GENERAL DYNAMICS
Ordnance and Tactical Systems–Canada

SUCCEEDING...
in a changing world

"IM-EM Technical Symposium"
Rome, Italy
May 20th, 2015

DNAN-Based Explosive Filling Process Toxicological Studies

Nathalie Lahaie
Pierre Pelletier
Isabelle Laroche
Daniel Lavigne
Dr Claude Émond

Outline

- Introduction
- Background
- Tests and results
- Actions taken
- General comments
- Summary
- Future work

Introduction

- Involvement of GD-OTS Canada with DNAN based explosives for many years.
- Work on internal R&D projects and some PM CAS contract with many formulations of this type (PAX-21, PAX-25, PAX-34 (OSX-4), IMX-104 (OSX-7), PAX-48 (OSX-8), OSX-12) covering different processing aspects presented in previous IM/EM TS.
- Work with PAX-21 at production level (60mm mortars) and qualification of IMX-104 in 60 and 81mm mortars
- Health problems encountered by some R&D technicians working in melt-pour pilot plant during tests involving PAX-48 formulation.
- Prepare and execute a test plan to improve understanding of the situation (causes and acceptable levels)
- Define appropriate actions to protect adequately people working in contact with this type of explosive.

Background

- Cases of skin rash and respiratory irritation encountered by technicians in the R&D melt-pour pilot plant working with PAX-48 formulation.
- Half masks with cartridges were worn followed by full face masks with cartridges and hood but the symptoms were still observed
- Up until work with PAX-48, no indication of such problem had been encountered with other DNAN based explosives (PAX-21, IMX-104, OSX-12)
- Hypotheses:
  - Link with PAX-48 material (more dust)?
  - Problem developed over time contact with DNAN based formulation?
  - Could rashes come from reaction of NTO with sweat (Why not observed with IMX-104)?
- Information received on similar indications by other organizations in relation with IMX-101.
- Discussions with people from different organizations (PM CAS, US Army surgeon general organization, BAE OSI, NAMMO, DRDC Valcartier) to exchange data on the situation.

Background

- Review of PAX-48 for comparison with other DNAN based formulations to list the differences in view of further study.
  - More dust observed in PAX-48 boxes compared to the other DNAN based explosive or composition B
    - This was mentioned to BAE OSI but it was not observed there and they had no explanation)
  - RDX dissolves partly in DNAN while HMX does not (as proven by a lower melting point and exotherm onset of IMX-104 compared to PAX-48 which are very similar formulations)
  - Particle size analysis of RDX and NTO recovered from IMX-104 and HMX and NTO from PAX-48 showed:
    - NTO particles were similar in size for both compositions
    - RDX particle size had a average value of about 30 microns and no particle below 5 microns
    - HMX particle size had a average of 10 microns with an important quantity below 5 microns.
  - Chemical analysis of recovered dust showed about same amount of DNAN, more HMX and less NTO than the data from the batch it was coming from.

Background

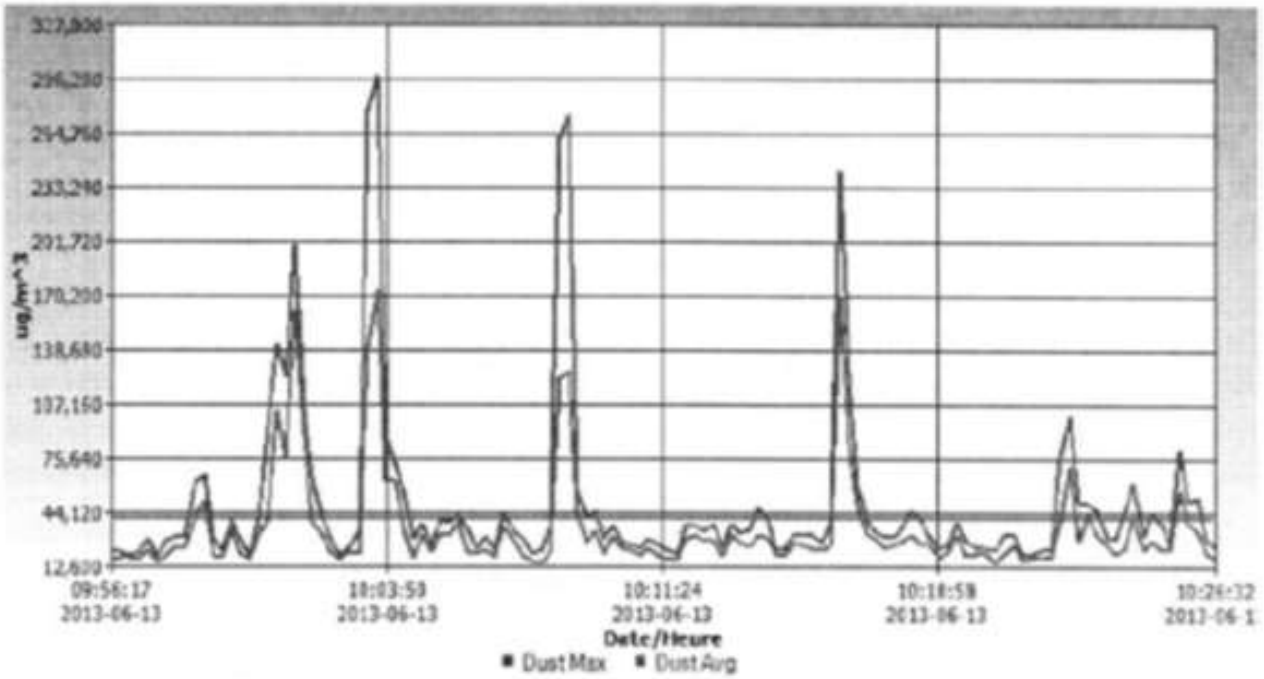
- Personal Protective Equipment until additional information was obtained
  - PPE selected based on review of data available from different sources and what other people were wearing and unknowns
    - TVEK coverall tied with tape at the wrist and ankle
    - 3M HEPA filter system with air supply system fitted on a hood with a part worn inside the coverall
    - 2 pairs of gloves on top of each other
    - Conductive shoes

Tests and results

- Sampling and preliminary analysis
  - Locations:
    - Pilot plant laboratory and production workshop at different points were conducted (all these stations are one level and connected to each other except for the last one):
      - Box emptying station
      - Melting kettle area
      - Holding kettle area
      - Filling station
      - Cooling stations
      - Funnels removal station
      - Fuze cavity reaming station
  - Analysis
    - Large quantity of DNAN at the box emptying station and funnels removal
    - Important DNAN vapor concentration observed near the kettle and filling stations
    - Important amount of DNAN vapors at the cooling station (solidified needles observed on the walls)
    - Results showed very small particles at the reaming station

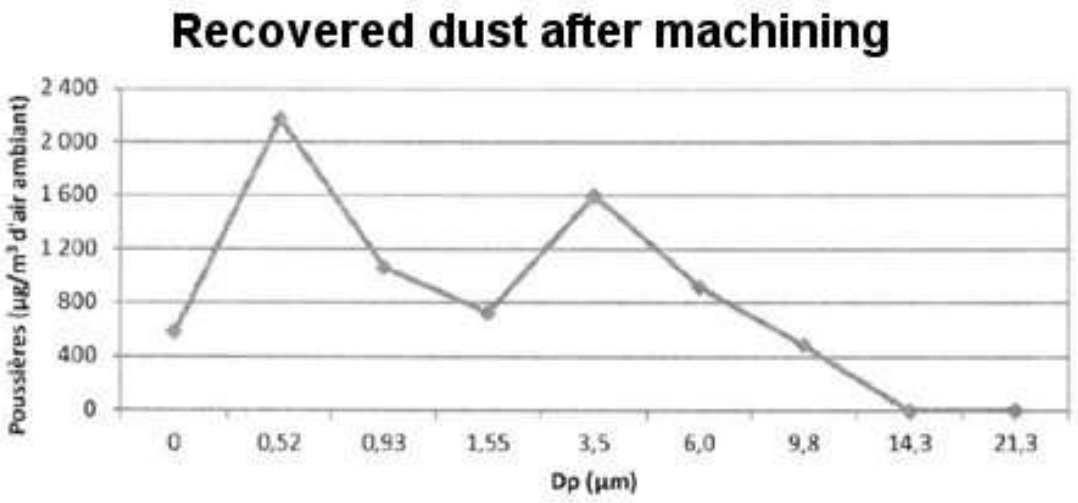
Tests and results

- Dust analysis - Quantities
  - On average, amount of dust is high compared to PM10 ACGIH (150 µg/m^3)
  - Highest values at the loading station (where explosive boxes are emptied)
  - High peaks (more than 100 x the limit) observed during explosive transfer.



Tests and results

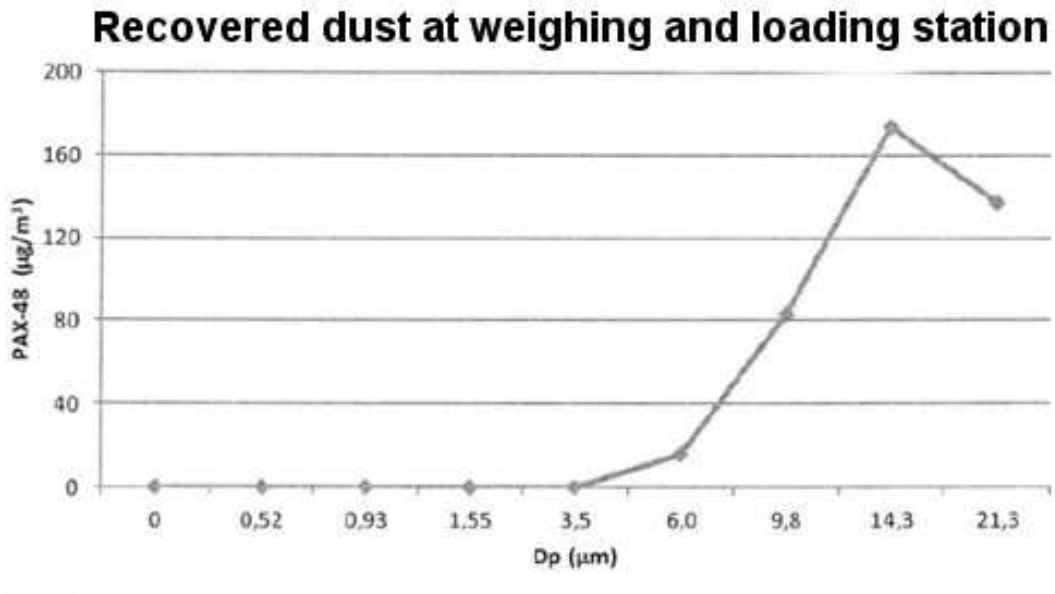
- Dust analysis – Particle size
  - Objective: Analyze relation between possible irritation and very small particles
  - Worst case: Output of the vacuum cleaner used for reaming and sectioning; very fine dust



  - New vacuum cleaner with HEPA filter: no more dust recovered

Tests and results

- Dust analysis – Particle size
  - PAX-48 weighing and loading station

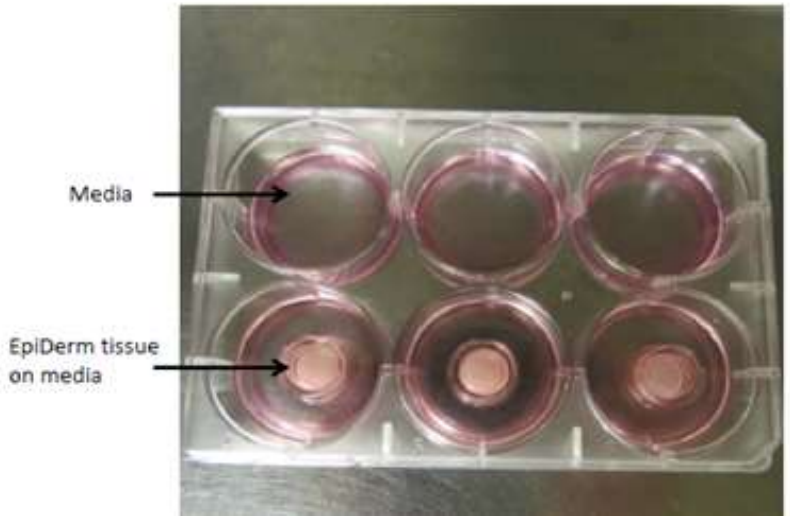


  - Particle sizes above 3.5µm PAX-48 but some below 5µm
  - Some evidence from CNRC-BRI that PAX-48 can cause skin cells irritation after 5 hrs exposition.

Tests and results

- Dust studies – Skin reaction
  - Tests performed based on hypothesis developed by the team (CRIQ, toxicologist and GD-OTS Canada representatives)
  - Tests performed by National Research Council Canada – Biotechnology Research Institute (NRCC-BRI)
  - Tests performed on synthetic skin (Human 3D EpiDerm).

Figure A1. EpiDerm™ tissues before treatment



Tests and results

- Dust studies – Skin reaction (cont.)
  - First series : DNAN, NTO2, NTO6 et HMX with 1hour exposure according to test protocol for cell kits
    - Materials dissolved in water
    - Filtering on a 0.22 microns filter
    - NTO2: Dissolved in water (pH=2)
    - NTO6: Dissolved in water (neutralized)
    - Negative results
      - % of dead cells
      - 12 proteins (biomarkers)
    - Conclusions
      - pH of 2.26 pour le NTO in water (matches a weak acid so 1hr exposure may not be sufficient)
      - HMX almost insoluble in water (3.562 mg/L)
      - No indication of dust irritation

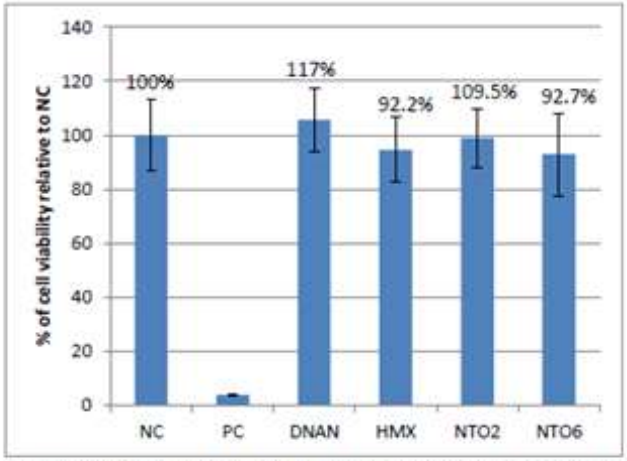


Figure 1- Summary of cell viability following 1 h exposure to different test samples. Each bar represents the average of 3 replicates ± SD.

Tests and results

- Dust studies – Skin reaction (cont.)
  - Second series: PAX-B, PAX-R et PAX-D with 1 et 5 hours exposure
    - Dust contact
      - PAX-B: Flakes
      - PAX-R: Dust at bottom of boxes
      - PAX-D: Dust from machining

    - Results
      - % of dead cells : PAX-B 5h significant, PAX-R and D non-significant
      - Interleukin 1 and 8 detected: 1 = cell stress, 8 = inflammation
    - Conclusions and recommendations
      - PAX-48 is skin irritant after about 5 hrs exposure
      - Which ingredient(s)?

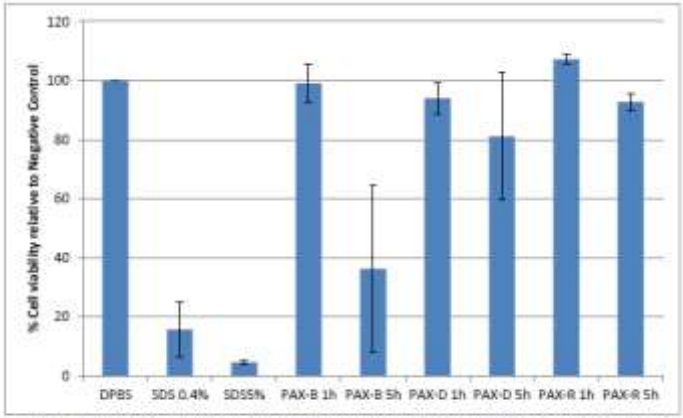


Figure 3- Summary of cell viabilities following 1 or 5 h exposures to different test samples. Each bar represents the mean of three replicates ± SD. DPBS indicates the negative control and SDS 5% indicates the positive control with values 100% and 4.6%, respectively.

Tests and results

- Dust studies – Skin reaction (cont.)
  - Third series: DNAN, NTO and HMX
    - 1, 2 and 3 hours exposure (Original plan: 1, 3 and 5 hours)
    - Exposure to solid crystal materials
    - Results
      - % of dead cells : negative results
      - Interleukin 8 (inflammation) reaction detected with NTO only
    - Conclusions et recommendations
      - NTO appears to be skin irritant but exposure time is not sufficient to kill cells.
      - Redo tests for 4 hours with the individual components and the three types of PAX-48 samples (flakes, dust from box and machining dust)

Tests and results

- Dust studies – Skin reaction (cont.)
  - <u>Fourth series:</u> DNAN, NTO et HMX, PAX-B, R and D
    - 4 hrs exposure
    - Exposure to solid crystal materials and dust
    - Results
      - % dead cells : 60% for NTO, PAX-48 More than 20% for PAX except for machining dust
      - Interleukin 8 (inflammation) reaction detected with NTO, PAX-B and PAX-D
      - Order of toxicity (skin irritation) NTO > (PAX-48B ≈ PAX-48D > PAX-48R > (DNAN ≈ HMX)

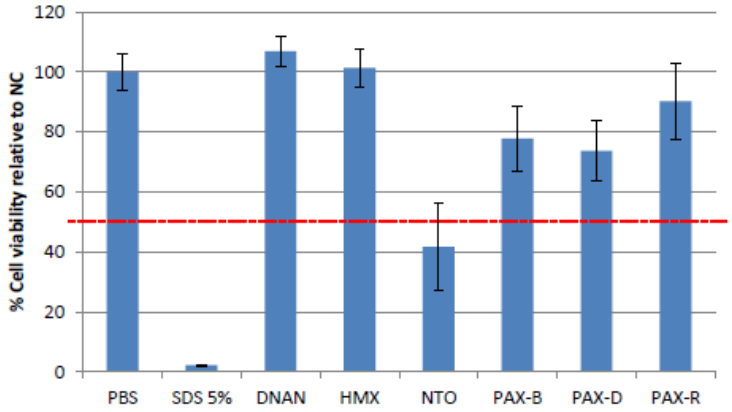


Figure 6. Summary of cell viabilities following 4 h exposure to different test samples. Hatched line indicates the irritancy threshold. NC indicates negative control. Each bar represents the average of 3 replicates ± SD.

Tests and results

- Polar and heavy VOC (Volatile Organic Compounds)
  - Less sensitive method but enable to get the more heavy and polar VOCs (amines and more specifically DNAN)
    - DNAN detected when cleaning the kettle at levels up to à 80 µg/m^3 (limit 90 µg/m^3)
    - Areas close to kettle and cooling stations showed DNAN level close to the limit
  - References about DNAN
    - Skin and mucous membrane irritant
    - Eye irritant
    - Sensitizer material

Tests and results

- Contact with synthetic sweat
  - Test objective: Study degradation of the PAX-48 components (DNAN, NTO and HMX) when put in contact with synthetic sweat.
  - Hypothesis: Solubilisation of NTO in sweat involving a chemical reaction to form an acid yielding irritation.
  - Method: Testing of the amount of each component after 30 and 120 minutes.
  - Could have been a way to discriminate between the effect of the three components.
  - Result: No difference in time in the quantity the three components.

- Cleaning water acidity (pH measurement)
  - Drain leachate: 3.80
  - Beginning of cleaning operation : 2.54
  - End of cleaning operation : 2.65
  - The acidity rises very fast when NTO is added to water
  - Some PAX-48 was found in the drains

Actions taken

- Pilot plant facilities
  - Improve ventilation in the whole area
    - Some limitation because it is important to ensure that this does not induce temperature changes that could influence the control of the processing parameters
    - Replace vacuum cleaner with one with HEPA filters at the fuze cavity reaming station
  - New measurements taken:
    - Improvement was observed but still above half the limit value so the equipment is still worn during production with PAX-48
    - Measurements taken after time without filling with PAX-48 in production showed that the values for DNAN were still high so the a clean up of the workshop was undertaken and check of values reduction before permission was given not to wear the full PPEs.
    - For some reason, DNAN vapors appears to be more difficult to remove than TNT vapors based on sampling.

Actions taken

- Production facilities:
  - Note: All the operations conducted on the same floor in two rooms
  - Improvement of system to handle bag out of the box and bring it to a system to cut the bag open in a closed area away from the operators
  - Enclosing conveyer belt bringing the material to the kettles (including metal detector)
  - Install systems to pick up vapors and better closing system for the kettles (melting and holding operations)
  - Improve ventilation in the whole production area
    - Some limitation because it is important to ensure that this does not induce temperature changes that could influence the control of the processing parameters
  - Improved ventilation and system to pick up dust at the funnels removal station and system enclosure
  - Studies showed that the dust at the reaming station was coming from the vacuum cleaner so it was changed by one with HEPA filter
  - Thorough general clean-up of the facilities
  - Humidity control

General Comments

- It takes a lot of time, efforts and money to perform all the studies involved to understand the situation
- Teaming between organization interested in the subject should be set to get the most of the resources available.
- It is important to take the best actions to ensure that operators do not become afraid of working with DNAN based explosives.
- When large production are involved, the actual protection equipment used at GD-OTS Canada become cumbersome and it is difficult to increase the production rate
- So far we have done our tests on PAX-48 but we are starting to work with IMX-104. We are applying the same rules for the time being but a as new data will be come available we hope to be in a position to review the situation.

Summary

- Studies are being performed at GD-OTS Canada to understand the cause of skin rash and respiratory irritation encountered by technicians in the R&D melt-pour pilot plant working with PAX-48 formulation.
- Preliminary analysis of differences between PAX-48 and other DNAN explosive formulations but except for larger amount of dust no difference was clear
- Dust sampling at different station in the melt–pour pilot plan and the largest amount was collected at the box emptying station (at some time the value was about 100 the limit.
- The study of the dust size led to change the vacuum system for the reaming station by one with an HEPA filter.
- Tests on artificial skin reaction seem to point towards NTO as the source of irritation but the mechanism still needs to be studied and the time to obtain reaction is long compared to the usual testing standards.
- The level of DNAN vapors was close to the limit close to the kettle and cooling stations as well as when cleaning the kettles.
- Modifications were done to both the pilot plant melt-pour laboratory and production plant to reduce the dust and DNAN vapors along with a thorough clean up of the workshops.

Future work

- Continue the toxicity studies work with experts outside GD-OTS Canada to obtain a better understanding of the causes of the reactions mentioned by the workers to be able to adjust the equipment (process equipment and PPEs)
- Perform the studies with IMX-104 to complete the analyses and understand possible differences
- Review the situation after taking additional measurements to review the use of PPEs.
  - Study possible separation of work areas

Acknowledgements

- Frank Cantin, Lise Phillips, Carol Jalbert, Marie-Claude Béluse, Alexandra Ducharme, Claudine Martel, from GD-OTS Canada for the preparation of samples and involvement in tests presented
- Dr Geoffrey Sunahara and Dr Mahsa Hamzeh, CNRC-BRI
- Marie-Josée Pinard from GD-OTS Canada Valleyfield for some material analysis
- Patrick Brousseau and Sonia Thiboutot from DRDC Valcartier for discussions on different aspects regarding the DNAN based explosives ingredients.
- Mike Erwin, Virgil Fung, Alberto Carillo from BAE OSI for helpful technical discussions on the characteristics of the formulations.
- Dr Mark Johnson, LTC Joseph Llanos from US Army Health organization for discussions on testing methods and available toxicity results.
- Phil Samuels, PM CAS for information on results from toxicity tests conducted in the US

Questions

- Points of contact for additional information:

Pierre Pelletier (Until August 2015)

GD-OTS Canada

Phone : 450-582-6345

Fax: 450-581-9771

E-mail: Pierre.Pelletier@can.gd-ots.com

Isabelle Laroche

GD-OTS Canada

Phone: 450-581-3080 extension:

Fax: 450-581-9771

E-mail: Isabelle.Laroche@can.gd-ots.com