Topics in Energetics

Research and Development

CENTER FOR ENERGETIC CONCEPTS DEVELOPMENT SERIES

ENERGETICS SCIENCE AND TECHNOLOGY SERIES

TOPICS IN ENERGETICS RESEARCH AND DEVELOPMENT SERIES

Topics in

Energetics

Research and Development

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Preface

In most modern defense systems, energetic materials are of critical importance. Consequently, there is an active research and development program at many laboratories and universities worldwide. The CECD is involved in several aspects of this research activity. Our Energetics Science & Technology series is comprised of books reporting activities in different parts of the world. Two volumes on work in China and Central Europe have already been published, and additional volumes are in progress. The motivation for this series is to provide a comprehensive collection of information on this critical technology and identify the energetic materials research being conducted across the globe.

Topics in Energetics Research and Development is planned as a companion series. The motivation for this series is to highlight selected and recent advances and discuss relevant topics in energetics research and development (R&D).

The five individual topics presented within this inaugural edition when viewed collectively articulate the need for a coordinated and sustained effort addressing the DoD's needs and future challenges.

Some experts hold the view that all the benefit of advancements in energetic materials has been obtained, and that the opportunity for new capabilities built on energetics is behind us. We hope to provide a cogent view that in fact a new era in energetics is upon us, wherein the use of modeling and simulation will allow entirely new capabilities to be developed from first principles, enabling exciting new advancements which were only ideas in the past.

This edition was prepared collaboratively under the Energetic Concepts Development Cooperative Agreement, N00174-09-2-0023, between the Naval Surface Warfare Center, Indian Head Explosive Ordnance Disposal Technology Division and the University of Maryland's Center for Energetic Concepts Development.

The authors acknowledge Ania Picard for the overall production of the book. Dylan Hazelwood was part of the team designing the cover. Kunal Sakpal assisted in formatting and designing activities. We would also like to acknowledge the numerous continuing discussions with colleagues which have provided much useful insight.

College Park, MD

Executive Summary

Energetics is a critical enabler for the development of new capabilities driven by asymmetric warfare requirements and joint force needs. Eight studies conducted on energetics since 2000 have concluded that energetics research is important, however, suffering from a lack of DoD attention. These studies concluded that the DoD technical tasking and investment strategy is near-term focused, reactive, and threatens the long-term technological superiority of the US warfighter, current gains are based on previous technology investments, and without investments in future technologies, sustained technological superiority is at risk.

The level of foreign investment in energetics continues to grow. Others are moving swiftly to exploit known technological opportunities and breakthroughs in energetics at a time when the US investment continues to decline. Energetics is an area where we have been surprised in the past and there is high risk of surprise in the future. A coordinated investment and execution strategy is necessary to take advantage of opportunities presented by energetic materials research, development and manufacturing technologies. The overarching issue is one of ensuring a critical national defense capability which is nurtured and maintained.

With the observation that new defense acquisition programs for platforms would benefit from smaller weapons without sacrificing either the range or effectiveness, there appear to be two intertwined issues that combine to frustrate the development and deployment of new energetic materials. The first is the fact that the development and use of new advanced energetic materials in the systems engineering process is seldom considered. The second is a lengthy, highly empirical development process with timelines that are long in comparison to the timelines for developing a new ship, aircraft or combat system. Addressing these issues may be a key long range facilitator for important advances in the military capability of our nation.

An inexpensive approach to facilitating the innovation process via analytical tools is discussed in Chapter 3. We note that today ordinary laptop computers can perform computations that were reserved only for supercomputers a decade ago. Exascale computing (10^{18} operations per second) is projected to be implemented by 2018, and could revolutionize the way computer simulation is used in science and technology, enabling hitherto-inaccessible high-fidelity predictive simulations. There is every expectation that the field of energetics science will benefit from such a capability by not only improving a fundamental understanding of the reactive behavior of high explosives, but also improving munitions design at the component as well as the system levels. At present, prevailing explosives design practices are heavily dependent on the designer's experience and intuition. Even when modeling and simulation (M&S) tools are used in design, they are mostly system specific and have high levels of empiricism and inaccuracies, particularly with regard to the response of the energetic material in a munition. Physics-based models are needed that can address non-scalable issues inherent in the response of complex, composite energetic materials (EM). Transforming the M&S design tools from empirically-driven to a physics-based capability will allow for the exploration of novel, more advanced materials and concepts, will reduce reliance on costly, time-consuming full-scale testing, and will provide faster design and implementation of technology solutions at a substantially reduced risk.

The computational tools capabilities described fall roughly into two categories. Tools that fall within the first category allow accurate a priori prediction and description of the full spectrum of chemical and physical properties of candidate new (notional) and existing EM structures and formulations. Capabilities in the second category are those that will lead to understanding of fundamental physics and chemistry controlling the initiation, sensitivity and behavior of EM subjected to insult. Establishing these capabilities is paramount for physics-based design of advanced weaponry using new materials. Most of the existing tools in this category have not yet resolved many challenges rooted in the multiscale, stochastic issues both in space and time under extreme conditions of pressures and temperatures, but efforts to overcome these challenges are underway.

There is significant ongoing energetic materials research underway worldwide. We briefly review the following countries: United Kingdom, Germany, Sweden, Poland, Japan, South Korea, France, Russia, India, and the Czech Republic. This focus of the review is on recent developments.

In the UK, work is going on in the area of Energetic Polyphosphazenes. In the search of increased safety in PBXs (Polymer Bonded

Explosives, Plastic Bonded Explosive), energetic polyphosphazenes [PolyPZ] are studied at the Atomic Weapons Establishment Aldermaston, at Cranfield University and at QinetiQ.

In Germany, the main research area at Ludwig-Maximilian University (LMU) in Munich, Germany is high (secondary) explosives. Other research has been conducted at LMU using high-nitrogen compounds.

In Sweden, the Swedish Defense Research Agency (FOI) around Dr. Nikolaj Latypov has focused their work predominantly in four areas. They are Nitro aromatics, O-nitro esters, N-nitro and gem-poly-nitro-aliphatic compounds, and Energetic salts. Over past years, FOI has also developed various products in the area of energetic materials.

In Poland, there are two main centers in which fundamental and applied research on energetic materials is continually performed – the Military University of Technology in Warsaw (MUT), and the Warsaw University of Technology (WUT). In recent years, at MUT, several topics have been explored, but the most interesting results were obtained in application of combustion processes of energetic composites for the synthesis of ceramic and carbon nanomaterials. Researchers at Warsaw University of Technology are searching for new energetic compounds and synthetic routes, and at present the main purpose of this work is the optimization of the synthesis of polycyclic nitroamines.

In Japan, the development of high energetic materials (HEM) for the next generation pyrotechnics and propellants started in 1970s following efforts in the USA and Europe, and three kinds of HEM; GAP, HAN and ADN were successfully synthesized. Further, it should be stressed that the N5+ formation was recognized for the first time in the world in 1998 by The National Institute of Advanced Industrial Science and Technology (AIST). R&D efforts are also underway for propulsion applications utilizing GAP and HAN.

In South Korea not much original synthetic work on energetic materials has been carried out. The Agency for Defense Development (ADD) in Korea developed the so-called "ADD Method-1" to predict the performance and sensitivity of new explosive materials.

Russia has gained tremendous experience to date in designing high energy materials (EM) sourced from polynitrogen and nitrogen-oxygen compounds, in particular heterocycles and carcass structures such as CL-20, etc. A number of unique methodologies that enable insertion of explosophoric groups into target structures have been developed. The Zelinsky Institute of Organic Chemistry RAS stands among the EM synthesis pioneers.

A major advance in EM chemistry is associated with a concept of stabilized polynitrogen-oxygen molecules building based on the charge alternation principle. In the Soviet Union, dinitramide ammonium salt (ADN) served a basis for propellants used in strategic missiles of various deployment modes, and was produced on a multi-ton commercial scale. ADN enables highly efficient smokeless fuels with improved performance, e.g. lower missile launch detectability, and is used on super-precision laser guidance systems. Apart from providing high energy efficiency, new fuels are also environmentally friendly. Currently, many countries, including Russia, are carrying out intensive research in the area of ADN and applications of other dinitramide salts as universal oxidizers for 'green propellants'.

In India, high energy materials (HEMs) is a generic term used for explosives, propellants, and pyrotechnics. The most important application of HEMs is in support of the country's defense capabilities. In order to keep pace with developments all over the globe and to ensure self-reliance in the field of HEMs, India has developed some newer and better molecules.

The military research in the Czech Republic includes all aspects of armament systems. The research into explosives is often done in cooperation with Explosia or more precisely the Research Institute for Industrial Chemistry (VUPCH) and the University of Defense in Brno. The four most important topics researched are emulsion explosives, application of demilitarized explosives in slurry explosives with focus on W/O mixtures, preparation and synthesis of cyclic nitramines, and studies of secondary explosives with high thermal stability. Also researchers at the University of Pardubice constantly monitor improvised explosives and their properties. Some of their research on TATP has recently been published.

Energetic materials research in Australia is done only at the Defence Science and Technology Organisation (DSTO) labs, with specific projects being contracted out to some universities. There has not been much new work published by DSTO over the last few years. The Australian Defense Studies Centre, UNSW@ADFA, Canberra has focused on the synthesis and characterization of new high nitrogen compounds. Azoxytriazolone (AZTO) is a new chemical species discovered by this research group, and preliminary results indicate it may possess potential as a new insensitive high explosive. The group is studying methods of synthesis of AZTO and other related compounds, and also investigating their solid-state and solution properties.

There is significant interest in energetic materials outside the DoD. The non-DoD areas where energetic materials are used are probably recognized by most. These include NASA, commercial access to space and Department of Energy (DoE) and their research related to improved strategic explosives. Other examples include an automobile airbag, explosive bolts and cutters, extracting oil and gas from shale and tar-sand fields, and a potential emerging application is in gas generators (e.g., hydrogen) for storable/replenishable batteries. Additionally, some energetic compounds are found in the pharmaceutical industry (e.g., nitroglycerine and other nitro/nitrate compounds). Finally, the theories, technologies and models developed in the research and advancements of energetic materials are often applicable to non-related industries, such as the development of protection systems and energetic material detectors used by the Department of Homeland Security (DHS). This expanded use of energetic materials is evidence that energetic materials are becoming more and more common in our daily lives.

The drivers for improvements in DoD energetic materials (i.e., safety, reliability, “green”, and performance) are the same as those which are making the energetic material more commonplace outside the DoD. There is, however, a low potential payoff for private support of energetic material research due to high cost and low ROI. The continued and consistent development of new energetic material technologies is only possible with continued DoD funding. The extensive non-DoD use of energetic materials should be recognized as a positive spin-off of DoD energetic material support, and should help to solidify the DoD need for continued investment in this area of research and development.

Author Biographies

Davinder K. Anand is Professor of Mechanical Engineering and Director of the Center for Energetic Concepts Development, both at the University of Maryland, College Park. He received his doctorate from George Washington University in 1965. Dr. Anand was Senior Staff at The Applied Physics Laboratory of the Johns Hopkins University from 1965-1974. From 1991-2002, he chaired the Department of Mechanical Engineering at College Park. He has served as a Director of the Mechanical Systems Program at the National Science Foundation, and his research has been supported by NIH, NASA, DoE, DoD, and industry. He has lectured internationally, founded two high technology research companies (most recently Iktara and Associates, LLC), published twelve books and over one hundred and seventy papers, and has one patent. He is a Distinguished Alumnus of George Washington University, and was awarded the Outstanding and Superior Performance Award by the National Science Foundation. Dr. Anand is a Fellow of ASME and is listed in *Who's Who in Engineering*.

Millard S. Firebaugh retired from the United States Navy in 1995 as a Rear Admiral after more than 33 years' service as an Engineering Duty Officer. Since then, he has been involved in various technical and business activities, including nearly 8 years as a Vice President and the Chief Engineer for General Dynamics, Electric Boat Corp. Subsequently he was COO of SatCon Technology Corp. He is now Minta Martin Professor of Practice at the University of Maryland in College Park Center for Energetic Concepts Development. Firebaugh holds the American Society of Naval Engineers' Gold Medal, the US Navy Distinguished Service Medal and is a member of the National Academy of Engineering. Dr. Firebaugh received his Sc.D. in Ocean Engineering in 1972 from MIT.

Yasuyuki Horie is the Senior Scientist, Energetic Materials, Munitions Directorate, Air Force Research Laboratory (AFRL), Eglin Air Force Base, FL. Dr. Horie has more than 30 years of experience in the area of high-pressure shock compression of condensed matter with focus principally on thermochemical behavior of both inert and energetic materials. He has pioneered the development of models for shock-induced phase transition and a statistical burn model of explosives, as well as a discrete element method for granular media. Dr. Horie has published and edited dozen books and more than 120 refereed journal and proceedings papers. He is also known for his work on the shock synthesis of refractory compounds and ceramic composites such as nickel aluminides and diamond/TiC composites. He holds a patent on the latter. Dr. Horie has served on various technical committees and professional societies, and has promoted international research collaboration. Dr. Horie received his Ph.D. in 1966 in Physics from Washington State University.

Robert E. Kaczmarek is a senior staff member to the Deputy Technical Director of the Naval Surface Warfare Center, Indian Head Explosive Ordnance Disposal Technology Division (NSWC-IHEODTD). Mr. Kaczmarek has over thirty years of weapon system development, acquisition, and organizational leadership experience. At NSWC-IHEODTD his assignments have included Weapons Engineering Department Head, Technology Development Department Head, and Research, Development, Test and Evaluation Department Head. In 2011, Mr. Kaczmarek was assigned as a Senior Visiting Research Scholar to the University of Maryland's Department of Mechanical Engineering Center for Energetic Concepts Development. Mr. Kaczmarek earned a Bachelor's degree in Chemical Engineering from the State University of New York at Buffalo in 1981 and a Master's degree in Engineering Administration from the George Washington University in 1987.

Robert A. Kavetsky is currently the President and Executive Director of the Energetics Technology Center, a research and development organization in Charles County, Maryland conducting research and engineering programs for the Department of Defense and other agencies. During his 32 year career in the Department of the Navy he led efforts in hypersonics and undersea weapons, and was appointed the first Warfare Center Liaison to the Office of Naval Research where he established the N-STAR program, a Navy-wide effort aimed at reinvigorating the science and technology community within the Navy's Warfare Centers. Mr. Kavetsky received a B.S. and M.S. degrees in Mechanical

Engineering and a Master of Science degree in Engineering Administration from Catholic University. He has co-authored six books, and a wide array of papers addressing both technical and workforce policy issues.

Thomas M. Klapötke received his Ph.D. in 1986 (TU Berlin), post-doc in Fredericton, New Brunswick, habilitation in 1990 (TU Berlin). From 1995 until 1997 Klapötke was Ramsay Professor of Chemistry at the University of Glasgow in Scotland. Since 1997 he has held the Chair of Inorganic Chemistry at LMU Munich. In 2009 Klapötke was appointed a Visiting Professor at CECD, University of Maryland. Klapötke is a Fellow of the RSC (C.Sci., C.Chem. F.R.S.C.), a member of the ACS and the Fluorine Division of the ACS, a member of the GDCh, and a Life Member of both the IPS and the National Defense Industrial Association. Most of Klapötke's scientific collaborations are between LMU and ARL in Aberdeen, MD and ARDEC in Picatinny, NJ. Klapötke also collaborates with ERDC in Champaign, IL. He is the executive editor of Zeitschrift für Anorganische und Allgemeine Chemie, the Subject Editor in the area of explosives synthesis of the Central European Journal of Energetic Materials and an editorial board member of Propellants, Explosives and Pyrotechnics, the Journal of Energetic Materials, and the International Journal of Energetic Materials and Chemical Propulsion. Klapötke has published over 600 papers, 28 book chapters, and 8 books.

Robert D. Lynch received his Ph.D. in 1977 (Vanderbilt University, Nashville, TN), and conducted post-doctoral research at Vanderbilt University Hospital. He worked as a propellant chemist with Thiokol Corporation (1978-1980 in Huntsville, AL), Talley (1981-1982 in Mesa, AZ) and Atlantic Research Corporation (Gainesville, VA). At Atlantic Research and later Aerojet (which bought the assets of ARC in 2004), he progressed to the position of Executive Director, Technology. In 2011, Dr. Lynch accepted the opportunity to focus fully on research as a Technical Principal becoming the Subject Matter Expert (SME) on propellants and energetic materials. He is responsible for oversight of advanced propellant development efforts, basic research of new ingredients (identification, modeling, synthesis and application of such ingredients); and applied research of propellants. He has over 50 publications and patents in propulsion, propellant technology, engineering solutions, insensitive munitions, and fire suppression. He has served as session chair and presented papers at numerous domestic and international symposiums for JANNAF, NDIA and AAIA and was the Meeting Chair for the NDIA IM International meeting in 1996. He is a member of the US delegation for DEA 5660 (Data Exchange

Agreement) group for energetic materials. He also serves on the CPIAC JANNAF Journal of paneled papers as a Board of Directors Charter Board Member.

Betsy M. Rice is the Team Lead of the Multiscale Reactive Modeling Team within the Weapons and Materials Research Directorate at the U.S. Army Research Laboratory, Aberdeen Proving Ground, MD. She is responsible for initiating, planning, and personally performing research investigations to determine microscopic details of the physical and chemical processes of materials of interest to the Army, including energetic materials and materials related to armor/armaments. Dr. Rice's expertise lies in the theoretical chemistry areas of classical molecular simulation and quantum mechanical molecular characterization directed toward advanced modeling of materials that are critical components of several DoD weapons and S&T mission areas. She is a technical advisor to laboratory peers, to the Research, Development, and Engineering Center (RDEC), industry, program managers, academia, and other government agencies in her area of expertise. Dr. Rice also holds the position of Senior Scientist at the High Performance Computing Software Application Institute for Multiscale Reactive Modeling of Insensitive Munitions. She has published over 80 reports, journal articles and conference papers, and nine book chapters relating to molecular simulations of energetic materials. Dr. Rice has received the U.S. Army R & D Achievement Award (1997, 2003, 2008), the ARL Achievement Award for Best Technical Publication (1999, 2007), and Army Research Laboratory Fellow (2000). Dr. Rice received her Ph.D. in Chemistry in 1987 from Oklahoma State University.

James M. Short is an international leader in energetics, focusing on combustion. He studied detonation physics at the University of California at Berkeley. After that he was a protégé of the eminent detonation physicist, Sigmund J. Jacobs, and explosives chemist, Mortimer J Kamlet. In 1983 Dr. Jacobs selected Dr. Short to be the chairman of the International Detonation Symposium. Dr. Short remained chairman of the Symposium for more than 20 years. In 1980, Dr. Short invited Professor Ding Jing of the Beijing Institute of Technology and three other Chinese Professors to participate in the Seventh International Detonation Symposium. In 1987, Dr. Short was privileged to represent the United States in Beijing and offer three papers at the International Symposium on Pyrotechnics and Explosives. Since 2011 he has served on the Foreign Advisory Board of the International Autumn Seminar on Propellants, Explosives and Pyrotechnics. At this seminar, the 15th in the Czech series on New Trends in Research of

Energetic Materials, he joins the Scientific Committee. Now as the Executive Editor of the Journal of Energetic Materials (http://www.tandf.co.uk/journals/titles/07370652.asp), he is privileged to publish the work of European energetic scholars, and he also encourages energetics scholars to publish in the Central European Journal of Energetic Materials.

Contents

Chapter 1

Future Capabilities for Energetics R&D

Robert E. Kaczmarek and Robert A. Kavetsky

The changing nature of military conflict requires the continued development of new war-fighting capabilities. Energetic materials and systems with substantially enhanced performance, reduced sensitivity, and controlled energy release are critical enablers for the development of future capabilities. The continued development of science and technology in the area of energetics is of critical importance to the United States (US) national security.

This military-unique capability and its critical workforce historically have had, and will continue to have a significant impact on future weapon systems, military operations, and homeland security.

1.1 A National Issue

Eight studies conducted on the subject of energetics since 2000 have concluded that energetics research is important, however, suffering from a lack of DoD attention. These studies in general have concluded that: the DoD technical tasking and investment strategy are near-term focused, and mostly reactive; the near term focus threatens the long-term technological superiority of the US warfighter; current gains are based on previous technology investments; and without investments in future technologies, sustained technological superiority is at risk.

The level of foreign investment in energetics continues to grow. Others are moving swiftly to exploit known technological opportunities and breakthroughs in energetics at a time when the US investment continues to decline. Energetics is an area where we have been surprised in the past and there is high risk of surprise in the future.

Perhaps the most critical current need for ever vigilant and robust research and development in energetics is that of Ballistic Missile Defense of the United States from rogue nations and limited ballistic missile launches aimed at the United States. A recent National Academies/National Research Council report, *Making Sense of Ballistic Missile Defense: An Assessment of Concepts and Systems for U.S. Boost-Phase Missile Defense in Comparison to Other Alternatives*[1,2], while not discussing energetics directly, makes the real case for continuing significant, perhaps disruptively advanced, improvements in propellants and warheads for ballistic missile interceptors.

Energetics is a critical enabler for the development of new capabilities driven by asymmetric warfare requirements and joint force needs. The following considerations would be addressed by a long-term energetics research and development program.

- Significant improvements in the energy density and power of weapon payloads.
- Development of a coherent, long-term vision or strategy regarding energetics research, development, and manufacturing.
- A revitalized energetics research, development and manufacturing technology human resource base.
- A systematic and continuous monitoring and assessment of energetics research, development and manufacturing technology investment around the globe.

1.2 Critical Warfighting Enabler

The US will continue to face military conflict of an asymmetric nature. In this environment, there is advantage in the precise application of force, avoiding collateral damage. Historically we sought more powerful energetics and weapons for symmetric warfare, while we now seek smaller weapons designed to prevent collateral damage while disabling the warfighting capability of the enemy. Energetics needed for future warfighting needs are driven by the need to minimize collateral damage, the need for flexibility to adjust to a wide range of targets, the need for small and lethal packages that will enable both the weaponization of unmanned vehicles, and increase the range/loitering capabilities of these new systems.

To ensure success, the US warfighter needs the best available weapons. The US forces have been able to successfully identify the targets and precisely navigate weapons to the targets, and in most cases destroy the targets, however, many targets in the Afghanistan and Iraq conflicts proved hard to destroy. These included hard and deeply buried bunkers and caves and highly mobile targets. There are many lessons to be learned from these recent conflicts and there are many opportunities for marked improvement in weapon lethality.

For the first time the US used thermobaric weapons in Afghanistan and Iraq. These weapons are effective because they have a long pressure pulse, due to transient combustion of metal fuel clouds following the initial detonation. While thermobaric weapons have been around for many years, the fundamental chemistry and physics of the transient combustion reactions are largely unknown. Experiments and modeling are required to provide a fundamental understanding of these complex coupled reactions. Because of the lack of fundamental understanding of the physics and chemistry of the transient combustion of metal fuel clouds, much of the design of thermobaric weapons to date is by “trial and error”.

In addition to research needed to address current deficiencies, research in energetics is also required to address future needs. The warfighter will need smaller weapons, but without giving up any performance. The weapons will have to have higher energy density in order to make the smaller weapons perform as if they were larger. This will require higher energy density both of propellants and explosives, a capability that is not achievable with our current set of ingredients.

The warfighters will increasingly want more from energetics. They will seek missiles that can go faster and farther to destroy enemy targets. They will require tailorable applications, to include changeable lethality, depending on the target and situation. **This necessitates making energetics experts equal partners in the systems engineering process, just like experts in airframes, sensors, and guidance systems.**

Meeting the DoD's objective of smaller platforms with increased lethality is only possible through the use of higher energy density explosives and propellants in combination with precision targeting systems. The direct result of this combination will be enhanced penetration, longer range, smaller warheads and reduced logistics support.

Key energetic materials-related research areas identified as having high promise are:

- Advanced fuels and oxidizers
- Advances in CHNO and CHNOF chemistry
- Metallic additives
- Nanostructured materials
- High-nitrogen species

- All-nitrogen species
- Reactive Materials
- Exotic materials and novel physics

1.3 New Horizons

In recent years, energetic materials research in the US has been focused on insensitive materials for use in insensitive munitions (IM). Insensitivity is an issue of critical importance, and programs related to the IM objective must be continued. The level of emphasis on IM, however, has limited development programs for other materials, and may have led to missed opportunities for improved systems. An expansion of the objectives of energetics research with a focus on performance is needed to recover for lost time in multiple areas - these include detonation, formulation chemistry, combustion physics, combustion chemistry and molecular synthesis. Materials design based in quantum chemistry and solid mechanics is defining revolutionary first principle approaches to energetic materials, and offers opportunities for significant advancement rather than incremental improvement.

While new materials have been synthesized in the laboratory, very few of these new materials have been implemented. There have been no major advances in materials in the propellant industry in the last four decades. Some new explosive formulations have transitioned into weapons systems, however, this is an area that can further benefit from the introduction of new energy storage and release concepts to improve performance.

Substantial performance advantages can be realized by both using newly formulated energetic materials and developing an understanding of their behavior and properties. Using first-principle-based design approaches we can revolutionize many of our most fundamental concepts of energy storage within weapon systems, facilitating the development of new weapons based on advanced energetic materials that would result in significant benefits to US warfighters with shorter times to target, longer standoff distances, and greater destructive power. It is estimated that, if we chose to, we could see significant improvements in conventional weaponry and a fundamental new understanding of energy storage and release within the next two decades.

Historically, efforts in the area of energetic material synthesis have been directed toward ingredients that contain only carbon, hydrogen, nitrogen, and oxygen (CHNO explosives). For many decades HMX (a powerful and insensitive nitramine explosive) was the benchmark against which high energy CHNO ingredients have been compared. In 1987, the Navy first synthesized CL-20, a powerful new material found to be more energetic than HMX. The traditional methodology for the formulation of new energetic materials such as CL-20 has been a combination of testing, experience, intuition, and trial and error. As the need for rapid deployment of new advanced weapons systems has grown over recent years, so too has the need for an optimized development process in the formulation of customized advanced energetic materials become more apparent. Recent developments in computational chemistry and physics-based modeling, chemical synthesis and formulation, and material science provide the key insights that will enable breakthroughs in the performance of energetic materials.

New tools are emerging that can accelerate the development of new energetic materials while reducing both the cost and time necessary to verify their performance. These tools include:

- Computational modeling and simulation
- New characterization techniques
- Improved processing methods
- Advanced munitions effects modeling and simulation

During the last fifty years the output of military high explosives has increased by approximately forty percent. Future weapon systems will be smaller, and unless a greater percentage of their mass is going to be energetic materials, achieving the same energy output will require higher energy density materials (HEDM).

Is there room for further improvement? Figure 1.1 shows the mass-based energy density spectrum and the relative position of conventional high-energy chemistry within it. Conventional hydrocarbons based on oxygen and nitrogen (CHNO) explosive materials are at the low end, on the order of 103 J/gm. New CHNO-based molecules combined with advanced approaches for achieving high surface areas and mixing components may be able to increase this figure several-fold - this would be the equivalent of several centuries of progress. The figure shows that there may be even greater potential for HEDM when utilizing alternative approaches. Some of these are currently only at the conceptual stage, while others are just entering the basic research stage.

1.4 Critical Workforce

Historically, the number of scientist and engineers (S&Es) in the US engaged in energetics research, development, and manufacturing technology has been relatively small compared to the numbers in other scientific fields. Recent trends show that this already small number is on the decline.

It can take five years or longer to fully train a college graduate with a science or engineering degree to work with energetic materials. The long lead-time to train S&Es to work in this field coupled with the anticipated retirements in the upcoming years will result in a knowledge gap in this critical defense technology area.

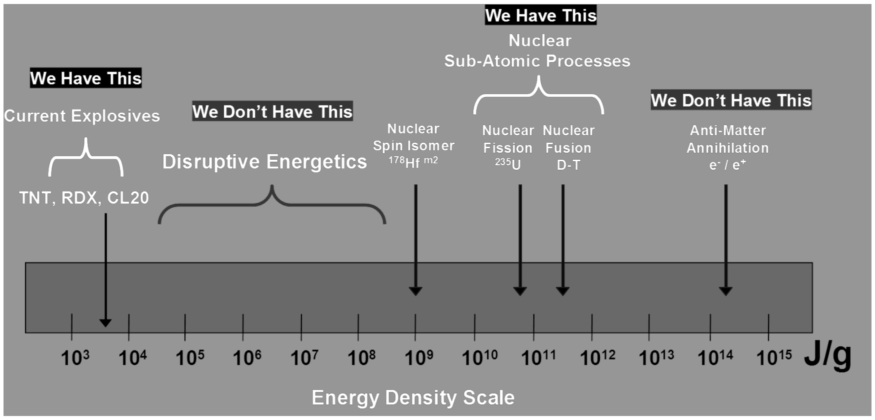


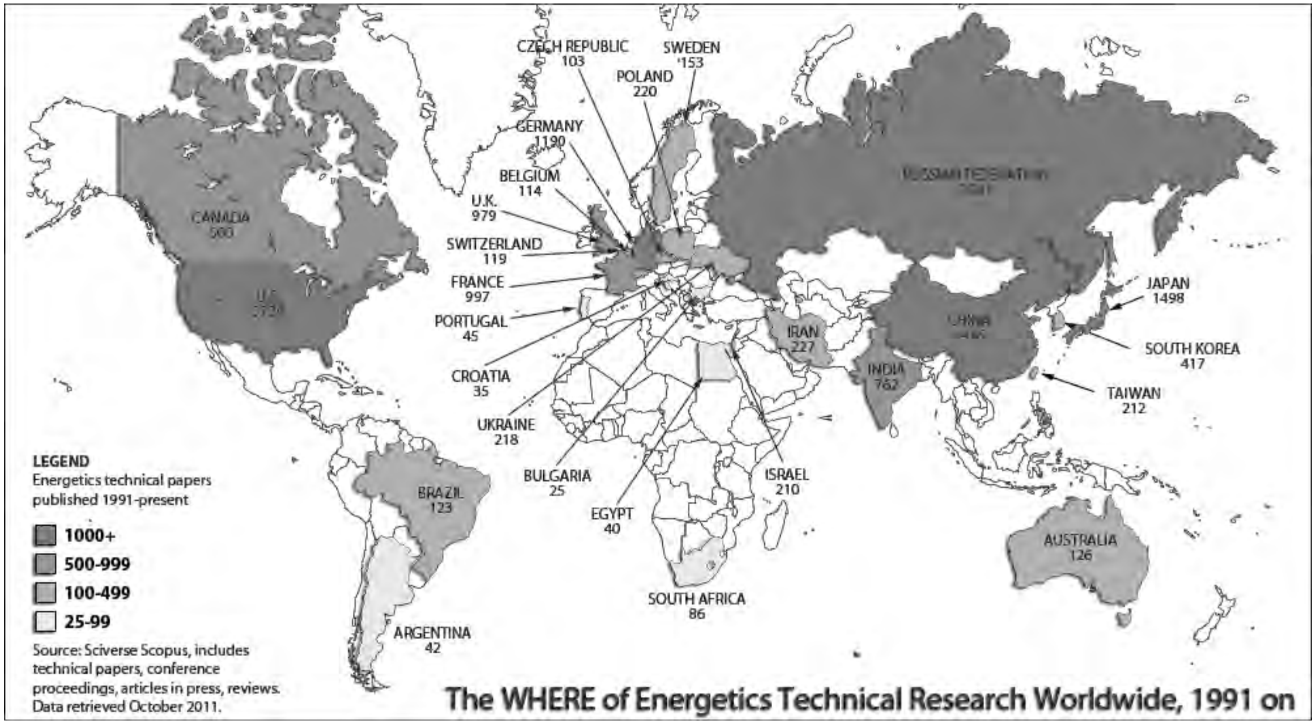
Figure 1.1: Mass-based energy density spectrum (J/g)

The deficiency in energetics materials research, development and manufacturing technology funding has impaired the ability of the DoD laboratories to attract and retain people with the critical skills need for technology development.

Current workforce trends will likely result in serious gaps in the number of S&Es engaged in energetics as the current generation of workers retires over the next several years.

The shrinking size of the US S&E workforce engaged in various aspects of energetics R&D raises an important question: what can be done to preserve this critically important defense technology area?

Unlike some other weapon systems technologies, energetics requires a strong government presence, not just to provide requirements, but also to lead the research and technology development. This is due to the lack of a commercial outlet for the technology and the low profit potential for industry. And, just like other weapon system competencies, the drawdown in the numbers of government personnel will begin to affect the ability to achieve the required breakthroughs.



LEGEND

Energetics technical papers published 1991-present

- ▨ **1000+**
- ▨ **500-999**
- ▨ **100-499**
- ☐ **25-99**

Source: Sciverse Scopus, includes technical papers, conference proceedings, articles in press, reviews. Data retrieved October 2011.

The WHERE of Energetics Technical Research Worldwide, 1991 on

Figure 1.2: Energetics research worldwide

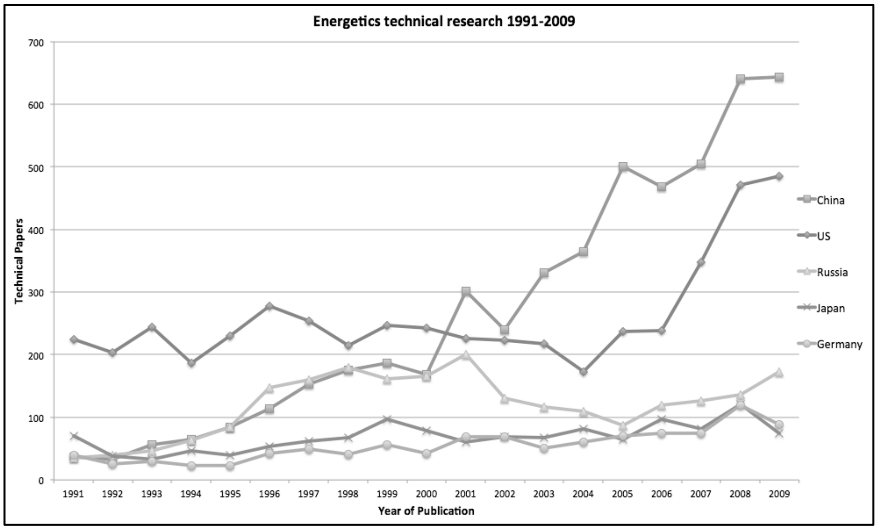


Figure 1.3: Energetics research worldwide

1.5 Emerging Technology Surprise

There are clear indications that foreign states are investing heavily in energetics research, development and manufacturing technologies, and as a result they may well be exploiting technological breakthroughs.

Other nations are not standing idly by. CL-20, developed through research in the US, is the most powerful energetic ingredient that is available today. Today, France, Sweden, China, Russia and other countries have made CL-20, and are trying to weaponize propellants and explosives incorporating this powerful ingredient. China has an extensive program in energetic ingredients, propellants and explosives. Their programs have many Ph.D.s working in energetics who were originally educated in the US. Without increased research there is no doubt that the US will fall behind. The "new" ingredients we are investigating today were developed by us or, in most cases, by the Russians, 20 years ago. We have stood still, others will not.

Figure 1.2 shows the worldwide summary of open literature scientific journal articles on energetics while Figure 1.3 depicts the US overtaken by China in yearly output of energetics literature.

Foreign organizations are now moving swiftly to exploit known technological opportunities/breakthroughs in energetics. Energetics is an area where we have been surprised in the past and there is high risk of surprise in the field in the future. How does a democracy such as ours prevent technological surprise? Maintain the technological initiative and ensure that intelligence is timely.

1.6 Recommendation

A coordinated investment and execution strategy is necessary to take advantage of opportunities presented by energetic materials research, development and manufacturing technologies.

A defined systematic approach that recognizes the long-term nature of energetics development timelines is required. This approach should focus, enhance, and accelerate Service and Agency programs with the aim of achieving new and novel energetic materials suitable for aircraft- and missile-delivered payloads with energy densities up to 10 times that of TNT within the next ten years. Enhanced energetic payloads will increase the lethality of current and future weapon systems and provide more credible, non-nuclear options for the hardest and deepest targets. A successful investment strategy for advanced energetics should pursue the following three tracks simultaneously:

- In the near-term, the first track includes advanced fuels and oxidizers, metallic additives for propellants and explosives, reactive materials, and enhanced blast explosives.
- In the mid-term, the second track includes nano-energetics, all nitrogen compounds, structural bond energy release, and meta stable atoms and molecules.
- Over the long-term, the third track includes the class of excited nucleon states, such as nuclear spin isomers. These are energetic metastable states of the nucleus with possible energy densities approaching a few percent of nuclear fission.

While only the first track is expected to yield some near-term practical candidates for new and novel energetic materials, the recommendation is for a balanced investment in all three tracks.

Finally, international energetics research, development, and manufacturing technology activities should be systematically and continuously assessed.

1.7 Conclusions

There is a requirement for continued effort in energetics research, development, and manufacturing technology to prepare for future weapons systems requirements and to counter emerging and disruptive technologies. The overarching issue is one of ensuring that our critical national defense capability is nurtured and maintained. Energetic materials research, development, and manufacturing technology have been, and should continue to be a key component of our nation's defense institution. A coordinated and sustained effort is required to focus the energetics community on addressing the warfighting challenges of the future. The best sustainer of technological capability is a robust program aimed at fielding new systems that extend the reach and power of our forces while diminishing their vulnerability. Together, the recommendations provided comprise a structured perspective. Innovation to achieve significant goals requires visionary leadership, competent scientists and engineers, challenging work, and state-of-the-art facilities. Of particular importance, is the state of the workforce in energetics. Absent a revitalized energetics workforce pursuing energetics research and development for new advanced weapon capabilities we are in stark danger of losing the capability for this activity we now possess, endangering a uniquely military capability we cannot afford to be only second-best at in the future.

References

1. The National Academies Press (2012), "Making Sense of Ballistic Missile Defense: "An Assessment of Concepts and Systems for U.S. Boost-Phase Missile Defense in Comparison to Other Alternatives," Committee on an Assessment of Concepts and Systems for U.S. Boost-Phase Missile Defense in Comparison to Other Alternatives; Division on Engineering and Physical Science; National Research Council.
2. The study specifically concerns itself with a) countering short-range, medium-range, and intermediate-range ballistic missile threats from rogue states to the deployed forces of the United States and its allies; and (b) defending the territory of the United States against limited ballistic missile attack.

Chapter 2

Systems Engineering Opportunities in the Development and Deployment of Energetic Materials

Millard S. Firebaugh

2.1 Concern

New defense acquisition programs for platforms, that is ships, aircraft and vehicles, for which one of the platform missions is to carry weapons with warheads to destroy targets, would benefit from smaller weapons without sacrificing either the range of the weapon or the destructive effects of the warhead it delivers. Such a benefit would be enabled by new advanced energetic materials. But the ship, aircraft or vehicle program is usually structured to carry weapons already fully developed and in use, based on energetic materials already proven in service. A more comprehensive view of the engineering of the super-system of platform and weapons would include trade-offs based on the merits of advanced energetic materials. But, the current state of energetic materials technology and the lack of adequate cross-disciplinary orientation in the leadership of defense acquisition combine so that such trade-offs are not usually or readily made.

2.2 Issues

There appear to be two intertwined issues that combine to frustrate the development and deployment of new energetic materials for military applications in the US armed forces. Addressing these issues may be a key long range facilitator for important advances in the military capability of our nation. First, in addressing new complex weapon and delivery system programs the development and use of new advanced energetic materials in the systems engineering process is seldom considered. The technical leadership for the acquisition of new platforms, that is ships, aircraft or vehicles, does not generally include individuals with comprehensive knowledge of energetic materials and the requisite level of awareness of what alternatives new energetic materials could offer in the systems engineering of a new or enhanced capability. Second, the development of new higher performance energetic materials for use in new munitions is a lengthy, highly empirical development process with timelines that are long in comparison to the timelines for developing a new ship, aircraft or combat system. As a result, in the engineering of a new weapon or a new delivery system for new weapons, engineers who might think of addressing new energetic materials as a part of the systems engineering process find that the new materials development process would be lengthy, probably very speculative as to outcomes and not compatible with timelines for getting a needed new capability into service.

Of course, there have been monumental examples in which this was not the case. The development of the submarine launched ballistic missile included the development the energetic materials for solid rocket propulsion. Systems engineering, including energetic materials in the systems engineering process, delivered a new capability of surpassing importance in national defense on a timeline that was critical in addressing the emerging threat. The resulting submarine launched ballistic missile greatly simplified the design of the strategic missile submarines resulting in an affordable system with high reliability and operability. But, for system developments that do not rise to the highest possible level of urgent national need and for which established energetic materials can somehow do the job, trade-offs exploring the extent to which improved energetic materials might be the key to a less costly system or a system with superior performance are mainly absent from the defense systems engineering process. As a result, the weapon and the platform that carries the weapon into battle may be larger and more costly to acquire, maintain and operate than might have been the case if the development of improved energetic materials had kept pace.

The underlying physics of energetic material reactions in propellants and explosives is exceedingly complex, non-linear, and transient, making mathematical analysis very challenging. Only recently have computational methods and the computers upon which to apply these methods approached the capability necessary to abet a transition of energetic material synthesis and analysis from mainly empirical methods to processes mainly guided by the results of numerical analysis. A transition of the science and engineering of energetic materials from an almost exclusively empirical process to one in which computation based analysis is used at every step in the process, as a reliable guide in sorting through the many decisions made at each step of a complex development, now appears to be feasible. This kind of transition from empiricism to computer based numerical analysis of a major part of the basis of understanding the complexities of energetic materials performance would be similar to the transformation of hydrodynamics and aerodynamics that occurred in the 1980's when computational fluid dynamics began to be applied as a basic analysis tool in the design of ships, aircraft and equipment. Computational fluid dynamics offered designers many new possibilities for quickly investigating higher performance systems with small expense compared to the earlier extensive use of physical model tests in flow facilities like wind and water tunnels and model basins. Computational fluid dynamics facilitated both the informed consideration of multiple options in early stage design and a degree of optimization not theretofore available to the designer due to cost and time constraints. Today in aero and hydrodynamics expensive physical model testing is generally of a confirmatory nature after most of the analytic work has been done using computational fluid dynamics.

In the case of the design, development, manufacture, handling and eventually disposal of energetic materials the complication of the dire consequences of an inadvertent triggering of the reaction of the material places a very high burden of proof on any computational methods that would substitute for the traditional empirical methods. While these concerns pose a high threshold for the validity of computational methods they should not be an impediment to development of these methods. Indeed, in one very specialized application of energetic materials computational methods of analysis are being successfully applied in lieu of very expensive and politically unacceptable physical tests.

What is proposed is that the systems engineering process for future advanced weapons and weapon delivery capabilities should routinely include the possibility that new energetic materials might result in a higher performance or less costly overall system. And, a computer based modeling and simulation capability for new, higher performance energetic materials along with a revitalized R&D program would facilitate the process, allowing system trades involving the energetic materials to be made as a part of other design considerations on a compatible time scale with other parts of the overall system work breakdown structure and development schedule.

2.3 Systems Engineering Basics

Consider a military requirement for a ship, vehicle or aircraft to find, engage and destroy the enemy's offensive capability. The requirements that generally dominate the design of the ship, vehicle or aircraft relate strongly to mobility, sensors and weapons. How fast and how far? What must be sensed? What types of weapons will be carried? How many and how big are they? These considerations are the main determinants of the size of the ship, vehicle or aircraft. With size, to first order goes cost. With respect to the weapons that will be carried the smaller the weapons are that will meet the requirement the less the over-all system will cost. How can the weapons be made smaller. For most weapons, now and for some time to come, energetic materials are used to propel the warhead toward the target and the damage mechanism for the warhead is initiated by a detonation of energetic materials. There are exceptions to this very basic weapon technology. For example, laser weapons depend on very different technology for the damage that the weapon can inflict on the target. In some postulated applications the electromagnetic rail gun may depend only on the kinetic energy of the projectile, traveling at a very high velocity, to inflict damage to the target. In other applications the electromagnetic rail gun may launch a projectile that employs energetic materials as part of the damage mechanism of the projectile. But, for conventional guns and missiles both propulsion of the warhead from the launcher to the target and the damage inflicted by the warhead on the target is accomplished by the use of highly energetic materials. If new more energetic materials can be applied in the design of these weapons such that more energy can be released for less volume of material, then for a particular application requiring the destruction of a certain target at a prescribed range, the weapon can be smaller. If the weapon is smaller, then the other elements that support the weapon in the overall delivery system, that is the ship, aircraft or vehicle that takes the weapon to the battle, can be smaller and therefore cost less.

An excellent definition of systems engineering systems engineering is as stated in the NASA Systems Engineering Handbook, SP-610S, June 1995.

> "*Systems engineering is* a robust approach to the design, creation, and operation of systems. In simple terms, the approach consists of identification and quantification of system goals, creation of alternative system design concepts, performance of design trades, selection and implementation of the best design, verification that the design is properly built and integrated, and post-implementation assessment of how well the system meets

> (or met) the goals. The approach is usually applied repeatedly and recursively, with several increases in the resolution of the system baselines (which contain requirements, design details, verification procedures and standards, cost and performance estimates, and so on).Systems engineering is performed in concert with system management. A major part of the system engineer's role is to provide information that the system manager can use to make the right decisions. *This includes identification of alternative design concepts and characterization of those concepts*[1] in ways that will help the system managers first discover their preferences, then be able to apply them astutely. An important aspect of this role is the creation of system models that facilitate assessment of the alternatives in various dimensions such as cost, performance, and risk."[2]

Alternative design concepts provided by the systems engineer in the process summarized in the above statement are naturally limited by the intellectual range and depth of the system engineers' experience. Historically, the skill sets of systems engineers in the platform business and those in the weapons business are developed in different organizations with limited overlap and cross-organizational fundamental knowledge and insight. The leadership at the level of broad cross-technology organizational ties, managing large complex entities, are, in our present construct, above the level at which systems engineering is being practiced. What is needed is a recognition that those directly involved in the new systems engineering process need to have a broader deeper understanding of the cross-disciplinary range of options. In the vocabulary of systems engineering as discussed in the NASA Systems Engineering Handbook the leadership needs to be schooled in the concept of a supersystem and the implications for supersystem engineering in determining the extent of relationships to be examined in addressing a new military requirement.

> "Every system exists in the context of a broader *supersystem,* i.e., a collection of related systems. It is in that context that the system must be judged. Thus, managers in the supersystem set system policies, establish system objectives, determine system constraints, and define what costs are relevant. They often have oversight authority over system design and operations decisions."[3]

2.4 Opportunity Lost

This author is very familiar with a specific example of a major acquisition that would have resulted in a considerably less costly end product had a different set of trade-offs been made to accommodate a planned higher performance weapon. That is to say, had the supersystem engineering been done more thoughtfully. The missing trade-off would have considered the over-all benefits in the design of a new platform that would have accrued had a very specific technological challenge been addressed with improved, more highly energetic materials in the design of the weapons the platform was designed to carry.

In the early 1980s plans were laid for a new US Navy attack submarine that would be much quieter than previous designs. A factor in developing the plan for the new submarine class, the SEAWOLF Class, was that it should be designed incorporating features such that it could eventually accommodate a new quiet torpedo. The new very quiet torpedo would complement the new very quiet submarine so that in an engagement with enemy ships the stealth of the SEAWOLF Class submarine would be secure until the weapon detonated on the target, rather than being compromised by a noisy weapon in the water. The noisy weapon could alert the target ship allowing for the possibility of evasion maneuvers and counter-attack. The allocation of resources to support the new submarine fully subscribed the available budget for submarine and submarine systems acquisition. So, in the long range plan for advances in submarine warfare, funding for the complementary quiet weapon would come at a later time in future budgets no longer burdened with the development costs of the new submarine. Very preliminary engineering estimates of the impact of quieting technology in a future torpedo development concluded that a quiet torpedo would need to be larger than the extant MK 48 torpedo to retain tactically relevant sensors, range and speed while also accommodating quieting technology. The practical way of providing for additional volume in the torpedo stowage and launcher equipment seemed to be to utilize a larger diameter torpedo tube. A guesstimate of what additional volume might be needed was made and the submarine design continued on that basis.

At the time the judgment that a larger diameter torpedo tube would be required was not challenged and no system trade-offs were made along the lines of developing new more energy dense propellants and warheads such that volume would be made available within the traditional torpedo tube diameter to include quieting in the weapon design. The system impacts of the larger diameter torpedo tubes were very substantial and costly to implement, resulting in a considerably larger submarine requiring a larger power plant to achieve the required speed. No careful cost analysis was made then or since of the impact of this single decision. But, the costs were very significant. A reasonable guess would be that the weight of the ship was on the order of 10 per cent larger than it would have needed to be had the design envisioned weapons no larger than the MK 48 torpedo. In today's dollars that could amount to as much as $200M per hull.

Had the funds used to accommodate a larger diameter weapon been used instead for the development of more energetic materials the submarines could have cost a lot less and the US Navy would have its new quieter weapon for the same investment. Of course, there is no guarantee that investment in the energetics for a new torpedo would have been successful in achieving the objective and this decision analysis benefits from hindsight. But, this chain of events remains an example of a possible important systems engineering opportunity missed for lack of development of new energetic materials. At the time, of course, there were no computational tools available to evaluate alternatives for new energetic materials for fuels or warheads that could have kept pace with the trade-offs being done in the early months of the program during which the basic characteristics of the submarine were being determined. Even so, judgments based on a technical dialog with experienced energetics professionals in government and industry might have created a level of confidence that the needed new more highly energetic materials could be developed in time to support the objective.

How was this opportunity missed? The process of programming for the SEAWOLF Class submarines, evaluating the state of technology that would be needed in the program, structuring related research and development and designing the ship involved many very experienced technologists and Navy planners. Many first rank engineers and scientists in government and industry committed their best efforts for months to define the programmatic and systems engineering path that this program took. Those familiar with the rhythms of major defense acquisition programs will readily understand that the SEAWOLF program was executed with all of the requisite oversight from within the Department of the Navy, the Office of the Secretary of Defense and the Congress. But, at no time was a voice heard asking if the design trade-offs should consider alternate means of achieving the desired quiet weapon, through a process involving improved energetic materials for higher performance, within the conventional weapon launcher volumes. An examination of the basic organizational structure of submarine programs suggests that intensive immersion in very specific technical areas of expertise, even in over-all leadership positions, is required to fully understand and manage the risks inherent in establishing overmatching technological superiority in arguably one of the most demanding physical and war-fighting environments. Some of the contributing technical areas and knowledge only come together organizationally at a level so broad that the impetus and opportunities to seek comprehensive cross-disciplinary analysis do not come to light. In the special case of energetics in which the work is intensively empirical and in which the centers of excellence with physical isolation for safety tend to breed a measure of insularity, cross-disciplinary interaction is all the more difficult.

It would, of course, be very speculative to be specific as to exactly how the right kind of thinking about the super-systems engineering connections in SEAWOLF could have been made. The connections between the power density of energetic materials in propellants and explosives relate to the weapon performance in range and destructive effect. There are other issues in the systems engineering of the weapon, including weapon guidance, maneuverability, speed, seeker, self-noise and radiated noise all subject to the basic hydrostatics and hydrodynamics of a submerged body in the water. All of these factors and many more would have come into play in attempting a new design with more powerful energetics. And, it is possible that the effort would have brought to light considerations that would render the concept un-executable. Indeed there was a small R&D effort made at the Pennsylvania State University Applied Research Laboratory for an alternative fuel for a torpedo engine. But, that effort was not pursued to any great extent and was not linked to any SEAWOLF submarine design trade-offs.

In the decision made that SEAWOLF should accommodate the future quiet weapon, the Navy made the collective and un-challenged judgment that the only way to retain the weapon performance in all of the above factors and have the volume necessary to include additional design elements such as coatings or engine isolation or quieter weapon propulsors would be to make the weapon larger in diameter. Therefore there would be more volume in which to work out the quieting features. Of course, bigger diameter means larger surface area and frontal area meaning more resistance, but the resistance increase relates mainly to surface area which is increasing as the square of the diameter while fuel capacity would be some function of the cube. In all of this, presumably the other weapon performance requirements were to stay about the same. But the judgment that the quieting of the weapon could be achieved with a bigger diameter was not based on an exacting analysis.

If the technologists were really on top of their game, they would have recognized that more powerful energetics could have provided an alternative path to quieting by means of a volume reduction in the weapon warhead and power plant for equivalent range and destructive effect, allowing the vacated volume to be used for silencing features in the weapon design.

Now back to the super-systems engineering issue. If the energetics had been already developed by a far-sighted RDT&E effort, or if tools were available for the rapid and safe development of new energetic materials on time scales compatible with the design of the submarine, then a decision could have been made to attack the weapon performance issue with energetic materials RDT&E rather than with more and very expensive volume in the design of the submarine.

But, parallel development of energetics and a weapon and a platform, while it has happened as in the case of POLARIS is not our usual *modus operandi*. And, absent something like a national emergency, we don’t have the perspective, tools or relationships to pursue such parallel approaches to improving capability.

Probably, the community of energetic materials scientists and engineers could help in the cross-disciplinary super-systems engineering effort by focusing some of their own effort in systems engineering. In the interests of economy of resources and in eliminating duplication of effort considerable emphasis has been placed on mechanisms to discourage practitioners in a particular technical specialty, in this case energetics, from straying out of their specialty. Such a restrictive, if well intentioned, efficiency measure may have the effect of restricting needed insight into the engineering of the super-system, leading to the potentially much greater inefficiency of inadequate systems engineering. The energetics material technologists should be challenged to engage in aggressive dialog as to the possibilities for new advanced energetic materials to participate in the systems engineering trade-offs in defining the super-systems for future weapon delivery.

2.5 Opportunities for the Future Missile and Platform Supersystems

The chart below illustrates progressive size increases in submarine launched ballistic missiles from the A-1 POLARIS missile carried by USS GEORGE WASHINGTON (SSBN- 598) through the D-5 TRIDENT II missile carried by the OHIO Class SSBN’s. As requirements developed for longer range missiles carrying more re-entry vehicles the missiles got bigger.

Similar growth in the size of individual units occurs in some other missile programs. For example, the body of the Standard missile, SM-2 Block III/IIIA/IIIB Medium Range is 13.5 inches. The body of SM-2 Block IV Extended Range is 21 inches. Both of these units can be launched from the cells of a MK 41 Vertical Launch System. The MK 41

VLS is designed for considerable flexibility to accommodate missiles of various lengths and diameters. The external dimensions of the launcher can be configured in several sizes as well to accommodate various sized ships. However, if the size of weapons that can be launched from the MK 41 VLS continue to increase a ship that employs the Mk 41 VLS launcher will not be able to carry as many weapons in the future. The USS ARLEIGH BURKE (DDG-51) Class that is now the principal surface combatant of the US Navy carries two MK 41 VLS launchers. From inception through FY 2012, the US Navy has procured 66 DDG 51 Class ships. More are planned for future year procurements. The early DDG-51 Class ships are designed for a service life of 35 years and the later ships for 40 years. The point is that there are many of these ships with their MK 41 VLS launchers and they will be a mainstay of the surface forces of the US Navy for many years. During the long time of service of these ships it may be anticipated that weapon requirements will change and to the extent that history is a guide there will be pressures for weapons with greater capability. But, if greater capability means bigger, then these ships will have to carry fewer weapons. And at some point the Navy will want to transition to a new larger and substantially more expensive ship to restore the capacity of the ships for numbers of weapons.

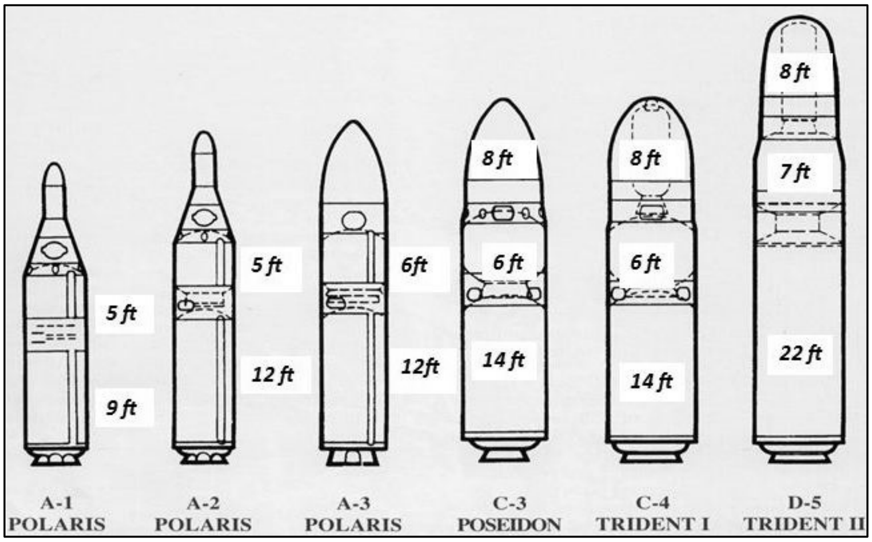


Figure 2.1: The dimensions of 6 fleet ballistic missiles[4]

New advanced energetic materials could offer a means by which the future desired greater capability missile could be realized within the dimensions of the largest missile that is compatible with the MK 41 VLS system of today.

Recently, the missions of the Navy's AEGIS system, that includes the ships that carry the system and the radar and combat control system that detect targets and control the missiles to intercept and destroy the targets, have expanded to include aspects of ballistic missile defense. This new mission will add to pressures for larger missiles with more acceleration and range to engage ballistic warheads at altitudes above the atmosphere. Indeed the development of offensive ballistic missiles with longer range and larger payloads including decoys will have to be countered with the development of more powerful anti-ballistic missiles carrying more sophisticated intercept devices that can cope with the decoys and still find and destroy the actual incoming warheads. This technological battle between offense and defense has the potential to become even more expensive if the missile sizes increase in such a way as to require larger launch equipment, afloat or ground based. Larger launchers afloat almost certainly means larger ships. And, larger ground based launchers imply larger construction efforts. As a matter of urgency, efforts should be undertaken to avoid those higher costs by the development of more powerful energetic materials.

A similar challenge has arisen with respect to the weaponizing of unmanned aerial vehicles (UAVs). Quite imaginatively, the initial weaponization of UAVs has been carried out by re-purposing helicopter weapons for use with UAVs. Now some efforts are being made to design smaller munitions specifically for UAVs some models of which can be quite small. With more powerful energetics UAV weapons can be made smaller without sacrificing lethality. Some UAV designs such as the US Navy X-47B stealth UAV designed for carrier based operation will need a family of stealth weapons that can be carried inside the aircraft envelope. These will have to be small weapons. For small weapons to have large effects new more powerful energetic materials will be needed.

2.6 Path Ahead

Absent a determined effort to develop new, more powerful energetic materials, both explosives for warheads and propellants weapons tend to increase in size in order to increase performance. As weapons increase in size, all of the costs of making the weapons and the even greater costs of producing larger platforms to deliver the weapons increase substantially. Investment in new more powerful energetic materials can forestall the impetus to larger platforms. Investment in technology for much more computationally based tools for modeling and simulation of all of the steps in the energetic materials value chain would be an important step in facilitating the kind of front end supersystem engineering needed to provide new capabilities at reasonable costs. And, lastly leading energetic materials scientists and engineers should engage as leading participants in the systems engineering of future weapon delivery systems.

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Chapter 3

Moving Energetics Science from Empiricism to an Advanced Computation-based Analytic Scientific and Engineering Basis, Facilitating Innovation

Betsy M. Rice and Yasuyuki Horie

3.1 Introduction

Today ordinary laptop computers can perform computations that were reserved only for supercomputers a decade ago. Exascale computing (10^{18} operations per second), projected to be implemented by 2018[1], could revolutionize the way computer simulation is used in science and technology, enabling hitherto-unaccessible high-fidelity predictive simulations. There is every expectation that the field of energetics science will benefit from such a capability by not only improving a fundamental understanding of the reactive behavior of high explosives, but also improving munitions design at the component as well as the system levels. At present, prevailing explosives design practices are heavily dependent on the designer's experience and intuition. Even when modeling and simulation (M&S) tools are used in design, they are mostly system specific and have high levels of empiricism and inaccuracies, particularly with regard to the response of the energetic material in a munition. Physics-based models are needed that can address non-scalable issues inherent in the response of complex, composite energetic materials (EM). Examples include chemistry, hydrodynamics, and geometry interaction, to name a few. Continued reliance on full-scale testing to develop munitions does not lend itself to rapid sensitivity studies and optimization of the effects of component parts, and the system level response. This inadequacy is particularly noteworthy in the design of explosives for survivability that involves a large variable set which is almost impossible to evaluate in an experimental framework. Historically, engineering design specifications of EM are based on ranking and protocol tests designed to address its performance and safety features. There is a statistical methodology commonly referred to as "Design of Experiments" used to deal with a large set of parameters, but the results are limited to the scale and scope of experiments used and do not provide a true predictive capability of macroscopic response based on fundamental physics and chemistry parameters linked to engineering and continuum models. Transforming the M&S design tools from empirically-driven to a physics-based capability will allow for the exploration of novel, more advanced materials and concepts, will reduce reliance on costly, time-consuming full-scale testing and will provide faster design and implementation of technology solutions at a substantially reduced risk.

While collecting the materials for this chapter, we were mindful of the article by L. Kadanoff in which he writes "excellent computer simulations are done for a purpose: the most valid purposes are to explore uncharted territory, to resolve a well posed scientific or technical question, or to make a good design choice".[2] The topics discussed here are chosen with the Kadanoff criteria in mind. Additionally, due to space and time limitations, we intentionally limited the selection of topics to those that we believe address the most pressing challenges or demonstrate the most potential. Therefore, many great contributions made by our colleagues at universities and DoE laboratories are not discussed here in detail. Rather, our emphasis is placed on three areas: Virtual Design, Novel Energy-Releasing Concepts, and Multiscale M&S in Energetic Systems Design. Obviously there are many other areas where M&S has made and will make significant contributions in advancing energetics science and technology. One notable example relates to insensitive munitions (IM); however, this area deserves special treatment and will not be discussed here. Rather, our focus will be on issues that are fundamental to energetics science and technology, rather than *system specific problems* such as IM and collateral damage.

The capabilities described herein roughly fall into two categories. Computational tools that fall within the first category allow accurate *a priori* prediction and description of the full spectrum of chemical and physical properties of candidate new (notional) and existing EM structures and formulations. Descriptions and examples will be given of how these capabilities are used to screen or design new EM in Section 3.2. A similar suite of design tools for energetic formulations is given in Section 3.3, whereas applications of theoretical capabilities to explore novel, non-traditional materials for potential energetic applications is described in Section 3.4.

Capabilities in the second category are those that will lead to an understanding of the fundamental physics and chemistry controlling the initiation, sensitivity and behavior of EM subjected to insult. Establishing these capabilities is paramount for physics-based design of advanced weaponry using new materials. Most of the existing tools in this category have not yet resolved many challenges rooted in the multiscale, stochastic issues both in space and time under extreme conditions of pressures and temperatures. Efforts to overcome these challenges through establishing multi-scale approaches for prediction of EM response based on fundamental physics and chemistry parameters will be described in Section 3.5.

3.2 Virtual Design of New EM

Maintaining and advancing energetic materials (EM) research, development and manufacturing technologies in the current fiscal climate presents substantial challenges. The traditional trial-and-error approaches for the synthesis, formulation, testing and fielding of a new energetic material have extreme time and dollar costs. These costs have become even greater in recent years due to additional constraints imposed to address statutory requirements both for IM compliance[3] and for environmental hazards associated with the development, processing, and handling of EM[4]. In light of these costs and current fiscal realities, innovative strategies are required to transform the overall research, development and manufacturing process leading to optimal performance and maximum efficiency at a minimum cost. A key innovation is the use of M&S tools for computationally constructing and assessing new materials before actual production. These tools can be used for a variety of purposes, including discovery of novel chemistries, assistance in design of new synthesis routes, and exploration of new materials and concepts for non-traditional storage and release of propulsive and explosive energy.

Until the mid-1980s, developmental efforts for new energetic materials were almost singularly focused on synthesizing new materials with higher energy densities. In the mid-1980s, new IM Programs were initiated in the DoD, thus expanding energetic material requirements to include reduced sensitivity as well as enhanced performance. In 1990, Congress established the Strategic Environmental Research and Development Program (SERDP) to address DoD environmental issues, including those associated with all stages of the lifecycle of EM (e.g., waste streams in synthesis, emissions ground contamination in training and in theater, stability during storage, and demilitarization). Thus, by the early 1990s, development requirements for new EM not only increased but became more stringent and diverse, thus increasing the need for reliable, efficient computational capabilities to predict properties of EM that are related to performance, sensitivities and environmental hazard for the purpose of screening candidate materials. Without these, the only way candidates can be screened is through synthesis and experimentation to produce the data necessary to assess potential performance or hazard. Such a time and resource-consuming procedure is inefficient, expensive, and generates potentially significant waste streams when applied to poor candidate materials. Thus, the DoD has made significant investments into development of these tools to obviate the synthesis and testing for probable poor performers, thus allowing time and resources to be expended on the most promising materials.

The majority of the computational tools that have been developed to date predict properties related to performance or vulnerability. Until the 1990s, the tools were highly empirical, since computational constraints precluded the use of accurate fundamental first principles methods (i.e., quantum mechanics [QM]) for the prediction of these properties. Many of the tools were similar in spirit to the QSAR/QSPR (Quantitative Structure-Activity Relationships and Quantitative Structure-Property Relationships) methodology used in the pharmaceutical community in drug design. A QSAR or QSPR is a simple statistical correlation between material behavior and properties with "molecular descriptors" such as chemical composition and constitution[5]. While useful, such empirical correlations are not extensible beyond the chemical classes of materials for which the correlations were established, thus limiting their predictive capacity to treat novel chemistries. Additionally, the correlations often do not provide physical insight into material behavior or response. For example, Brill and James[6] report "153 nearly linear correlations" between molecular and bulk material parameters with sensitivity to initiation for one class of explosives and argue that their existence "cloud rather than clarify understanding". Although the QSAR/QSPR approach is limited in the information that is revealed, it is quite useful as a quick screening tool for the purpose of EM design. Efforts have been made to develop more physically meaningful molecular descriptors based on QM predictions of molecular properties, thus linking the fundamental electronic structure of an isolated molecule with its macroscale behavior or properties.

Development of QM-based descriptors for EM, however, was not practical before the 1990s. Until then, the computational requirements for QM calculations limited their application to simple polyatomic systems that were much smaller than those of conventional energetic materials. Thus, approximate semi-empirical QM methods, in which some of the more computational costly portions of a full QM calculation are eliminated, were developed and applied to predict properties of EM. However, the performance of the tools was inconsistent, the results are questionable, and the tools are non-transferable and limited in applicability. In the early 1990s, however, a viable alternative QM methodology emerged that was sufficiently accurate for the development of predictive tools, but had modest computational resources, such that large polyatomic systems and even condensed phase systems could be treated. This method, Density Function Theory (DFT), is suitably accurate for use in developing molecular descriptors, and in providing a characterization of molecular and condensed phase properties and chemical reaction. Advances in DFT have resulted in a series of useful computational tools that are now available to EM developers for use in virtual design, screening of candidates and evaluation of notional materials. These tools predict measurable quantities of molecules such as structure, vibrational states, rates of reactions, energies of reactions, and other similar spectroscopic and thermodynamic properties or condensed phase properties, such as structural, thermodynamic and transport properties, shock Hugoniot properties, phase transitions/equilibria, and condensed phase energy transfer and chemical reaction. Additionally, the ever-increasing advances in high performance computing and algorithms ensure that even more sophisticated and powerful capabilities will be available to make *a priori* determinations of other key properties that are indicative of performance in a weapons system, vulnerability, or environmental hazard.

Summaries of computational capabilities for prediction of chemical and physical properties related to performance and sensitivity of conventional CHNO explosives are given in Refs [7-10]. More recently, efforts have focused on developing capabilities for prediction of environmental hazard and high-nitrogen explosive fills.[11,12] Brief descriptions of key capabilities and how they can be utilized in the design and synthesis of a new EM are given below:

Determining Stability: A first step in computationally-aided design of new energetic molecules might be to determine whether the molecule can exist at the ambient state. This can be easily and accurately determined through QM predictions of its equilibrium molecular structure. A molecule is in a local equilibrium when it does not spontaneously decompose or react. Failure to predict a stable structure provides crucial information to the synthetic chemist, not the least of which is to abandon attempts to synthesize the target. However, the calculations will also allow for a theoretical explanation as to why a molecule is not stable, and provide information for modification of the desired target to achieve the requisite stability. Once a molecule has been determined to be kinetically stable, assessment of whether it would have suitable properties for a high performing EM with acceptable vulnerability characteristics begins.

Thermochemical Properties: Conversion of an EM to its products often involves numerous chemical steps in which energy is either absorbed or released; the overall energy released in conversion of an EM to its final products is related to its performance. Reaction energies can be quantified theoretically by QM predictions of the Heats of Formation of both reactants and products in individual reaction steps. The heat of formation of a material provides a measure of its energy content and is a critical parameter used in standard thermochemical codes to assess potential performance in a gun or warhead.

Reaction Path Mapping: Although thermochemical properties such as Heats of Formation and Heats of Reaction describe energy content of a material or the amount of energy released or absorbed in a reaction, they do not reveal any information about reaction mechanisms, i.e., the manner in which products form. For example, the complete conversion of an EM to final products usually involves several steps, with the first often requiring energy to form intermediate species. The intermediates must then react with other intermediate or reactant species to form the final products. The rates at which the reactions occur are related to the energy needed to cause the reaction to occur, the degree of steric hindrance, and the ease with which a reactive encounter can be accomplished. Thus, while the thermochemical properties of a proposed EM might be good, the ease with which the product can form might be poor due to substantial energy or steric requirements. Direct observation of atomic-level details of chemical reactions cannot be accomplished except through QM reaction path mappings; these provide crucial mechanistic details that might influence the reaction. QM reaction path mappings are also useful for determining viability of synthesis routes. QM mappings often identify features on the reaction path that might preclude formation of the target, such as formation of unexpected intermediates or other products. QM reaction path mappings can also lead to consideration of non-energetic features of the reaction that might hinder synthesis, such as improper reaction conditions. QM mapping is useful to identify alternate (and often unexpected) reactions; by understanding the details of the various reaction mechanisms, it is envisioned that experimental conditions can be established in which targeted product formation (which influences performance) can be obtained. The concept of targeted product formation is the basis of a relatively new area of research, quantum or coherent control, in which experimentally controlled fields, informed by quantum mechanical calculations through closed-loop learning, dynamically drive a chemical reaction or other molecular process to a desired result.[13]

Crystal Density: Detonation velocity and pressure are proportional to the density of an EM; thus, this is a critical parameter for evaluation of potential performance in a warhead. Methods for *a priori* predictions of crystal density for EM range from completely empirical group-additivity methods to quantum-mechanically-based approaches. The empirical group additivity approach, parameterized with available experimental information or assuming chemically reasonable descriptions are limited in applicability to the chemical families used in the parameterization, and cannot be used reliably on the more exotic new compounds that are being synthesized (e.g., high-nitrogen materials), since the database used for parameterization is sparse. QM-based procedures have little or no reliance on experimental information, and thus are inherently transferable to different chemical families, since QM calculations are generally applicable to diverse chemical systems. A demonstration of the method applied to 289 molecular and ionic crystals composed of conventional CHNO and newer high-nitrogen energetic materials produced results that had an overall root-mean-square deviation of 4% and 5% for neutral and ionic crystals, respectively.[14] However, predictions for approximately one-third of the compounds had unacceptably large deviations from experimental values, indicating that the method would benefit from further refinement. Subsequent studies[15, 16] showed that electrostatic corrections to the procedure described in Ref. 14 improved QM crystal density predictions; application of the electrostatic corrections to the same suite of molecules in Ref. 14 confirmed this result, reducing the rms deviations for neutral and ionic crystals to 2.7% and 3.7%, respectively.[17]

A more elaborate computational procedure is one in which not only is the crystal density estimated, but details about the atomic arrangement within the crystal and different polymorphic forms are predicted using information only about its molecular constituents. Such information is particularly useful, since different conformational and packing polymorphic forms of EMs often have significantly different performance, stability and vulnerability properties. Although the development of a computational procedure to generate a probable crystal structure using the information of a single molecule has been described as "one of the most fundamental challenges in condensed matter science,"[18] it has the potential to be an extremely cost-effective, efficient

EM design tool. Several methods have being developed for *ab initio* crystal structure prediction,[18] however, only one has been utilized and developed for used in EM design.[19] While applications have demonstrated that the method is promising, substantial research investments are still needed to make this computational capability a cost-effective, efficient and robust design tool. The benefit of this approach is that it is inherently improvable, mainly by inclusion of QM descriptions of the interatomic interactions, advances in algorithms and computational platforms, and algorithm development for robust global optimization procedures.

Sensitivity: Capabilities to predict initiation resulting from impact, friction, electrostatic discharge or thermal loading are lacking, most likely because the initiation phenomenon is an intricate mix of thermodynamic state-dependent material (microstructural) and molecular properties. This is reflected in the relatively little success in establishing a predictive capability based on fundamentals of a single molecule. Most efforts[7-10] have focused on developing QSPR-type tools that relate impact sensitivity (as measured using a drop hammer test[20] with molecular descriptors, since this is the more prevalent type of experimental data available. To date, there is no one single computational tool that can adequately describe the response of all chemical classes of EM to impact; rather, the tools appear to work within families of energetics. Due to the failure of identifying a suite of tools for predicting sensitivity using molecular descriptors, efforts are growing to explore the influence of microstructural features on explosive sensitivity, through multiscale modeling approaches. This methodology will be described in Section 3.4 and not covered here.

Environmental Screening: Several key policy and regulatory drivers[21] prompted the development of predictive capabilities for screening new EMs for environmental hazard, As outlined in a protocol to address environmental, safety and occupation health (ESOH) risks in the development of new energetic materials, M&S approaches to evaluate performance, sensitivity and ESOH risks should be used at the earliest stages of EM development for use as “a basis for go/no-go decisions regarding further development”.[22] As outlined in Ref. 22, the majority of predictive tools to determine environmental impact and risk are based on QSAR/QSPR approaches, with one prominent suite of tools developed by the Environmental Protection Agency (EPA) [23] to estimate environmental fate and physical/chemical properties for use in predicting fate, transport and toxicological properties. While widely used within industry, these tools are not well-suited for either traditional or notional

EMs; further, they cannot predict toxicities of ionic compounds, an emerging class of environmentally-benign EMs. Accordingly, alternative QSPRS using quantum mechanical molecular descriptors were developed to predict ESOH risks of energetic materials for both conventional and novel (e.g., high-nitrogen) energetic materials. Physical properties that correlate to environmental fate, transport and effects (FTE) of compounds can be predicted using quantum mechanically-based methods; efforts have been successfully validated against available experimental data.[24] Additionally, estimates of aquatic toxicity for some novel energetic materials were obtained from models developed using fathead minnow and daphnia (water flea) data for a wide variety of nitrogen-containing compounds (both explosive and non-explosive). Similarly, additional models are under development to assess other forms of ecotoxicity, such as impact to green algae and earthworms.[25] Environmental aspects, however, present substantial challenges to M&S; QSPR/QSAR approaches cannot, for example, adequately assess parameters such as persistence that are influenced by "site-specific factors such as rainfall, temperature and organic carbon content of the soil".[22] However, large-scale condensed phase QM and classical molecular dynamics calculations are now being attempted to explore the behavior and breakdown of materials on model soils and in aqueous environments.[26] Some of the obstacles in developing predictive capabilities for FT in soils are reviewed in Ref. 27.

Overall, progress has been made in establishing practical computational chemistry tools that can be used for the purpose of design, assessing and screening of notional EMs before investing in synthesis and scale-up. One can envision application of quantum-informed QSPR approaches to predict properties of interest to the EM designer other than those detailed here, such as burning rate, melting point or other phase transition temperatures, compatibility, solubility, or vapor pressure and physical properties that correlate to FTE. All that is required is a sufficiently large set of experimental information that can be used for establishing the correlations. Unfortunately, availability of sufficient experimental data often becomes a limiting factor in the exercise of this approach, especially with regard to environmental screening as mentioned previously.

As it is often difficult to assign physically-reasonable explanations for the correlations, it would be advantageous to develop computational tools that will move away from QSPR/QSAR approaches to more physically-meaningful models and simulations. Of particular utility will be those in which dynamic process can be observed at the atomic level, such as condensed phase initiation reactions, or those that simulate crystal growth and control of polymorphism. Such advanced M&S tools for computationally constructing and assessing new materials before production will result in significantly reduced, developmental times, while meeting the goals of producing environmentally-acceptable energetic materials that meet or exceed lethality, performance and vulnerability requirements of current materials.

3.3 Virtual Design of Energetic Formulations

While the previous discussions in Section 3.2 have centered on numerous first principles models to provide guidance primarily to scientists engaged in the search of new energetic materials, an even greater need exists for design capabilities of novel formulations using new or existing energetic materials. The Air Force has extensive ongoing efforts to develop software to guide the formulation process, referred to as a design studio. The concept involves the creation of an architecture under which models of the formulation process are encoded and the results evaluated for energetic performance, IM response, survivability (as discussed below), producibility and cost.

As opposed to the virtual process for designing new energetic materials, in which candidate materials can be easily screened at the atomistic level, formulation of new energetics is a multi-step/mutli-level process. This multi-step/multi-level process requires specialists at one end who can perform the QM calculations and chemists who actually make trial mixes at the other end. In general, these are typically not the same people with the same areas of expertise. The skill set required to understand, develop and perform DFT or QM level calculations is significantly different from the skill set needed to process materials to form a new formulation. In the latter case, all of the inherent non-theoretical realities impose themselves at the bench level, and that cannot be resolved by first principles models. These include real crystals with shapes that are far from regular or the effect of microns-thick viscous flow between those particles, thus introducing concerns over actual versus desired surface wetting. Thermal effects, stirring rates, agglomeration, optimum time to add plasticizers, cross-linkers, etc. and other processing procedures greatly influence the resulting formulation. As a result, actual formulation work is generally performed on a trial-and-error basis, particularly with respect to particle fit. Within such an Edisonian process, the best formulators are those with years of experience in actually performing the work, recording both the positive and negative results and thus developing practical know-how. The most successful formulators have the ability to understand user needs and apply his practical know-how to design a formulation that will satisfy the user's requirements. Recognizing the need to retain and exploit this practical know-how while still desiring some level of M&S to provide formulation guidance, the Air Force Research Laboratory (AFRL) has embarked on the development of a collection of models which will not only provide a digital library of readily accessible formulation data but also some level of prediction of the results of the formulation in terms of energetic performance, IM performance, survivability (for Hard and Deeply Buried Target applications), producibility and cost. It is anticipated that the overall structure will work in two ways, that is, by the user/formulator as the optimizer or through use of coded optimization algorithms.

Under the user-directed approach, an individual can design a formulation based upon a given set of requirements. He selects a binder system, energetic crystals, fuels, oxidizers, etc. through a GUI menu. For example, if the selection is a cast cure, HTPB type binder system, the design tool, through the GUI interface, provides recommendations of plasticizers, cross-linkers/catalysts, bonding agents, wetting agents, etc., as well as providing a selection of other alternative components. Each component of the formulation, of course, affects the cure rate, physical properties, producibility, etc. of the formulation (Note: ultimately, the process parameters and material properties need to be captured through knowledge of the components and in-line physico-chemical modeling, but at present they will be determined through independent models or through the existing database). Calculations of the required equivalent weights/percentages of each of the ingredients are performed to finalize the proposed formulation. Information on vacuum requirements, temperature, expected pot life, is provided. From this formulation, estimates of performance are made using thermochemical codes (e.g., the CHEETAH code which provides JWL parameters, energy, detonation velocity and detonation pressure). From these, performance in specific applications can be estimated by calculating, for example, expected fragmentation distributions based upon the detonation pressure. Insensitive munition response can be estimated based upon anticipated burn rates as well as particle size and distribution. In essence, the code provides the user the means to evaluate the proposed formulation prior to mixing any test batches.

Under the second approach, the user is replaced with an optimization algorithm, in this case DAKOTA[28], which optimizes the formulation against a set of constraints or requirements and an objective function. DAKOTA (Design Analysis Kit for Optimization and Terascale Applications) is a software toolkit developed by engineers at Sandia National Laboratories to provide a flexible, extensible interface between analysis codes and iterative systems analysis methods. DAKOTA contains optimization algorithms using gradient and nongradient-based methods, parameter estimation with nonlinear least squares methods, uncertainty quantification with sampling, reliability, and stochastic finite element methods, and sensitivity/variance analysis with design of experiments and parameter study capabilities.

Obviously, the aforementioned methodology is not first principles; however, merging the virtual design tools described in Section 3.2 with emerging formulation predictive capabilities envisioned in this section will strengthen this important component of the DoD energetics effort. Until the formulation design tool is populated, given the budgetary requirements, every effort must be made to retain the experience of the formulators who have served over the past 30-40 years. The objective of this approach is to capture that experience, update it with models as they improve and enhance the capabilities of those personnel actively engaged in the formulation part of DoD energetics.

3.4 Exploration of Novel Energy Releasing Concepts Using M&S

The dream of EM synthesis is to create molecules that are usable and store energy many times that of existing molecules. But it is generally acknowledged that the discovery of new, more powerful, but still practical explosive molecules has been stagnant over several decades now. At present there is not much more than a dozen that are in military application. There has been no practical molecule synthesized that exceeds the energy density of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL20), discovered about 20 years ago. Recent attempts are reviewed in Ref. 29. Additionally, there exists a not-well-recognized work that showed the existence of a first principle limitation on stored energies for systems of separated ionic species.[30]

An obvious alternative to developing more energetic molecules is to add energetic constituents to explosive compositions consisting typically of energetic crystals, binder materials, and additives such as metal particles. Heterogeneous compositions have advantages in that the response can be tailored to the application including non-intentional reactions as may occur in an accident environment. Binders lock constituent particles into locations to ensure reaction transport occurs in the required time scale. With the exception of TNT, most binders have been inert. However, inert binders can be replaced with energetic binders as well. Efforts based on metal additives are associated with a variety of names that reflect either the composition and/ or mechanisms. They are Metal Augmented Charge (MAC), Solid Fuel Air Explosives, Thermobarics, Shock-Dispersed Fuels, Hybrid Energetics, Structural Energetics, etc. In these materials the phenomenon of detonation may be fundamentally different and is referred as non-ideal detonation or heterogeneous detonation, where energy release may occur in many stages. Although there is intense activity in formulation design using metal additives[31], questions remain of how, when and where we can (if we can) burn the particles to generate additional energy and/or gaseous products to enhance the working fluid. Since typical explosives do not contain excess oxygen (many of them are in fact oxygen deficient), burning additional fuels in the explosive product gas does not necessarily result in a significant energy gain. In addition there are still inadequately understood questions such as heating of the particles and speed of particle combustion in the environment of not only the explosive product gas, but also subsequent expansion into air, to name a few. Unlike explosives, metallic fuels and oxygen are not combined at the molecular level; consequently the art of releasing energy from metals or other energetic materials using the power of detonation energy requires a deep understanding of not only the explosive's detonation, but how it interacts with other energetic materials, including air. To exploit the high energy density stored in reactive materials requires the understanding of the entire process from beginning to end, including terminal effects. The process includes detonation, breakup of case, and near and far field transport of explosive gas and particulate fragments. A complicating factor is that the transport events take place in air; as a result, product gas, fragments, and air create a complex high temperature reactive flow that resembles a volcanic eruption and subsequent hyper-clastic flows. Such complex, inherently multi-scale multi-physics phenomena can only be captured through multi-scale modeling and simulation.

M&S can also be used to identify and explore novel non-traditional energy-releasing concepts that cannot be easily examined using current experimental methodologies. One of the more promising concepts being explored involves release of stored structural energy in the form of stress or strain in metastable states of materials. This concept, termed Structural Bond Energy Release (SBER), originated from interesting experiments performed by Bridgman,[32] in which he first compressed various non-detonable organic and inorganic materials to high pressures in a diamond anvil cell (DAC), and suddenly introduced a shear. For several of these systems, this combination of pressure and sudden shear resulted in explosions; in fact, Bridgman reports that several non-detonable materials "detonated" under these conditions. Whether or not these are "true" detonations in a formal sense, the result was energetic enough to destroy both the samples and the DAC.

These experiments generated little interest in the United States scientific community, with one notable exception: Edward Teller, the "father of the hydrogen bomb" reported that table sugar would explode in a Bridgman experiment.[33] Conversely, the former Soviet Union (FSU) developed large research programs for exploring the physical and chemical responses of materials subjected to high hydrostatic pressure plus shear deformation (HP+SD). FSU efforts are reported to have begun in the mid-1960s at the Institute of Chemical Physics of the USSR Academy of Sciences under the direction of N. S. Enikolopyan. Enikolopyan was especially interested in polymerization under HP + SD conditions, but performed other investigations of chemical reactions of organic and inorganic substances under HP + SD. He observed that the "nature of occurrence of chemical reactions in solid substances" was radically different from "the occurrence of these same reactions in gas and liquid phases"—i.e., the reaction rates were higher than in the liquid phase, and were not dependent on temperature. Also, solid phase mass transfer rates, usually very slow, were substantially accelerated over that of the liquid phase reactions. In a dramatic demonstration of the acceleration of chemical reaction due to mechanical stressing, Enikolopyan subjected thermite mixtures (which produce non-explosive, exothermic solid-solid reactions) to Bridgman experimental conditions[34]. The result was a "cold detonation", i.e., a detonation wave in a solid that does not form gaseous products and which occurred at room temperature. He reported that all types of "characteristic reactions" occurred, but the solid-solid reaction rates were several orders higher than in the liquid phase, and that the rates of mass transfer were accelerated by 8-12 orders of magnitude higher than what is usually observed in the solid phase. Additionally, the mass transfer and reaction rates were not temperature dependent.

While it is clear that mechanical action on a system can accelerate chemical reaction (breaking or formation of chemical bonds), the fundamentals of the mechanochemical processes are unknown. Questions exist as to whether the mechanical action a) breaks covalent bonds, thus creating reacting centers, or b) whether the weaker intermolecular bonds in solids are broken, resulting in micronized structures in which reacting centers are optimally aligned for thermal activation, or c) whether the mechanochemical response is due to a combination of both mechanisms. Whatever the result, mechanochemical reactions appear to be distinguished from conventional thermally-activated solid state chemical reactions. A recent review on mechanochemical synthesis states "*The review of published data demonstrates that many organic syntheses can be carried out by the mechanochemical method; however, systematic research in this field is barely carried out and can hardly be expected in the near future*."[35] Activity in this area is starting to grow in the United States, but still is limited to very few groups, with virtually no activity devoted to theoretical exploration, and most work relating to EM devoted to exploration of Reactive Materials. However, M&S, unlike experiment, is not affected by the extreme conditions of HP + SD experiments that render obtaining and interpretation of experimental information difficult, and is well suited to provide a theoretical interpretation of the experimental findings of Bridgman, Teller and Enikolopyan of accelerated chemical reactions in pre-stressed solids. Identification of the conditions and factors that control conversion of the materials to products under HP + SD conditions can then be used to develop capabilities for the design and implementation of disruptive energetic materials in which the energy release is mechanochemically controlled.

Mechanically stressed solids can produce other types of *autowave behavior* such as rheological explosion (i.e., material response similar to that observed from seismic activity due to sudden releases of stress along fault lines or tectonic plates) or self-sustained failure waves. A simple example of explosive energy release due to self-sustained failure of a non-energetic material can be found in Prince Rupert's Drops. A Prince Rupert's drop is a tadpole-shaped piece of glass that is formed by dropping a blob of molten glass into cold water. Under these conditions, the outer surface of the drop cools faster than the inner core. As the core cools, it contracts, thus producing both surface and internal stresses that result in very unusual mechanical properties. The bulbous end of the drop can be subjected to blows from a hammer or compression by pliers without damaging the material. However, if the thin tail of the drop is broken, the drop shatters explosively into a fine powder. The explosive energy release is a simple manifestation of rapid relaxation of surface tension and internal stresses. In like manner, rapid release of internal stresses within systems that are similar to Prince Rupert's drops could be used for novel energy release applications. For example, nanoparticles are known to contain stored structural energy, as evidenced by theoretical calculations for nanoparticles of Ge, Si, Au and diamonds.[36-38] This stored structural energy is due to surface reconstructions on the nanoparticles that act on the core. Theoretical explorations into characteristics of nanodiamonds (ND) report the surface reconstructions compress the core to internal pressures estimated to be in excess of 50 GPa—a tremendous quantity of stored structural energy for a ND.[39] The authors of this study hypothesized that sudden rupture of the reconstructed surface of the ND might allow for a sufficiently rapid release of residual stresses in the core that might result in an explosive event, similar to that observed in the Prince Rupert's drops.

QMD simulations of hypervelocity impacts of two ND were performed to explore this hypothesis.[39] Upon impact, a portion of each ND is sheared and compressed; as the particles separate, the material in the exposed core expands into the vacuum, ejecting a variety of small clusters and atoms moving at high velocities. As the expansion and ejection of core material into the vacuum proceeds, the remainders of the parent fragments flatten relative to the original spherical shape. Producing highly reactivity species in this manner in an atmosphere containing potential reaction partners could lead to explosive exothermic reaction, such as combustion. First principles explorations such as these can also be used to explore more fully the role of surface morphology on stored structural energy. For example, theoretical calculations on Ge and Si and Au indicate that passivation of these surfaces with species such as hydrogen can change the degree of surface relaxation and corresponding action on the core. Thus, such calculations can be used to guide the design of nanoparticles in terms of energy content, as well as provide information as to experimental conditions required to achieve the rapid relaxation required to produce the explosive energy release.

Although the theory indicates that structural energy is stored in ND and can be released explosively, experimental verification has not yet been obtained, perhaps due to impurities that might diminish the magnitude of the internal stresses. For example, most commercially-available ND is formed through detonation synthesis of a mixture of explosives; the resulting particles contain substantial quantities of impurities and a non-diamond surface structure whose exact morphology is under debate.[40] Spectral measurements of this ND subjected to high hydrostatic compression indicated a thinning of the graphitic outer shell became thinner with pressure, and no evidence of explosive energy release. Laser heating of this type of ND showed an energetic response, with the first of two studies reporting a "violent" decomposition of the ND due to a 3-fold volume expansion and accompanying CO and CO_2 gas release after laser excitation.[41] The event is characterized as "bursting" of the ND that is similar to that of popcorn popping. The second of the two studies showed a 10-fold expansion in volume after laser excitation; accompany spectral measurements led the authors to conclude that photolysis of nitroso species within the ND caused a pressure induced "popcornlike conformational change of ND".[42] Although the samples used in the experiment and the resulting material response are not directly comparable with those of pure samples used in the theoretical study, the responses suggest stored structural energy that can be released; further theoretical exploration into ND doped with impurities could shed light on the degree of the stored structural energy and could provide guidance into its controlling its release.

Structural energy in the form of stress and strain can also be trapped in metastable material states attained through subjection to extreme temperatures and/or pressures. Such extreme conditions substantially modify the electronic structure within the material, allowing for different bonding arrangements resulting in the destruction of covalent bonds leading to atomization or metallization, or, in the case of molecular solids, to non-molecular polymeric phases.[43] Significant structural energy stored in the metastable phases is then available for release upon transition back to the lower energy ground state and, if harnessed, could be used for military applications. Polymeric forms of CO, estimated to have stored structural energy approaching or exceeding that of conventional high explosives, can be synthesized with modest pressure (5 GPa) at room temperature, and are recoverable at the ambient state (although the samples slowly decompose thereafter), and have shown explosive decomposition.[43] The polymeric form of nitrogen is also of considerable interest since energy available for release upon the transition to the triply-bonded diatomic molecular ground state has been estimated to be as much as three to five times that of conventional EM.[44] Several polymorphic forms of nitrogen have been predicted from first principles calculations; however, to date only the cubic gauche form of polynitrogen has been synthesized under extreme conditions.[45] Recovery at ambient conditions has not yet been achieved. Theoretical predictions indicate that a pure crystal of cg-N should be recoverable at the ambient state, suggesting that the instabilities of the synthesized form might be due to defects or impurities. QMD simulations were used to explore the shock response of cg-N, in order to determine its potential as an advanced energetic material.[46] In the simulations, a shock wave was initiated through the crystal through flyer plate impact. Passage of the shock wave induced numerous complex phase transformations, within which defects were formed and absorbed the shock energy, slowing the compression wave as the simulation progressed. Although reaction of the shock filament occurred well behind the shock front, the energy release was not sufficient to sustain shock propagation. The shock response of the material is due to the unusual mechanical properties of this form of polymeric nitrogen, and the simulations have suggested that this form is unsuitable for use as a high explosive, although it has the potential to be a gas generator. While disappointing, these theoretical simulations refocused attention to other potential forms of polymeric nitrogen as better candidates for an advanced EM. For example, material from a highly defected region of the shocked cg-N in Ref. 46 was used to find a porous low-pressure crystalline structure.[47] Quantum mechanical dynamics simulations of the structure revealed instabilities in the material, allowing for a computational "removal" of the instabilities in the material to produce a low-pressure, low-temperature stable structure. Also, there is experimental evidence that there are other, less stable amorphous forms of polymeric nitrogen, but they have not characterized nor are they recoverable at the ambient state. Theoretical predictions[48] of these more sensitive forms of polymeric nitrogen have identified sources of instability: that of dangling bonds. QM calculations of the amorphous form in which all dangling bonds are capped by hydrogen atoms have shown that the material stability can be substantially increased. Thus, this is a dramatic example of the power of M&S in identifying factors that control stabilization of metastable materials.

To summarize, M&S, particularly those using first principles approaches, can be used in a variety of ways to identify and theoretically demonstrate novel energy-releasing materials and concepts that would otherwise not be easily found (or even possible) through trial-and-error experimentation. M&S allows for determination of factors that control amounts and rates of energy release, and provides guidance for experimental stabilization of non-traditional EMs such as those described herein for implementation in military applications. Finally, M&S can be used to rapidly and efficiently determine the viability of exotic energy-releasing concepts that have the potential to produce cutting-edge advances in disruptive military technologies.

3.5 Multiscale M&S in Energetic Systems Design

To demonstrate the importance of careful design of energetic systems, one need look no further than the obvious desire of military forces to house important assets either for safety or security, in hardened, underground bunkers. Figure 3.1 is a picture of a structure used to house German submarines during WWII after being attacked by a weapon known as Grand Slam[49]. The roof was approximately 15 feet of reinforced concrete. The explosive fill was TORPEX, a mixture of RDX, TNT and aluminum powder. In general, TORPEX is relatively sensitive to mechanical loading as happens during a penetration event; therefore, the nose of such a weapon is typically filled with an inert material to cushion the impact. As Grand Slam was used with great success during WWII, it is hard to argue with its design. It is also an indication of the excellent engineering by the designer (B. Wallis). The Grand Slam weapon was essentially hand made. The TORPEX was poured into the bomb cavity and allowed to cool slowly over a month, to reduce voids and cracks that might make the explosive fill more sensitive.

While Grand Slam remains an engineering marvel, targets have gotten harder, defenses are better and the structures themselves are better designed to minimize blast damage. As a result, more energy is required on target and the fills are subjected to greater loads. Therefore, the warhead designer must understand the loads the weapon will be subjected to, the duration of those loads, the end game lethal requirement, and all fuzing considerations. This information must be passed on to an explosive formulator with the skills required to meet the weaponeering requirements. Therefore, the formulator's toolbox must contain a means to estimate performance, survivability, IM response and typical processing requirements.

Figure 3.1: Grand slam bunker buster WWII

In general, thermo-chemical performance codes such as JAGUAR[50] or CHEETAH[51] are available and have been developed to such an extent that for most explosives, the calculated performance is within a few percent of measured performance. However, we cannot yet calculate other performance attributes to the same level of predictability as that demonstrated by thermo-chemical codes for energy output and equilibrium thermodynamical properties. Non-predictable properties are typically screened using small scale tests with specific systems for specific threats. As noted by B. Asay[52] that "even with all of the study and the hundreds of years of experience (black powder, first explosive, is said to be discovered in China in the 11th century), we still cannot predict with any precision, in general, what will happen to an explosive if we hit it, heat it, drag it, drop it, or do anything else outside of its design envelope." This inability reflects the fact that chemistry initiates, responding to local temperature conditions. In the case of mechanical insults, it is generally believed that mechanical deformation due to, say impact or other type of insults, produces hot spots which grow over time and may cause unintended chemical initiation of the fill, and results in subsequent explosive reactions or even detonation. Thus, non-predictable properties are typically screened using small scale tests with specific systems for specific threats and the prevailing practice of explosives design is heavily dependent on designer's experience and intuition. Even when M&S tools are used in design, they are mostly system specific and have a high level of empiricism and associated inaccuracies.

This inability to predict explosive response can be attributed to a lack of appropriate models that capture the influence that material heterogeneities inherent in explosive formulations impose on its response. Most military explosives are heterogeneous composites of materials, at least one of which is a high explosive. With a few exceptions, most explosives crystals come in powder form, and are consolidated with a binder to form a solid explosive charge for use as booster or main charge. The term "formulation" is typically used for development of main charges which are composites of materials, at least one of which is a high explosive, consolidated with a binder. A formulation is designed to provide necessary energy output that delivers desired effects, be it blast or fragments moving at high speeds or other types of effects such as shaped charge jets or any combination thereof. Currently-used explosive fills are composites made of explosive crystals that are bonded together with other constituents such as metal particles, oxidizers, and minor constituents to help assure mixing and chemical compatibility. The metallic and oxidizer particles are added not only to boost performance, but also to create system specific effects. Typically main charges are fabricated by a melt-cast or cast cure process, depending on the choice of the binder. The result is an inherently heterogeneous microstructure as shown in Figure 3.2 (comparable microstructures are seen for concrete and geological materials).

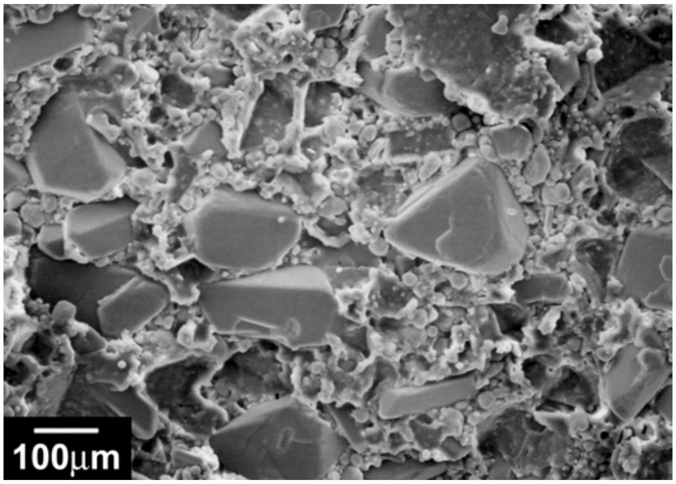

Figure 3.2: Microstructure of modified PBXN-109

The distributions of, for example, particle size, size distribution, and particle morphology are obviously probabilistic unless of course some bias exists because of processing (e.g., clustering of particles resulting from inadequate mixing or preexisting strong agglomeration). One of the profound consequences of the heterogeneous composition and the processing is that a) important microstructural attributes of the explosives become stochastic at the grain scale, and b) calculations (and measurements) of an explosive's response to thermo-mechanical stimuli (hitting, heating, dragging, scraping, etc.) must address multiscale issues both in time and space: averaged quantities are not adequate to describe the first-order influence of small scales or short time events on much larger scales or long time events. What is worse, the aforementioned stochastic microstructure attributes cause stochastic physico-chemical processes that are induced by external stimuli. Hindrances to establishing the requisite predictive capability are compounded by a) experimental difficulties resulting from the extreme pressures and temperatures created in the EM response and b) a lack of fundamental understanding of chemistry and hydrodynamics under the extreme conditions and temperatures that need to be represented in the models.

Despite these difficulties, it is critical that a predictive capability for energetic design be pursued. Otherwise, there will be perpetuation of current M&S tools that have high levels of empiricism and inaccuracies. These uncoupled models will never be sufficient to extrapolate beyond existing threats, and thus there will be continued reliance on full-scale testing to parameterize the models. This, in turn will increase program cost and schedule risk in the design, development and fielding of weapons that utilize the EMs. M&S based design will allow for cost-efficient, expedient exploration of new capabilities and effects, will reduce reliance on costly and time-consuming experimentation and will lead to the modeling, analysis and understanding of a vast array of energetic materials and complex formulations. Ultimately, this capability will enable cost-efficient, expedient design of new advanced weaponry.

The predictive capability must be an integrated suite of multiscale modeling and simulation (MM&S) tools so that the variety of complex processes and structures at time and lengths scales ranging from the atomistic (nanoscale) through continuum (mm and above) can be properly modeled. As stated earlier, most of the existing M&S tools are based on continuum mechanics. Current models have limited physical descriptions and extensive simplifying assumptions and approximations. The models use constitutive parameters and relations that describe physical and chemical properties and processes of materials that dictate material response; often these parameters and relations are empirically derived. Thus current continuum capabilities are oversimplified, and are not agile and transferable between multiple materials and threat scenarios. The atomistic scale models used in EM research are fairly mature; however, computational restrictions preclude direct application to the time and length scales larger than the nano-regime. Thus, atomistic modeling of EMs usually depicts overly simplified, highly idealized systems within which the aforementioned microstructural heterogeneities that control material response are not included.

M&S capabilities to address the intermediate (mesoscale) regime that corresponds to microstructure are in the earliest of development for use in EM research; little to no experimentation to interrogate this time and spatial regime is available to ensure that the models and simulations are valid. Mesoscale understanding is the lynch pin of explosives research that stands between molecular scale physics and macroscopic or system level response behavior. Materials are considered homogeneous both at the microscopic and macroscopic scales, but as shown in Figure 3.2, they are inherently heterogeneous and stochastic. Unfortunately, that is the scale that needs to be bridged to connect synthesis to performance.

Thus, the current state of MM&S for EM response consists of a collection of disjointed models at various scales (with very few at the crucial mesoscale); further, those currently used for munition design do not incorporate sub-continuum M&S descriptions of various thermophysical, chemical and mechanical materials processes that affect threat response. Instead, the simplest of MM&S efforts involve replacing empirically-derived constitutive parameters and/or relations that describe relevant chemical and physical properties of the system (e.g., pressure-dependent strain rates, chemical kinetics, or material equations of state) with sub-continuum M&S results. Even this is insufficient to enable a robust predictive capability: the zeroth-order approximations inherent in the current hydrodynamic models of EM hinder their applicability to a wide range of materials and threat scenarios, despite the quality of the constitutive parameters that are provided. Thus, in addition to developing sub-continuum M&S capabilities to produce detailed descriptions of microstructural heterogeneities, chemical reaction, and energy flow resulting in EM response, the physical descriptions (the physics) within hydrodynamic models of EM must be improved in order to accommodate the subscale information.

Recognizing these deficiencies, the DoD has invested in developing M&S programs for Energetic Systems Design that are evolving to address the multiscale issues. Efforts underway include the development of (i) mathematically rigorous multiscale modeling methodologies capable of coupling behaviors from the atomic scale through full scale system, (ii) computational simulation frameworks built around this methodology into which techniques for investigating behaviors at the various scales can be effectively integrated, and (iii) proof of concepts of the developed core technologies using synergetic interactions with experimental work. One key effort was initiated in 2008, in which the ARL and ARDEC, under DoD High Performance Computing Modernization Program support, established a Software Applications Institute for Multiscale Reactive Modeling of Insensitive Munitions (MSRM-IM). The MSRM-IM mission is to establish, demonstrate and disseminate a completely-coupled framework of MM&S tools for use in developing and optimizing new IM and for improving existing munitions to meet IM compliance. The MSRM-IM technical program, coordinated with Army, AF and Navy mission programs, intends to accomplish that mission by enabling M&S capabilities that will adequately capturing the effects that microstructural heterogeneities inherent in composite EMs impose on macroscopic events through MM&S of EM Response. This software development activity builds on existing core programs in traditional M&S of EM at ARL, ARDEC, and Institute partners at AFRL and NRL. For example, mission efforts at ARL and ARDEC were augmented to support the MSRM-IM by providing the basic and applied research required to develop or refine methods and theories for implementation into MSRM-IM software and to provide advanced experimentation to validate theoretical results. Army teams have focused on developing sub-micron dynamical simulation methods to generate details of microstructural deformation and damage for use in higher scale codes. Crucial scale-bridging technologies allowing for multiscale depiction of chemical events in an EM are being developed by MSRM-IM Institute partners at the AFRL. AFRL researchers are developing meso-level reaction models for use in continuum level simulations; inputs for the reaction models will use results from the finer-scale models of microstructural damage calculated by the ARL Institute team. ARDEC researchers, in turn, are working with AFRL to couple the quantum-informed mesoscale reactive burn model with detonation hydrocodes. Finally, the fundamental chemical rules used in the meso-level reaction model are being generated from QM calculations by Institute partners at the NRL. This tri-service activity represents cutting-edge advances in continuum level modeling of EM response to insult through proper descriptions of microstructural heterogeneities and energy release, and will be used for development of IM-compliant munitions. DoD is also leveraging efforts at DoE laboratories under the DoD/DoE Joint Munition Program MOU (TCG-I, III); within which MM&S methods and software are being developed to address some of the numerous technical challenges within this area.

From a warhead design perspective, the reliability of the overall weapon system must be understood in order to perform required weaponeering. Current targets may require penetration events with durations of hundreds of milliseconds to a second. This requires that the fill be designed to minimize hot spots which may be controlled through particle size, shape and type, binder selection and solids loading. Inadequate control of these issues is known to have produced premature initiation of the explosive fills for use in high speed penetrator weapons that are subjected to large inertial and shear forces that cannot be tested by conventional safety tests.

Efforts are underway at AFRL/RWME to develop an entire M&S system which will address these concerns. The on-going AF efforts at the Munitions Directorate are very complimentary to the MSRM-IM program at ARL and ARDEC: that of changing the paradigm of explosives design/ formulation process from one that is characterized by phrases such as “empirical”, “*ad hoc*”, “qualitative”, and “disjointed”, to one that is M&S-based, and can be characterized by phrases such as “integrated”, “quantitative”, and “analytical”. Ultimately, the change will result in not only reducing weapon development cost and time, but also increased explosives reliability and optimum performance.

The AF efforts comprise several components that address key issues at the grain scales where the heterogeneous nature of the materials must be explicitly represented. The first is the capability to relate hot spot dynamics to microstructure attributes, such as packing density of crystals, particle size distribution, binder and crystal properties. Currently this component is based primarily on two codes in two spatial dimensions: a Cohesive Finite Element Code (XCFEM developed at Georgia Tech)[53] and a hydrocode developed at Louisiana State University (denoted LSU code hereafter)[54]. The major differences between the two are (1) XCFEM includes fracture and is primarily concerned with non-shock deformation, and (2) the LSU code is used to simulate high-pressure shock compression without binder and fracture effects. Limitations of 2D calculations are well known, but these capabilities will give basic characterization of fracture, frictional heat generation, and thermal conductivity that might be useful for future 3D studies. It is thought that trends and relationships observed in 2D will provide a useful guide to future 3D studies.

The main features of XCFEMX are:

- fully dynamic finite deformation kinetics and kinematics, coupled thermal-mechanical constitutive descriptions of materials, rate-dependence, strain/thermal softening, and heat generation and conduction;
- ability to predict and track arbitrary intragranular, transgranular and interfacial fracture, and contact;

- accounting of bulk (viscoelastic, viscoplastic) and interfacial frictional heating;
- accounting of actual or computationally synthesized microstructures with any combination and any number of hyperelastic, elastic-viscoelastic, elastic-viscoplastic constituents; and
- choice of loading/boundary conditions: prescribed velocity (strain rate), impact loading, and non-reflective boundary.

The LSU code is a combined finite and discrete element method that is well suited for problems involving heterogeneity. This combined method uses the finite element method (FEM), coupled with a radial return stress update algorithm, to numerically integrate the time-dependent, 2D conservation principles and visco-plastic flow rule governing deformation of individual particles, and uses the discrete-element method (DEM) to account for interactions between particles. The DEM is based on a distributed, conservative potential-based penalty method whereby the normal contact traction between particles is estimated by penalizing their penetration, and frictional tractions are estimated using a penalty regularized Amonton's Coulomb law. Particles are discretized using constant strain, triangular finite elements, where each particle consists of several hundreds of elements. A temporally second-order accurate, explicit numerical technique is used to integrate the FEM equations for nodal displacements and temperatures.

The second major component of the AF efforts is an ignition model using the hot spot dynamics that captures the collective essence of stochastic material properties as well as deformation processes at the grain scale. The aforementioned meso-scale modeling principally accounts for hot-spot formation enabling spatial and temporal characterization of hot-spot size and temperature distributions that are important for ignition but are difficult to experimentally resolve. By combining predicted inert hot-spot distributions with thermal explosion data and analysis, it is possible to estimate both the distribution of hot-spot ignition times and the local fraction of ignited mass as a function of wave strength for a material having a prescribed composition and meso-structure. This information is then used with a stochastic theory to estimate the early time ignition (or local ignition) probability of the material as a function of wave strength. Local ignition, which occurs at the particle scale, is a necessary precursor to global ignition associated with a measurable event. The stochastic theory currently under development is an extension of the theory first developed by Terao[55] to estimate the ignition probability of reactive gas mixtures based on measured thermal explosion time data. The resulting theory is a first step in establishing a framework for constructing physics-based ignition performance maps for different materials using resolved meso-scale computations. This map summarizes the variation in local ignition probability with deformation wave strength (usually expressed by the effective temperature behind waves). Such maps would provide engineers with an additional tool to assess the relative impact sensitivity of explosive formulations.

The third and final major component of the AF efforts is the creation of a virtual design environment where designers can formulate explosives or raise "what-if" questions and get answers based on real-time interactive simulations. With virtual design tools, they can test their hunches and see consequences in a trade space between, say, performance and ignition probability. This software couples the models and information gathered from the first two steps with continuum mechanics structure codes which will allow not only predict survivability but also provide margin. One of the essential aspects of engineering is the ability to design a structure based upon a set of requirements and then meet a predetermined factor of safety or margin requirement. Currently, explosive survivability is based upon a comparison between the predicted response of the fill to a penetration event and various test results such as the Intense Pressure and Friction Test[56]. Since the data scatter in those particular tests is not well defined, the designer simply selects an arbitrary level below the minimum reaction observed in the test. For a weaponeer, this does not provide a well-defined tabulated design space in which he has confidence. The proposed approach is to link the meso-scale data into a continuum approximation coupled with target specific effectiveness requirements, and evaluate and modify the overall design concept as required to meet not only the mission requirements but also to provide the design margin. If a specific lethality requirement is known and coupled with survivability (Ignition Probability) information, the designer can select his options based upon normal risk/performance trade-offs leading to an overall engineered solution.

The virtual design environment is a significant enhancement over current capabilities and its potential impact in advanced weapon design should not be underemphasized. For example, one penetrator bomb contains about 5000 lbs. of explosive encapsulated within a few inch thick casewall. However, given the large amount of explosive used, the statistical likelihood of a measureable defect in the fill is high. Since the energetic crystals in AF explosives are controlled through MIL Specs (5% Class 1 RDX and 200 micron Ammonium Perchlorate), the potential for defected crystals (e.g. uncoated or cracked crystals, etc.) is relatively high. Measureable voids and other macro-scale defects exacerbate hot spot formation at the meso-scale. The penetration event for such a bomb is relatively long, allowing multiple cycles for compression, expansion and relative motion of the fill within the case. This motion, particularly near interfaces, allows for inter/intra granular friction, cracking and, perhaps, the development of hot spots which begin small scale energy release thereby increasing the temperature. Normally, reducing the solids loading reduces hot spot formation since crystals should be further apart and more easily fully coated. Survivability should obviously increase. However, reducing the solids loading reduces the energy introduced into the target thereby rendering the weapon less capable. The trade-off becomes a matter of required lethality versus required survivability. However, if that trade-off is well posed, the weaponeer can then assess all of the risks, from the ability of the platform to penetrate enemy airspace to that of the energetic fill to provide the lethal defeat mechanism in the target space to accomplish the mission objectives. Currently, if a warfighter requests a survivability estimate of the explosive fill against a given target, only qualitative estimates can be provided. The goal of the virtual design environment is to change qualitative estimates to quantitative.

In summary, the brief description of Army and AF efforts in MM&S in Energetic Systems Design in this section clearly show that there are numerous unsolved issues to be addressed, technology gaps to fill, and grand challenges both in theory and computer simulation. However, continued development of these capabilities will produce short and long term payoffs for advanced gun, missile and rocket propulsion, naval bombardment, and hard and deeply buried target technologies. New materials that will deliver greater lethality in these weapons systems will be produced through exploiting MM&S information to design materials with specific performance properties (including burn rates, controlled energy release and flame temperature, superior mechanical and rheology properties, low vulnerability, and hypervelocity propulsion). Predictive capability is a must for making design choices [see Kadanoff in Section 3.1] and will enable exploration of new capability and effects, while ensuring cost avoidance, schedule savings and increased system reliability.

3.6 Acknowledgements

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Chapter 4

Energetics in the Rest of the World

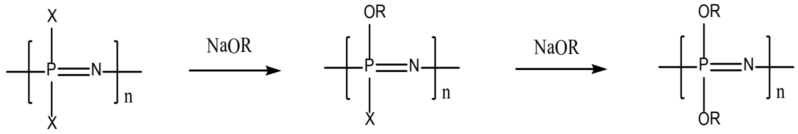
Thomas M. Klapötke and James M. Short

In this chapter the authors give a brief overview of energetic materials research ongoing in "the rest of the world" with special emphasis on the following countries: United Kingdom, Germany, Sweden, Poland, Japan, South Korea, France, Russia, India, and the Czech Republic. This review is not exhaustive in scope. The focus is on recent developments.

4.1 United Kingdom

Energetic Polyphosphazenes

In the search of increased safety in PBXs (Polymer Bonded Explosives, Plastic Bonded Explosive), energetic polyphosphazenes [PolyPZ] are studied at the Atomic Weapons Establishment Aldermaston, at Cranfield University and at QinetiQ. The polyphosphazenes are synthesized from poly[bis(2,2,2-trifluoroethoxy) phosphazene] or polydichlorophosphazeneby displacement of the CF3CH2O or Cl groups by potentially energetic alkanoxy groups (Scheme 4.1). The latter may contain (i) protected diolfunctions which can subsequently benitrolysed to dinitrato moieties (nitratopolyPZs), or (ii) azido groups (azidopolyPZs). The extent of substitution, and hence the energetic content and physical properties of the polymer, can be varied by suitable choice of experimental conditions.



Polyphosphazene I II

Scheme 4.1: Polyphosphazene

Where R is the potential energetic side group and X is the CF3CH2O or Cl group. Progressive substitution of the side group yields multiple products (I or II) with controllable physical properties. Some typical examples of energetic polyphosphazenes are:

linear $[NP(OCH_2CF_3)_{2-x}(OCH_2CH(ONO_2)CH_2ONO_2)_x]_n$

linear $[NP(OCH_2CF_3)_{2-x}(OCH_2CH_2CH(ONO_2)CH_2ONO_2)_x]_n$

linear $[NP(OCH_2CF_3)_{2-x}(OCH_2CH_2CH_2CH_2CH(ONO_2)CH_2ONO_2)_x]_n$

linear $[NP(OCH_2CF_3)_{2-x}(OCH_2CH_2CH_2N_3)_x]_n$

linear $[NP(OCH_2CF_3)_{2-x}(OCH_2CH_2CH_2CH_2CH_2CH_2N_3)_x]_n$

where n is the degree of polymerization and x is the degree of substitution ($0<x\leq2$). For structure I, $0<x<2$; when $x=2$, formed when X=Cl, the products are homopolymers (structure II). The basic reactions (substitution and nitrolysis) have been scaled up from g to kg scale.[1]

Attractive properties of the energetic PolyPZs are (i) rubbery binders, (ii) compatibility with many common energetic fillers viz. HMX, FOX-7, HNS, TATB, (iii) improved performance and hazard characteristics compared with existing binders e.g. polyGLYN, (iv) generally low Tg values.[2] In addition, the azido systems, promising as binders in propellants, may be cured, utilizing uncatalysed ‘click chemistry’, with methylene bis(p-phenylenemaleimide) as curing agent, i.e. without isocyanates.

LLM-105 [2,6-Diamino-3,5-dinitropyrazine 1-oxide]

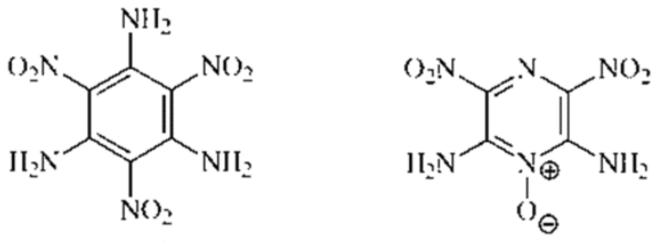
LLM-105 is a relatively new ‘IM’ explosive, which originated at Lawrence Livermore National Laboratory. LLM-105 has characteristics similar to, if not better than, those of TATB (Scheme 4.2, Table 4.2).

Table 4.1: Physical properties of energetic PolyPZ compounds

Polymer	Decomposition Energy DSC (J g^{-1})	Density (g cm^{-3})	Energy Density (J cm^{-3}) [%higher than PolyGLYN]	Glass Transition Temperature (°C)
Homo PolyPZ (II)				
C3 dinitrato PolyPZ	2690	1.69	4550 [57]	-32.5
C4 dinitrato PolyPZ	2880	1.65	4750 [63]	-23.8
C6 dinitrato PolyPZ	2760	1.45	4002 [38]	-35.2
C3 monoazido PolyPZ	1825	1.35	2465	-73
C6 monoazido PolyPZ	1665	1.16	1930	-99
Mixed Substituent* PolyPZ (I)	2020-2430	1.52-1.65	3333-3792	-13 to -55
PolyNIMMO**	1300	1.26	1638	-33.0
PolyGLYN**	2000	1.45	2900	-30.0

* Mixed Substituent PolyPZ (I) indicates that the polymer contains a random mixture of energetic and non-energetic (X =CF3CH2O) substituents along the -P=N-P=N-P=N- chain.

** Established carbon- based reference energetic polymers.



TATB LLM-105

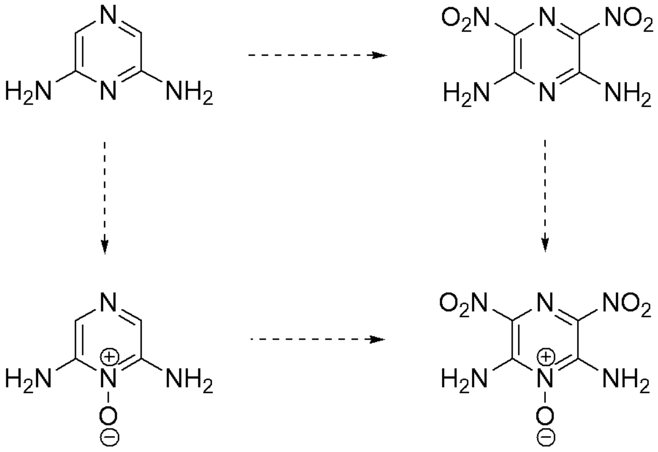
Scheme 4.2: Structures of TATB and LLM-105

Table 4.2: Physical properties of TATB and LLM-105

Compound	Dec. (°C)	Density (gcm^{-3})	V_{calc} (ms^{-1})	P_{calc} (kbar)
TATB	350	1.93	7870	278
LLM-105	354	1.92	8730	359

LLM-105 exhibits low impact and friction sensitivity. It is somewhat more sensitive than TATB but still relatively insensitive and yet more energetic. The energy content is ~81% of HMX, ~20% more than TATB.

Unfortunately, there is at present no efficient synthesis of LLM-105. The commonly used 4-stage, synthetic route from the expensive 2,6-dichloropyrazine gives an overall yield of ~46%. Research groups at AWE Aldermaston and Cranfield University have explored alternative routes to LLM-105,[3] the most interesting of which involves nitration of 2,6-diaminopyrazine 1-oxide. However the best yield of LLM-105 by this route was only 57% (nitration stage only). The starting material for this synthesis may be prepared by 2 routes. An alternative route, involving nitration of 2,6-diaminopyrazine, was complicated by side reactions (Scheme 4.3).



Scheme 4.3: New potential routes to LLM-105

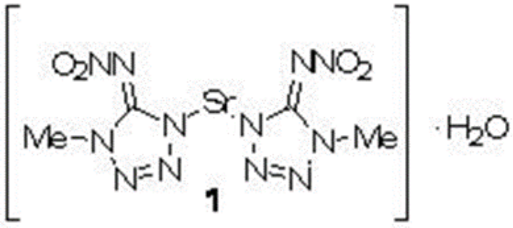
4.2 Germany

The main research area at Ludwig-Maximilian University (LMU) in Munich, Germany is high (secondary) explosives.[4a,b] Other research has been conducted at LMU using high-nitrogen compounds:

- RDX Replacements (HEDM, High Energy Density Materials)
- Lead-free Primary Explosives
- High Oxidizers (HEDO, High Energy Density Oxidizers)
- Nitrogen-Rich Propellants
- Energetic Polymers
- Non-Polluting Pyrotechnical Compositions (visible)
- Alternative Magnesium/Teflon/Viton-Flares (MTV)
- Infra Red Illuminants
- Agent Defeat Weapons (ADW)

High-Nitrogen Pyrotechnics

In the area of perchlorate-free red light illuminants, LMU developed high-Nitrogen strontium containing salts as colorants (Scheme 4.4) that were used by Army Armament Research, Development and Engineering Center (ARDEC) to design high-nitrogen based pyrotechnics.[5a,b] In this context, the full-up prototype testing of perchlorate-free hand-held signal formulations for the US Army's M126A1 red star parachute hand-held signal has been described. Compared to the perchlorate-containing control, the disclosed formulations were found to be less sensitive toward various ignition stimuli while offering superior pyrotechnic performance. Militarily, the new formulations provide further evidence that development of shorter hand-held signals in an environmentally conscious way is a realistic and obtainable goal (Table 4.3–Table 4.5).



Scheme 4.4: Molecular structure of strontium bis-(1-methyl-5-nitriminotetrazolate) monohydrate

Table 4.3: Perchlorate-free formulations A and B

Formulation **A**		Formulation **B**	
Components	Wt %	Components	Wt %
Strontium Nitrate	39.3	Strontium Nitrate	39.3
Magnesium 30/50	29.4	Magnesium 30/50	35.4
PVC	14.7	PVC	14.7
Bis-Tetrazolate **1**	9.8	*Bis*-Tetrazolate **1**	3.8
Epon 813/Versamid 140	6.8	Epon 813/Versamid 140	6.8

Table 4.4: Small-scale performance of formulations A and B against the control

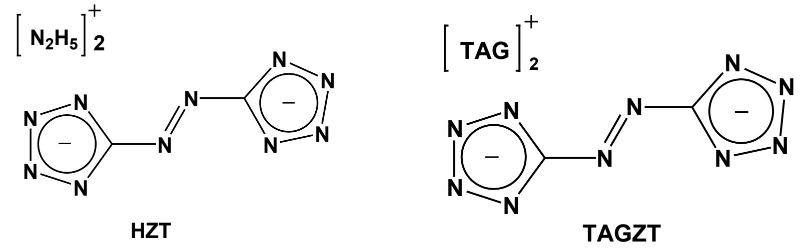
Formulation	Burn Time [s]	Luminous Intensity [cd]	Dominant Wavelength [nm]	Spectral Purity [%]
Control	32.2	423.5	623.0	86.4
A	39.4	544.3	620.6	89.1
B	35.6	812.8	618.2	90.6

Table 4.5: Performance of formulations A and B against the perchlorate-containing control at the prototype level

Formulation	Burn Time [sec]	Luminous Intensity [cd]	Dominant Wavelength [nm]	Spectral Purity [%]
Military Requirements	50.0	10,000.0	620 ± 20	76.0
Control	54.0	17,194.9	613.1	88.6
Formulation A	63.3	16,285.0	612.5	89.9
Formulation B	55.1	24,490.1	612.7	91.6

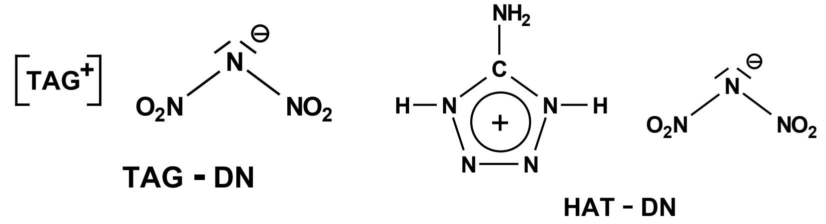
High-Nitrogen Energetic Materials

Researchers have almost reached the upper bound of energy content limit for CHNO-based molecules. To further increased energy content research into different molecular structures and molecular make-up is ongoing. Materials with high nitrogen content offer advantages over those with carbon backbones, including the potential for increased energy content. Research at LMU into molecules with high nitrogen content (>50%) has shown potential for increased energy content. High-nitrogen compounds such as hydrazinium azotetrazolate (HZT) and triamino-guanidinium azotetrazolate (TAGZT) (Scheme 4.5) [1,2],[6a-c] are nitrogen rich and have desirable ingredients for erosion-reduced gun propellants. However, due to the unfavorable oxygen balance, such compounds are not suitable as energetic fillers in high explosive compositions. Their effectiveness in gun propellant formulations is being explored at the Naval Surface Warfare Center, Indian Head Explosive Ordnance Disposal Technology Division by Dr. Christine Michienzi.



Scheme 4.5: Chemical structure for HZT and TAGZT

TAG-DN or HAT-DN (Scheme 4.6) are high-nitrogen compounds with favorable oxygen balances. These compounds are more suitable for high-explosive formulations. Both are in the preliminary stages of laboratory investigation (Table 4.2).[7a-c] Materials with an oxygen balance close to zero are also suitable as powerful ingredients in solid rocket propellants. An increase of the I_{sp} of only 20 s would be expected to increase the payload or range by ca. 100%. Figure 4.1 shows the computed I_{sp} for an isobaric combustion (at 20 bar) for AP/Al (70:30), HAT-NO3, HAT-DN and TAG-DN.



Scheme 4.6: Structures for TAG-DN and HAT-DN

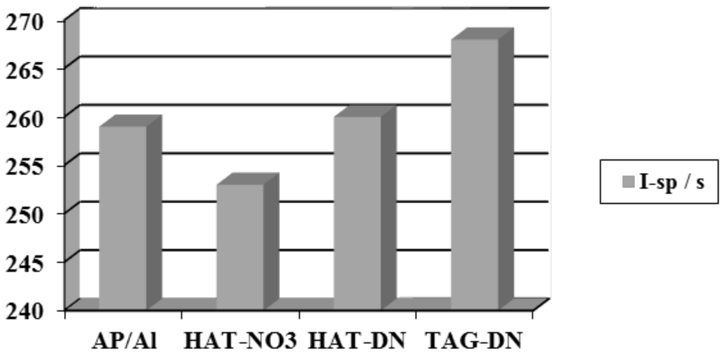
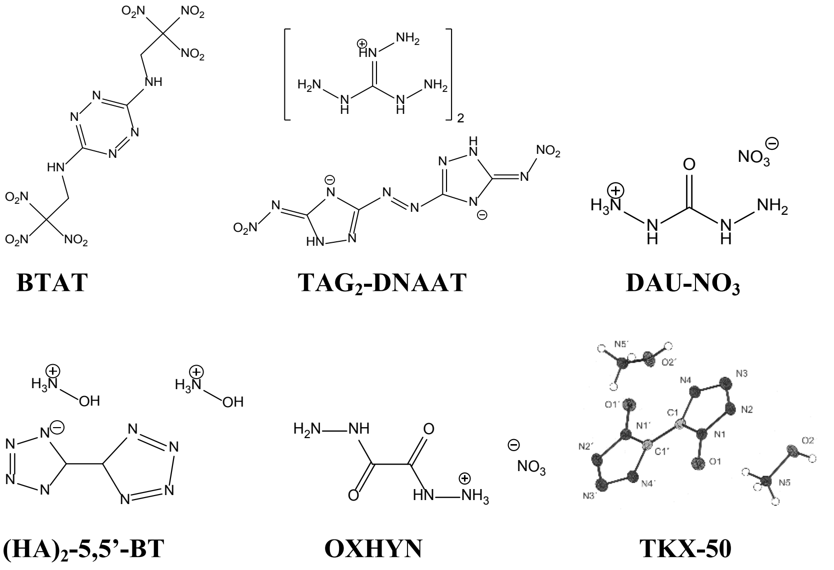


Figure 4.1: Computed specific impulses (I_{sp}/s)

In the area of high-performing insensitive secondary explosives, amongst others, the following molecules were developed at LMU: BTAT, TAG_2-DNAAT, DAU-NO_3, $(HA)_2$-5,5'-BT, OXHYN and TKX-50 (Scheme 4.7, Table 4.6).[8a-b]



BTAT **TAG_2-DNAAT** **DAU-NO_3**

$(HA)_2$-5,5'-BT **OXHYN** **TKX-50**

Scheme 4.7: Molecular structures of BTAT, TAG_2-DNAAT, DAU-NO_3, $(HA)_2$-5,5'-BT, OXHYN and TKX-50

Table 4.6: Physical properties of BTAT, TAG$_2$-DNAAT, DAU-NO$_3$, (HA)$_2$-5,5'-BT, OXHYN and TKX-50

	IS / J	FS / N	$T_{dec.}$ / °C	VoD / m s^{-1}	p_{C-J} / kbar
BTAT	7	168	189	9261	389
TAG$_2$-DNAAT	>40	>360	212	8694	282
DAU-NO$_3$	11	>360	200	8829	317
(HA)$_2$-5,5'-BT	10	240	200	8858	343
OXHYN	11	>360	270	8655	327
TKX-50	20	120	221	9686	424

4.3 Sweden

In recent years, the Swedish Defense Research Agency (FOI) around Dr. Nikolaj Latypov has focused their work predominantly on the following areas:[9a-f]

1. Nitro aromatics (TNT and similar)
2. O-nitro esters (nitrocellulose, nitroglycerin)
3. N-nitro and *gem*-poly-nitro-aliphatic compounds (RDX, HMX, CL-20, BDNPA etc.)
4. Energetic salts (AN, AP, ADN)

The most investigated methods currently used for creating energetic moieties in energetic materials are:

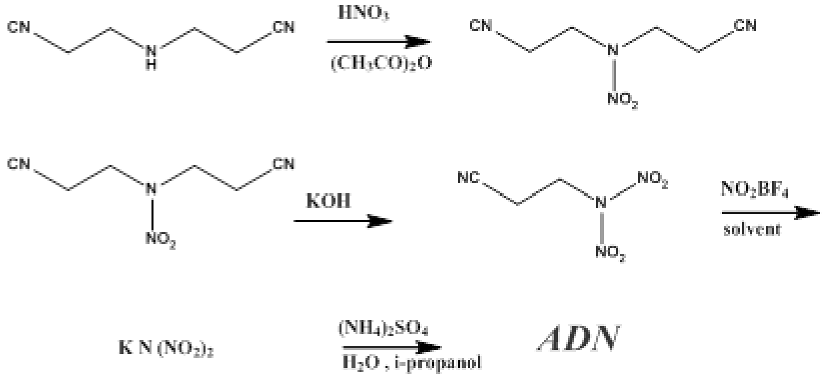
- -C, -N, -O nitration by "mixed acids", nitric acid alone or admixed with catalysts, -huge amount of literature could be found elsewhere (syntheses of NG/NC, TNT, RDX / HMX etc)
- Oxidation of nitroso-, amino- groups and oximes (synthesis of gem- dinitro compounds, e.g. Hexanitrobenzene, TNAZ)
- Special methods like reactions named after: T. Curtius, K.F.Schmidt, and, more recently introduced Sandmayer, Kaplan-Schechter and VNS methods (synthesis of BDNPA / F , TATB and nitro heterocycles)

Over the past years FOI has developed various products in the area of energetic materials:

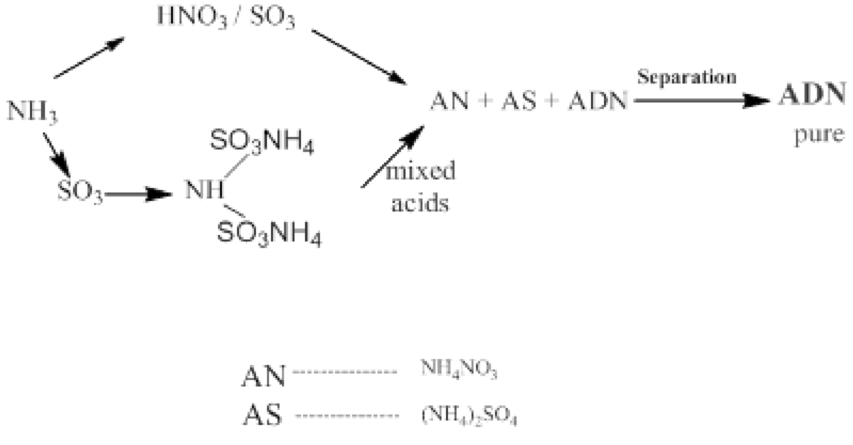
- Dinitramide and its salts

- N,N’-dinitro-urea
- N,N’-dinitro-guanidine
- Nitramide and derivatives
- Di- and tri- nitro methane and salts thereof
- 1,1-diamino-2,2-dinitro-ethene (FOX-7).

Large emphasis has been put on the development of suitable synthesis strategies for ammonium dinitramide (ADN). In addition to the original “organic” method (Scheme 4.8) there is now also an additional “inorganic” method for making ADN (Scheme 4.9):

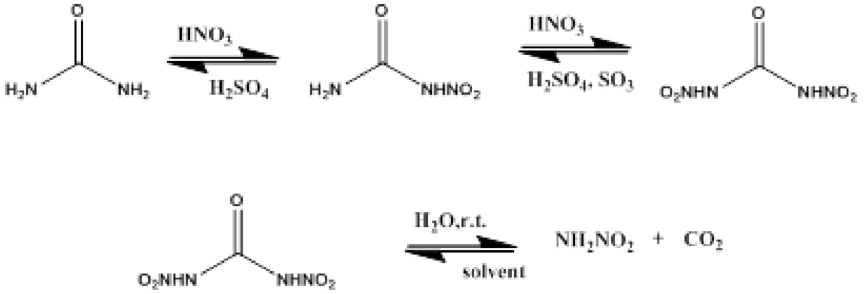


Scheme 4.8: Original “organic” method for making ADN

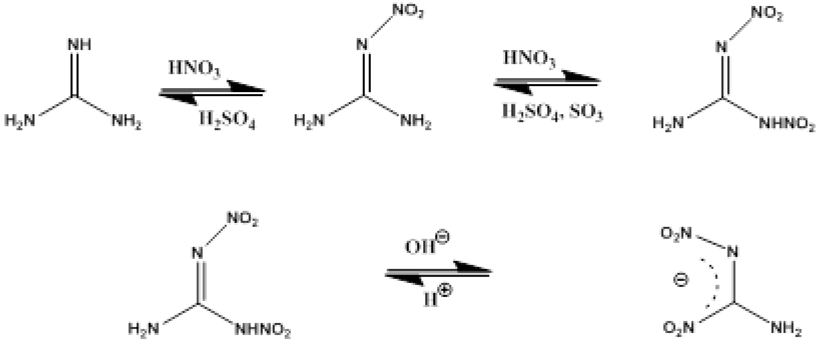


Scheme 4.9: “Inorganic” method for making ADN

Furthermore, a great deal of effort has been put into the synthesis of N,N'-dinitrourea and N,N'-dinitro-guanidine compounds (Scheme 4.10 and Scheme 4.11).

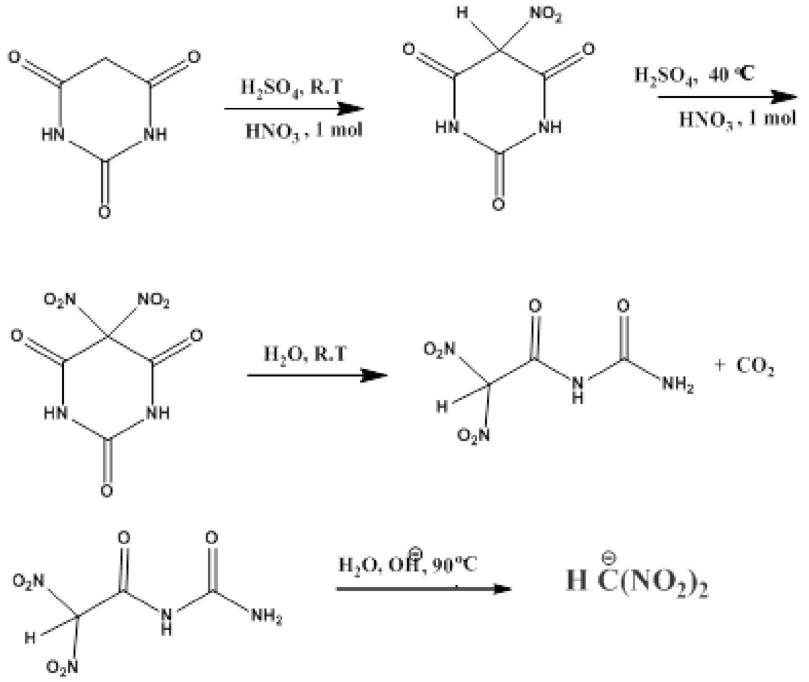


Scheme 4.10: Synthesis of N,N'-dinitro-urea and nitramide



Scheme 4.11: Synthesis of N,N'-dinitro-guanidine and salts thereof

Last but not least, the synthesis of *gem*-dinitro-aliphatic compounds and salts of dinitromethane has attracted considerable attention at FOI (Scheme 4.12).



Scheme 4.12: Synthesis of *gem*-dinitro-aliphatic compounds and salts of dinitromethane

4.4 Poland

In Poland, there are two main centers in which fundamental and applied research on energetic materials is continually performed, i.e. Military University of Technology in Warsaw (MUT) and Warsaw University of Technology (WUT).

In recent years, at MUT, several topics have been explored, but the most interesting results were obtained in the application of combustion processes of energetic composites for synthesis of ceramic and carbon nanomaterials.[10-17] For example, silicon carbide nanowires were efficiently produced via self-combustion high temperature synthesis (SHS) rout from silicon-bearing poly(tetrafluoroethylene) mixtures.[10-12] Similarly spontaneous highly exothermic reactions between sodium azide and various halocarbon compounds (including fluorinated graphite) in the presence of ferrocene give carbon-encapsulated iron nanocrystallites and various carbon nanoparticles with interesting structure and properties.[13-17]

Primary and secondary explosives are extensively studied at MUT. The main effort is put into the search for new compounds and composites with high performance and reduced sensitivity to external stimuli. A good example of such compounds is polymeric tris(4-amino-1,2,4-triazole)copper(II) perchlorate.[18,19] It has been confirmed that $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ detonates when exposed to flame, is thermally stable (decomposes above 250°C), moderately sensitive to friction (10 N) and has high initiating performance (priming charge to PETN approx. 150 mg). These properties indicate that it can be used as replacement for lead azide as it shows promising properties with respect to stability, sensitivity, energetic properties, and initiating performance. Also other complex copper perchlorate with 4-amino-1,2,4-triazole of $[Cu(C_2H_4N_4)_4(ClO_4)(H_2O)](ClO_4)_2$ is of interest as an additive in pyrotechnics and propellants.

The aim of the development program for secondary explosives is to discover and test possibly insensitive replacements of currently used mixtures of TNT with RDX or HMX and RDX/HMX/wax compositions. Of course the new explosives should have equivalent performance, at least. To achieve this RDX or HMX is being replaced with less sensitive energetic ingredients, namely 3-nitro-1,2,4-triazol-5-on (NTO) and 1,1-diamino-2,2-dinitroethene (FOX-7).[20-22] Additionally the composites include some additives to aid in processing to achieve good press-/melt-processing capability. The formulations are tested to determine sensitivity, stability and energetic characteristics. In each case, the design of a new formulation starts with thermochemical calculations. As it was expected, it is impossible to reach Comp B performance by using exclusively NTO and TNT. Therefore ternary compositions have been prepared. Beside TNT and NTO, they contain 20 or 40% of RDX. Formulations containing NTO or FOX-7 and HMX can be used as replacements for phlegmatized RDX. In the mixtures with NTO, HMX must constitute 40% at least, but when FOX-7 is used as an insensitive ingredient 25% of HMX is enough to reach the expected performance.[22]

A search for new energetic compounds and synthetic routes is performed by researchers at Warsaw University of Technology.[25-27] At present, the main purpose of the works is the optimization of the synthesis of polycyclic nitroamines, especially CL-20 (HNIW). The optimization is accomplished by means of a mathematical experiment planning theory with the steepest descent method. As a result of the study an improved yield of some hexaazaisowurtzitane derivatives was achieved.

4.5 Japan

Development of high energetic materials (HEM) for next generation pyrotechnics and propellants in Japan started in 1970s (following USA and Europe), and three kinds of HEM; GAP, HAN and ADN were successfully synthesized. Further, it should be stressed that N_5^+ formation was recognized for the first time in the world in 1998 by the National Institute of Advanced Industrial Science and Technology (AIST). Some R&D is underway for propulsion applications using GAP and HAN.

4.5.1 GAP

Two kinds of liquid prepolymer, di-ol and tetra-ol GAP are available and used in each favored application. Rather soft cured GAP can be prepared with di-ol prepolymer and used as a fuel binder of composite propellants, and harder cured GAP with tetra-ol prepolymer as a solid fuel of ducted or hybrid rockets. The combustion mechanism of GAP was fully investigated by Wada et al., and it was found that the role of combustion residues is significant and the burning rate is governed by "Blow off mechanism".[28]

Recently, significant interest has been focused on debris free propulsion systems in deep space. Solid rocket motors have occupied the main role there due to their simplicity and high propulsive performance, but they have been criticized because of their combustion product; metal oxide particles. Liquid or hybrid rockets may be the alternative, however, their volumetric disadvantage hampers their use in this application. Thus, the development of non-metalized solid propellant is necessary and the mixture of GAP/AP is considered as a promising candidate. Figure 4.2 shows the I_{sp} curve of GAP/AP propellant as a function of GAP content at the typical nozzle expansion ratio used in deep space applications. I_{sp} is maximum at 20wt% of GAP and only 8% lower than the typical metalized composite propellant, which should be accepted considering the strong environmental requirement. Linear burning rate characteristics and mechanical properties of this propellant are modest and this propellant attracts wide attention now.

Development of a GAP based ducted rocket started in 1980, guided by Kubota N. in the military area. The system is composed of two combustion chambers, and GAP burns in the first stage as a gas generator (GG). Combustion gas of GAP, still fuel, and entrained air burn in the ramjet stage completely. A high performance and thrust controllable system was realized experimentally,[29] and the flight test has been successfully completed.

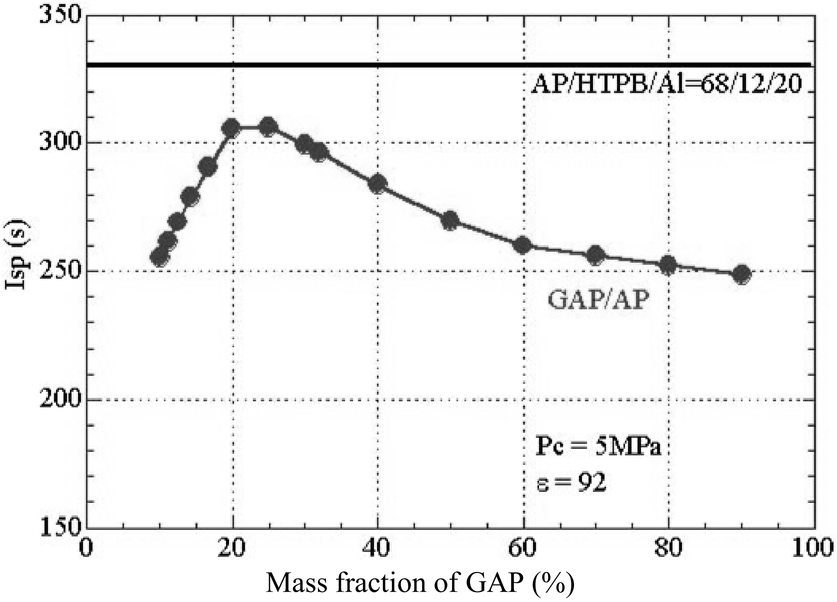


Figure 4.2: I_{sp} of GAP/AP propellant

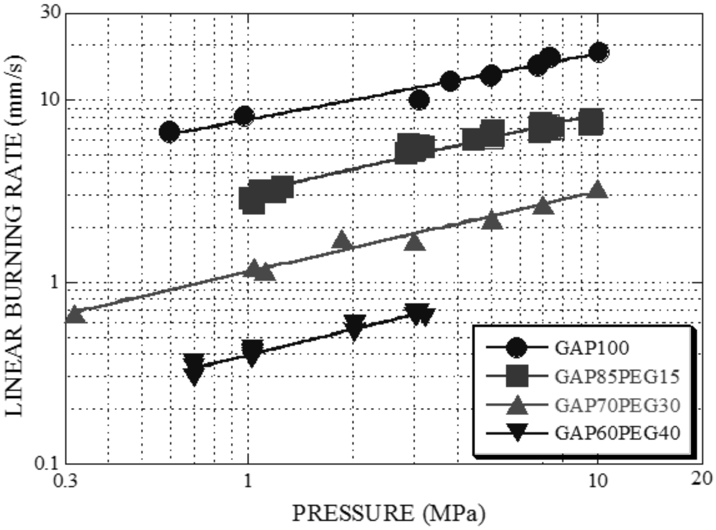


Figure 4.3: Linear burning rate of GAP/PEG mixtures

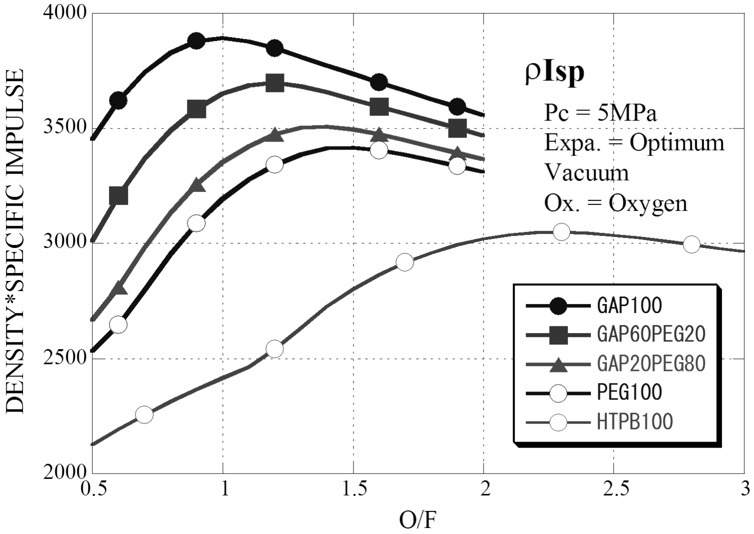


Figure 4.4: Comparison of density specific impulse of GAP, GAP/PEG, PEG, and HTPB as a function of O/F ratio with oxygen

The application of GAP to hybrid rocket motors has been studied.[30] GAP is suitable for a gas hybrid rocket system because the system uses fuel rich solid GG. The fuel gas from GAP GG is mixed with oxygen at the secondary chamber and burn there, which is similar to the ducted rocket. The linear burning rate of GAP is high, however, the tailoring by the mixing with inert polymer is possible, and polyethyleneglycol (PEG) was selected as the inert diluent. Linear burning rate was effectively lowered with the PEG addition and the pressure index was kept constant (Figure 4.3). Figure 4.4 shows the comparison of propulsive performance; density I_{sp} of GAP, GAP/PEG, PEG and HTPB. As is shown in Figure 4.3, GAP and GAP/PEG mixtures, and even PEG are superior to HTPB due to the low density of HTPB. Study of traditional hybrid rocket; so called as boundary layer type, has also been conducted, and GAP and GAP/PEG mixtures were tested as solid fuels. Firing tests up to 1000N were successfully carried out (Figure 4.5) and higher surface regression rates were obtained. The versatility of GAP gas hybrid system was also shown experimentally. In this test, the ability of quench, re-ignition and delivery of a progressive pattern (see secondary chamber pressure) which is useful for small satellite acceleration with a minimum perturbation of attitude was demonstrated (Figure 4.6).

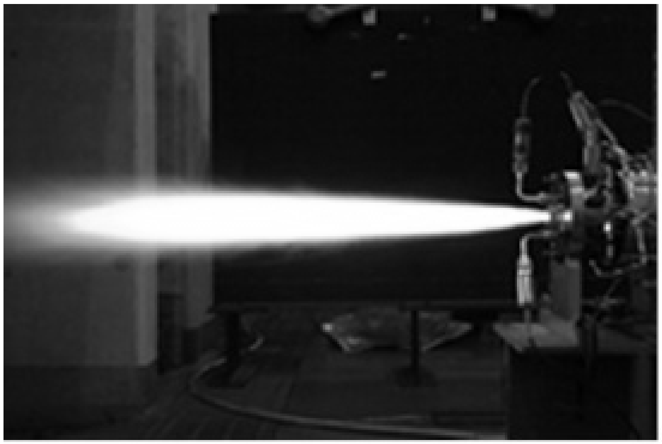


Figure 4.5: GAP hybrid motor burn

4.5.2 HAN

Research into HAN based liquid gun propellants and liquid oxidizer for hybrid rocket has been conducted, however, the intensive combustion characteristics of these solutions at high pressures have hampered their applications. The mechanism of very high burning rate was clarified such that the violent gas nucleation production by the superheat of water in the two phase region at burning surface is responsible and care must be taken for the content of water.[31,32] A new composition which includes AN and methanol at a mass ratio of HAN/AN/water/ methanol=95/5/8/21 was developed to realize a low burning rate, and the development of the thrusters for rockets and satellites using this solution is underway. Table 4.7 compares the representative properties of hydrazine and this HAN solution, and it is shown that the propulsive performance (density specific impulse) of the HAN solution exceeds hydrazine by approximately 70%. Further, another merit; low toxicity is indispensable for manned programs and has an advantage at the ground activities cost.

One flight test was successfully conducted in 2010. A mockup of a supersonic vehicle, 4.6m in length and with a total weight of 6000kg, was lifted up to a 37.5km height by a balloon and then separated as a pretest of the flight test with the supersonic engine. The mockup entered free fall and its attitude was controlled with nitrogen gas jets. Two HAN thrusters were equipped with the mockup and helped the acceleration at the freefall. In Figure 4.7, two thrusters can be identified at the end of the body in silver color. After the separation from the balloon, HAN thrusters operated for 30 seconds with the aid of preheated catalysis beds at vacuum and -50C environment. The same pressure pattern as ground tests, and 230s of I_{sp} were recorded, and this success promotes the applications of HAN thrusters to other Japanese space programs.

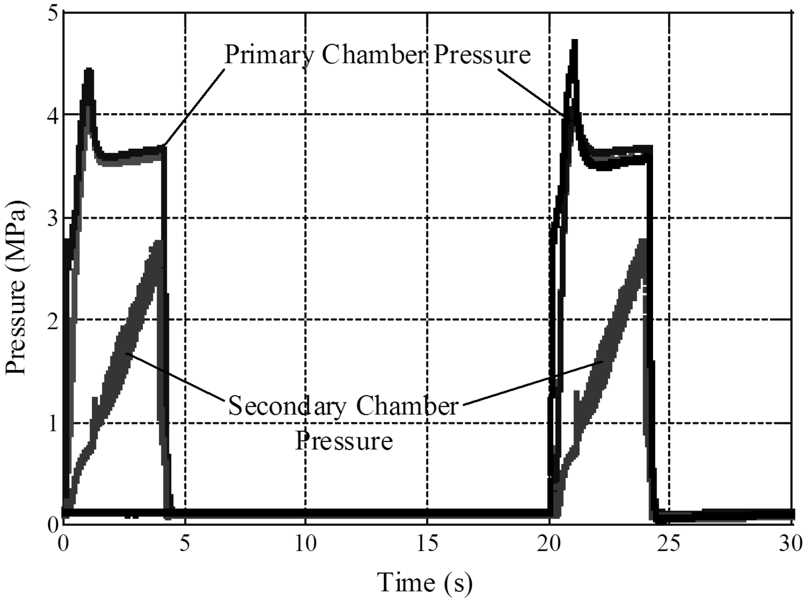


Figure 4.6: Demonstration of progressive patterns, extinction and re-ignition at gas hybrid system

Table 4.7: Comparison of hydrazine and HAN solution

	Hydrazine	HAN solution
Density (10^3kg/m^3)	1.0	1.4
Melting point (C)	1.4	-68
Isp (s)*	233	276
ρIsp (10^3skg/m^3)	233	386
Toxicity	high	low

*Pc=0.7MPa and ε=50

Figure 4.7: Flight test mockup

4.5.3 N_5^+

Polynitrogens were extensively investigated theoretically from 1980s, however, no experimental proof of their existence was reported until 1998. Matsunaga et al.[33], succeeded in synthesizing N5 cation for the first time in the world and made a significant contribution in this area. Cyanuric triazide (C_3N_{12}, Figure 4.8) was selected as a starting material owing to the highly electron-withdrawing cyano groups to get reactive nitrogen species. Cyanuric triazide was photolyzed and ionized by a Nd:YAG pulsed laser at room temperature in vacuum, and ionized fragments were observed by means of MS/MS. A strong peak at 70 of m/z was detected and identified as N_5^+ rationally.

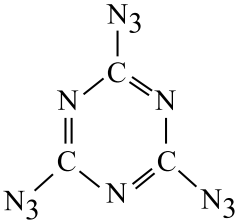


Figure 4.8: Cyanuric triazide

4.6 South Korea

While not much original synthetic work on energetic materials has been carried out in South Korea, the Agency for Defense Development (ADD) in Korea developed the so-called "ADD Method-1" to predict the performance and sensitivity of new explosive materials. Because the ADD Method-1 required laborious computational procedures to find the global minimum in a potential energy surface, a new revised approach, the ADD Method-1(2D) excluding conformational search procedures, and offers a useful way to design novel HEDM compounds.[34] In order to develop potential high-density energetic materials knowledge of the formation mechanism and of explosive performance studies is important. Kim et al. performed mechanistic studies on the formation of melamine and nitro-substituted 1,3,5-triazine derivatives and their explosive properties using Møller-Plesser perturbation methods and density functional theory.[35]

4.7 Russia

Russia has gained tremendous experience to date in designing high energy materials (EM) sourced from polynitrogen and nitrogen-oxygen compounds, in particular heterocycles and carcass structures such as CL-20, etc. A number of unique methodologies that enable insertion of explosophoric groups into target structures have been developed. Zelinsky Institute of Organic Chemistry RAS stands among the pioneers of EM synthesis.

A major advance in EM chemistry is associated with a concept of stabilized polynitrogen-oxygen molecules building based on the charge alternation principle. As the concept evolved, a new high-energy functional group – N_3O_3 (N-nitrodiazenoxides,[36] a new heteroxyclic system – 1,2,3,4-tetrazin-1,3-dioxides [37] and a new polynitrogen-oxygen anion – N3O4 (dinitramide salts) [38] were achieved. In the Soviet Union, dinitramide ammonium salt (ADN) served as a basis for propellants used in strategic missiles of various deployment modes and was produced on a multi-ton commercial scale. ADN enables highly efficient smokeless fuels with improved performance, e.g. lower missile launch detectability, and is used on super-precision laser guidance systems. Apart from providing high energy efficiency, new fuels are environmentally-friendly, which is of special importance in the context of ever-increasing environmental standards, whereas in the combustion of ammonium perchlorate fuels supertoxicants – dioxins are generated.[39] Currently a lot of countries, including Russia, are carrying out intensive research into the area of ADN and applications of other dinitramide salts as universal oxidizers for ‘green propellants’.[40,41]

Highly promising investigation is ongoing into synthetic methods and properties of EM in the N-polynitroalkyldiazen-N-oxide series ($XC(NO_2)_2N(O)=NR$, where R = Alk, Ar, Het, X=H, Hal, Alk, NO_2). Rather stable compounds of this series among aliphatic, aromatic and heterocyclic derivatives have now been prepared.[42]

Simple one-step methods to prepare derivatives of small nitrogen-containing heterocycles such as diaziridines – potential propellants for liquid fuel rocket engines [43] and 1,3,3-trinitroazetidine – a powerful fusible explosive [44] were developed. Extensive research is underway into a series of high energy derivatives of various azoles where significant advances were made particularly in constructing high energy furazan and furoxan derivatives. Combinations of these cycles between themselves and with other polynitrogen heterocycles, e.g. pyrazole, trazole, tetrazole, pyrazine, tetrazine, etc., afford a great diversity of linear ensembles of heterocycles and annelated intermediates enriched in nitro, azido, azo, azoxy, and nitramino groups. On this basis, methods for preparing hydrogen-free polynitrogen compounds built from C, N and O atoms were elaborated. Approaches to the correction of the EM physicochemical properties in a broad range (e.g. m.p. from -50 to 400°C) were identified through varying functional group combinations.[45-50] Analogous research is performed in the series of tetrazole derivatives.[51]

In the pyrazole series general methods were developed for the synthesis of mono-, bi- and polycyclic polynitropyrazoles, including a new type of nitrogen-containing energetic molecules – mesoionic 2-(dinitropyrazolyl)-1,2,3,4-oxatriazol-5-ates. A pioneering synthesis of TATB-like aminodinitropyrazoles was implemented to result in 4-amino-3,5-dinitropyrazole and 5-amino-3,4-dinitropyrazole characteristic of unique sensitivity within this class and comparable with RDX in performance.[52,53] General methods of polynitropyrazole N-functionalization [52,54] by explosophores such as N-nitro, N-amino, N-difluoroamino, N-hydroxy, and N-fluorine groups were developed. Preparative procedures to synthesize isomeric 1,3,4- and 3,4,5-trinitropyrazoles were designed. These were shown to be excellent starting compounds, unique in their synthetic capabilities, for the synthesis of diverse polyinitropyrazole intermediates.[52,55]

Non-conventional methods to prepare EM are being developed, in particular with the use of alternative solvents – ionic liquids [56, 57] and supercritical liquids. Liquid and supercritical CO_2 are employed as environment-safe solvents in preparing N-nitramines from secondary amines and N,N-dialkylcarboxamides. A system ‘nitric acid-acetic anhydride',[58, 59] Nitrogen oxide (V) or its mix with HNO3 (nitrooleum)[60] served here as a nitrating agent. N-nitramine yields are comparable with results attained by the known methods, however owing to CO_2's inertness to oxidants and its ability to efficiently remove heat from the reaction zone, nitration processes have acquired improved explosion and fire safety. This method is used for the synthesis of compounds with several nitramine groups.

Principal research efforts related to the experimental study of EM thermochemical properties and energy aspects of detonation initiating processes are implemented in Semenov Institute of Chemical Physics RAS.[61] Major advances in researching the kinetics of the low-temperature decomposition of numerous homogenous and heterogeneous EM were achieved in Institute for Problems of Chemical Physics RAS (Chernogolovka).[62] This basic research dealing both with individual nitro compounds and with ammonium perchlorate to include model formulations and prototype solid rocket propellants (SRP) on its basis have laid a robust scientific foundation for addressing various practical issues related to the storage and operation of these substances and formulations.

Research within the stationary and non-stationary homogenous propellant theory initiated by Zeldovich and Novozhilov was evolved by Merzhanov with a focus mainly on the theory of EM ignition and thermal detonation.[63] Original kinetic instruments were designed for investigating the kinetics of split-second reactions.[64] The latest developments include the design and testing of a set of instruments where as a result of a so-called "electrothermal explosion" realized in the condensed phase, it is possible to measure with quantitative accuracy the kinetic parameters of reactions with characteristic transformation times below 1 ms in the $900^{o}K – 3600^{o}K$ temperature range.

Many approaches[65] to the estimation of EM basic properties were developed in Russia, including additive schemes and molecular mechanics, quantum chemistry methods, the QSPR methodology for identifying quantitative structure-property relationships, and Artificial Neural Networks. A novel concept of the *in silico* search of novel energetic structures with a promising set of physicochemical characteristics was proposed.[66] Based on the original classification of EM structural features and using experimental data on the EM decomposition mechanism, a new method for the modeling of thermal decomposition processes for organic compounds was developed.[67] The method allows the generation of a variety of possible thermal decomposition reactions of energetic compounds at different steps of decay, even at the deepest ones. A significant amount of research was undertaken in quantum chemistry and computer modeling for the decomposition of nitro compounds.[68]

4.8 India

High Energy Materials (HEMs) is a generic term used to categorize explosives, propellants and pyrotechnics. These are generally perceived as 'devil' during war and considered as an 'evil' during handling, transportation and storage, but prove to be an 'angel' due to their innumerable applications in almost all walks of life. The most important application of HEMs in India is for defense preparedness. In order to keep pace with the developments all over the globe and to ensure self-reliance in the field of HEMs, India has developed some newer and better molecules.

The HEMs have been classified in the following classes based on a single most important property, and their status and intended applications in India are:

- Thermally stable or heat-resistant explosives (DATB, TATB, HNS, PATO and its nitro derivatives, DIPAM, TPM, PYX, NONA, BTATNB, PAT, SAT, BTDAONAB etc.).
- High Performance (high density and high velocity of detonation) explosives (TNGU, TNPDU, HNIW/ CL-20, TNABN, DNCC etc.)
- Melt-Castable Explosives (TNT, Tris-X, TNAZ, DNBF etc.)
- Insensitive High Explosives (IHEs - TATB, ADNBF, NTO, DINGU, ANTA, TNAD, FOX-7, FOX-12, PL-1 etc.)
- Energetic Binders [PNP, GAP, NHTPB, Poly (NiMMO), Poly (GlyN) etc.] and Plasticizers [NG, EGDN, DEGDN, TEGDN, BTTN, BDNPF/ A, Bu-NENA etc.] for explosives / propellants.
- Novel Energetic Materials synthesized with the use of dinitrogen pentoxide (N2O5) Technology [NHTPB, Poly (NiMMO), Poly (GlyN) , ADN etc.]

The new thermally stable explosives reported by India are: 1,3-Bis(1,2,4–triazolo–3–amino)–2,4,6–trinitrobenzene[BTATNB], 5–Picrylamino–1,2,3,4–tetrazole (PAT), 5,5'–Styphnylamino–1,2,3,4– tetrazole (SAT) , N , N' - Bis (1, 2, 4 – triazole – 3 – yl) - 4, 4' – diamino 2,2',3,3',5,5',6,6' – octanitroazobenzene [BTDAONAB]. The data on BTATNB [69] indicates that it is slightly more thermally stable (m.p.3200 C as compared with 3100 C for PATO) coupled with better insensitivity towards impact and comparable friction sensitivity. A

Table 4.8: Most promising thermally stable explosives and their properties

Name	Melting Point °C	Density gcm^{-3}	Impact Sensitivity (h$_{50\%}$) cm	VOD Ms^{-1}	Salient Properties and Applications
1,3,5-Triamino-2,4,6-trinitro benzene (TATB)	>350	1.94	Very Insensitive	8,000	Explosive with unusual insensitivity, heat resistance and respectable performance. Used for space, nuclear and special military applications (high speed guided missiles).
Tetranitro dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)	494 (Ignition)	1.85	Very Insensitive	7,250	Stable upto 354^0C and very impact insensitive. Used for FLSC and high temperature resistant detonators.
2,6-Bis (picryl amino)-3,5-dinitro pyridine (PYX)	460	1.75	63	7,450	Slightly impact sensitive. Regarded as a substitute for HNS. Used for thermally stable perforators for oil and gas wells.
N,N'-Bis(1,2,4-triazol-3-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazobenzene (BTDAONAB)	Does not melt/show any change upto 550 and gives exotherm at 550.	1.97	87	8321	Most thermally stable explosive reported so far. Reported recently on a laboratory scale. Needs further evaluation.
BTATNB	320 (with decomposition)	1.98	165-170	7610	Slightly better than PATO
Polynitropolyphenylenes (PNPs)	286-294	1.8 – 2.2	--	--	Thermally stable binder for pyrotechnic formulations

Table 4.9: Important properties of some newly reported explosives

Name	**Melting Point ^{0}C**	**Density gcm^{-3}**	**Impact Sensitivity cm**	**VOD m s^{-1} (calculated)**	**Remarks**
PL-1	336	2.02	170	7861	Slightly inferior to TATB in terms of thermal stability and VOD but better in respect of density. Appears to be a potential IHE.
ANTA	240	1.82	> 170	8460	May be useful for formulations where insensitivity coupled with thermal stability is required.
DANTNP	> 330	1.84	> 170	8120	--
PADNT	198-201	1.85	135	6628	Useful for safe and insensitive explosive/propellant formulations
2,5,7,9-Tetranitro-2,5,7,9-tetra-azabicyclo (4,3.0) nonane-8-one (TNABN)	> 230	1.92	115	9015	Promising blend of explosive properties and insensitivity to impact and friction

comparison of thermal and explosive properties of PAT (deflagration temp. =203^0C, and calc. VOD=8126ms^{-1})[70] and SAT (deflagration temp. =140^0C, and calc. VOD=8602 ms^{-1})[71] reveals that PAT is more thermally stable than SAT but more sensitive to impact and friction. The most thermally stable explosive reported so far is BTDAONAB, which does not melt up to 550^0C.[72] This has been reported at laboratory scale and needs further detailed investigation.

As a result of extensive studies on thermally stable explosives, India has also zeroed down to TATB keeping in view ease of synthesis and scale-up, purity, yield and properties, for space, nuclear and special military applications.[73] It is being manufactured at pilot plant scale through the sym. trichlorobenzene route similar to other countries. A comparison of thermal stability and other parameters of most thermally stable explosives is given in Table 4.8.

Similar to other countries, India has also developed 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazaisowurtzitane (HNIW/ CL-20)[74] by following the method of Neilsen and co-workers.[75] The intermediate HBIW/TAIW is available on pilot plant scale whereas attempts are being made to scale up the laboratory method to pilot plant scale and also to bring down the cost of manufacture of CL-20. As regards IHEs, our emphasis is on TATB and NTO, both available at pilot plant scale and PL-1 and formulations based on these two IHEs will shortly be available for several applications. Energetic plasticizers such as nitroglycerine (NG), ethyleneglycol dinitrate (EGDN), diethyleneglycol dinitrate (DEGDN), triethyleneglycol dinitrte (TEGDN), 1,2,4-butanetriol trinitrate (BTTN), bis (2,2-dinitropropyl) formal/ acetal [BDNPF/A], butyl-N-(2-nitroxyethyl) nitramine[Bu-NENA], bis(2-azidoethyl) adipate [BAEA][76] etc. have been developed, and are being used for several explosive/ propellant formulations. However India has not given its due share to the development of energetic binders, except for some work on glycidyl azide polymer (GAP), energetic thermoplastic elastomers such as 3,3-Bis (azidomethyl)oxetane [BAMO], 3-azidomethyl-3-methyloxetane (AMMO) and their copolymers (as binders for gun/ rocket propellants) and polynitro polyphyenylene (PNP as binder for pyrotechnic formulations).[77]

A number of new explosives have been synthesized, their structures established, characterized for thermal and explosive properties and evaluated for their intended appplications.[78-83] The data on thermal and explosive properties of some aromatic nitrate esters suggest that 1,3,5-Tris(2-nitroxyethyl nitramino)-2,4,6-trinitrobenzene is a potential substitute of PETN.[78] An explosive called 2,4,6-Tris (3',5'-diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazene [designated as PL-1] is a new thermally stable and insensitive explosive which on comparison with TATB suggests that it is slightly inferior to TATB in terms of thermal stability (M.P., °C : TATB ≈ 350 and PL-1 ≈ 336) and calculated VOD, ms^{-1} (TATB ≈ 8000 and PL-1 ≈ 7861) but it is better in respect of density (density, gcm^{-3} : TATB ≈ 1.94 and PL-1 ≈ 2.02) whereas sensitivity to impact and friction is comparable.[79] Another study on 3-Amino-5-nitro-1,2,4-triazole [ANTA] and its derivatives concludes that ANTA and 4,6- Bis (3-amino- 5-nitro -1H - 1,2,4–triazole–1-yl)–5-nitropyrimidine [DANTNP] may find application in propellant/explosive formulations where insensitivity coupled with thermal stability is of prime importance.[80] The study on 4-picrylamino-2,6-dinitrotoluene [PADNT] leads to the conclusion that its handling is safe and at the same time, it possesses a good thermal stability.[81] PADNT may also be an attractive option as a new energetic ingredient for the development of safe and insensitive explosive/propellant formulations. The compound 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo(4,3,0) nonane-8-one [TNABN] possesses a promising blend of explosive properties and insensitivity to impact and friction.[82,83] Important properties of some newly reported potential explosives are given in Table 4.9. The method of their synthesis, properties, structures and likely intended applications are described in texts by Agrawal and Hodgson.[84a,b]

For warhead applications, RDX and HMX in conjunction with TNT (a melt-castable explosive) are main explosive fillings. In view of the cost, RDX is a preferred explosive but HMX is used in its place in order to meet the requirements of enhanced performance. CL-20 based formulations are still in the developmental stage. The technology of a wide range of RDX and HMX based cast PBXs (with HTPB as a binder) has been established and simultaneously the technology of pressed PBXs has also been established.

Different types of solid rocket propellants - extruded double-base (EDB) propellants, cast double-base (CDB) propellants, composite propellants (CPs), nitramine based propellants, composite modified double-base (CMDB) propellants and fuel rich (FR) propellants are available for use in various rockets/missiles for defense applications. These propellants are mainly available in cartridge loaded mode. In recent years, India's Defense Research and Development Organization (DRDO) has embarked upon the development of case bonded composite propellant (HTPB and AP based) motors of various configurations and sizes. Apart from propellant development, ferrocene based burning-rate modifiers,[85] inhibition techniques (thread winding technique and inhibitor sleeve technique,[86-91] insulation liner, binder and eco-friendly high performance oxidizers (which are essential constituents of propulsion systems) are also available.

A number of gun propellants (varying in their formulation, geometric size, method of manufacture depending on the ballistic requirement of a particular system) for various weapons of Army, Navy and Air Force have also been developed by India, along with other components of ammunition such as primers, igniters, additive liners and coated cambric cloth containers.

Pyrotechnics are among the oldest explosive devices known to a man and the Chinese are usually credited with their invention. Indians have also developed a large number of pyrotechnic formulations and pyrodevices for producing special effects - light, heat, delay, smoke and sound, etc. Many of such stores - delay cartridges, illuminating and IR flares, illuminating candles, smoke bombs, etc. have been developed at DRDO, the technology has been transferred to the Director General of Ordnance Factories (DGOF), and they are being manufactured in bulk at Ordnance Factories to meet the requirements of Services.

Red phosphorus (RP) is an extremely versatile material and is of special interest for many military applications, mainly for producing screening and signaling smokes. In view of its need for greater stability, easier handling, and environmental and occupational safety, there is a lot of research in this area all over the globe, including India, especially for smokes effective in IR region.[92,93]

Basic lead azide (BLA) has been developed as an alternative to lead azide (LA) and service lead azide (SLA). It is safer to handle and possesses necessary power to detonate high explosives. The technology has been transferred to DGOF, and detonators based on BLA are manufactured by Ordnance Factories on a regular basis.

4.9 Czech Republic

The military research in the Czech Republic includes all aspects of armament systems. Research into explosives is often done in cooperation with Explosia, or more precisely VUPCH, and the University of Defense in Brno.

Below are four of the most important topics being researched:

1. Emulsion explosives (W/O) were originally developed as first class permissible explosives for a company named Istrochem in Bratislava.[94] Along with the development of new explosives the performance of these W/O systems was tested,[95] the micromechanism of initiation of detonation was studied for blasting agents and fortified blasting agents,[96] and studies were undertaken of the fortification effect of W/O explosives by small grain propellant grains.[97]

2. The application of demilitarized explosives in slurry explosives [98] with focus on W/O mixtures.[99,100]
3. The preparation and synthesis of cyclic nitramines *cis*-1, 3, 4, 6 - tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX)[101,102] a ε - 2, 4, 6, 8, 10, 12 - hexanitro - 2, 4, 6, 8, 10, 12 - hexaazaisowurtzitane (ε-HNIW)[103] and plastic bonded explosives on their bases.[104-107]
4. Studies of secondary explosives with high thermal stability. [108-111]

Moreover, Zdenek Jalovy is/was working on CL-020, TNAZ, FOX-7 and other interesting secondary explosives. In addition to the above mentioned topics researchers at the University of Pardubice constantly keep an eye on improvised explosives and their properties. Some of their research on TATP has recently been published.

4.10 Australia

In regard to general area of energetic materials research in Australia work is done only at the Defence Science and Technology Organisation (DSTO) laboratories, with specific projects being contracted out to some universities. There has not been much published by DSTO over the last few years. The Australian Defense Studies Centre, UNSW@ADFA, Canberra has focused on the synthesis and characterization of new high nitrogen compounds. Insensitive high explosives are an important area of research interest due to the increased requirement for safer energetic materials. Azoxytriazolone (AZTO) is a new chemical species discovered by this research group[112], and preliminary results indicate it may possess potential as a new insensitive high explosive. The group is studying methods of synthesis of AZTO and other related compounds, and also investigating their solid-state and solution properties.

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Chapter 5

Energetic Materials Outside DoD

Robert D. Lynch

With the Chinese first-century discovery of black powder as a means to propel a projectile, the world became introduced to the world of energetic materials. It took nearly thirteen centuries for man to progress from the use of energetic materials for projecting fireworks to their first experimental use in battle (beginning as early as the 14th century). For the next six centuries, the desire for improved energetic materials was driven by the need for better gun propellants and explosives.

The energetic material advancements over the past 50 years have, until recently, been almost exclusively driven and controlled by governmental branches which control defense; for the U.S. this branch is the Department of Defense (DoD). The defense desire for better energetic materials is both for improved explosives and for methods to propel rockets further and more precisely.

With the recognition then that the U.S. DoD drives and controls current energetic material advancements and that the purpose of this book is to describe the contribution of advanced energetic materials to the strength of the DoD, one might ask "Why devote an entire chapter to energetic materials outside DoD?" The simple answer (as depicted in Figure 5.1) is that the off-shoot of the government's support of energetic materials has significantly affected the lives of every American and improved our living and social conditions. Also, since the use of energetic materials is becoming more common-place, one might question: if energetic material technology development is becoming self-sustaining then are DoD funds no longer needed? To answer these questions, this chapter evaluates the broad range of areas where energetic materials are used in our daily lives, how previous DoD advancements have impacted use of energetic materials outside the DoD and the potential for self-sustainment of energetic material research without DoD support. This chapter will show that without continued past and future government support of energetic materials, our American way of life would have been and will be significantly altered.

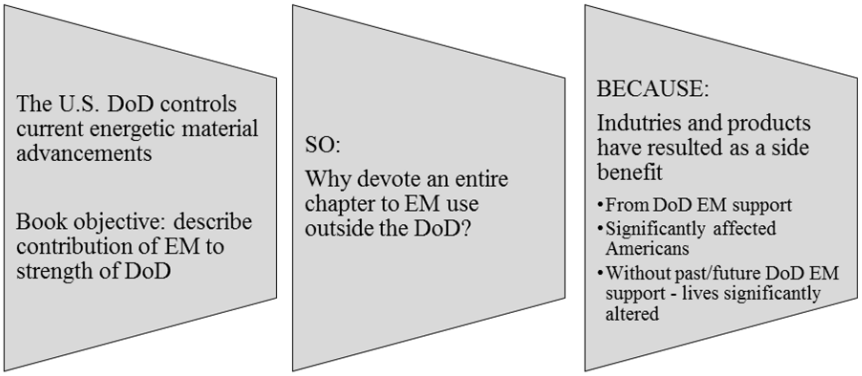

Figure 5.1: Why address non-DoD energetic material use?

The obvious non-DoD areas where energetic materials are used are probably recognized by most. These include:

- NASA for access to space and maneuvering in space
- Commercial access to space and
- Department of Energy (DoE) and their research related to improved strategic explosives

Additionally, there are several commercial areas where the use of energetic materials is quickly recognized. These include:

- Commercial hunting supplies for the local hunters
- Propellants for model rockets for the backyard “rocket-man” hobbyist
- Commercial explosives for demolition and construction
- Explosives and pyrotechnics for typical special effects seen in theater and movies and
- Rocket launching and pyrotechnics for those fireworks we all enjoy on the 4th of July or other local and significant celebrations.

Beyond these obvious areas, there are many not-so-obvious somewhat-surprising applications of energetic materials to our daily lives. The same energetic material technologies which make large interceptors fly or are used to propel the shuttle from its launch pad are the key technologies making possible the near-instantaneous inflation of an automobile airbag. Energetic materials are also the key component to explosive bolts and cutters used in some emergency removal of roofs at accident scenes as well as powder actuated nail guns. Energetic materials are used to improve the efficiency of extracting oil and gas from shale and tar-sand fields. Even more recently, energetic materials have been the source of gas and products which provide protection from fires for some government aircraft and private automobiles (literally "fighting fire with fire"). A potential emerging application of energetic materials is the use of them as gas generators (e.g., hydrogen) for storable/replenishable batteries. Additionally, some energetic compounds are also found in the pharmaceutical industry (e.g., nitroglycerine and other nitro/nitrate compounds). And finally, the theories, technologies and models developed in the research and advancements of energetic materials are often applicable to non-related industries including the development of protection systems and energetic material detectors used by the Department of Homeland Security (DHS). This expanded use of energetic materials is evidence that energetic materials are becoming more and more common in our daily lives.

The drivers for improvements in DoD energetic materials (i.e., safety, reliability, "green," and performance) are the same as those which are making the energetic material more common place outside the DoD. First, and foremost, use and application of energetic materials need to be safe. The work brought about in the DoD effort to develop LOVA (low-vulnerability ammunition) and IM (insensitive munitions) has resulted in materials which are safer and less prone to accidental initiation. For non-DoD applications, the second criteria of importance, related to and closely following safety, is reliability. For most non-DoD applications, reliability is so important that the materials must be proven to a very high level of acceptance. In many cases, the current state-of-the-art (SOTA) is not sufficient; yesterday's SOTA is the only thing acceptable. More recently, the DoD recognition of the impact of energetic materials on the environment and the research involved in developing green materials and processes/procedures is directly applicable to the non-DoD energetic material users. And, of course accomplishing safer, greener and more reliable energetic materials is a moot point without maintaining or improving on their performance. This need for high performance also makes some of the non-DoD applications more feasible.

As the energetic material industry becomes safer, more reliable, greener, etc. and their use finds more ways into our daily lives, a “snow-balling” effect could occur. Acceptance of energetic materials may drive further use of energetic materials to the point where energetic materials become common place and new applications and uses of energetic materials will be found to make our lives safer and more enriching. Even if this evolutionary acceptance of energetic materials doesn’t occur in the future, the use of energetic materials will continue to play an important role in our lives and the application of safe and efficient energetic materials will be a driver in our society.

The evolution of energetic materials from a novel source for propulsion into our daily lives has only occurred because of the advancements in energetic materials within the DoD. Even though energetic materials are used more routinely and in multiple areas, the advancements of energetic materials is, in large part, attributed to the government funding of energetic materials primarily within the DoD (but also within the DoE). The cost to produce and manufacture energetic materials prohibits most industries from additional research in this area. As a result, the vast-majority of advancements in energetic materials are a result of government-funded efforts.

In summary, the use of energetic materials in the non-DoD areas is, for the most part, feasible only because of the DoD investments and efforts over the years. Without continued government-funding of advanced energetic for the past half century, many of the non-DoD applications of energetic materials we experience in our daily lives would not have occurred.

The remainder of this chapter explains and justifies this position. We will first evaluate what is required to develop an energetic material and thus understand if private industry is in a position to do so. We will then evaluate what the requirements should be when developing new energetic material technologies. Finally, we will evaluate each of the types of organizations and industries summarized above. In this final assessment we will evaluate what effect prior DoD investment has had on the development of a specific industry/organization and the ability of that industry/organization to sustain energetic material research without future DoD support.

5.1 Required Effort to Develop Energetic Material Technologies

Before we look at uses of energetic materials outside the DoD, we need to first understand what is required for a company or organization outside the DoD to develop a new energetic material or technology. By doing so, we can better understand the cost involved for a non-DoD enterprise to support such an effort.

Private, for-profit companies need to justify expenses based on the return on their investment (ROI). It is impossible for a profit making company to justify an expense if the gain on the investment does not exceed the cost on investment (i.e., a negative ROI). The larger the projected-return, the more likely that company is to invest in the effort. As depicted in Figure 5.2, four factors are considered in ROI evaluations and will be assessed here as a means to determine the potential success associated with a private company investment in a specific endeavor. These four factors are further discussed below and assessed as they relate to investment in energetic material efforts. As revealed below, collectively, these factors result in high risk with a low projected-return on an investment in energetic materials. This makes it difficult for private industry to justify such efforts unless unusual circumstances occur.

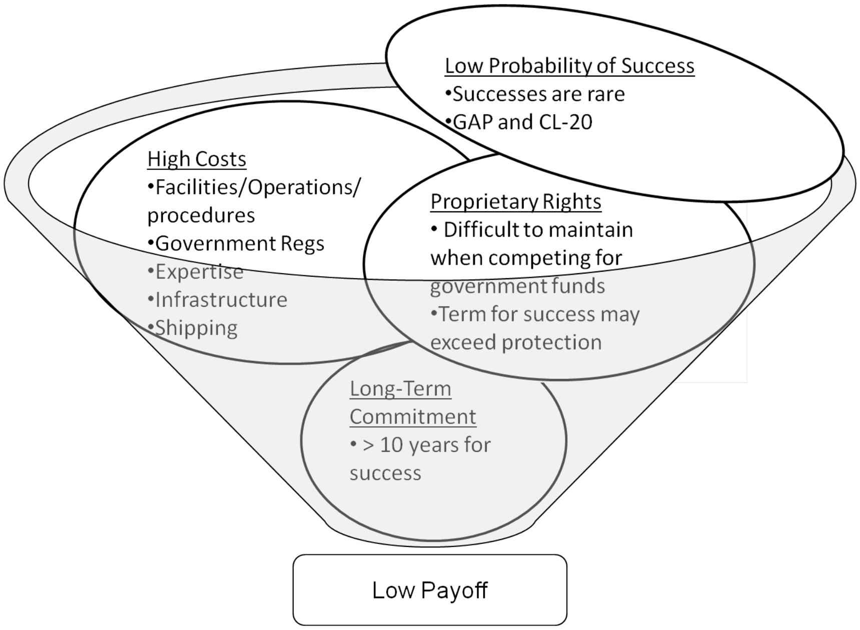

Figure 5.2: Factors affecting low payoff

5.1.1 ROI Cost

High costs are associated with energetic material development because of the special process and approaches required to address the inherent needs of safety, environmental, and etc. The safety issue was recognized when efforts were first begun in the 1940s and the procedures to achieve reliable safety have resulted in numerous established approaches. Because of this inherent need for extensive procedures, high initial and sustained costs are required for developers of energetic materials. Many factors result in this high cost.

1. Facilities – Special facilities are required and these facilities are expensive. Operations need to be located in a facility which controls a blast if an accidental initiation occurs. This requires special cells to be built which are structurally sound to contain or direct a blast away from personnel and other facilities. These specialized cells require thick, reinforced concrete and special design considerations. They also require substantial open ground-space around the operating facility to meet required separation from adjacent work areas (i.e., quantity distance, QD, requirements).
2. Operation Apparatus – Specialized operation apparatus within a facility is required because most operations must be conducted remotely. Thus, the operations must be controlled from outside a cell and/or at an acceptable distance from the cell while still being able to observe and monitor the operation in real time. This results in the need for monitoring systems and remote operations and procedures. Additionally, much of the testing apparatus is unique to the industry. In many instances, the test apparatus has to be developed at the site because it is not commercially available. The operators also need to be trained on site for operation of such apparatus.
3. In-place Procedures – Nearly every step associated with preparing, handling, producing, storage, preparing for shipping, and etc. requires understanding and instituting safe procedures to protect personnel and facilities. These procedures require years to properly develop and incorporate as routine steps within a company. Significant training of individual operators is also a key part of this.
4. Expertise – There are few college or university programs within the U.S. that develop experts in the areas of energetic materials. The education background of most of the current U.S. experts is chemistry and engineering degrees. The energetic material

expertise of personnel, for the most part, has been developed at the expense of the supplier or the government. Experts are trained within the industry not at a university. Typically, the industry assumes that a minimum of about three years is required to allow personnel to be competent in this area. Many more years of training are required before a level of expertise is achieved. (As a side note, with minimal current funds for energetic materials research, the work force is shrinking.)

5. Extensive Government Regulations – Over the years, the U.S. government has developed numerous procedures and regulations for an energetic material organization to be aware of and comply with. These are not only for safety but also for environmental regulation and enforcement. The company must be up to date with the latest procedures and is subject to frequent audits. This requires management knowing and enforcing the regulations and each operator being trained and following the regulations.
6. Infrastructure Required – As examples above have shown, the unique hazards and environmental issues associated with developing energetic materials requires an extensive in-place infrastructure to conduct energetic material research. This includes environmental experts, security around the clock, and safety experts. For each of these, the management needs to stay up to date with the latest and extensive government procedures. For the environmental management, understanding of on-site and off-site disposal as well as environmental regulations associated with a material's use and application needs to be understood. For the security manager, keeping up with the latest government procedures and reporting regulations for personnel and the ATF (Bureau of Alcohol, Tobacco, Firearms and Explosives) procedures for storing energetic materials are at the top of the list. For the safety manager, assuring the latest procedures are followed and newest requirements are incorporated into the company's procedures and facilities is required. Each of these is subject to multiple reviews and audits and the company is expected to pass these without any incidents.
7. Shipping and Transportation – In order to receive and/or ship materials from a facility, understanding the extensive regulations and continuous updating of regulations and training handlers is required. Receiving any material goes well beyond simply requiring an MSDS; it requires understanding the potential sensitivity of the material and having a plan in place to immediately support and handle the material. Shipping material requires conducting the proper testing prior to shipping (which

> can be very expensive by itself), understanding how to package the material or item, and making sure the correct shipping approach is used for transporting of the material. Since procedures change, frequent re-training is required. The result of the regulations and requirements surrounding shipping energetic materials is typically a costly procedure requiring a team of experts to oversee the effort.

5.1.2 ROI Probability of Success

A low probability of success is associated with developing new energetic material technologies especially when the desired technology is a new ingredient. The current energetic-material priority is new ingredients which offer more performance, acceptability sensitivity and are low cost.

Over the past 30 years, only two new ingredients: CL-20 (a complex-structure nitramine in the family of HMX and RDX developed by the U.S. Navy) and GAP (glycidyl azide polymer developed by the U.S. Air Force) have had any impact on potential DoD production programs. Both were first identified in the late 1970s to early 1980s and neither was considered for production applications until the late 1990s. Neither has yet to be used in a large U.S. DoD production program.

Since all the materials which are easily synthesized or obtained have been used for decades, the next step is to identify and synthesize materials which are less-obvious and more difficult to obtain; further lowering the probability of future successes. There are literally millions of potential ingredients which could provide the required advantage. However, out of the literally-millions of compounds, few (if in fact any) will still survive after undergoing the scrutiny required to achieve an acceptable and useful compound. Factors eliminating a material from use can be:

- Physical (e.g., readily decompose at relatively-low temperatures)
- Chemical (e.g., readily react with other ingredients commonly used)
- Safety (e.g., are sensitive to shock or other stimuli)
- Environmental issues (e.g., require synthesis procedures which incorporate unacceptable environmental risks) or
- Cost (e.g., can only be synthesized via a multi-step process and/or each with low yield)

Unfortunately, evaluating these elimination factors can, for the most part, only be completed once material is in hand. Projections based on models are becoming more common place but the real proof is in the final assessment based on evaluation of the material. Numerous ingredients have been evaluated to date but still, at best, only minimal success has occurred.

5.1.3 ROI Proprietary Rights

In order for a company to justify a high return on an investment, they must be able to justify that the investment will put their product in a unique and advantageous position for future sales. If a new product or material is developed and allows the manufacturer to achieve something not possible with other approaches or solutions, then it is easier to justify investment. Furthermore, the longer this unique position exists, the higher the potential sales and thus the higher potential return on the investment. The complication comes into play when the product is to be used by the U.S. government. The U.S. government can legally allow a non-inventor the rights to the product or material (with compensation to the inventing company per Federal Acquisition Requisition, FAR, Subpart 27.2) thus removing most of the advantage of the inventing company. This results in a much more difficult justification of new energetic material work by private industry. Recent FAR changes have only exacerbated this situation. This is more extensively discussed in 5.3.5.

5.1.4 ROI Duration of Commitment

Historically, a long-term commitment has been required for success to be realized for a new energetic material technology. As stated previously, the probability of identifying a useable ingredient or technology is very low. However, even when overlooking this factor and assuming that a valuable ingredient will be identified with the first and only effort, a long-term commitment is still required. The application of a new ingredient to a final delivered product is probably ten to fifteen years away, much longer than the payoff intended by private contractors for the use of their internal funds. This is primarily due to the extensive characterization and use required before an ingredient is considered sufficiently safe and reliable for use as an energetic ingredient. The new material requires extensive characterization to address the in-depth scrutiny. Environmental, sensitivity, repeatability of the raw ingredient and end-product use, long-term storage and effect on the end product (e.g., mechanical properties, processing, detonation rate, etc.) and development of low-cost synthesis routes are a few of the issues that need extensive characterization and understanding prior to use in an end product.

5.1.5 Summary

In summary, four factors result in low potential payoff for private support of energetic material research. These are:

- the high cost associated with energetic material research,
- the low probability of success,
- the difficulty in maintaining proprietary rights when applied to government use and
- the long-term commitment to achieve success

Without a reasonable return-on-investment, a private company will not invest in a new effort. This will be further discussed in Section 5.3 wherein we will consider each private entity and the probability of a return on an investment by each of those industries and/or organizations.

5.2 Advanced Energetic Material Requirements for non-DoD Applications

The requirements associated with energetic material advancements for DoD use discussed in this book are nearly-identical to the required improvements needed for application outside the DoD. These include making energetic materials safe to the user, making them very reliable, making them have minimal (and preferably no) deleterious effect on the environment, having them efficiently perform their intended need with no side effect and doing all this at a minimal cost. How each of these requirements contributes to the acceptance of energetic materials outside the DoD is depicted in Figure 5.3 and further discussed below.

5.2.1 Safety

Not so very long ago, a safe energetic material was considered an oxymoron. How can something that is intended to explode, burn or otherwise result in a notable event, be safe? With energetic materials, safety is an obvious concern and one that is universal not only to the user within the DoD (e.g., the soldier) but especially for other industries where the eventual user is not trained in the use of safe procedures. The question of safety can be broken down into three complementary aspects:

- Knowledge of risks

- Regulations and
- Implementation of lessons learned

Throughout the 70-year history of the DoD studies and implementation of energetic material use, experiences associated with each aspect have become extensive and provide a substantial data base for non-DoD reference.

Knowledge of risks is dependent on the experience associated with these materials and, for new materials, the use of standardized safety tests. These tests are common within the propulsion and explosive industry and establish a comparison of known and new materials. For the most part, this data is shared by the community and open to non-DoD uses. However, the testing and interpretation of results is based on years of experience and can easily be misunderstood or incorrectly applied by the novice. Numerical simulation codes (computation of aerial pressure waves, speed and mass of fragments, etc.) complement the standard tests and provide additional information for improved safety.

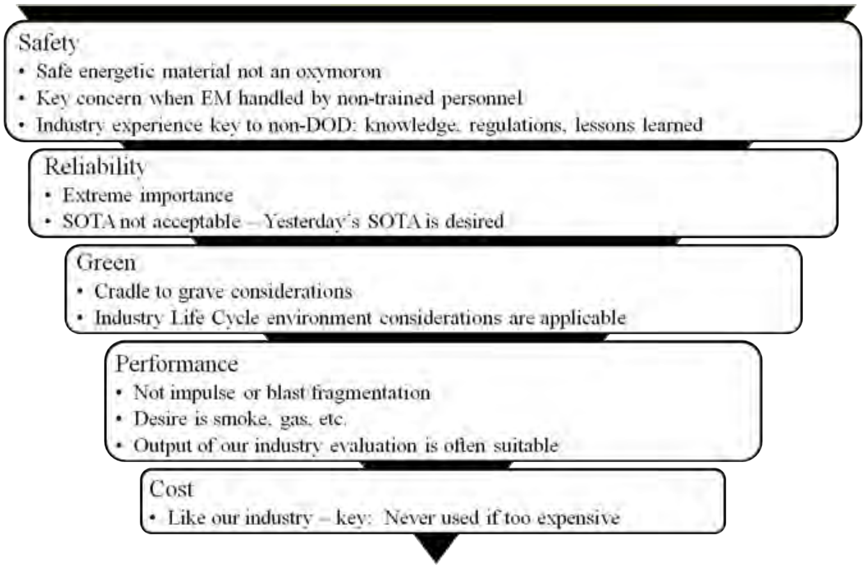

Figure 5.3: Energetic material requirements for non-DoD applications

Regulations have been established over the years and enforced at a government level. These include industrial safety and supplementary rulings that classify energetic materials and industrial operating conditions, and specify the aspects to be integrated in workplace safety studies. For the most part, each of the private companies that work with the DoD have also established safety regulations which mimic, or go beyond, the DoD regulations. These regulations and procedures are available to the non-DoD areas and in most cases are also required for the non-DoD use.

There have been numerous safety lessons learned in DoD uses over the past 70 years. The initiatives for insensitive munitions (IM) and low vulnerability ammunition (LOVA) concepts grew out of the lessons learned. The result of these initiatives has been numerous advancements in making energetic material use safer. For example, de-confinement arrangements that significantly attenuate the effects of an accidental operation in the human and environmental environment are known and can be applied. Use of venting to reduce an energetic materials response to an accidental-stimulus is another example.

5.2.2 Reliability

For non-DoD applications, the second criteria of importance, is reliability. In most instances, a failure cannot be tolerated even if that failure is a non-initiation but especially if the failure is a detonation or explosion. As a result, reliability for the non-DoD areas of use is normally so important that even using today's state-of-the-art (SOTA) is not sufficient. Most often the non-DoD user is looking for yesterday's SOTA. By doing so, it is assumed that the capability of the material has been further proven and reliability becomes acceptable.

A good example of this dependence on reliability is NASA's selection of propellants for the space shuttle. When the space shuttle was being developed in the mid-late 70s, the SOTA binder technology was the hydroxyl-terminated polybutadiene (HTPB) binder. However, since this technology was still relatively new, NASA went with a technology that was used in the 1960s for large solid boosters. They basically chose to go with "yesterday's-SOTA" choosing a propellant based on a copolymer of poly butadiene and acrylonitrile.

5.2.3 Environmentally Friendly ("Green")

For the non-DoD user, environmental concerns become a factor in every aspect of energetic material use from "cradle to grave." Each step in development and use (synthesis, production, formulation, testing, training, demilitarization, and cleanup) of an energetic material requires consideration of its impact on the environment. And, the impact on the environment is strictly controlled by government agencies such as EPA.

During development, types of solvents and use of heavy (restricted) metals as catalysts or reagents need to be considered. Disposing of these solvents and metals can become costly and minimize the use of materials dependent on them.

During testing, residual materials need proper disposal procedures to avoid impacting the environment.

Finally, during use, liberation of toxic or environmentally non-friendly gases and bi-products must be avoided. Over the past fifteen to twenty years, the recognition by DoD of the impact of energetic materials on the environment has become a significant driver in the research associated with energetic materials.

Procedures developed by the DoD community for evaluating and assessing "green" aspects can be applied to the non-DoD user world. For example, during the competitive-development stages of airbag inflator formulations, a key aspect was the quantity of asthma-causing effluent in the exhaust. The use of thermochemistry calculations, a common tool used in the propellant industry, provided the required information to identify the asthma-causing effluent. Once identified, it was merely a matter of re-formulating with the aid of the thermochemistry runs to obtain asthma-friendly formulations.

Each aspect of environmental impact on the cradle-to-grave scenario of a material, commonly referred to as life-cycle environmental issues, is considered by the DoD. As a result, the use of "green" development and use procedures has become common place with energetic materials thus making their use more compatible with non-DoD needs.

5.2.4 Performance

When one refers to performance for DoD applications, one is typically speaking of impulse-related parameters (propulsion) and blast capability (warheads and explosives). Typically, impulse and such related properties are not the primary performance consideration for non-DoD applications. The desired output could be anything from smoke to sparks to heat to gas volume to detonation/blast output. As a result, high performance for DoD applications does not necessarily translate into high performance for non-DoD applications. Nonetheless, the characterization and assessment of energetic materials conducted by the DoD for various applications will usually provide the necessary information needed to assess the capability for non-DoD use. As an example, again I refer to the theoretical thermochemistry properties of a propellant which are routinely calculated for all propellants and energetic materials. These theoretical calculations normally provide much of the information, e.g., gas volume, products, and etc., used by the non-DoD user to determine the effectiveness of a material.

5.2.5 Cost

For most of the non-DoD world, the cost of a material or item simply gets passed to the user. As a result if the item has a unique capability only available with an expensive item, it may find its way into use by the mainstream user. However, a high cost will significantly minimize the use of the item especially if a lower-cost approach is already available. Thus, lowering the cost becomes advantageous for increased use.

Low-cost is also a primary driver within the DoD. Many materials have been considered but eliminated due to the high potential cost for synthesis or preparation.

Low-cost not only includes the cost of the material but the cost to develop the material. Again, during the competitive years of automobile airbag inflators, the driver was for extremely low cost. The cost of an automobile inflator as sold by the manufacturer to the automobile industry was in the single-dollars range. This is an almost unbelievable cut in cost from typical $100,000-plus price ranges for rocket motors, the technology on which the airbag inflator is based. Here, the low-cost rocket motor industry approaches were inadequate and the inflator manufacturers had to develop their own procedures, tests and materials.

5.3 Non-DoD Organizations and Industries Using Energetics

The expanded use of energetic material outside the DoD is evidence that energetic materials are becoming more common in our daily lives. For the most part, these industries have grown out of the wealth of technology that has been developed through DoD funding of energetic materials. Also, little to no additional funding is being provided for energetic material research by these companies and organizations.

As stated previously, there are numerous non-DoD areas where energetic material use is common place (Table 5.1). These include other U.S. government departments (i.e., Department of Energy, Department of Homeland Security, Department of Justice and NASA); businesses closely associated with government contracts (i.e., propulsion industry and commercial houses for access to space), and other industries which rely on energetic material for their products and/or service.

In this section, we look at each of the non-DoD users of energetic materials. This discussion is restricted to U.S. operations. The emphasis of the discussions is as follows.

Table 5.1: Non-DoD use of energetic materials

Organization	Product/ Mission	Reliance on Past DoD Technologies	Funding Source?	
			Past	Future Potential
DoE	Nuclear material policy responsibility • Explosives to initiate or replace nuclear materials • HEAF primary responsibility for non-nuclear EM	• Largest non-DoD EM $ • Does not rely on DoD successes • DoE/DoD MOU for cooperative research	Yes[i]	Yes[i]
NASA	Nation's civilian space program & aeronautics/aerospace research • DoD in IHPRPT and RP-21 • EM funds directed towards reliability • No one Org controls EM funds	Yes-for initial launches Takes advantage of past SOTA	Yes[ii]	Yes[ii]
DHS	Protecting the U.S. and protectorates from terrorist attacks	• EM Detection/test (airport security) • Understanding EM to offset terrorist capabilities • Blast protection	No	No
Aerospace Contractors	• Provide products containing EM under government contract • Desire latest SOTA and pushing technology	• Highly reliant on DoD funding • Internal funding for EM ingredients is limited	Yes[iii]	Yes[iii]
Commercial Space Access	• Low-cost access to space • Safe, reliable old technology	DoD technology was basis for propellants	No	No

Gas Generators	Gas generator products for exhaust to perform specific function (e.g. airbags, fire ext., replenishable batteries)	• DoD technology was basis for starting EMs • Significant previous funding by airbag industry	Yes	No
Specialty Tools	Gas generator products which propagate blast wave	DoD technology was basis for starting EMs	No	No
Fireworks/ Special Effects	Provide explosions, smoke, loud noises, fireworks, etc. in presence of personnel	• Industry established before DoD existed • Primary dependence in 100+ yr old technology	No	No
Explosives	Deliver precise blast capability for destruction and removal	• Industry established before DoD existed • Primary dependence in 100+ yr old technology	No[iv]	No[iv]
Model Rockets	Propellant grains for the back-yard rocketeer	DoD technology was basis for starting EMs	No	No
Hunting Supplies	i.e. bullets - only included for completeness	Totally independent of DoD development	No	No
Pharmaceutical	Provide pharmaceutical products for health care	None	Yes[v]	Yes[v]
Other	Application of related EM technologies • Computer models • Analysis techniques	EM technology development required development of these technologies	No	No

[i] Most DoE funding of EM is for explosives, minimal for propulsion

[ii] Most NASA funding is for reliability and safety, not performance increase

[iii] Private industry EM typically for formulation development not new ingredients
-No payoff for new ingredient work; lack of patent protection and long-term payout.

[iv] Occasionally the commercial explosives industry required/s developing specialized products

[v] Pharmaceutical industry funds development of new chemicals which coincidentally are EMs

- Understand the impact of DoD funding of energetic materials on other aspects of our lives, and
- Determine if these other industries are a source of funding for future energetic material research and technology development.

5.3.1 Department of Energy (DoE)

The U.S. Department of Energy (DoE) is a Cabinet-level department of the U.S. government responsible for policies regarding energy and safety in handling nuclear material. Its responsibilities include the nation's nuclear weapons program, nuclear reactor production for the U.S. Navy, energy conservation, energy-related research, radioactive waste disposal, and domestic energy production. It is comprised of about 35 laboratories conducting research and development.[1]

The majority of the DoE's energetic materials effort is associated with nuclear materials and reactions. Even though nuclear materials are energetic materials, they are considered outside the scope of this book. However, the DoE does conduct research and has on-going efforts with non-nuclear energetic materials. Outside of the U.S. DoD energetic materials funding, the DoE probably has the largest energetic materials budget. Their work is primarily with explosives which can either initiate or replace nuclear materials.[1]

The DoE and DoD have a cooperative agreement for a Joint Munitions Program (JMP) in place under a Memo of Understanding (MOU) to share research funding. Within this JMP are several Technical Coordinating Groups (TCG). TCG-III is the designated task for the DoE and DoD energetic materials cooperative research. The mission of TCG-III is to provide new energetic materials technology. This research includes: discrete molecules in a range of particle sizes and crystal morphologies; formulations of joint interest to DoD as well as the DoE; mechanistic understanding of energetic material properties and behavior; and computational tools for high performance and insensitivity. The DoE laboratories most frequently associated with non-nuclear energetic materials research, i.e., Lawrence Livermore National Laboratory (LLNL), Sandia (SNL) and Los Alamos (LANL), are involved in this JMP TCG-III.[2]

LLNL's High Explosives Applications Facility (HEAF) is the "Energetic Materials Center of Excellence" within the DoE National Nuclear Security Administration. As such, the areas of expertise include high explosives and other energetic materials. Its mission is to provide expertise to government agencies including DoE, DoD, TSA, Homeland

Security, the FBI and other law enforcement and government intelligence organizations.[3]

The HEAF research contributes to the nation's understanding of energetic materials by developing new explosives in the synthesis and formulation laboratories, conducting explosives properties testing, developing experimental diagnostics, designing and executing basic explosive's properties research, studying explosives at the micron scale, and utilizing multiple firing tanks for larger scale explosives experiments. These efforts provide better understanding to the fundamental physics and chemistry of energetic materials, particularly with regard to their stability, sensitivity, and performance.

Guiding all of these activities are computer codes developed by HEAF personnel that mimic energetic materials and the very rapid physical and chemical processes that govern their detonation. The codes reflect longstanding Livermore expertise in simulating extremely short-lived events such as nuclear detonations. Continually refined by experimental data, the codes are paving the way for an unprecedented understanding of energetic materials at the molecular level. Many of these codes are nearly 15 years old and are commonly used in the energetic materials industry to better understand new and current materials. These include:

- ALE3D – a hydrodynamic code used in safety analyses such as cookoff simulations spanning a wide time span,
- CHEETAH – a code which transforms predicted formation energy and density of molecules into performance measures such as detonation velocity, pressure, energy, impulse and impetus, and
- TOPAZCHEM, PALM – codes to predict changes in thermal and chemical properties caused by different accident, battlefield and aging scenarios.

HEAF has made multiple energetic material contributions to weapon development, homeland security, and counterterrorism. Examples include:

- Conventional weapon development, including special-purpose weapons, armor penetration, and infantry protective equipment design,
- Development of new safer explosives for military and commercial use,
- Counterterrorism, including improvised explosives,
- Basic explosives research and development,

- Development of next-generation high-speed diagnostics for explosives research, and
- Development of environmentally focused processes such as molten salt oxidation of explosives for safe and clean disposal of explosive-waste.[3]

In summary, as a government organization, the DoE does support development of new energetic material technology and takes advantage of the advancements made from DoD funding. However, the DoE funding is directed mainly at explosives with minimal emphasis on propulsion and energetic material advancements for propulsion.

5.3.2 National Aeronautics and Space Administration (NASA)

As the executive branch agency of the U.S. government, NASA is responsible for the nation's civilian space program and aeronautics and aerospace research. Since February 2006, NASA's self-described mission statement is to "pioneer the future in space exploration, scientific discovery and aeronautics research." Although this mission goes beyond propulsion, certainly a key part of the mission is accessing space and maneuvering in space. Each of these requires use of energetic materials resulting in energetic materials being a key technology required for NASA.[4] With the recent announcement by NASA that it had selected a design of a new Space Launch System that will take the U.S. astronauts farther into space than ever before and provide the cornerstone for future human space exploration efforts by the U.S., the emphasis on energetic materials has been put to the forefront of requirements for NASA.

NASA is comprised of two Mission Directorates: The Human Exploration and Operations (HEO) and Science. The HEO Mission Directorate leads NASA’s human exploration in and beyond low-earth orbit. It oversees the International Space Station, commercial space transportation, advanced explorations, and launch services associated with human and robotic exploration programs. The Science Mission Directorate strives for a deep scientific understanding of our planet, other planets and the solar system.[5] Both Directorates are involved in use of energetic materials for propulsion (access to space and within space). As a result, there is no one organization which oversees the advancement of energetic materials for NASA.

NASA’s involvement with energetic materials range from the large space shuttle boosters to small motors used to help maneuver spacecraft in orbit. Each shuttle solid booster contained over 1.1 million pounds of propellant and produced up to 3,300,000 pounds of thrust. This compares dramatically with very low-thrust electrically-powered spacecraft propulsion systems.

NASA’s vision to enable global leadership in aerospace propulsion by responding to current and future propulsion needs of our country requires a close association with the U.S. DoD efforts. NASA is a member of the U.S. DoD core propulsion organization referred to as JANNAF (Joint Army, Navy, NASA and Air Force). NASA has also been involved in the propulsion industries’ Integrated High Payoff Rocket Propulsion Technology (IHPRPT) program and the more recent Rocket Propulsion for the 21st Century (RP-21) program. The vision of each of these programs is to advance technology of propulsion. As a result, NASA stays closely associated with the latest advancements occurring within the DoD and with DoD contracts including advancements associated with energetic materials.

As one can imagine, as open as the NASA missions are to public review and oversight, the primary driver becomes safety and reliability. One only needs to think back to 1986 and the impact of the Space Shuttle Challenger incident to realize how important reliability and safety are for NASA. As a result, NASA engineers may not be as interested in the latest technology as they are in yesterday’s technology to insure reliability.

In summary, as a government organization, NASA supports development of new energetic material technology through participation in efforts such as IHPRPT and RP-21. NASA also takes advantage of the advancements made from DoD funding. However, the NASA funding is directed more towards high reliability and safety rather than pushing technology to achieve performance.

5.3.3 Department of Homeland Security (DHS)

The United States Department of Homeland Security (DHS) is a cabinet department of the United States federal government, created in response to the September 11 attacks, and with the primary responsibilities of protecting the territory of the United States and protectorates from and responding to terrorist attacks, man-made accidents, and natural disasters. Whereas the Department of Defense is charged with military actions abroad, the Department of Homeland Security works in the civilian sphere to protect the United States within, at, and outside its borders.[6]

The vision of homeland security is to ensure a homeland that is safe, secure, and resilient against terrorism and other hazards where American interests, aspirations, and way of life can thrive. This vision leads to five missions, two of which require use of energetic materials as a key component to their efforts:

- Preventing terrorism and enhancing security
- Securing and managing our borders [7]

Most of the energetic material research conducted within DHS is overseen by the Science and Technology Directorate of the DHS. Places within the DHS where advanced energetic materials and technologies are primarily applied include:

- Detection and testing of energetic materials including at airport security lines,
- Understanding advanced energetic materials in an effort to stay ahead of the capabilities and technologies used to conduct terrorist activities, and
- Materials and technologies to protect against energetic material explosions, shaped charge jets, and etc.

However, since the need for DHS is primarily immediate use, reliability becomes a primary factor. As such minimal funds are put into developing new technologies. Instead the DHS seeks technologies, materials, and items ready for immediate use. For the most part, yesterday’s SOTA is sought to increase the reliability and understanding of the materials and technologies.

In summary, as a government organization, DHS requires use of energetic material technology but primarily applies established technology rather than support development of new technology. DHS also takes advantage of the advancements made from DoD funding.

5.3.4 Department of Justice

The United States Department of Justice (often referred to as the Justice Department or DOJ), is the United States federal executive department responsible for the enforcement of the law and administration of justice, equivalent to the justice or interior ministries of other countries. It has become the world's largest law office and the central agency for enforcement of federal laws.

The mission of the DOJ is to enforce the law and defend the interests of the United States according to the law; to ensure public safety against threats foreign and domestic; to provide federal leadership in preventing and controlling crime; to seek just punishment for those guilty of unlawful behavior; and to ensure fair and impartial administration of justice for all Americans.[8]

Like the DHS, the DOJ need is primarily immediate use and again, reliability becomes the driving factor for use of new technologies. As such minimal funds are put into developing new technologies. This author could not find an organization within the DOJ responsible for development or identification of new technologies relying on energetic materials. It appears instead the DOJ seeks technologies, materials, and items ready for immediate use. For the most part, yesterday's SOTA is sought to increase the reliability and understanding of the materials and technologies.

In summary, as a government organization, DOJ requires use of energetic material technology but primarily applies established technology rather than support development of new technology. DHS also takes advantage of the advancements made from DoD funding.

5.3.5 Private Aerospace Industries

There are several private companies which primarily work government (i.e., DoD) contracts for propulsion and warheads (i.e., propellant and explosives). Each of these companies routinely handles and works with energetic materials. For each, the majority of their work is conducted under government contracts mostly from a prime contractor and to a lesser extent, directly from the government.

Each private corporation has the basic mission of providing the best-value energetic unit (motors, gas generators, warheads, etc.) possible. To do this, they are required to build units which meet the requirements of the contract at a low cost. Any internal funding spent by any of these companies is spent with the intent of providing an advantageous position on a future (preferably relatively near-term) contract. This results in a constant balance between latest and best performance/technology and low cost.

At the core of each company is the desire and ability to work with energetic materials and conduct research to make the best and most technically-advanced product. The search for improved energetic materials, be they better raw ingredients or a better formulation, is a key part of the in-house research dollars for each company. Additionally, their personnel who are experts in this area also receive some funding from the U.S. DoD through direct contracts with the government laboratories. For the past fifteen years, most of this funding has been associated with the Integrated High Payoff Rocket Propulsion Technology (IHPRPT) program[9]. This government funding has provided the opportunity for most of these private contractors to be involved in identifying and developing new ingredients and applying these ingredients in new formulations.

The internal funds set aside by each company to work energetic materials are primarily directed toward formulation work and not raw-ingredient efforts. Since, by law, any technology developed by private industry can be assigned by government to another contractor on a government contract, and since most of the work conducted by these companies is for government work, the potential payoff for advancing the technology is minimal. Internal funding is typically only applied to an area where the proprietary rights to an advanced technology can be maintained. Over the years, each of these private contractors has learned to protect the technology and processing associated with a new formulation. This results in internal funding of energetic materials being applied to the development of new formulations for general application and technology advancement. Thus the internal funds provide an appropriate advantage for that company for future contract work.

Conversely, there is very little money spent by private contractors on development of advanced energetic ingredients. This results from two factors: the fact that the government can deem patents useable by a competitor for a government contract and the fact that the effort involved to bring a new ingredient into use in a production product takes a decade or two. Each is discussed further below.

Applying a new ingredient to a new product offers minimal if any advantage to the original inventor of that ingredient. Once a new ingredient is used in a unit, a competitor can quickly and easily determine the ingredient by analysis of the ultimate product. Thus, maintaining a new ingredient as company secret is nearly impossible. Alternately, patenting a new ingredient would not provide an advantageous position since the government could use the patent on a contract with a competitor (with compensation to the original inventor). The best way to protect a new ingredient would be to establish the synthesis of that ingredient as a company secret thus it is not open to the competitor. However, re-developing a synthesis approach is typically accomplished by experts in the field and at best this gives the original inventor an advantage of a year or two. In summary, any new material that results from internal funding will quickly become open to use by competitors. This thus minimizes or eliminates any advantage that a company would have from advancing the technology making it difficult at best and probably impossible to justify funding.

The second roadblock to private contractor internal funding for new ingredients is the time taken and low-probability of success in bringing a new ingredient into a high-volume production product; the true goal for each and every private contractor. The application of a new ingredient to a final delivered product is probably ten to fifteen years away, much longer than the payoff intended by private contractors for the use of their internal funding. Furthermore, the probability of success for a new ingredient to have a real impact in the industry is minimal (Note the CL-20 and GAP experience noted in Section 5.1.2).

Nonetheless, the private contractors maintain involvement in the development of new energetic material technologies and maintain experts in this field. Support for this primarily comes from DoD contracts but some in-house funding also supports this expertise.

In summary, the technology and expertise exists within the private industries to advance the state of the art for energetic materials. Some private contractor internal funding is used for developing new formulations. Because internal funding of new ingredient technology is a high-risk low-payoff endeavor, minimal or no funding is set aside by private industry for this work.

5.3.6 Commercial Access to Space

For the past approximately 15 years, there has been a recognition that the future for space flight lies not within NASA programs but within the private sector. The ultimate goal is to provide commercial service to space just as commercial aircraft currently provide services via air to other locations and other countries. The intent is to provide service for passengers and ultimately goods and supplies to a distant planet.

Since about 2006, NASA has acknowledged that the future for space transportation lies within the private sector. This resulted in the formation of NASA’s Commercial Orbital Transportation Services (COTS) and Commercial Resupply Services (CRS) programs. The first is to develop vehicles for delivery of crew and cargo to the International Space Station. The second is to coordinate the actual deliveries. Unlike previous NASA projects, the spacecraft resulting from the COTS program are financed and owned by private companies.[10] The spacecraft are designed to serve commercial customers but also can provide contracted services to the U.S. government on an as-needed basis. The issue for this endeavor is more challenging than existent commercial space transportation because it requires precision orbit insertion, rendezvous and possibly docking with another spacecraft. These NASA efforts lend financial support to potential commercial access-to-space providers.

The potential for spawning a new industry with initial high profit margins has resulted in new companies developing technologies for future commercial space opportunities. These companies must continue to compete with the current propulsion providers. The goal of these new companies is to build spacecraft for access to and orbiting in space. Such aircraft must be highly reliable. The result is that the technologies incorporated into future systems are yesterday's SOTA and development of new energetic materials is not considered. Again, new energetic material use in such spacecraft is probably only applicable a few decades out and the opportunity for an advantageous position is nearly non-existent (as discussed previously).

In summary, the companies addressing commercial access to space incorporate the established energetic material technologies developed through DoD funding. However, since the emphasis is on reliability and safety, the likelihood of this industry developing new energetic material technologies is very low.

5.3.7 Gas Generant Industries

The most successful spin-off product that has resulted from the government's expenditure of funds for energetic materials (i.e., propulsion) has been the development of gas generators for unique applications. By far, leading the product field in this area is use of the gas generators to inflate airbags for automobile safety. Other potential applications are with the use of gas generators for fire suppression (units currently exist in police cars using energetic materials) and potentially to provide a source of reusable/replenishable batteries.

In the mid 1990s, the development of advanced energetic materials for airbags was highly competitive and a slight advantage could result in very-large volume production and thus company profit. Since this industry was private by nature, any patented inventions were held proprietary by the inventing company and provided an immediate advantage to that company. This resulted in significant private-industry funding of new ingredients and new ingredient technologies. This effort took advantage of the work previously funded by the DoD in areas such as use of new ingredients like GAP. Numerous new technologies and patents were established. For a few years, the airbag industry was the only source of funds for development of new ingredients outside the government. These technologies developed in the airbag industry even found application to DoD propulsion and munitions area (e.g., improved AN phase stabilization, improved methods for application of GAP). Currently, the automobile airbag is basically a commodity within the automobile industry resulting in only minimal funding by private airbag suppliers for new energetic ingredients and no recent advancements in this technology have occurred.

The use of an energetic material to initiate at a specific time and provide a high volume of air (and for fire suppression, a high volume of a suppressant ingredient) closely mimics the function of an automobile airbag. As a result, the technology of gas generators for fire suppression grew out of the airbag technology. Since, to date, the use of gas generators for fire suppression has found niche-market opportunities but has not been incorporated into a high volume product, the market is very limited and the opportunity for profit is minimal. The result has been limited funding of new technologies especially new energetic material technologies.

The most recent potential opportunity for gas generators to find a commercial product home is in the use of gas generators to release gas as a source to replenish a battery. This technology requires an energetic material to provide an exhaust product (e.g., for a hydrogen battery). Since this is still a new and unproven potential market, no funding outside of previous Small Business Innovative Research (SBIR) funds has been expended in this area and no private sector corporation has provided significant funding of this technology.

In summary, several years ago, the airbag industry was a viable source for commercial funding to advance the technology of energetic materials. Since the airbag has become a commodity, airbag suppliers no longer support additional energetic material research. The other potential commercial gas generator industries also have not provided any significant energetic material technology funding. Unless one or more of these alternate gas generator opportunities becomes highly profitable and competitive, funding of energetic material technology will not occur within the private gas generator product industry.

5.3.8 Specialty Tools

Outside of the use of gas generators for automobile airbags, the most common use of energetic materials in our daily life is their use in specialty tools. Whereas the gas generators for airbags, fire suppression and replenishable batteries are dependent on exhaust materials (i.e., gas and/or solid effluents) these energetic materials propagate a shock which translates into a useful action. Pyrotechnic fasteners, pyrotechnic rescue cutters and nail guns are examples of such use of these energetic materials.

A pyrotechnic fastener or explosive bolt fastener incorporates a remotely activated (typically an electric current) pyrotechnic charge.[11] These have found applications in space to ensure separation between rocket stages. Compositions of the energetic material vary depending on the desired burning rate and required amount of energy and volume of gas produced. These compositions have grown out of the near 70-years of DoD funding of energetic materials. There is no intended improvement in these materials or potential for additional energetic material funding.

Pyrotechnic rescue cutters have resulted from the application of the use of a pyrotechnic material to a 50-year old "jaws of life" technology. The introduction of the pyrotechnic material can cut the weight of the cutter in half and at less than half the price. Again, the compositions used have grown out of the near 70-years of DoD funding of energetic materials. There is no intended improvement in these materials or potential for additional energetic material funding.

A "direct fastening" powder-actuated tool, sometimes referred to as a powder actuated nail gun, is used in construction and manufacturing to join materials to hard substrates (e.g., steel and concrete). This device relies on a controlled explosion created by a small energetic material charge. There are both high-velocity and low-velocity types. The energetic material directly impacts the fastener driving it into the hard substrate for the high-velocity version. It activates a piston in the low-velocity version. Powder-actuated technology was developed prior to the establishment of the DoD, during WWII. The high velocity fastening systems were used to temporarily repair damage to ships by fastening steel plates over damaged areas. The current materials are sufficient for any and all applications and there is no need for additional energetic material research to improve these products.[12]

In summary, each of these products, as well as other similar current or potential products, is designed for a niche-market. As such, there is minimal potential for investment by these manufacturers for energetic materials. Thus this product line is not seen as a source of potential funding for energetic material technology.

5.3.9 Special Effects and Fireworks

A common use of energetic materials is the use of pyrotechnics for special effects and fireworks. Pyrotechnic materials are capable of undergoing self-contained and self-sustained reactions for the production of heat, light, gas, smoke and/or sound. These effects are used to provide explosions, flashes, smoke, flames, fireworks, and etc. for entertainment purposes such as movies, plays and musical performers. They are also the basis for that Fourth of July fireworks celebration we have all enjoyed and flares we use to indicate an emergency.

The industries providing these sorts of special effects and specialty uses are end-users. These industries require highly reliable and safe products. They have relied on not only the technologies developed by the DoD over the past 70 years, but even older technologies based on early fireworks and pyrotechnic development. There is no source of funding for new energetic material technology within this industry.

In summary, this is an industry that would have existed even without DoD investments and is not a source for future funding of energetic material research.

5.3.10 Commercial Explosives

The commercial explosive industry pre-dates the DoD and other U.S. government agencies. This industry to a great extent relies on old and reliable energetic materials such as dynamite, TNT, HMX, NG, and etc. These established materials have proven reliable and continue to be the primary source for explosions and detonations. Occasionally, a specialty area arises where tailored or unique blast capability is required. Examples are directed blasts for building collapse or for filling holes/crevices with advanced explosives. Recent funding of slurry explosives has occurred due to the need to be able to pour explosives down holes, cracks and crevices. In general, some funding has been provided by the commercial explosive industry but it has been minimal and infrequent.

The common area of work between commercial explosive suppliers and the DoD is the coordinated efforts to classify explosive-safety for packaging resulting in the adaptation of HM 181, UN classifications for explosives packaging.

In summary, the commercial explosive market relies primarily on very-old technology that pre-dates or nearly pre-dates the DoD. Even though this industry is an obvious user of energetic materials, because it is so well established and nearly a commodity, it is not a source of funding for advancing the technology of energetic materials.

5.3.11 Petroleum Industry

Energetic materials have been evaluated to help eliminate the U.S.'s dependence on foreign oil. Fracturing approaches using propellants and gas generators can supplement or replace hydraulic fracturing to optimize the amount of oil obtained from a pay zone.

In the petroleum industry, many stimulation techniques are used to maximize flow of oils from reservoir rocks. After initial drilling, oil remains in the spaces and pores of reservoir rocks. Increased production is achieved when these spaces are connected to the well and the oil seeps into the well. The process to achieve this increased production is called well fracturing. Fracturing can increase the production of a well by 1.5 to 30 times the initial rate of flow, as well as the overall production from 5 to 15%. Also, a well can be fractured multiple times during its production life.[13]

This process has evolved over time from explosive fracturing to hydraulic fracturing to, more recently, fracturing with propellants or gas generators. The slower, longer burning of the propellants results in further propagation of the flow path. This approach can be used in areas where hydraulic fracturing is not effective. The use of energetic materials typically reduces the time required for well fracturing and at a lower cost.

The energetic materials used in the petroleum for well fracturing are based on the technologies developed under DoD funds. Minimal or no funds have been expended by the petroleum industry to develop these energetic materials and future funding is also unlikely.

5.3.12 Model Rockets

An obvious application of energetic materials to commercial products is the area of model rockets. Since model rockets require propellant to launch into the air of our back yard or over a public park, it is obvious that this industry requires energetic materials. However, again, above all else, these model rockets must be reliable and safe. As a result, these rockets incorporate very-old technology which has been developed and reliably demonstrated through nearly 70 years of DoD funding. The model rocket industry provides no funding to advance the technology of energetic materials.

In summary, this is an industry that has relied on the propellants developed with DoD funding from decades ago. It is not a source for future funding of energetic material research.

5.3.13 Commercial Hunting Supplies

Since commercial hunting supplies include use of energetic materials, i.e., bullets, it is included in this section for completion. Most readers recognize that the technology that goes into gun ammunition dates back many centuries for common gun powder with refinements in the mid-1800s (guncotton and nitrocellulose) and the late 1800s for the development of smokeless powder[14]. The current technology for bullets is sufficient for all hunters' desires. The opportunity for a bullet manufacturer's payoff by investment in energetic materials is non-existent.

In summary, this is an industry that would have existed even without DoD investments and is not a source for future funding of energetic material research.

5.3.14 Pharmaceutical Industry

Some readers may find it surprising that the pharmaceutical industry is included in this discussion of non-DoD users of energetic materials. However, if one thinks about it, nitroglycerine, a common ingredient for rocket motors and explosives, is a common medicine prescribed in the medical industry for treating heart conditions.

When looking at advanced energetic materials for high performance (impulse or blast), chemical groups considered commonly include nitro-groups (e.g., nitroglycerine), nitramines which include a nitro-group attached to a nitrogen (e.g., HMX and RDX, and etc.) and nitrate salts (e.g., ammonium nitrate). These same nitro-groups and nitrates are also very important in the medical field and are the basis for many new pharmaceuticals developed over the past several years.

Even though this industry has probably never benefited from DoD investment in energetic materials, there is an opportunity for the energetic material industry to benefit from the multi-billions of dollars invested annually by the pharmaceutical industry[15]. As a large, competitive industry with high-volume and high-profit products, there is significant payoff for pharmaceutical companies to invest heavily in development of new ingredients; and, they do. Coincidentally, some of these new ingredients are energetic materials. The pharmaceutical industry contains numerous experienced and skilled chemists for the identification, development and synthesis of new ingredients. The successes have been numerous.

In summary, the pharmaceutical company has not relied on the DoD as a source of energetic materials. But it is currently the best source of non-DoD funding for new energetic compounds, especially when referring to new nitro-compounds and new nitrate salts.

5.3.15 Application of Energetic Material Technologies to Other Areas

Over the many years of developing energetic materials, related technologies have been developed which have been applied in other non-energetic material areas. To best understand the value of the multiple years of DoD investment, these enabling technologies need to be considered.

The development of explosives has coincided with computer codes developed to evaluate very rapid physical and chemical processes that govern their detonation. These computer codes have found utility in related areas such as evaluating safety of structures and “bomb-proofing” structures. These codes are also being used to develop new and improved helmets for soldiers for protection from blast.

Understanding how propellants burn has required in-depth studies of combustion and efficiency. Again, a knowledge base and computer codes have been developed which have been incorporated by multiple industries including fire suppression and automobile industries.

Understanding how propellants behave from a structural view point has been a key part of the past 70 years of research. Computer codes have been developed and refined which assess and establish a propellant's usefulness based on standard tensile properties. The expertise and codes developed within the propellant industry have been applied by other industries based on composite filled materials (e.g., rubbers and composite cases).

In summary, in addition to actual energetic materials that have been developed under DoD funding, several related technologies have been developed which have directly affected the U.S. citizens' life and have improved the safety and reliability of non-related products.

5.4 Potential Effect of DoD Energetic Materials Support on Non-DoD Energetic Materials Use

In Section 5.3, we looked at each of the non-DoD users (U.S. only) of energetic materials with the intent of:

- Understanding the impact of past DoD funding of energetic materials on other aspects of our lives and
- Determining if, within these other industries, a source of funding exists for future energetic material research and technology development

This evaluation of the non-DoD users has revealed that the evolution of energetic materials from a novel source for propulsion into our daily lives has primarily occurred because of funding by the DoD for the advancement of energetic material technologies. Even though energetic materials are used more routinely and in multiple areas, the advancements of energetic materials in the U.S. is nearly-exclusively attributed to the DoD funding. The cost to produce and manufacture energetic materials prohibits most industries from additional research in this area significantly limiting non-government funding of research in energetic materials.

Without continued government-funding of advanced energetic materials by the DoD, no significant technology advancements can be expected. As discussed in Section 5.3, the probability of funding by other users of energetic materials is nearly non-existent. The one exception is the development of new pharmaceuticals where there is cross-over between medicines and energetic materials (primarily with the nitro-group and nitrate salts).

Thus DoD dollars put into energetic materials will strengthen each of the U.S. industries involved with energetic materials and help to make them safer, more advanced thus more competitive world wide, and environmentally friendly.

As the energetic material industry becomes safer, more reliable, greener, etc. and their use finds more ways into our daily lives, a "snow-balling" effect could occur. Acceptance of energetic materials may drive further use of energetic materials to the point where energetic materials become common place and new applications and uses of energetic materials will be found to make our lives safer and more enriching. Even if this evolutionary acceptance of energetic materials doesn't occur in the future, the current uses of energetic materials will continue to play an important role in our lives and the application of safe and efficient energetic materials will be a driver in our society.

5.5 Summary

This chapter has shown that the extensive use of energetic materials in non-DoD areas has, for the most part, only been feasible because of government investments. Without past consistent government-funding of advanced energetic materials research, most of the non-DoD applications of energetic materials we experience in our daily lives would not have occurred. Additionally, this chapter has shown the low-probability of our country to sustain energetic material research without DoD funding in this critical area. It is expected that this trend will continue in the distant future.

The continued and consistent development of new energetic material technologies is only possible with continued DoD funding. The DoD is the only real source of energetic material funding. The successes associated with past (and probably future) DoD energetic material investments have made the American way of life simpler. This extensive non-DoD use of energetic materials should be recognized as a positive spin-off of DoD energetic material support and help to solidify the DoD need for continued investment in this area of research and development.

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