Current Strands of Research in DERA on the Chemistry of Energetic Materials and Insensitive Munitions

by Simon P Philbin
Chemical Technology Department, Building X3,
DERA Fort Halstead, Sevenoaks, Kent TN14 7BP, United Kingdom
Tel. +44 1959 515629, Fax. +44 1959 516041, Email spphilbin@dera.gov.uk

1. Abstract

Over the past several years there has been a considerable effort within DERA towards the development of new and improved energetic materials and their corresponding formulations. This paper will give an overview of such activities whilst addressing a number of key technology areas, namely:

- Energetic binders synthesis and development, including plasticisation and polymerisation studies.
- Characterisation studies of new ingredients and formulations, including compatibility, stability and thermal analysis.
- Clean technologies towards the synthesis of existing energetic materials using a variety of environmentally friendly solvents such as supercritical fluids as well as the use of solid supported reagents.
- Synthesis of nitrogen heterocyclic compounds and nitrogen cage molecules.
- Development of new explosive and propellant formulations and investigation of processing aspects.

Current chemistry research within DERA is part of a highly integrated programme funded by the UK MoD, which is aimed towards the provision of advanced energetic materials. As part of this programme activities carried out include the synthesis of new molecules, development of new materials, characterisation and scale-up as well as formulations and processing studies. This chemistry work is also backed up by molecular modelling activities.

2. Background

Energetic materials are an important engineering sub-component of weapon systems in use by all three of the armed services. There is an increasing pressure to develop weapon systems which are safe [i.e. they meet insensitive munitions (IM) requirements], reliable, cost-effective and have a predicted long life. Within DERA there are currently a number of projects which are focussed towards the development of new energetic materials technologies and these can be broadly assigned to the following four categories:

(i). Development of new energetic binder systems.
(ii). Synthesis and characterisation of energetic filler compounds.
(iii). Investigation into new processing technologies.
(iv). Assessment and development of new formulations for application as propellants and/or explosives.

This paper describes a number of approaches towards the development of new energetic ingredients and their corresponding formulations as well as addressing the importance of designing the compositions to have IM characteristics from the beginning. It is also recognised that IM properties for an energetic system can be developed by the use of alternative technologies such as novel rocket motor cases or liners.

3. Development of New Energetic Binder Systems

Historically, there has been extensive work carried out within DERA on the development of binders such as polyNIMMO and polyGlyN [1]. These binders have now been transferred to industry and are commercially available from ICI Nobel Enterprises in Ardeer, Scotland. Energetic binders synthesis work within DERA has now moved on to look at new systems which offer improved performance over those currently in use.

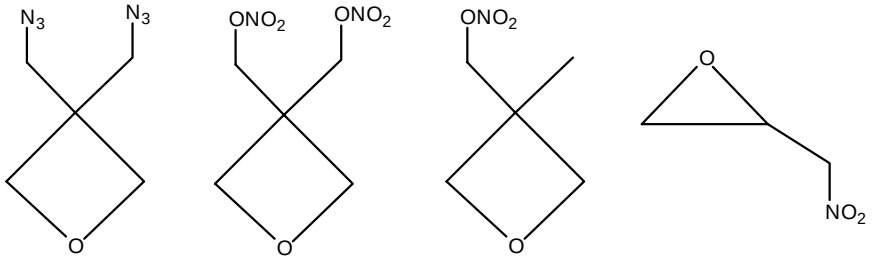
Energetic binders play a pivotal role in the development of IM technology and it is essential that binders are developed with the necessary properties. The binders must have the correct physical properties, i.e. have a sufficiently low Tg, as well as hopefully providing energy to the system and not diluting down the power of the composition as is the case with HTPB.

3.1 Energetic Thermoplastic Elastomers (ETPEs)

The development of energetic thermoplastic elastomers (ETPEs) for insensitive munitions applications is currently being investigated. Such binders should have ideal properties for processing whilst also contributing to the energy of the system. Additionally, at the end of the munition life-cycle it should be possible to recycle and re-use the formulation ingredients.

A number of possible routes to energetic thermoplastic elastomers (ETPEs) have been assessed. Initially, both (AB)n and ABA copolymers were investigated but it was decided early on that ABA block copolymers would have the most attractive physical properties. Within the ABA block copolymer system, where A represents the hard block and B represents the soft block, there is a dependence of the physical properties on temperature. The glass transition temperature (Tg) of the soft block defines the lowest temperature of service use whilst the melting point (Tm) of the hard block influences the maximum temperature of service use, which lies just below the Tm. The UK temperature range for air carriage energetic systems is –54 deg. C to +70 deg. C. With existing energetic binders this requirement is difficult to meet, however, with ETPEs it is believed that such an operating range is achievable.

3,3-Bis(azidomethyl)oxetane (BAMO) and 3,3-bis(nitratomethyl)oxetane (BNMO) [2] are both known hard block monomers whilst 3-nitratomethyl-3-methyloxetane (NIMMO) and glycidyl nitrate (GlyN) are both known soft block monomers.



BAMO BNMO NIMMO GlyN

The traditional synthesis of ABA block copolymers, such as styrene-butadiene-styrene materials, involve anionic polymerisation of styrene followed by sequential addition of butadiene followed by styrene and then finally termination of the reactive ends. However, anionic polymerisation cannot be used with energetic monomers due to attack of the azido or nitrato groups by the initiator. Consequently, cationic methods of polymerisation have been investigated.

The polymerisations of GlyN and NIMMO were re-investigated to improve molecular weights and hence produce the required blocks for ETPE preparation. In earlier studies sequential cationic polymerisation was ruled out as a way of producing ABA materials. GlyN was polymerised with HBF_4 and 1,4-butanediol whilst BF_3OEt_2 and 1,4-butanediol were used in the polymerisation of NIMMO. The polymerisation of BAMO was achieved using a BF_3.THF/alcohol system. Once the hard and soft blocks have been produced then the next challenge is to link them together.

The most common method for linking hydroxy teminated polymers is via the use of isocyanates. A range of linking reactions were carried out based on isocyanates in addition to the development of alternative systems. Currently a number of linking reactions are under investigation and it is hoped that the synthesis of a suitable ETPE will be achieved in the near future.

3.2 Energetic Plasticisers

Within the energetic binders context there is also work currently being carried out on the assessment and development of new energetic plasticisers [3]. Plasticisers are used to extend the service temperature range of an explosive/propellant, enhance the physical properties of the system as well as to improve processing. It is envisaged that energetic plasticisers will increase the overall energy of the system as well as modify the vulnerability and ballistics behaviour of the formulation.

It is recognised that with the development of new energetic binders such as GAP, polyNIMMO and polyGlyN there is also a requirement for a new series of energetic plasticisers which are compatible with these binders. Consequently, in order to further extend energetic binders technologies in support of IM applications it is important that a new range of energetic plasticisers are developed.

A range of plasticisers based on a cyclic tetramer of NIMMO and linear oligomers of NIMMO and GlyN were investigated. Early studies were focussed on the synthesis and investigation of the cyclic tetramer of NIMMO, however, this material has a relatively high Tg and is therefore a poor plasticiser.

More promising results were obtained from studies involving the low MW oligomers of NIMMO and GlyN. The plasticisation of both polyNIMMO and polyGlyN using these oligomeric plasticisers was assessed. A range of other known plasticisers such as TMETN, BTTN and BDNPA/F were also investigated so as to act as a benchmark to the new plasticisers. A database of properties was therefore built on approximately twelve plasticisers with information on energy, hazard, effect on lowering Tg, miscibility, volatility, migration, stability and compatibility parameters obtained.

In this comparison the oligomeric plasticiser of GlyN had very promising properties as did a more conventional mixture of TMETN/BTTN (70:30) as well as BuNENA. Molecular modelling of the plasticiser properties was carried out under contract by researchers at ICI Wilton which gave valuable information on plasticiser behaviour. The quantitative structure property relationship (QSPR) technique was used to predict properties of the new plasticisers which in some cases correlated well with experimental data.

Current and future work on energetic plasticisers is based on assessment of their processing properties, properties which depend upon the complete formulations with

crystalline fillers and larger scale behaviour. The two most promising candidates for further investigation are the oligomeric plasticiser of GlyN and BuNENA.

4. Synthesis and Characterisation of Energetic Filler Compounds

The synthesis of inherently insensitive energetic ingredients in order to impart IM characteristics to a formulation is an established method for improving the safety and handling of munitions. Consequently, over the past several years there has been considerable effort within DERA to prepare such molecules (Section 4.3). There is also effort being directed towards the synthesis of very high energy compounds (Sections 4.1) as well as development of clean syntheses of energetic ingredients (Section 4.2).

4.1 High Nitrogen Content Explosives

There is currently a highly innovative project towards the synthesis of high nitrogen content explosives being carried out within DERA. Molecular modelling studies have predicted that these compounds will have major/massive improvements in performance over current nitramines such as RDX and HMX. A range of different approaches are being employed in this study and it is acknowledged that the synthesis and development of filler compounds with higher performance than CL-20 has to be a long term goal.

In order for weapon systems to become more lethal and have a greater range then new more efficient high energy explosives and rocket propellants are required. For conventional explosives based on carbon, hydrogen, nitrogen and oxygen the performance limits have almost been reached. Therefore, alternative molecular structures which have a high nitrogen content are under investigation. It has been shown by computational theoretical studies that caged nitrogen allotropes are capable of existing as stable species. Molecules such as octaazacubane (N_8) and tetraazatetrahedrane (N_4) are predicted to be significantly more powerful than both HMX and CL-20.

Synthetic methods have been investigated which are based on the preparation of novel high nitrogen heteroatom cages and caged nitrogen. Extensive molecular modelling was carried out on all target high nitrogen molecules using the Cheetah code. It was found to be essential that modelling activities were highly integrated with laboratory studies so that all experimental activities were targeted and efficient.

4.2 Environmentally Friendly Nitration

There is a raft of environmental legislation which is either in place or about to be implemented, such as the Montreal Protocol, which addresses the banning of toxic solvents such as chlorinated hydrocarbons. Consequently, there is extensive work on the development of clean technologies for the production of energetic materials being carried out. This work is primarily based on the use of solid supported nitrating agents but is also aligned to previous studies which utilised supercritical or liquid carbon dioxide as the reaction medium.

Nitration is an underpinning chemical reaction in the development of energetic materials and insensitive munitions. The development of clean technologies in the production of energetic materials is designed to reduce the environmental impact of manufacturing such compounds due to the increasingly stringent environmental legislation. Current clean nitration strategies under investigation include the following approaches:

Solid Supported Nitration Activities [4]

(i). Systems which eliminate the use of strongly acidic solvents or chlorinated hydrocarbons as reaction media.

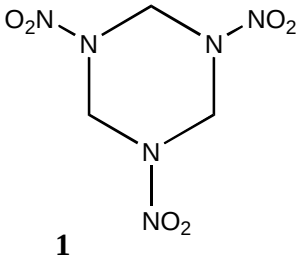
(ii). Technologies which enable simplification of the synthetic work-up and permit recycling of solvents and spent reagents.

(iii). Systems where the selectivity of positional attack on precursor molecules is increased thereby reducing by-product formation and the need for post-reaction work-up.

Use of Alternative Solvent Systems

(iv). Investigation of alternative reaction media such as supercritical and liquid carbon dioxide.

Nitration systems have been developed which are based on both clays and zeolites and it has been shown that dinitrogen pentoxide can be used to nitrate a number of energetic precursor compounds in environmentally friendly solvents such as hexane. The use of the aforementioned techniques has been applied to the clean synthesis of a number of strategically important materials such as RDX (**1**), TNT (**2**) and EGDN (**3**) with varying degrees of success.



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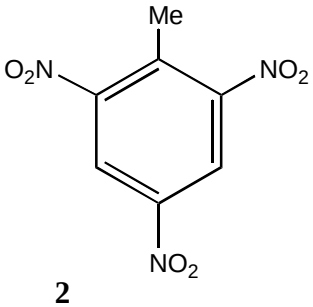

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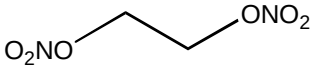

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Environmentally friendly nitration has also been used to prepare energetic plasticisers and their precursors and it is hoped that future studies will focus down on a small number key high energy ingredients. Particular success has also been achieved in the nitration of amine compounds to form nitramines by dinitrogen pentoxide in liquid carbon dioxide.

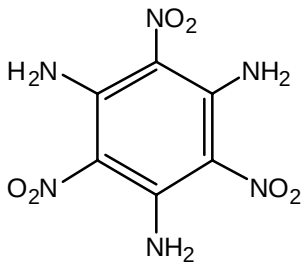
In conjunction with the clean synthesis of energetic filler compounds there has also been effort directed towards the polymerisation of NIMMO and GlyN in supercritical carbon dioxide. Both polymerisations were achieved under standard BF_3OEt_2/1,4-butanediol and HBF_4/1,4-butanediol initiation conditions.

4.3 Assessment of Existing High Energy Insensitive Materials

A number of recent studies have been carried out on the evaluation of the synthetic routes of a range of high energy insensitive materials which have structures analagous to that of TATB (**4**). These compounds include 2,6-diamino-3,5-dinitropyrazine-*N*-oxide (PZO) (**5**), 2,5-damino-3,6-dinitropyrazine (ANPZ-i) (**6**) [5] and 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) (**7**) [6].

Synthesis experiments here are based on a series of organic reactions such as aminations, nitrations and *N*-oxidations. Modification of reaction techniques is often

important and the use of alternative reagents, such as nitronium tetrafluoroborate in sulpholane for nitration reactions, has been investigated.



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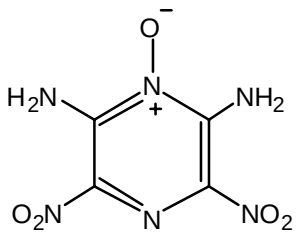

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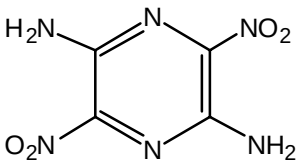

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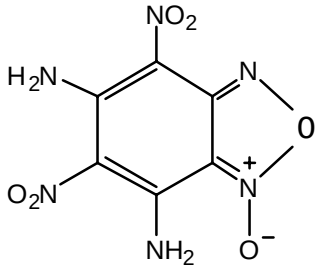

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Future work in this area is likely to concentrate on scaling-up the synthesis of key nitrogen heterocyclic compounds for evaluation in small scale formulations studies. Initially, the provision of hazard assessment data from small scale testing will be important as well as information on the stability and compatibility of these new energetic ingredients. Assessment of scale-up will include obtaining reaction heats of formation.

4.4 Characterisation of Existing High Explosives [7]

A number of levels of characterisation are carried out on all energetic ingredients. In the first level simple chemical characterisation is performed and then as the material becomes more well defined additional physical characterisation is carried out. Both CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)] and ADN (ammonium dinitramide) have been extensively evaluated for use in new energetic materials formulations.

Compatibility studies have shown that CL-20 can be formulated with ammonium nitrate, polyGlyN and an appropriate plasticiser. The thermal stability and compatibility of ADN in a range of materials has been measured for application in rocket propellants. Consequently, a much greater understanding of the curing behaviour of polyNIMMO with ADN has been obtained. Furthermore, methods for the modification of ADN particle size and shape have been developed so that optimised particle properties have been obtained for propellant applications. A range of potential stabilisers for use with ADN have been investigated, however, initial results indicate that any improvements in thermal stability have been quite small.

5. Investigation of New Processing Technologies

Within DERA there are a number of alternative processing technologies which are currently being developed. There are a range of different benefits which can be

achieved through the development of alternative processing techniques, some of which are as follows:

- Improved ease of processing of energetic formulations.
- Cheaper production of energetic formulations.
- Modification of ballistics and vulnerability parameters.
- Demilitarisation/re-cycling potential.
- Commercial spin-off.
- Safer processing.

Twin screw extrusion (TSE) is currently being investigated which has been shown to offer a high quality of mix as well as having a number of other benefits over more traditional forms of mixing. The TSE facility at DERA Fort Halstead is currently in the final stages of commissioning and it is envisaged that once this facility is operational it will be an ideal processing platform for newly developed ETPEs.

The use of supercritical fluids (SCF) as an aid to processing is also being looked at. It is known that processing materials in SCFs allows for the possibility to control particle size, which has the effect of altering the properties of the material. The production of energetic materials with a reproducible particle size is currently being pursued so that a greater control of the properties of the energetic ingredients can be achieved.

6. Assessment and Development of New Formulations for Application as Propellants and/or Explosives [8, 9]

There is currently a significant amount of activity within DERA towards the assessment and development of new and improved formulations for application as both next generation propellants and explosives. There is a need for lower vulnerability explosives with higher performance which have improved survivability in hostile environments. Explosives work is closely aligned to gun and rocket propellant activities.

There exists considerable effort towards the development of next generation rocket propellants. This is because it is believed that the performance limit has almost been reached for double base (NC/NG) rocket systems whilst composite systems, such as AP/HTPB/nitramine, suffer from smoke and signature problems . New systems are being developed which offer high energy, minimum signature and clean exhausts for the weapon platform. Multidisciplinary studies are focussed on a platform of capabilities which include assessment of processability, mechanical properties, signature (plumes modelling) and safety/vulnerability of the formulation.

There is also effort being directed towards risk reduction activities associated with introducing new energetic materials technology into service. Due to the safety considerations of using energetic materials the risks for putting new weapon systems into service are amplified. Consequently, the qualification of a series of new insensitive explosives and propellants for both UK and NATO service (under STANAG 4170) is being addressed. Through the provision of testing data on hazard and mechanical properties to the UK Ordnance Board (OB) it is envisaged that systems with lower vulnerability and improved performance will be developed.

7. Conclusions & Future Work

It is essential that IM properties are addressed as early as possible in the development of new energetic ingredients and therefore all new chemistry programmes are designed with this in mind. Within DERA there is currently a

number of different activities being carried out towards the development of new energetic materials technologies and insensitive munitions. A range of assessment activities are under investigation which are aimed towards developing a number of energetic formulations for a variety of applications such as next generation gun and rocket propellants and main charge explosives. As part of this assessment it is vital that key parameters such as performance, hazard properties, compatibility and stability are reviewed periodically. Consequently, a range of complementary activities are carried in order to achieve this, namely; molecular modelling, small scale hazard testing as well as physical characterisation such as DSC and related thermal analyses.

The development of energetic binder systems will continue via the synthesis of ETPEs based on ABA block copolymers, in conjunction with the exploitation of new energetic plasticisers. Work on energetic filler compounds is also on-going and will continue to focus on the provision of clean technologies for the synthesis of energetic materials as well as the synthesis and development of existing high energy insensitive materials and high nitrogen content molecules. As initial chemistry activities are concluded the most promising materials are evaluated as part of an overall formulations and processing programme. Finally, optimised compositions are identified for use in either explosive or propellant applications.

8. References

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