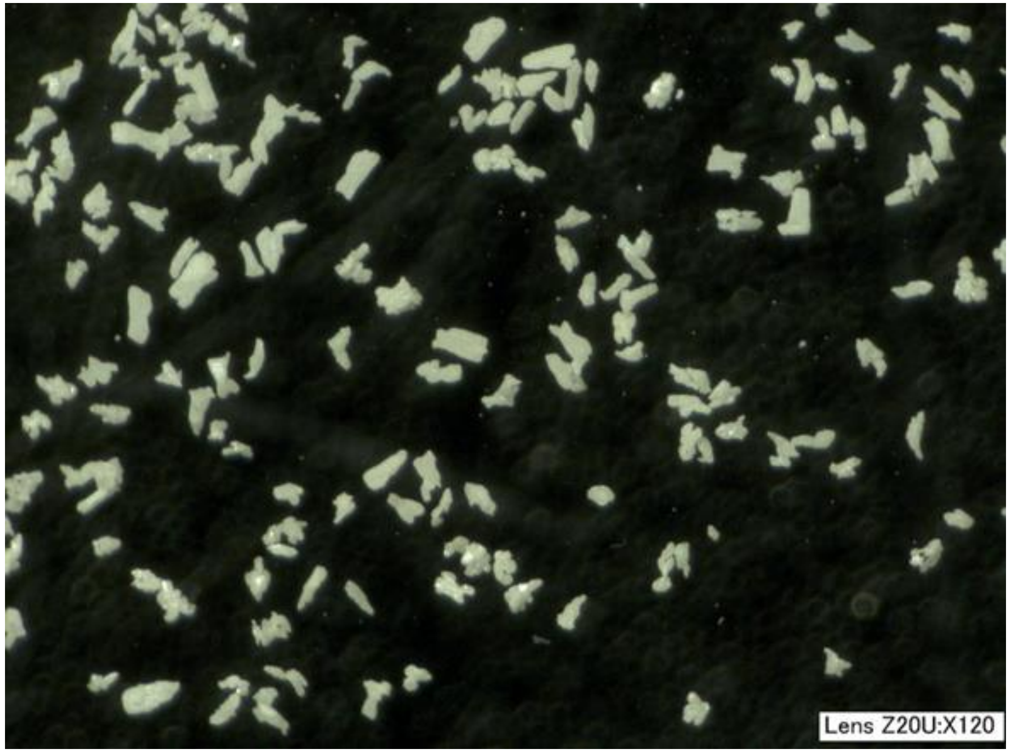
- Found in virtually all chemical detonators

- Produces the initial shock wave necessary for proper detonation of main explosive charge (RDX, HMX, HNS….)

- LA has its drawbacks:
  - Unstable in non-hermetic applications
  - Decomposes to hydrazoic acid gas in the presence of water and CO_2
    - Hydrazoic acid may react with metal components to form unstable metal azides (Copper)
  - Lower thermal stability than that of silver azide
  - Hazardous to environment/personnel and regulated as previously discussed
  - Remains friction and impact sensitive even under water!

Lead Azide Overview

Colloidal LA, 40X



RD-1333 LA, 120X

- Typically a white to beige powder which may darken slightly as it ages or on exposure to light

Silver Azide Overview

- Silver azide (SA) is a primary explosive, but has the following benefits over LA:
  - Lower friction and impact sensitivities (sensitivity highly impacted by crystal size and shape)
  - Thermally stable and demonstrates approximately 50°F advantage particularly near max use temp
  - Initiation/detonation properties similar to Lead Azide(cannot be dead pressed)
  - Nearly insoluble in water and generates low partial pressure of hydrazoic acid (precluding formation of other metal azides)
  - Generally considered less toxic to both environmental and human health perspectives relative to lead
  - Compatible with most metals including aluminum and copper (unless liquid water is present)
  - Compatible with most common explosives and inert componentry
  - We considered SA as the best candidate to replace LA in our products

Silver Azide Overview

Costain & Wells Process

- Common process used to produce SA

- Involves heating and distilling ammonia from an aqueous solution of sodium azide, silver nitrate and ammonium hydroxide

- The method produces a product with reasonably consistent particle size and morphology, good handling characteristics and a high bulk density

- But, differences where noticed when process transitioned from our Lab to Production Department:

  PSEMC thermal stability evaluation:
  Small scale (2 gram) Costain SA was close to 500°F (appearing to meet industry needs)
  Large scale (300 gram) Costain SA was ≤ 480°F

- Process improvement project launched

Silver Azide Overview

Costain & Wells Process Observations

- Method does not appear to be optimal for highly consistent product for use in commercial applications
  - Batch to Batch variations
  - Handling and loading difficulties

- Scaling up to > 100 gram levels uncovered the following observations:

  - Inconsistent morphology resulting from non-homogeneous concentrations of ammonia and water in the solution
    - Significant at the liquid surface and the liquid surface and glass interface
    - Adding a crystal modifier to improve morphology lowered thermal stability

  - Silver azide plating on reactor walls and stirring apparatus (creating uncontrolled morphology and more sensitive product)
    - Liquid surface to glass interface is an area of major concern (lead to formation of plates)

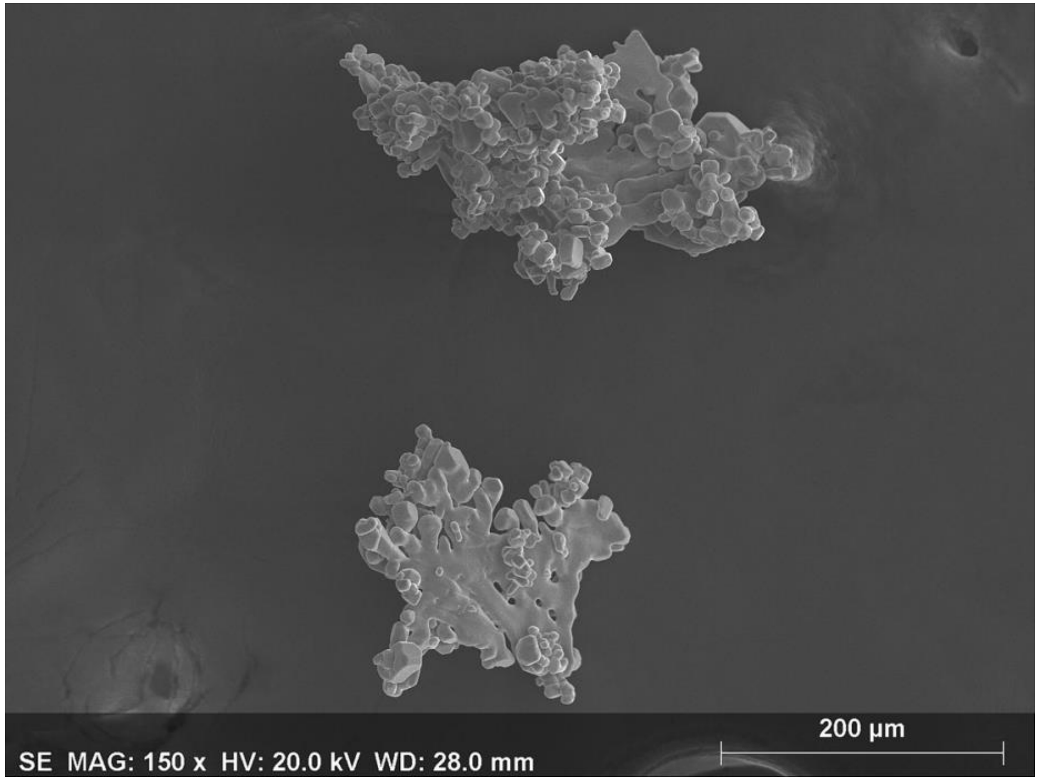
  - To maintain constant volume water has to be added at a rate which equals the ammonia evaporation

Silver Azide Overview

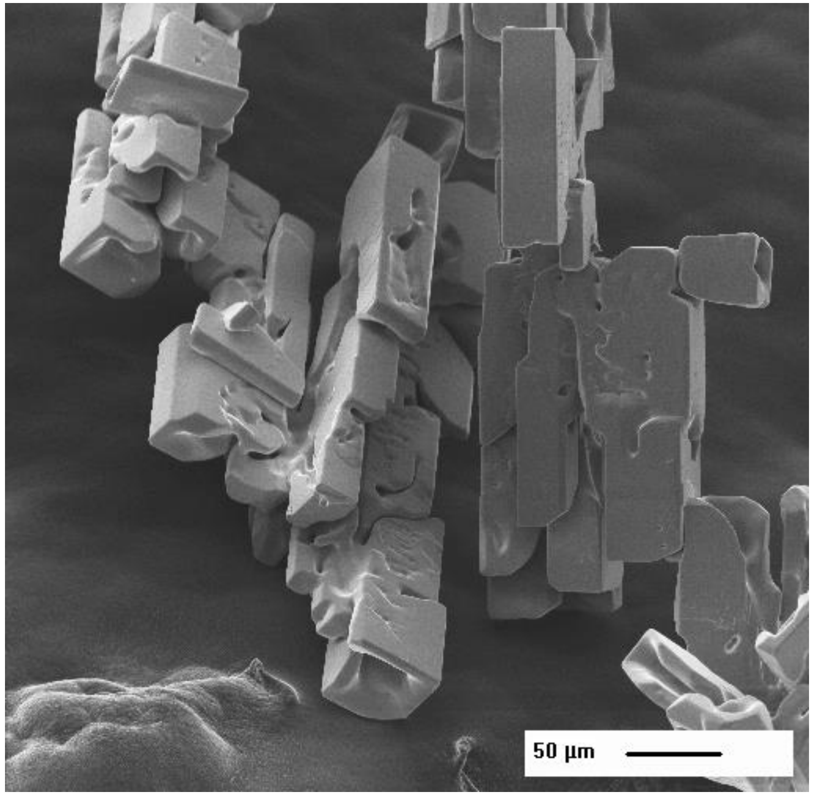
New Process (JF Method)

- A new process was developed to control and eliminate the Costain observations
- The new process (referred to as JF Method, John Fronabarger) adds an organic ester containing organic phase to the aqueous phase which more tightly controls the formation of silver azide crystals as the ester neutralizes the ammonia
- Advantages:
  - Higher purity SA with high thermal stability
  - Morphology is cubic throughout the production and between batches, granular and free flowing
  - Process appears to be inherently safer as personal exposure with the reaction is minimized (set-it and forget-it)
  - Crystallization is kinetically controlled vs. evaporation controlled
  - The reacting solution is homogeneous than the Costain & Wells method – concentration gradients minimized
  - Crystallization on reactor and stirrer do not occur
  - SA produced by this method may be used in detonator applications where temp exceeds 500°F for ≤ 24 hours

Costain vs. New (JF Method)

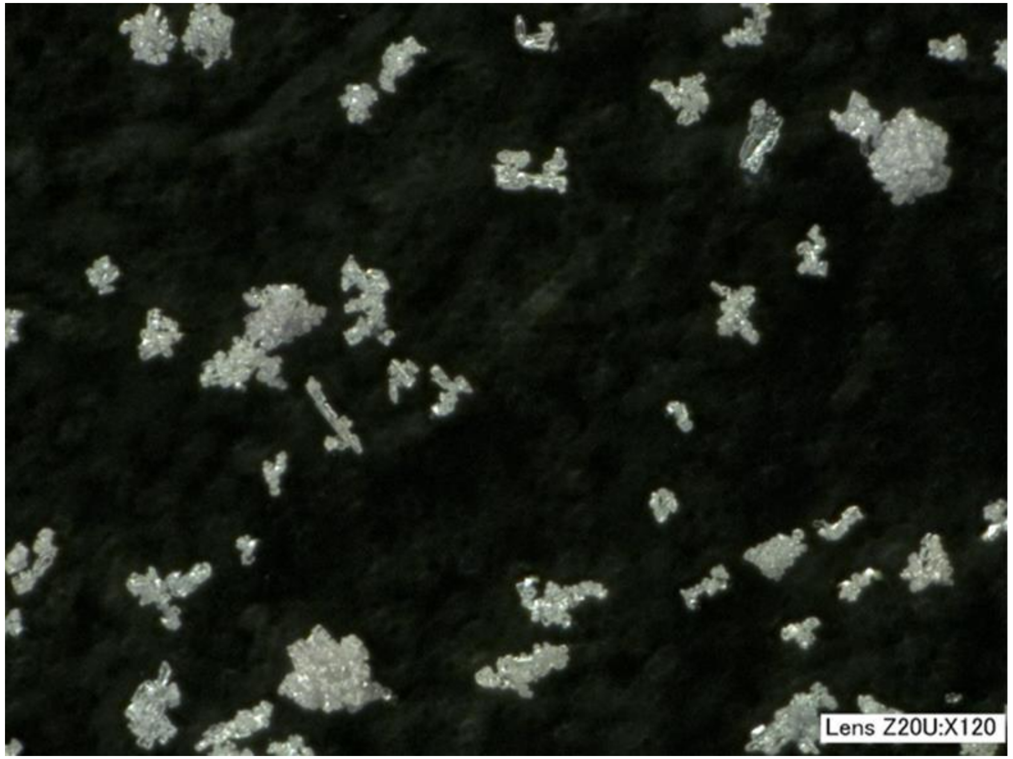


Costain SA, *150X* SEM

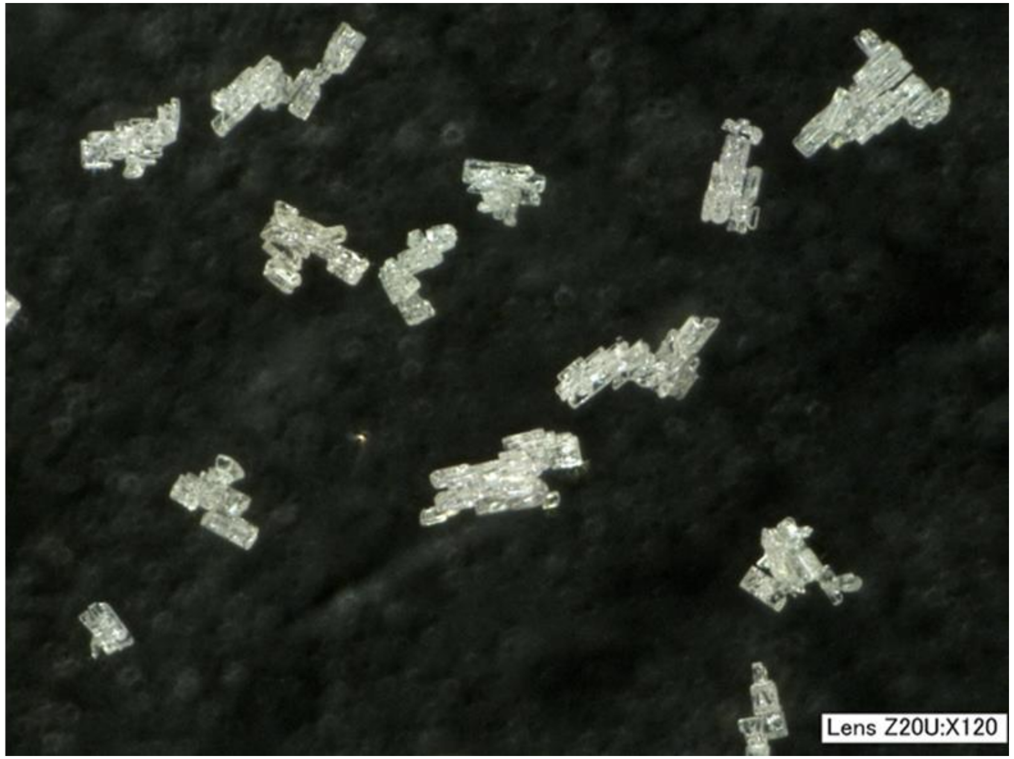


PSEMC SA, *250X* SEM, 200um (4M105)

Costain vs. New (JF Method)



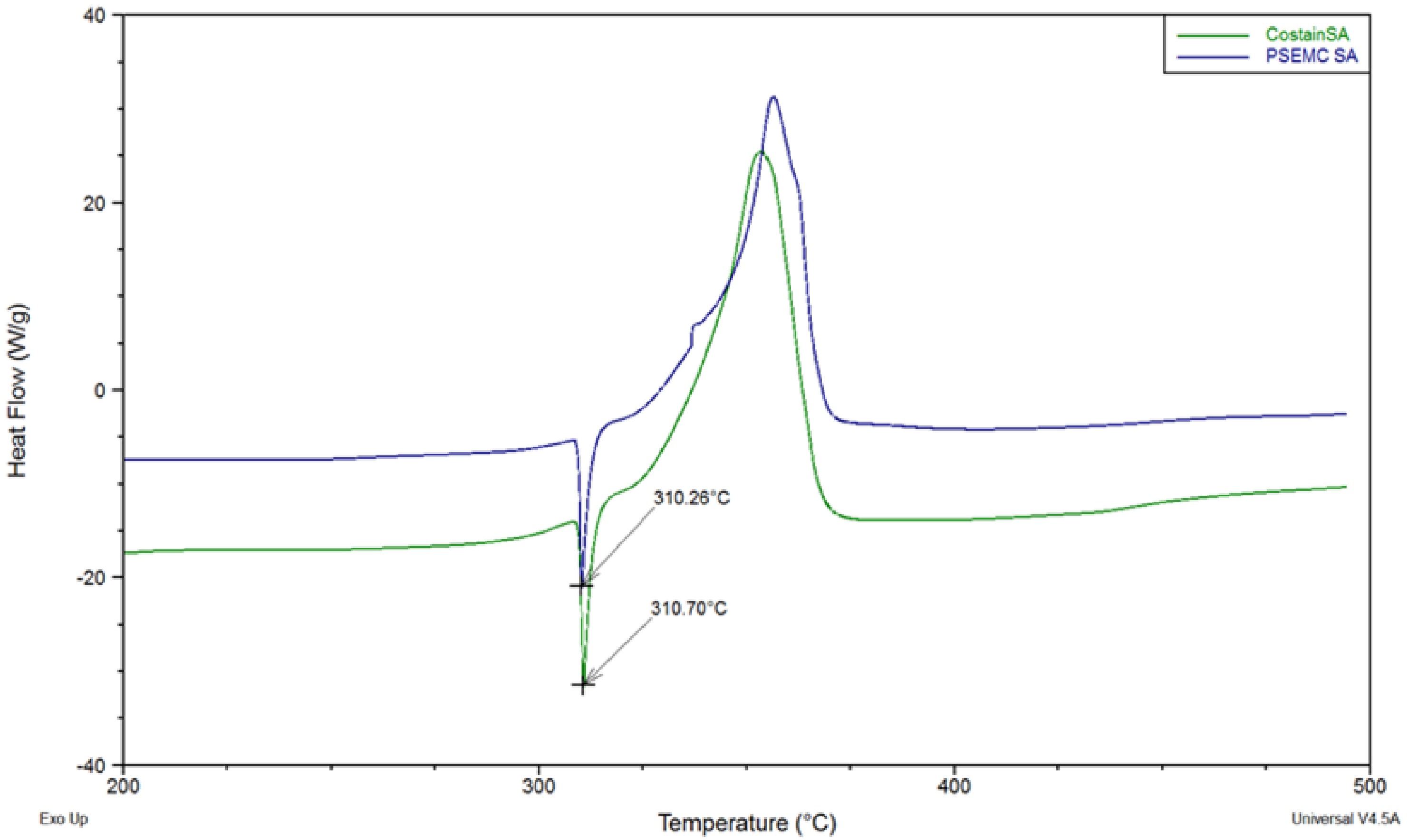
Costain SA, 120X



PSEMC SA, 120X, 200um (4M105)

Particle size may be controlled by varying reaction parameters

Results Comparison



- Comparison of DSC (and TGA) spectra of Costain and JF Method revealed little difference.
- Higher temperature capability of PSEMC SA has more to due with crystal morphology and density than with purity.

Results Comparison

- Tested in percussion fired detonators
- All results were acceptable
- Requirement = .050” minimum dent
- SA is also acceptable as a LA replacement in time delays

XWO101060 - HT Percussion Primer/Detonator 51-1965-4

		Destructive Testing per ATP	
SN	SA Lot	500°F, 12hrs	510°F, 12hrs
1	103	0.056	-
2	103	0.060	-
3	103	0.060	-
4	103	0.059	-
5	103	-	0.059
6	103	-	0.060
7	103	-	0.059
8	103	-	0.061
9	105	0.057	-
10	105	0.058	-
11	105	0.058	-
12	105	0.058	-
13	105	-	0.059
14	105	-	0.058
15	105	-	0.059
16	105	-	0.059

Industry Benefit

- Detonators capable of operating in high temperature fields or extreme depths such as Gulf of Mexico
- Manufacturing process produces highly consistent results
- Perforating jobs can be performed with non-lead containing detonators & time delays
- Increased potential to eliminate lead exposure in entire value stream: raw material, blending, handling, manufacturing, use, cleaning, scrap and redress activities

Acknowledgements

- International Perforating Symposium

QUESTIONS? THANK YOU!