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New trends in advanced high energy materials

Abstract: *In the last twenty years military explosives and energetic materials in general have changed significantly. This has been due to several factors which include new operational requirements such as Insensitive Munitions (IM), but is also due to the availability of new materials and to new assessment and modelling techniques. These permit more effective use of materials and a more detailed understanding of the processes involved in applying the technology. This article will outline some of the effects in addition to taking a glance at what the future might hold.*
Keywords: *Energetic materials, Insensitive munitions, Explosives*

LIST OF SYMBOLS

ADN	Ammonium dinitramide
AP	Ammonium perchlorate
CL20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
EURENCO	European Energetics Corporation
FOX 7	1,1-diamino-2,2-dinitroethylene
FOI	Swedish Defence Research Agency
F of I	Figure of Insensitiveness
GAP	Glycidyl Azide Polymer
GUDN	N-guanylurea-dinitramide
HNF	Hydrazinium nitroformate
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane
HTPB	Hydroxy-terminated polybutadiene
HTPE	Hydroxy-terminated polyether
HTCE	Hydroxy-terminated caprolactone ether
IM	Insensitive Munitions
I-RDX	Insensitive RDX
MSIAC	Munitions Safety Information Advisory Centre
NATO	North Atlantic Treaty Organization
NIMIC	NATO Insensitive Munitions Information Centre
Poly-NIMMO	3-nitratomethyl-3-methyloxetane polymer
Poly- GLYN	Nitratomethyl oxirane polymer
PBX	Polymer Bonded Explosives
RS-HMX	Reduced Sensitivity HMX
RS-RDX	Reduced Sensitivity RDX
STANAG	NATO Standardization Agreement
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TNT	Trinitrotoluene
UK	United Kingdom
UK MOD	United Kingdom Ministry of Defense
UN	United Nations
USA	United States of America
US PAX	Picatinny Arsenal Explosive

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INTRODUCTION

There are always two factors that drive developments. They are interconnected but can exist separately. The first is new technology or technological developments and the second is new requirements. The convergence of the two produces what is called a killer application which drives developments and markets.

It may seem strange to apply such an analogy to Energetic Materials but in a limited way this has indeed taken place. Without new technology it would not be possible to meet new requirements or even define new options, but without an awareness of new needs the technology would languish unused.

Within Energetics the need to reduce the vulnerability of munitions, now coupled with the need to manage their life effectively has meant that technology such as Polymer Bonded Explosives (PBX) has been developed and applied. This was only possible with the technology available, though it inevitably produced more questions than it answered. Any IM policy requires that the risk to users be quantified, and this means that it is necessary to have sufficient understanding of the processes involved to be able to predict the response well enough to meet the immediate requirement for service. Naturally these requirements also alter with time and experience so that this too is a continuing activity and leads to far greater investment in basic science and modelling than might have been predicted a few years ago.

To these requirements must now be added the need to do more with less; to be precise in delivery and action and so maximise effect with minimal collateral damage. Such a set of requirements cannot be easily met with the technology that existed even ten years ago. It requires basic understanding of materials, both old and new, and understanding of the processes of performance, vulnerability and ageing, so that these can be used in predictive modelling. The aim is to understand both the materials and how to use them properly to design weapons. Such an understanding can also lead to cost reductions and the ability to use existing materials more effectively.

It is worth examining the different aspects in turn, starting with materials.

INGREDIENTS AND MATERIALS

Scientific curiosity will always drive research, even though this may not always be understood by those who wish to solve their immediate problems. New methods of producing materials and new materials arise from this research, and the ability to undertake these studies is important within the technology. However, there are constraints.

Any new material must fulfil a real need or provide options not previously available. Until about 1990 performance drove that requirement, with an increasing awareness of Insensitive Munitions requirements acting as a constraint.

The changes in the requirements which must include the continuing uncertainty over what the requirements should be has slowed this development and several materials that once seemed certain to be used are still awaiting application. Many have been produced on laboratory scale and several on pilot scale, but only a few have made it beyond that, into demonstrator programmes even if not into any fielded munitions.

Ingredients can be divided into two classes, solids and binders. Looking first at binder technology, while HTPB (Hydroxy-terminated polybutadiene) has successfully made the transition from composite rocket propellants to Polymer Bonded Explosives (PBX) and other similar materials have been employed in the same role (e.g. HTPE Hydroxyl-terminated PolyEther and HTCE Hydroxy-terminated Caprolactone Ether), the expected transition to energetic binders has stalled. At present, military needs can be met with the materials that are already in service and Glycidyl Azide Polymer (GAP) or either 3-nitratomethyl-3-methyloxetane Polymer (PolyNIMMO) or Nitratomethyl Oxirane Polymer (PolyGLYN) have not really moved beyond technical demonstrator status.

It is worth outlining the logic for their development. It became clear that TNT was too brittle to meet developing vulnerability requirements and the use of inert polymer binders was proposed as a way to remedy this defect, drawing on the extensive rocket propellant expertise. (It is worth noting that melt cast options are again being examined as they continue to be easy to use and meet several needs very well.) While the mechanical properties were improved, the level of solid required for maintaining the performance level was high, and the argument ran that if energy were to be embedded in the polymeric chain then performance could be maintained while further improving mechanical properties at the same time.

Several materials were produced and studied, with many being able to produce explosives meeting UN transport class 1.6 (Extremely Insensitive Detonating Substance). However, the cost of the materials was high, and it was found possible to meet most current requirements with existing materials. Therefore at present these are still awaiting a system requirement. They are likely to have uses especially within high performance small warheads or specific types of rocket motor, but the requirement has not yet appeared or has not yet been sufficiently defined.

There is a similar story with solid fillers. CL20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) was produced in 1986 in China Lake and once the highest density form known to-date, the epsilon polymorph, was found, seemed likely to be used to replace HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane) where high performance was needed. It has around 15 per cent higher performance than HMX, and was formulated into a metal moving composition, LX19, for high performance shaped charges. This has 95.5 per cent by weight of CL20 and 4.5 per cent of Estane binder. Unfortunately, CL20 is a highly sensitive explosive. It has a Figure of Insensitiveness (F of I) of approximately 25 and high explosiveness, making it hard to use for low vulnerability compositions. It can, however, be desensitised and this has been achieved for the US PAX (Picatinny Arsenal Explosive) series of compositions as well as in rocket propellants (Balas, 2003).

CL20 is only one of the newly available solid ingredients. More recently FOX 7 (1,1-diamino-2,2-dinitroethylene) has been produced in Sweden by FOI (Swedish Defence Research Agency) and its production licensed to what is now Eurenco. FOX 7 (Karlsson, 2002) has roughly the same performance as RDX but appears to be much less sensitive. To-date the data confirm this and (Oestmark et al., 2006) have suggested that this is due to the graphite-like structure within the crystals, similar to that of TATB (1,3,5-triamino-2,4,6-trinitrobenzene), which allows a mechanism for internal flexibility. This may explain the vulnerability response and has also been noted in *N*-guanylurea-dinitramide, GUDN (Oestmark et al., 2006) sometimes known as FOX 12, which appears to offer similar vulnerability benefits, particularly in gun propellant formulations.

Other ingredients are older, particularly ammonium dinitramide (ADN), first synthesised in Russia in 1971 and employed as an oxidiser in rocket propellants. It has problems in use, being very hygroscopic and with low melting point (91-93.5°C), and also has a low F of I of around 25, though it can be desensitised. However, it is one of the few possible replacements for ammonium perchlorate (AP), now seen as posing significant environmental problems in the USA. Whether it can be used or not is as yet unproven, but it was in Soviet service despite the problems. Its possible applications are not limited to propellants but have also great potential for underwater explosives.

The European Space Agency and others have invested heavily in HNF (hydrazinium nitroformate) as an alternative oxidiser. However, this has even more stability problems than ADN and has not yet been proven to be suitable for use. Work is still progressing, but without definitive proof of its suitability it is unlikely to be investigated further.

The properties of FOX 7 illustrate the current approach. It appears to offer satisfactory performance while allowing the production of new low vulnerability materials which can contribute to IM solutions. It is benefits such as these which will drive new materials into use.

Yet as work is performed in understanding these materials, the same techniques can be used to modify and improve existing ingredients. Being able to control the morphology and size of crystals is now possible in ways not available until recently, and some surprising results have been obtained. Work over a decade ago shared amongst the UK, Netherlands and Norway showed that producing spherodised materials affected the shock sensitivity as well as affecting the processing characteristics. Since then others have examined ways of manufacturing materials and the benefits obtained by greater control of particle size and shape.

I-RDX (Insensitive RDX), or more generally RS-RDX (Reduced Sensitivity RDX), has emerged in the last few years. The first, I-RDX was produced by what is now Eurenco (the name is a Eurenco trademark). The evidence suggested that this version of RDX was significantly less sensitive than traditional grades, and therefore could be used to reduce the vulnerability of munitions through less sensitive fillings, for example in PBXN-109. Other manufacturers offered similar products within a very short time to the extent that NATO AC326 arranged a round-robin (Doherty, 2006) managed by MSIAC (Munitions Safety Information Advisory Centre) with various versions of RS-RDX and attempts to determine what made it different and how to encapsulate that within a STANAG. The study indicated that there was no simple answer to the question but that the properties of the crystal – surface, density, voids and flaws all played some part. Research continues in several laboratories throughout the world with the result that a greater understanding of the importance of such properties is being obtained. In the meantime RS-HMX (Reduced Sensitivity HMX) has been produced and is being offered by Chemring in Norway.

As it is unclear if these forms of existing materials do offer real vulnerability benefits both initially and during munition life, this is currently being examined and research is needed both on the materials and on the tools used to examine and assess them.

These materials are being applied within munition design as it has been developed in the West in the last 50 years. However, with the end of the Cold War, access was gained to the products of parallel research in Russia. The research was neither better nor worse, just different. Different materials had been developed and used, such as ADN, but more importantly different defeat mechanisms had been assumed, and blast for example was a far more important mechanism in Soviet weaponry than in NATO. It became clear that NATO did not know quite as much as it thought it did, and multiple programmes were started in order to examine mechanisms not previously considered.

This has led to the investigation of nano-materials, including nano-Aluminium produced by various processes; to studies of solid state reactions as a mechanism for rapid energy release; to the examination of blast mechanisms and non-ideal explosives for land weapons, and to looking again at many of the models and assumptions that formed the basis of munition design.

In addition entirely new routes are being investigated. Modelling predicted new very high performance materials such as polynitrogen and these are being sought experimentally. High nitrogen species of a more conventional type are being researched in Munich under the direction of Prof T Klapoteke.

While much of the work is being done in the US, FOI and Sweden have been particularly innovative. N_5^+ was made at Edwards AFB by Karl Christie, but N_5^- was detected by FOI. This is high risk, blue skies research, with no guarantee that any of these are really stable or that they will give the performance predicted. Already the figures quoted in some publications are being revised as greater understanding is obtained of the way such systems will behave. However, the predicted performance benefits make the gamble worth taking. One conclusion must be that there are other species worth researching: Fig. 1 (courtesy QinetiQ).

CHARACTERISATION AND ASSESSMENT

If we make new demands on our materials and require that they act with precision throughout their useful life,

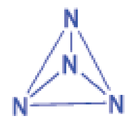
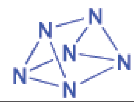
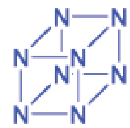
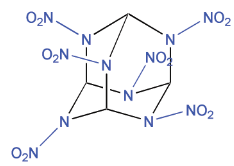
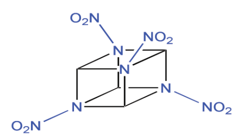
Tetraazacubane, N4		Detonation Velocity, 13.42 kms^{-1} Pcj, 770 kbar
Hexaazaprismane, N6		Detonation Velocity, 14.04 kms^{-1} Pcj, 933 kbar
Octaazacubane, N8		Detonation Velocity, 14.75 kms^{-1} Pcj, 1370 kbar
Hexanitrohexaazaadamantane		Detonation Velocity, 10.1 kms^{-1} Pcj, 519 kbar
Tetranitrotetraazacubane		Detonation Velocity, 11.25 kms^{-1} Pcj, 720 kbar

Figure 1: Detonic Characteristics of Nitrogen Species

we need to understand them clearly and also be able to predict their behaviour adequately to allow for both risk management and optimum use. The same tools that can be used for these predictions should also be capable of being applied in the design of weapons systems and of energetic sub-systems to meet new demands.

Traditionally, much of the science has been based on tests that simulate accidents or based on the analysis of the factors that contributed to accidents. It has meant that every nation had a large database of national results which did not easily cross-reference with those in other countries. Often this was based on priorities derived from accidents and the attempt to prevent them being repeated.

Closer links amongst allies meant that it became essential to be able to understand and accept tests from different centres. One of the most important tasks within the NATO CNAD Ammunition Safety Group remit is the development of common tests, released as NATO STANAGs, and the assessment of capability gaps which need filling. This was paralleled in the research area by closer collaboration on developing the tools and understanding needed to provide the means of better risk management. Major accidents such as that on USS Forrestal in the Vietnam War, Sir Galahad in the Falklands and Camp Doha in the First Gulf War emphasised the need for munitions that did what they were supposed to but were otherwise relatively inert, Insensitive Munitions! The development of the tools and materials to provide these has driven much of the research programme for the last 20 years (MSIAC, 2006).

As part of the coordination exercise, NATO created the NATO Insensitive Munitions Information Centre (NIMIC), where a small group of experts could support work in the national programmes through advice and analysis of available information. This was successful despite limitations on the information at their disposal and it took over preliminary protocols for problem analysis developed by the US, Canada, the UK and Australia using them to support the analytical development of an approach to IM. The UK has been and remains an active member of NIMIC, and now MSIAC (Munitions Safety Information Analysis Center), the successor with a broader remit. It remains important to UK forces that our allies have munitions as close as possible to our standard of vulnerability, since we will often work closely with them in joint operations (MSIAC, 2006).

Nevertheless this approach is only part of the story, and the tool development continues and seems to be accelerating. Detailed analytical examination of mechanisms such as blast has produced modelling tools that are more capable, though this again is driven by both need and technology and therefore has also partially become possible through computer development since computers can now do more, and so enable the models to get a little closer to acceptable reality. The diagnostic approach driven by models has meant that several questions have started to be answered, such as obtaining detailed physical and chemical properties; an understanding of what happens to a material under shock, and trying to establish what are the critical properties for predicting performance and vulnerability. As mentioned above, with these tools it becomes possible to begin to design materials for specific functions (Cumming, 2009).

Once there is an understanding of the basic components; their interactions and the way they behave with time, it is possible to develop validated tools for general use. Validation is important for while models can be seductive, they can only be approximations of reality and rely on the quality of the real measurements. It is equally important that the two groups, modellers and experimentalists interact to provide a continuous check on the direction and usefulness of both models and experiments. In several countries this is being attempted and groups have been working on the problem of assessing and predicting hazard so that it is possible to deal more effectively with existing problems as well as prepare to answer the questions likely to be posed by tomorrow's problems.

This approach can be cost effective and is being now pursued widely. With these types of tools it becomes possible to look again at ageing phenomena and provide support for Whole Life Assessment Policy development as well as the aforementioned design capability.

It is still necessary to undertake field tests and this is likely to remain the case for the near future. Any prediction requires validation and that can only be achieved with real tests. However the combination of small scale tests with the improved understanding of behaviour should make such tests increasingly confirmatory. It is clear, however, that this stage has not yet arrived. There are still important questions to be answered, in particular those associated with scaling factors in moving from small scale to large; rapid acceleration or deceleration, and the effect of ageing on munition response. That which passes IM tests may not pass after 5 years in storage. Properties change and the question cannot be answered sufficiently authoritatively to meet the requirements of a responsible owner, which is what the UK MOD aspires to be.

The increased interest in non-ideal explosives has identified areas where greater understanding is needed, and where civil experience can be used to fill the gaps. There is a need for a broader approach, to mutual benefit, and this seems to be developing.

It should be obvious from much of this discussion that collaboration in many forms plays a significant part in the research and assessment. Industry is trans-national, with munitions being equally trans-national, with the result that nations may be faced with similar assessment or procurement problems. It makes sense therefore to work together to develop a common technology approach and understanding especially since no one nation, not even the US, can afford to do all the necessary work alone. Networks already exist and are certain to develop.

CONCLUSION

Inevitably any review provides only a glimpse of the present position. It is possible to predict some of what will develop, but there will always be surprises. What is predictable includes continuing emphasis on reduced vulnerability; increased emphasis on life management and the minimisation of environmental impact, including recycling and the search for more benign materials. These are likely to drive the need for selected new or improved materials which assist in meeting requirements, and to drive studies on green munitions and the environment as outlined in the UK Defence Technology Strategy, an open document available on the Internet.

The need to provide flexible and precise performance in a cost-effective manner will need investment, but longer term options remain open. There are areas such as polynitrogen and non-traditional chemistry which should be investigated. Other scientific fields, such as materials science, can provide inspiration for new directions though links and the move away from traditional approaches.

Collaboration is also likely to increase, which may have the additional benefits of a broader base of experience and therefore, perhaps, a higher level of innovation.

The field is changing fast and in unpredictable ways, which makes it exciting while demonstrating that it is far from exhausted.

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