MSIAC Munitions Safety Information Analysis Center
*Supporting Member Nations in the Enhancement of their Munitions Life Cycle Safety*

# Bulletin

## In this issue



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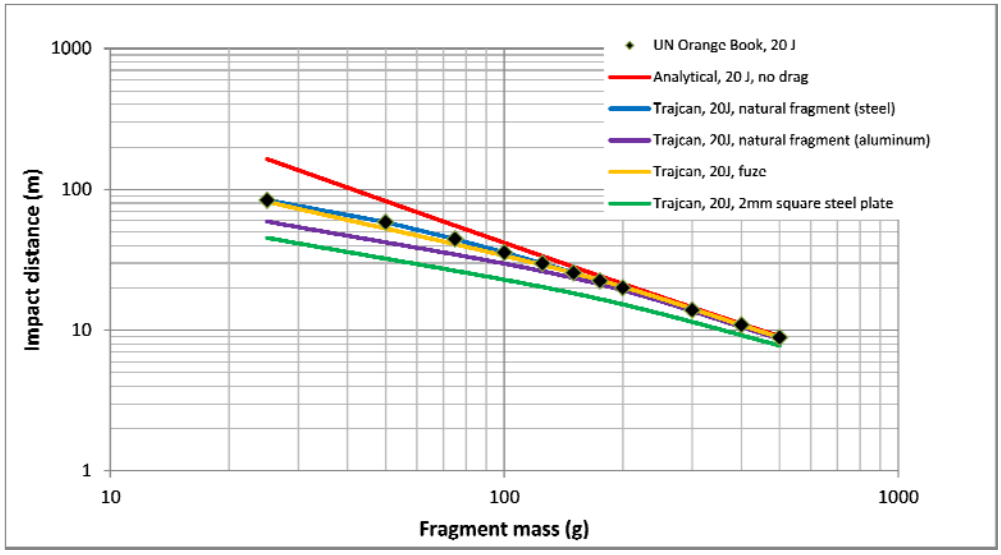
## Projection Criteria for Insensitive Munitions and Hazard Classification

This project has resulted in a paper that will be presented at the IMEMTS in Nashville, US (12-16 September 2016). The abstract of the paper is given below:

*"The origin of projection criteria for Insensitive Munitions and Hazard Classification was investigated. The distance-mass relations were reproduced using TRAJCAN trajectory analysis by using launch energies of 8, 20 and 79J and calculating the maximum impact distance reached by a natural fragment (steel) launched from 1 m height. The analysis shows that at the maximum throw distances, the impact energy is generally much smaller than the launch energy. For the launch energies of interest, the height reached by the projectiles is not enough to reach the terminal velocity before impacting the ground. Using maximum distance projections, new distance-mass relations were developed that match the criteria based on impact energy at 15m and beyond rather than launch energy. For near vertical projections the impact distance does not provide any information about the launch energy or impact energy. High velocity shallow trajectories can result in high impact energies, but collected data may be unrealistic due to ricochet effects. The smallest projectile masses in the distance-mass relations are in the transition region from penetration injury to blunt injury. For this reason, blunt injury dominates the assessment of injury or lethality. State of the art blunt injury models predict only minor injury for a 20J impact. For a 79J blunt impact, major injury is likely to occur with a small probability of a lethality. MSIAC recommends changing the distance-mass relation that distinguishes a munitions burning response to a 20 J impact energy criterion at 15 m."*




*Comparison between distance-mass relations in the UN Orange Book and trajectory calculations for various types of fragments.*

A more detailed overview of the results has been described in MSIAC Report O-168. Interested parties can download the paper and report through these links:

- https://www.msiac.nato.int/products-services/publications/o-168-projection-criteria-for-insensitive-munitions-and-hazard
- https://www.msiac.nato.int/sites/default/files/attachments/imemts_van_der_voort_160630.pdf

As this topic has the attention of many international colleagues we're looking forward to interesting discussions at the conference.

**Martijn van der Voort**
**MSIAC Safety of Ammunition Storage & Transport Specialist**
**&**
**Ernie Baker**
**MSIAC Warhead Technology Specialist**

# EXPERIMENTAL & THEORETICAL BASIS OF CURRENT NATO STANDARDS FOR SAFE STORAGE OF AMMUNITION AND EXPLOSIVES

Good progress has been made within the project "Experimental and Theoretical basis of current NATO standards for safe storage of ammunition and explosives". The results obtained so far have been presented at various meetings and have been reported in a paper for the Military Air Blast Symposium (MABS) which is to be held in Halifax, Canada (19-23 September). The work will also be presented at the OME symposium in the UK (1-2 November). Because the topic of this study is very broad and complex, we asked various international colleagues for their review and feedback.

The abstract of the paper is given below:

*"NATO standards for the safe storage of ammunition and explosives contain tables with so-called Quantity Distances (QDs). These distances are aimed to provide an acceptable protection level to surrounding Exposed Sites (ES) in the event of an accidental explosion of a Potential Explosion Site (PES). The development of the standards took place over many decades by explosives safety experts. The QDs are based on the analysis of a large number of explosives tests- and accident data. Based on additional testing and analysis accomplished in recent years, a comprehensive and transparent overview of the basis for the QDs is necessary in order to validate them and to eliminate inconsistencies.*

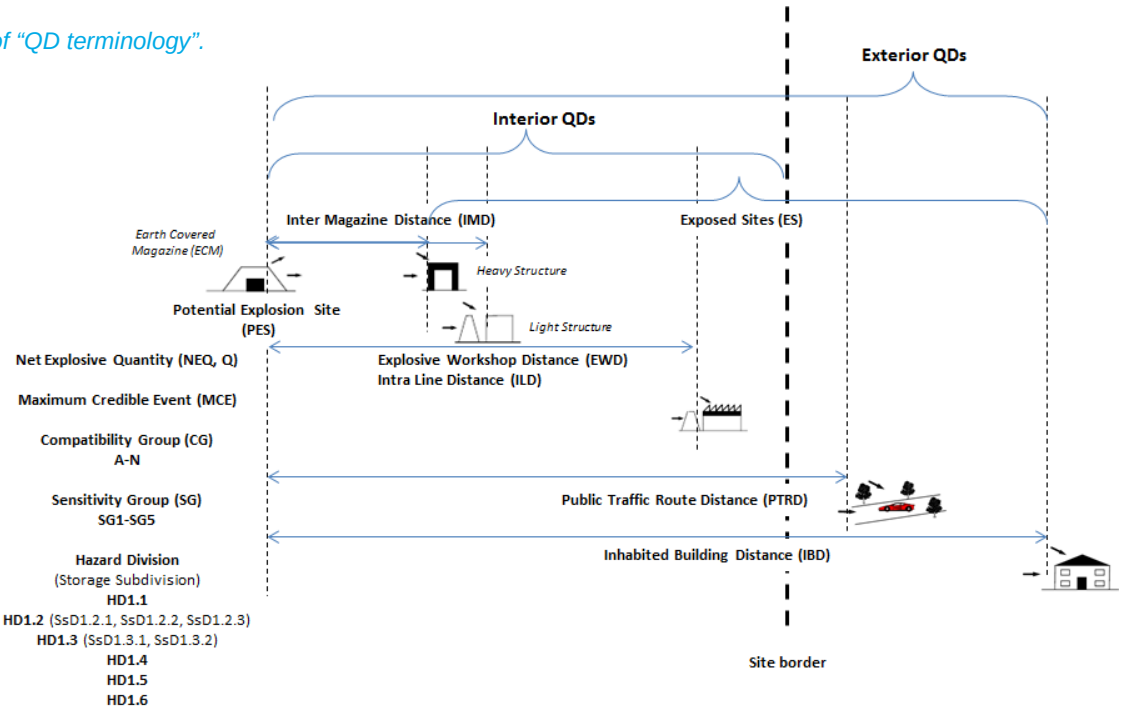
*The Munitions Safety Information Analysis Center (MSIAC) conducted a study on the experimental and theoretical basis of QDs. This paper presents a structured approach to QDs, starting with the amount of munitions involved in the munitions response, and then treating each explosion effect separately.*

*Relevant references that support the standards have been analyzed. QDs have been compared to state-of-the-art prediction models for blast wave propagation and observed damage. The basis of those QDs that are dominated by fragments and structural debris is discussed as well. Planned changes to the NATO standards, such as the implementation of QDs for small quantities of explosives, are taken into account. Knowledge gaps have been identified and recommendations for long term development have also been made. A more detailed report as well as a repository of all references will be completed towards the end of 2016."*

Interested parties can download the paper through this link: https://www.msiac.nato.int/sites/default/files/attachments/mabs_2016_p187_van_der_voort_msiac_basis_of_qd_lowres.pdf.

The paper concludes with an overview of those assumptions that make AASTP-1 and AASTP-5 conservative, but also addresses a number of aspects that may lead to potentially unsafe situations. A number of recommendations are given related to the

*Graphical overview of "QD terminology".*



harmonization of standards and to better address QDs for Insensitive Munitions.

Interesting recommendations for the long term are given as well:

- A development towards more physics-based QDs in combination with clear acceptance criteria in terms of explosion effects or consequences is recommended. QDs with a larger fidelity avoid the need to split up tables for different NEQ ranges, with associated discontinuity problems at the boundaries. It also avoids the need to make assumption for situations that require "No QD".
- More advanced debris IBD models could be used that take into account building parameters like dimensions, wall thickness and door properties, and also provide reduced QD in off-normal directions.
- The development of QDs could benefit from a closer cooperation with expert groups on testing and modeling of explosion effects and consequences. Examples are the Klotz Group and the AASTP-4 CWG. Ideally speaking the explosion effect models reported in AASTP-4 and QDs and FDs provided in AASTP-1 and AASTP-5 should be consistent.
- Instead of presenting QDs in table format, they could be provided by means of a calculation tool. This prevents human error, and also avoids issues about rounding and interpolation.

A number of the recommendations will be addressed in the upcoming Technical Working Group for AASTP-1 Part 1 (5-6 September) in preparation for the AC/326 SGC meeting (7-9 September).

The Stokes fellow project "Benefits of IM", which is currently being carried out by Ben Keefe (UK) has a direct link with this work. Ben will finish his project end of August, and a summary of Ben's findings will be mentioned in the next newsletter.

**Martijn van der Voort**
**MSIAC Safety of Ammunition Storage & Transport Specialist**

# ENERGETIC MATERIALS ROUND UP

We start with the sad news of the passing of two scientists both from the field of detonics and energetic research; Dr Carl-Otto Leiber (ICT), and Dr Igor Plaksin (University of Coimbra). Our condolences are with their families at this time; a loss also to the scientific community.

In this edition of the newsletter we review presentations and proceedings from three recent energetics meetings; 7th Nitrocellulose Symposium, 47th International Annual Conference of ICT and 19th New Trends in Research of Energetic Materials (NTREM). Our thanks go to Dr McAteer (Cranfield University) for providing the NTREM review.

Some promising secondary explosives and pyrotechnic materials, testing methodologies and collaborations between countries have been presented. Please refer to each symposium for greater details.

In this issue we were unable to cover other activities occurring around the nations; Gordon Conference, New Energetic Materials, International Pyrotechnic Symposium. Lastly we highlight some forthcoming meetings of interest for 2016/17.

## *7th Nitrocellulose Symposium*

The 7th Nitrocellulose (NC) symposium took place from 31st May to 1st June and was held in Montreal, Canada hosted by General Dynamics Ordnance and Tactical Systems (GD-OTS) at the Westin Hotel. The symposium had a similar level of attendance to that of the 6th symposium (110 people) with representation from 20 countries. Eleven out of thirteen MSIAC countries were represented (only Italy and Norway were absent).

The symposium, through 23 presentations, covered cellulose manufacture and its analysis, nitrocellulose manufacture and its analysis and characterisation for inclusion in propellants, and some propellant manufacture and additives.

*Process*

New methods were described for in-process control of mixed acid (Synthesia) by use of Density/Sound Velocity Receptor (DSR). The process allows real time measurements of mixed acid ratio (nitric, sulphuric and water) and was compared to standard laboratory techniques. The DSR method although quicker was not as accurate as the laboratory method.

Further development of Near InfraRed (NIR) spectroscopy for determining nitrogen percentage (%N) in nitrocellulose and mixed acid percentage was report mainly for industrial use (Manuco, Synthesia, Nitrochemie). This technique still requires calibration against the titrimetric method, and chemometrics to provide the correlation/calibration against variables such as temperature and changes in water content. The technique is still only useful for industries that are able to generate the primary calibration, which requires hundreds of samples.

Results of particle size analysis using imaging for characterising NC fineness to provide a particle size distribution rather than a single value were shown. This was backed up with theory and determining limits for fines/dust, agglomerates and fibres (GD-OTS). Having greater information on the shape and size distribution of NC should help in understanding the effect on propellant properties.

Findings from research into nitration of bacterial cellulose (QinetiQ) showed that solubility characteristics changed when compared to linters based cellulose. Batch nitrations of one grade were able to produce a nitration level of use for gun propellants but not for rocket propellants. Cost and availability of the bacterial cellulose suggest that this will remain a research product.

*Analysis*

A programme of work (Cranfield University) was underway to understand the degrees of freedom of NC and how to correlate chemico-mechanico properties of NC with those of propellant. Work continues on improving Gel Permeation Chromatography (GPC) to analyse nitrocellulose (AWE) by reducing dissolution time and the use of multiple detectors (low angle light scattering and viscometry). A direct chromatographic method is also sought to determine nitrogen percentage in propellants, after ageing, rather than using the indirect stabiliser depletion model (TNO).

Interesting work to understand thermal NG/NC stability using ARC was presented (CERL). They would like to understand the effect of decomposition across all heating rates; isothermal ARC data has given them slow decomposition regimes and they have fasting heating data (literature). New experimental techniques are required to access the intermediate regimes.

Friction and impact apparatus have been fully instrumented (CERL) to provide better information on reaction information to the aforementioned stimuli. Gas analysis ($CO/NO_x$), load sensors and pressure transducers were used to provide the analytical information.

*Safety*

An update was provided on a NC accident (AWE) and the work required to comply with the UK HSE. This included understanding the physical properties of the NC (resistivity) and solvent (ignition energies). This led to fundamental changes in process operation including elimination of NC drying, development of an indirect NC lacquer concentration method via viscometry, new lacquer production equipment and paste manufacturing process.

An accident with a US Navy CAD PAD (2007) led to the redevelopment of the cartridges (composite propellant) and the introduction of new In–Service Surveillance monitoring technology (US Navy).

*Propellants*

Work continues on the development of 'green' anti-oxidants & stabilisers for single and double base propellants (PB Clermont). The work has shown how families of compounds behave in stabilising NC-based propellants. This has led to the down-selection of 3 compounds (Curcumin, □-ionone and □-tocopherol) that have shown to provide stabilising effects according to STANAG 4582 and without the generation of N-nitroso compounds. Performance testing and qualification on the propellants has still to be achieved.

Modernisation of Mulwala required the re-qualification of Australian propellants (DST Group). Work continues on understanding the mechanical and ageing characteristics of the propellant.

LOVA propellant development (BAe) and IM testing was presented. The LOVA formulation used a thermoplastic elastomer (TPE) binder based on NC (up to 10 %), ethyl vinyl acetate (EVA; up to 8 %) and a plasticiser (up to 9%), combined with a nitramine (up to 80%) filler. The IM tests were promising (see presentation) with a pass for SCJ. The test set up (SCJ) and degree of confinement was not discussed. The LOVA propellant has been designed for the 120 mm and 105 mm artillery.

*Future*

The next symposium will be held in 2018 in Bergerac, France and hosted by Manuco. The objective for the next meeting will be to understand the science of cellulose, nitrocellulose and propellant formulation. The linkage and understanding between the three fields should then drive the requirement(s) for cellulose and nitrocellulose production.

## *47th International Annual Conference of ICT*

The theme for this year's conference was "synthesis, characterisation and processing". 24 countries were present with 250 delegates providing 39 oral presentations and 95 posters. Eleven of the thirteen MSIAC nations were present with absences from Italy and Spain.

*New Materials*

Work by Francois (LANL) showed the effect of particle size on the initiation characteristics of 3,3'-diamino-4,4'-azoxyfurazan (DAAF). A reduction in the particle size from 40 µm to <10 µm led to an increase in the initiation pressure (39.9 to 43.3 kbar) as determined by the GAP test. The work highlighted the potential use for DAAF in 'slapper' detonators.

Energetic ionic liquid research by Schaller (ICT) highlighted the plasticisation properties of 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN) with the energetic binder system GAP:N-100. Stability, via ARC, and mechanical testing showed that AMTN performs similarly to the BDNPA/F plasticized variant.

Work by Koch (Lutradyn) proposed an interesting replacement for red phosphorous compositions based on phosphorous (V) nitride ($P_3N_5$), which would not lead to $PH_3$ formation, that exhibited friction sensitivities of >355 N with oxidisers such as $KNO_3$, $KClO_4$ and $NH_4NO_3$. Work to date showed good thermal stability, and comparable yield factors and mass extinction coefficients for obscurant formulations.

Cooke (ARDEC) reported on diammonium 4,4',5,5'-tetranitro-2,2'-biimidazolate (DATNBI); an insensitive replacement for RDX with a higher decomposition temperature and less sensitiveness to impact and friction. A design of experiments approach to re-crystallisation of the 3-step synthesis product improved the crystal morphology to allow performance testing. Detonation velocity and pressure were less than predicted, requiring further work on understanding the variance.

*Formulations*

In the secondary explosive sphere two presentations were given, one on DNAN-based melt cast charges and the other on a FOX-7-based pressable charge.

Johansen (Chemring Nobel) provided qualification data on four melt cast compositions for use in 155 mm

ammunition (IM requirement); MCX-6002 (NTO/RDX/TNT; 51/15/34 wt%), MCX-6100 (NTO/RDX/DNAN; 53/15/32 wt%); MCX-8001 (NTO/HMX/TNT; 52/12/36 wt%); MCX-8100 (NTO/HMX/DNAN; 53/12/35 wt%). The ISGT highlighted the effect of casting density on initiation pressure for the MCX-6100 formulation (58.5 kbar @ 98.1 % TMD compared to 36.5 kbar @ 95.2 % TMD). Velocity of detonation and pressures for all formulations were lower than calculated values. Work continues, on the above formulations, to slow and fast heating threats (tube tests).

Coulouran (Nexter) presented the continuing development of FOX-7-based pressable formulations for booster applications. Work on XP/FOX-7, using class 4 (250 µm) FOX-7, showed good ambient pressing conditions, similar velocity of detonation and smaller ISGT result when compared to XP3264 (the RDX analogue).

An EU funded project, GRAIL, to develop green solid propellants based on ammonium dinitramide (ADN) and ammonium nitrate (AN) was presented by Winborg (FOI). This is a three year project represented by four nations (France, Germany, Sweden & Italy) with seven partners. The work will cover synthesis & prilling of ADN, phase-stabilised AN, propellant requirements, high energy fuel characterisation and combustion, $AlH_3$ development and motor testing. Initial work will also attempt to understand the effect of hexamine-stabilisation of HTPB/ADN systems.

*Posters*

There were a wide range of poster topics covering propellants, sheet explosives, ageing and spectroscopy. The scientific committee awarded the poster prizes to the following people:

1st Characteristic optimisation results of new insensitive energetic plasticizer for castable PBX with HTPB binder systems (**Jin Seuk Kim**, ADD, ROK, P72)

1st Analyzing the migration of plasticizers in powders by imaging spectroscopy (**H. Pontius**, ICT, DEU, P120)

2nd Effects of aluminium content and particle size on detonation reaction zone structure and aluminium reaction time in CL-20-based explosives (**D. Y. Liu**, Beijing Institute of Technology, PRC, P84)

3rd Towards green propellants (IV) (**A. Dejeaifve**, PB Clermont, BEL, P103)

The next meeting will cover the topics of reactivity and modelling to be held 27th – 30th June 2017.

## *19th New Trends in Research of Energetic Materials (NTREM)*

Authored by Dr Daniel McAteer, Cranfield University (d.mcateer@cranfield.ac.uk)

This year's NTREM conference invited researchers from the energetics community to share their research on the theme of "Modern experimental techniques and diagnostics for energetic materials". As always the conference was well attended, with 217 delegates from 26 countries coming together for the presentation of 127 papers which provided a lively debate on topics not limited to the prescribed theme.

*Testing and Evaluation*

Dr Miroslav Krupka was one of several invited speakers who gave a talk on the "Challenges in testing of energetic materials," which provided an invaluable insight into the work done at OZM Research. His talk covered many of the practical issues and technical obstacles encountered during the development and optimisation of the testing apparatus with which OZM have made their name.

In another of the invited talks, Prof. Jimmie Oxley, presented findings in her field of organic peroxide research related to the "Solvent suppression of ions in API mass spectrometry," an area which has become particularly significant in recent years given the use of peroxides in improvised explosive devices (IEDs). The talk concluded by warning that use of acetonitrile during mass spectrometric analyses may have the effect of reducing sensitivity of certain MS techniques to peroxides.

The late Dr Igor Plaksin presented work on the use of a multi-channel optical analyser developed at the University of Coimbra, Portugal which may be employed to provide detailed information on shock waves in both inert and energetic systems on a scale which allows for the reduction of sample sizes, a common objective in energetic materials testing.

Topics also covered in this field included the assessment of internal damage in RDX-based formulations by scanning electron microscopy (SEM) presented by the Netherlands Organisation for Applied Scientific Research (TNO), the qualification of a ammonium dinitramide

based satellite propellant, LMP-103S by Dr Stefan Ek of the Swedish Defence Research Agency (FOI) and an overview of the toxicological assessment of dibutyl phthalate replacements by the University of Coimbra, Portugal.

*Novel Materials*

Novel explosives are regularly presented at NTREM and this year was no different with many of the awards for presentations and posters being awarded to synthetic chemists.

Dr Leonid Fershtat of the N. D. Zelinsky Institute of Organic Chemistry was awarded best presentation for his work on the "Synthesis of (1H-tetrazol-5-yl)furoxan ammonium salts via a two-step dehydration/[3+2] cycloaddition approach," which represented a truly significant body of work. Mr Tomasz G. Witkowski of Ludwig Maximilian University, Munich was also recognised separately for his presentation and for a poster. The first of which presented work on the "Synthesis and investigation of the novel thermally stable explosive – TKX-55" which exceeds hexanitrostilbene (HNS) in thermal stability. Mr Witkowski's poster, "Investigation of initiating strength of detonators containing TKX-50, MAD-X1, PETNC, DAAF, RDX, HMX or PETN as a base charge", was also recognised by the scientific committee, as an exciting and academically gratifying piece of work which offered direct comparison of many well-known, newly developed explosives. The last of the presentations to be recognised by the scientific committee was Mr Anatoly Bragin's talk on the "Thermal decomposition and combustion characteristics of 5-amino-3,4-dinitropyrazole". A previously reported material which the researchers considered worthy of further study due to its potential to represent a compromise between the well-known pyrazole materials, 3,4-dinitropyrazole (the melt-cast TNT replacement being produced by FOI) and the highly energetic and unfortunately acidic 3,4,5-trinitropyrazole. In the final two posters to be recognised, "Highly energetic 1,1'-dinitramino-5,5'-bitetrazoles," by Mr Norbert Szimhardt delivered an extensive piece of work on a group of interesting new energetic materials while the "Synthesis and characterisation of 1,1'-azobis(3,5-dinitropyrazole): a stable, catenated N6, polynitro energetic compound," was an intriguing paper by Dr Ya-Nan Li and co-workers which offered a comparatively facile route to a $N_6$ catenated explosive similar in some respects to the renowned $N_{10}$ catenation of Davin Piercey's 1,1'-azobis(tetrazole).

*Initiation*

in the field of initiation there were fairly few entries, however an excellent piece of work by Dr Steven Dean of the United States Army Research Laboratory offered an in depth description and discussion of the diagnostics used in the development of a novel laser-driven flyer plate capable of travelling at velocities in excess of 1400 $ms^{-1}$.

*Modelling*

Modelling is often avoided by the experimentalists among the field but it is undoubtedly becoming a significant and unavoidable feature of energetic materials science. The NTREM conference has been fortunate in attracting exceptional speakers on this topic for many years and this year Dr Vitaly G. Kiselev of Novosibirsk State University gave another excellent talk on the use of quantum chemical calculations giving insight into the potential decomposition pathways for materials such as FOX-7 and TATB. In addition to this quantum chemical presentation, Dr Michael M. Nardai of Fraunhofer institute for Chemical Technology (ICT) spoke at length about the use of molecular dynamics simulations to probe the behaviour of polymeric networks with particular reference to the behaviour of HTPB.

As ever, the penultimate night of the conference was spent in Pardubice castle with excellent food, refreshments, company and even entertainment in the form of a choir and a troupe of fire dancers.

## *Forthcoming Meetings*

There are a number of energetics related meetings planned for the remainder of this year and 2017. Follow the links to the respective event for further details.

- **12-15.09.16:**
  Insensitive Munitions and Energetic Material (IMEMTS) in Nashville, TN, USA :
  *http://www.ndia.org/meetings/6550/pages/default.aspx*

- **26-28.09.16:**
  5th Australian Energetic Materials Symposium at Flinders University, Adelaide, Australia :
  *http://www.flinders.edu.au/science_engeneering/caps/research/ceem/aems/home.cfm*

- **26.06.17:**
  13th Workshop on Pyrotechnic Combustion Mechanisms in Karlsruhe, Germany:
  *http://www.lutradyn.com/home/wpc/*

- **27-30.06.17:**
  48th International Annual Conference of ICT in Karlsruhe, Germany :
  *http://www.ict.fraunhofer.de/en/conferences/conferences/jahrestagung_announcement.html*

- **22-25.05.17:**
  10th International Heat Flow Calorimetry Sumposium on Energetic Materials in Crane, USA
  *(no website to date)*

- **30.08-09.09.17:**
  4th Korean International Symposium on High Energy Materials (KISHEM-4) in Seoul, Korea :
  *http://www.kishem.co.kr/*

**Dr Matthew Andrews**
**MSIAC Energetic Material Specialist**

# MSIAC welcomes 2 trainees from ENSTA Bretagne until the 2nd of September

MSIAC is happy to welcome two French students from the post-graduate state engineering school ENSTA Bretagne, based in Brest (France), which belongs to the DGA (Direction Générale de l'Armement).

The school gathers military and civilian students from all parts of France, upon results of a national entrance examination. Military students are intended to become IETA (national engineers for armament).

Maud and Maxime are in the 2nd year of engineering classes and at the end of the 3rd year, they will graduate with a Masters Degree of Engineering diploma in Mechanics, with specialty in Energetic Materials. They are attending a 12-week internship within MSIAC, of which the main field of expertise perfectly matches their specialty.

### *Mitigation Technologies for rocket motors.*

Maud Chéneau will work on the mitigation technologies for rocket motors.

Producing insensitive munitions (IM) has become a problematic aspect for the munitions industry. To reduce the explosive response, several mitigation technologies could be used according to the type of munition, specific design constraints or the kind of threat it has to face.

The topic will focus on mitigation technologies available for rocket motors. A wide range of mitigating devices can be applied on solid propellant motors. The project intends to create a review document which summarizes the different mitigation devices which can be used with a rocket motor. The purpose of this document will be to provide an overview of the technologies with their detailed description, the threats against which they protect and their current use. This work will provide MSIAC nations with a state of the art on the mitigation technologies for rocket motors. The benefits will be to gain an understanding of these devices and to identify the difficulties in this achievement.

### *"Critical Diameter is Critical Information"*

Maxime Voisin will work on critical diameters.

Every new energetic material needs to be tested before being used by the military according to the NATO AOP-7. To properly perform these many of these tests, the critical diameter should first be determined.

Indeed, the propagation of a steady state detonation in an unconfined cylindrical explosive will only occur if its diameter is larger than a certain diameter, called the critical diameter, no matter how high the velocity of the initiating shock wave. The latter depends on the nature, the composition and the density of the tested material.

However, testing the explosives or propellants can be expensive and a very long process, so it is important for MSIAC nations to have the best and easiest way to estimate the critical diameter of an energetic material. Maxime is creating a review document of all critical diameter testing procedures, as well as conducting an analysis and correlations to properties of interest for munitions safety.

The analysis includes reaction to shaped charge jet impact, Held's criteria, large scale gap test results, detonation velocity and pressure, as well as other explosive properties.

If you are interested in these 2 topics and/or would like to contribute, please feel free to contact MSIAC (e.schultz@msiac.nato.int or m.andrews@msiac.nato.int).

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