



## Advanced Energetic Materials

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Committee on Advanced Energetic Materials and Manufacturing Technologies,  
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# ADVANCED ENERGETIC MATERIALS

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Committee on Advanced Energetic Materials and Manufacturing Technologies  
Board on Manufacturing and Engineering Design  
Division on Engineering and Physical Sciences

NATIONAL RESEARCH COUNCIL  
*OF THE NATIONAL ACADEMIES*

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## Preface

Advanced energetic materials are a critical technology for the defense of the United States. While many of these materials are routinely manufactured as commodities, several new concepts and formulations have great promise for both evolutionary and revolutionary applications. The Department of Defense is concerned with prioritization of scarce resources as well as maintaining and improving the knowledge base in this area.

To help address these concerns, the Office of the Deputy Under Secretary of Defense for Science and Technology and the Defense Threat Reduction Agency (formerly the Defense Special Weapons Agency) requested that the National Research Council, through the Board on Manufacturing and Engineering Design, conduct a study to investigate and assess the scope and health of U.S. research and development efforts in energetic materials.

The Committee on Advanced Energetic Materials and Manufacturing Technologies (see Appendix A) was charged with the following tasks:

- Review U.S. research and development in advanced energetics being conducted by the Department of Defense, the Department of Energy's national laboratories, industry, and academia from a list provided by the sponsor of the study.
- Review papers and technology assessments of non-U.S. work in advanced energetics.
- Assess important parameters, such as validity, viability, and the likelihood that each of these materials can be produced in quantity. Identify barriers to scale-up and production, and suggest technical approaches for addressing potential problems.
- Suggest specific opportunities, strategies, and priorities for government sponsorship of technologies and manufacturing process development.

The committee conducted five information-gathering meetings at which it received presentations from the Department of Defense, the Department of Energy, and the Central Intelligence Agency and from academic and industrial organizations (see Appendix B, "Meeting Agendas"). Additionally, committee members visited a representative group of advanced development and production sites.

The committee effort focused on the following six major technical areas, defined by the study's sponsor. Each is addressed in a separate chapter, following the Executive Summary and an introductory Chapter 1.



- New energetic materials synthesis and development (Chapter 2),
- Thermobaric explosives (Chapter 3),
- Reactive materials (Chapter 4),
- Nanomixtures and nanocomposites (Chapter 5),
- Advanced gun propellants (Chapter 6), and
- Exotic physics (Chapter 7).

Chapter 8 presents the major conclusions and recommendations of the study. Findings and recommendations on the respective technical areas are presented in Chapters 2 through 7. A supplement to this report contains information that was determined by the U.S. government to contain technical data whose export is restricted by the Arms Export Control Act. Requests for the supplement should be made to ODUSD(S&T)/WS, Suite 9030, 1777 N. Kent St., Arlington, VA 22209.

The scope of this study covered a broad range of materials. The committee is indebted to the experts who took the time to share their knowledge and insights. The committee also greatly appreciates the support and assistance of National Research Council staff members Sharon Yeung Dressen and Emily Ann Meyer in the development of this report.

Ronald L. Atkins, *Chair*  
Committee on Advanced Energetic Materials  
and Manufacturing Technologies

## Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's (NRC's) Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Robert Austin, Princeton University  
George Dieter, University of Maryland  
John W. Fischer, Naval Aviation, Science, and Technology Office  
George Lester, Consultant  
Fred Michel, Consultant  
Hyla Napadensky, Napadensky Energetics, Ltd. (retired)  
James O'Bryon, O'Bryon Group  
Lalitha Ramaswamy, University of Maryland  
Alfred G. Stern, Naval Surface Warfare Center, Indian Head

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Frank H. Stillinger of Princeton University. Appointed by the NRC, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.



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## Executive Summary

In response to a request from the Office of the Deputy Under Secretary of Defense for Science and Technology and from the Defense Threat Reduction Agency, the Committee on Advanced Energetic Materials and Manufacturing Technologies conducted a study of the scope and health of U.S. research and development efforts in energetic materials. The study focused on six major technical areas:

- New energetic materials synthesis and development
- Thermobaric explosives
- Reactive materials
- Nanomixtures and nanocomposites
- Advanced gun propellants, and
- Exotic physics.

Based on information gathered from meetings, site visits, and presentations from the Department of Defense, the Department of Energy, the Central Intelligence Agency (CIA), and academic and industrial organizations, the committee's major findings are as follows:

- Although all modern defense systems and weaponry rely on energetic materials as an explosive fill or a propellant from guns, rifles, missiles, and rockets, the U.S. effort in research and development of energetic materials is small, fragmented, and suboptimal, leaving this critical national technology area at risk.
- The suboptimal U.S. effort is characterized by severe resource limitations across the entire spectrum of energetic materials research and development, but particularly in the funding for scale-up and advanced development studies of potential new materials and in the training of replacements for the aging workforce.
- The current focus in the Department of Defense is on limited theater actions, with an emphasis on deployment of precision strike smart weapons that are smaller, cheaper, and at the same time more lethal against all target classes—demands that



advanced energetic materials can address.

- Current funding sources for the military services for advanced energetic materials research are most often narrowly focused on near-term individual service requirements associated with hyperbole in news accounts of foreign weapons effects, as well as overly dramatized intelligence reports of foreign capabilities.<sup>1</sup> Such short-term efforts can reflect perceived technology capability gaps. The resulting competition for scarce resources inhibits cooperative research and development efforts across the government aimed at more global national requirements.

In addition to the specific technical recommendations presented at the end of each chapter in the report, the committee offers the following two major recommendations:

**1. The committee recommends that the Department of Defense redirect attention and resources to focus on strategies for reducing transition barriers to scale-up.**

This effort should be closely coupled to the ongoing efforts of the services to improve target lethality and weapons effects. Such an approach would ensure an extensive technology effort from the energetic materials community and would help provide for an adequate supply of well-trained scientists and engineers to meet the nation's future defense requirements.

**2. The committee recommends that the Department of Defense consider centralizing its management of energetic materials research and development in order to achieve a longer-term, cross-service perspective.**

One possible approach to such a restructuring might include establishing an Energetic Materials Technology Office in the Office of the Secretary of Defense (OSD). Similar to the Office of Munitions, such an office would require a unique program element funding line as well as the charter and authority to lead a national, coordinated energetic materials technology thrust effectively. A clear benefit of this approach would be a robust and productive national effort in energetic materials technology.

The recently initiated Advanced Energetics Initiative could perhaps be the cornerstone of this national effort.<sup>2</sup> However, any approach to implementing this suggested office would require establishing broad oversight and coordination responsibility as well as authority over all the energetic materials programs of the Department of Defense and a charter to develop

---

<sup>1</sup> Backgrounder on Russian Fuel Air Explosives ("Vacuum Bombs"). Human Rights Watch, February 2000. Available at <http://www.hrw.org/press/2000/02/chech0215b.htm>.  
George Smith. 2002. Weapon of the Week: The Thermobaric Bomb. *The Village Voice*, December 18-24. Available at December 18-24, 2002. Accessed November 2003.  
Noah Shachtman. 2003. When a Gun Is More Than a Gun. *Wired News*, March 20. Available at <http://www.wired.com/news/conflict/0,2100,58094,00.html>. Accessed November 2003.

<sup>2</sup> The Advanced Energetics Initiative was proposed by the Office of the Secretary of Defense for maturing the fundamental technologies required to transition the next generation of energetics materials into field use.

cooperative engagement with and coordination of industrial and academic programs of the National Laboratories focused on energetic materials.

The overarching issue remains one of priority. Energetic materials are a key component of the nation's defense strategies. A coordinated and sustained effort in research, technology transition, and production technologies is needed to maintain the contribution of these materials to U.S. national defense.



# 1

## Introduction

There is no modern defense system or type of weaponry that does not rely on energetic materials—either in the form of an explosive fill or as a propellant (e.g., from guns, rifles, missiles, and rockets). In addition, energetic materials are used in a multitude of critical defense components ranging from shaped charges, actuators, and delay lines to detonators. U.S. defense needs for advanced energetics have been evolving rapidly in recent years. The needs for increased mobility, enhanced range and lethality, reduced or modified signatures, reduced collateral damage, and the capability to destroy hardened and buried targets combine to increase demand for enhanced conventional energetics. However, there are challenges to overcome before larger-scale manufacturing of enhanced energetic materials can take place or before fully fielded applications from the novel energetic materials technology base can be realized.

There continue to be indications that the former Soviet states are investing heavily in energetics research and development and may well be exploiting technological breakthroughs. For example, as indicated in a presentation to the committee, in 1986 Mikhail Gorbachev delivered a speech in which he implied that Soviet progress was being made in "non-nuclear weapons, based on new physical principles that approach nuclear weapons in strike capabilities."<sup>1</sup> A similar message was delivered by Russian Defense Minister Pavel Grachev in 1993 during a speech in which he discussed the possibility of achieving military technical superiority through the "creation of new models of high precision weapons, as well as weapons based on new physical principles that approach nuclear weapons in destructive force."<sup>2</sup> Recent reports indicate possible Russian use of advanced energetics in Chechnya. These foreign breakthroughs have the potential to place U.S. armed forces at a substantial technological disadvantage.

Many emerging technologies show promise for revolutionary changes—for example:

- Lighter-weight, longer-range missiles and rockets;
- Higher-performance, lighter-weight explosives;
- Reduced logistics and airlift requirements;
- Reduced sensitivity, resulting in increased safety and warhead penetration;
- Reduced or out-of-band plumes;

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<sup>1</sup> G. Ullrich, DoD. 2001. Presentation to the committee. July 31.

<sup>2</sup> G. Ullrich, DoD. 2001. Presentation to the committee. July 31.

- Increased stealth; and
- Designer weapons for neutralization of chemical and biological agents.

Enabled by advances in high-performance computing, modeling and simulation, new synthetic techniques chemistry, and the use of lasers, cryogenics, and high pressure to synthesize new molecules, recent U.S. energetics research has focused in the energy range between conventional energetics and nuclear fission.<sup>3</sup> Approaches for creating technologies with high energy and high rates of energy release range from the evolutionary to the revolutionary, and include the following:

- Shock-dissociated advanced fuels and oxidizers,
- Advanced CHNO/F (carbon-hydrogen-nitrogen-oxygen compound with fluorine) chemistry,
- Designer explosives with metallic additives,
- Nanostructured materials,
- All-nitrogen and hydrogen energetics,
- Reactive materials, and
- Exotic materials, such as nuclear excited state spin and shape isomers.

Many of these technologies are in the early stages of transition from theory to computer models to synthesis of small laboratory quantities for experimentation. The chemical structures of many of these materials are shown in Figure 1-1.

The introduction of an evolutionary improvement in energetics typically takes a decade or longer. This period spans the time from production of laboratory quantities through process scale-up, demonstration and validation in defense systems, bulk production, and introduction into inventories.<sup>4</sup> The revolutionary nature of many of these advanced energetic materials could mean that these basic steps will take significantly longer. The application of modern concurrent engineering techniques may substantially reduce the elapsed time for moving advanced energetic materials from theory to inventory. Modeling and simulation are likely to be useful in the safe and cost-effective scale-up of processes, equipment, and facilities for these materials.

Production processes for advanced energetics will likely range from modifications of conventional mixing, casting, curing, and pressing processes; to more novel techniques, such as the creation of nanocomposites by means of skeletal synthesis, solution crystallization, and gel mending; to the exotic, such as the use of advanced nuclear reactors. Given the limited commercial markets for many of these advanced energetics, it is anticipated that substantial government investment will be required to move these technologies into production.

The U.S. supplier base for high-performance explosives has been operating under increasing stress since the late 1980s. A report by the Department of Commerce, issued in 2001, predicts potentially serious employment issues with scientists, engineers, and production workers as a generation of workers retires in the next 10 to 15 years.<sup>5</sup> For

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<sup>3</sup> Conventional energetics are capable of releasing in the range of  $10^3$  joules per gram (J/g); nuclear fission can release approximately  $10^{11}$  J/g.

<sup>4</sup> T.L. Boggs, M.L. Chan, A.I. Atwood, J.D. Braun, P.S. Carpenter, M.S. Pakulak, and R.L. Hunt-Kramer. 1991. Propellant Development: From Idea to Motor, presentation to 28th JANNAF (Joint Army, Navy, NASA, Air Force) Combustion Subcommittee Meeting, CPIA Publication 573, Vol. III, October, pp. 317-357.

<sup>5</sup> National Security Assessment of High Performance Explosives and High Performance Components Industries. 2001. U.S. Department of Commerce, Bureau of Export Administration, Office of Strategic Industries and Economic Security. Executive summary available at

example, at the Naval Air Warfare Center at China Lake, a workforce of 10 to 12 employees was engaged in active research and development of new energetic compounds in 1985. Today, this effort involves only two to three people carrying out applied development on a single material.<sup>6</sup>

All of the armed services have steadily cut spending on R&D for munitions in recent years. Department of Defense funding for research, development, testing, and evaluation for munitions is expected to continue on a downward slope. By 2005, defense spending in this area is projected to be 70 percent below 1989's peak funding level of \$2.8 billion.<sup>7</sup>

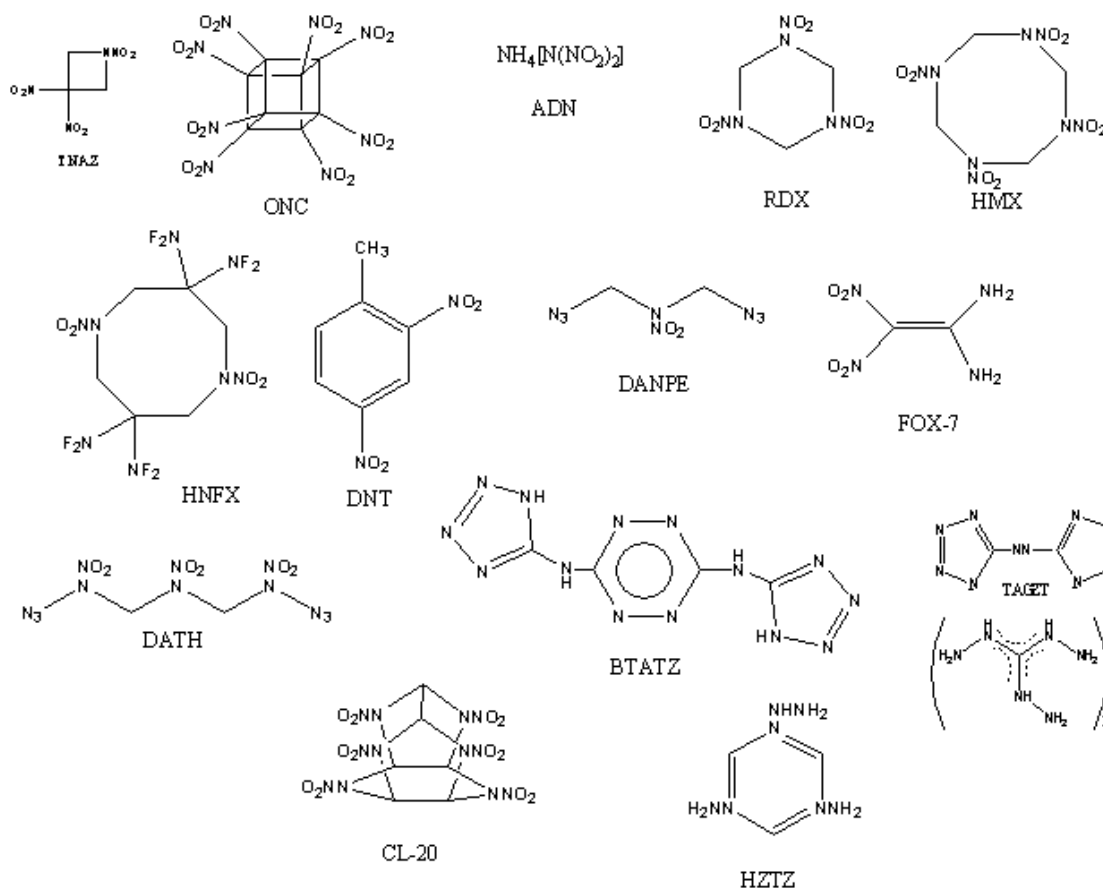


FIGURE 1-1 Molecular structures of selected energetic materials. (The acronyms for these materials are spelled out in Appendix C.)

<http://www.bxa.doc.gov/defenseindustrialbaseprograms/OSIES/DefMarketResearchRpts/ExplosiveComponentsIndustries.html>. Accessed September 2003.

<sup>6</sup> Robin Nissan, Head of the Chemistry and Materials Division, Naval Air Warfare Center Weapons Division at China Lake. 2003. Personal communication.

<sup>7</sup> Ullrich. See note 1 above.

## New Energetic Materials

### CURRENT RESEARCH FOCUS

In presentations made to the committee, the commitment of the U.S. Air Force, U.S. Army, and U.S. Navy to new energetic materials research on CHNO/F compounds was emphasized. Representatives of each service stated that new CHNO/F compounds will play a vital role in improving the capability of existing and planned systems. Each service presented research efforts focused on essentially unique suites of CHNO/F compounds. They all agreed that CHNO/F compounds continue to be the central and core ingredients for the vast majority of explosive and propellant formulations for the foreseeable future.<sup>1</sup> As such, this specialized field of synthesis needs to be a dynamic element of any initiative for meeting the emerging performance goals of future military ordnance.<sup>2</sup> It is important to note that the committee's task did not extend to verifying these service requirements presented to it.

The U.S. effort in the synthesis of energetic materials at present involves approximately 24 chemists, several of whom are approaching retirement. Few chemists are being trained to replace them.<sup>3</sup> The committee considers these scientists to be a national resource whose productivity in terms of new energetic compounds has been very high. If the level of effort that these scientists have contributed is not fostered and maintained, the United States will lose the technological edge that it has gained as a result of their work.

Attracting top synthetic chemistry talent to energetic materials research is possible only if the field is perceived to be scientifically exciting and financially stable. It has been argued that expansion of the synthesis effort is easily justified with respect to U.S.

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<sup>1</sup> R.S. Miller. 1995. Research on new energetic materials. Pp. 3-14 in Proceedings of the Materials Research Society, Vol. 418: Decomposition, Combustion, and Detonation Chemistry of Energetic Materials, T.B. Brill, T.P. Russell, W.C. Tao, and R.B. Wardle, eds. Warrendale, Pa.: Materials Research Society.

<sup>2</sup> J.M. Goldwasser, ONR, 2001, presentation to the committee, July 31; J.A. Lannon, RDC/Picatinny, 2001, presentation to the committee, July 31; M. Berman, AFOSR, 2001, presentation to the committee, July 31; D. Woodbury, DARPA, 2001, presentation to the committee, July 31; K. Kim, DTRA, 2001, presentation to the committee, July 31.

<sup>3</sup> T. Highsmith, Thiokol. 2002. Presentation to the committee. April 17.

competitiveness with other countries—for example, Russia and China, where the perception is that hundreds of capable scientists actively work in this area.<sup>4</sup> These numbers would suggest that the United States and Western nations should have faced major technological surprises from this large community investigating new compounds. While there have been notable exceptions, such as with ammonium dinitramide and aluminum hydride ( $\text{AlH}_3$ , or alane), the numbers and impact of foreign-generated new energetic materials have been comparatively small, calling into question the validity of this argument. Bigger is not necessarily better. This discussion does not, however, dilute the case for a continued, viable U.S. energetic materials synthesis program.

The need for a strong synthesis program today is inherently based on the new critical tactical requirements of the battlefield. These requirements are a result of new mission profiles and rapid turnover in other weapons system components and tactics that will fundamentally alter the mission requirements for new energetic materials. Using yesterday's energetic materials exclusively in today's (or even more so, tomorrow's) battlefield systems would be as effective as trying to run a Ferrari on kerosene. While it is generally accepted that new  $\text{CHNO}/\text{F}$  molecules will offer only incremental improvements to the currently employed materials, these improvements will lead to significant cumulative weapons system performance enhancement on target when coupled to technological advances in targeting, lethality, survivability, and advanced fusing, to cite a few areas.

### TRANSITION BARRIERS

It must be pointed out that over the past several decades, the products of the research of the energetic materials synthesis community have not successfully made the transition to military applications. One of the greatest barriers to capitalizing on current efforts is the lack of adequate and stable resources (including personnel) for synthesizing new materials and for shifting the most promising materials from the laboratory into fielded systems. Historically, the transition period from discovery of a new material to its availability in the field has been several decades. Very few materials complete that transition owing to the large number of requirements that a material must meet. These include the need to achieve high density, good mechanical properties, low sensitivities, good stability, low cost, ease of manufacture, and environmental acceptability.<sup>5</sup>

While the synthesis of new molecules is relatively inexpensive, full characterization, scale-up, and other processes necessary to introduce a new material into the military inventory require significantly more resources. In the current acquisition process, program managers cannot assume the inherent risk associated with research materials, since there is a good chance that major stumbling blocks will be encountered and system developers do not have the charter, or the resources, to invest in the development of new materials. Moreover, research managers are similarly resource-constrained. They cannot afford to support full characterization of emerging materials, which in the past has been the responsibility of the applied and advanced development community (i.e., the underfunded 6.2 and 6.3 program elements, respectively).

The Department of Defense (DoD) is essentially the only customer for these energetic materials. There is no question that the nation's capability to discover and to utilize new energetic materials is in decline. A significant, defense-funded energetic materials program would need to be implemented to stop this decline. Such a program should do the following:

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<sup>4</sup> H. Shechter, OSU. 2001. Synthesis of 1,2,3,4-Tetrazines Di-N-Oxides, Pentazole Derivatives, and Pentazine Poly-N-Oxides. Presentation to the committee. December 13.

<sup>5</sup> A. Sanderson. 1995. Proceedings of the NIMIC (NATO Insensitive Munitions Information Center) Workshop on What Makes a Useable New Energetic Material. NIMIC TR19950061. Listed online at <http://www.nato.int/related/nimic/reports/limited/limited.htm>.



- Become closely coupled to future weapons systems needs;
- Address the full spectrum of research, advanced scale-up, and characterization of advanced energetic materials;
- Focus on the qualification of new energetic materials for service use; and
- Train tomorrow's workforce.

## CURRENT CHNO/F ENERGETIC MATERIALS RESEARCH

The national energetic materials synthesis programs all have a common theme: beating the performance of the current, most energetic materials deployed in today's arsenal—namely, the nitramine explosives cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX).<sup>6</sup> The goal of new materials synthesis is generally focused on performance improvement. In most cases, target molecules are chosen only after theoretical predictions from extensively calibrated, empirically based computer codes indicate that the substance, if synthesized, will significantly improve performance in weapons applications. This approach to new conventional CHNO/F energetic materials can be characterized by recent U.S. successes, as detailed below. The chemical and molecular structures of such materials are shown in Figure 1-1 in Chapter 1.

## CHNO/F Targeted Energetic Materials Synthesis Programs

### *Caged Nitramines*

In the early 1970s, the Research Department of the then-Naval Weapons Center (NWC) in China Lake, California, conducted a short-term effort to synthesize hexanitrobenzene (HNB). This work was funded by Lawrence Livermore National Laboratory (LLNL). The successful synthesis of HNB catalyzed a multiyear effort of new CHNO (carbon-hydrogen-nitrogen-oxygen) compound synthesis at China Lake that culminated in 1987 with the synthesis of the caged nitramine explosive hexanitrohexaazaisowurtzitane (CL-20).<sup>7</sup> The caged nitramine effort was funded over almost a 15-year period by a number of sources, including the Office of Naval Research (ONR) Mechanics Division, internal NWC 6.1 (basic research), and 6.2 (applied research) funding.<sup>8,9</sup>

CL-20 has the highest density of all currently known stable nitramine explosives. (Density is an important physical property that couples directly to improved performance.) Lawrence Livermore National Laboratory has developed and fully characterized the performance and safety properties of a new explosive formula, Livermore Explosive Formulation 19 (LX-19), using CL-20 as the energetic component. CL-20, the single CHNO explosive currently in the transition process for qualification as an explosive and propellant ingredient, shows great promise. ATK Thiokol Propulsion has developed the scale-up processing protocol under DoD ManTech funding for large-scale synthesis of CL-20, and CL-20 is readily available for explosive and propellant developers to employ in future military applications.

<sup>6</sup> See Figure 1-1 in Chapter 1 for the molecular structures of RDX and HMX.

<sup>7</sup> See Figure 1-1 for the molecular structure of HNB and CL-20.

<sup>8</sup> A.T. Nielsen, A.P. Chafin, S.L. Christian, D.W. Moore, M.P. Nadler, R.A. Nissan, D.J. Vanderah, R.D. Gilardi, C.F. George, and J.L. Flippen-Anderson. 1998. Polyazapolycyclic caged polynitramines. *Tetrahedron* 54:11793-11812.

<sup>9</sup> A.T. Nielsen, ed. 1995. *Nitrocarbons*. Weinheim, Germany: VCH Publishing.

### Octanitrocubane

Researchers at the University of Chicago recently published the successful synthesis of one such target compound, octanitrocubane.<sup>10,11</sup> The work was supported by the U.S. Army's Armament Research, Development, and Engineering Center (ARDEC) and by the ONR Mechanics Division. A tour de force of modern synthetic chemistry, this work is illustrative of the value of sufficient and sustained support. However, octranitrocubane currently does not exhibit the predicted high density, and it is not yet clear whether cubane-based energetics will find a practical niche. In addition, the extremely long synthetic route of this material implies a high production cost, which may affect its application.

### Nitrogen Fluorine Substituted Nitramines

In several classes of explosives, the replacement of oxygen with fluorine may enhance many desired properties. For example, the introduction of difluoroamine groups into HMX may increase its density, performance, and specific impulse.

Particular advantages may be noted when the formulation includes metal ingredients. These expectations suggest that similar modifications should be investigated for a selected few of the more promising CHNO/F compounds that have been synthesized.

A comparison of two of the more common compounds can be seen in Table 2-1.

**TABLE 2-1 Comparison of HMX and HNFx**

Compound	Density (g/cm <sup>3</sup> )	P (GPa)	I <sub>sp</sub> (s)
HMX	1.90	37.4	272
HNFx	1.99 <sup>a</sup>	47.4 <sup>a</sup>	285 <sup>a</sup>

<sup>a</sup> calculated

The ONR Mechanics Division continues to fund synthesis efforts at the Research Department, Naval Air Warfare Center-Weapons Division (NAWC-WD), China Lake, and at the Naval Surface Warfare Center-Indian Head Division (NSWC-IH), pursuing fluorine analogs of HMX. In an essentially one-person effort over the last decade, a family of difluoroamine (NF<sub>2</sub>) substituted cyclic nitramines was synthesized, having calculated densities, heats of formation, and performance equal to or greater than those of HMX.<sup>12-14</sup> The first scale-up of these materials was initiated in 2002 with a small commercial contract as one task in the Advanced Energetics Initiative (AEI).<sup>15</sup> The goal of this project is to prepare sufficient gram

<sup>10</sup>P. Eaton and M.X. Zhang. 2002. Octanitrocubane: A new nitrocarbon. *Propellants, Explosives, Pyrotechnics* 27:1-6.

<sup>11</sup>M.X. Zhang, P. Eaton, and R. Gilardi. 2000. Hepta- and octanitrocubanes. *Angewandte Chemie, International Edition* 39:401-404.

<sup>12</sup>R.D. Chapman, M.F. Welker, and C.B. Kreutzberger. 1998. Difluoroamination of heterocyclic ketones: Control of microbasicity. *Journal of Organic Chemistry* 63:1566-1570.

<sup>13</sup>R.D. Chapman, R.D. Gilardi, M.F. Welker, and C.B. Kreutzberger. 1999. Nitrolysis of a highly deactivated amide by protonitronium. Synthesis and structure of HNFx1. *Journal of Organic Chemistry* 64:960-965.

<sup>14</sup>T. Axenrod, X-P Guan, J. Sun, L. Qi, R.D. Chapman, and R.D. Gilardi. 2001. Synthesis of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetranitro-1,5-diazocine (TNFX), a diversified energetic heterocycle. *Tetrahedron Letters* 42:2621-2623.

<sup>15</sup>The Advanced Energetics Initiative was proposed by the Office of the Secretary of Defense for maturing the fundamental technologies required to transition the next generation of energetics materials into field use.

quantities of HNFx, a gem-difluoronitramine substituted HMX analog, to confirm calculated physical and performance properties.

### TNAZ

Other work funded by ARDEC led to the synthesis and process for the commercial scale-up of 3,3,1-trinitroazetidene (TNAZ), a strained ring heterocyclic nitramine. TNAZ is one of the few new energetic materials found to be thermally stable above its melting point. However, in formulations studies, it has been found that TNAZ has high volatility that will severely inhibit its utility in military explosive and propellant applications.<sup>16</sup> Further limitations to its use include the processing, polymorph, and material costs.

### High-Nitrogen-Content Heterocyclic Molecules

Significant progress toward enhanced performance and increased stability is being made in the synthesis of high-nitrogen-content heterocyclic molecules. This area of synthesis is being funded in the Department of Energy (DOE) Laboratories, LLNL, and Los Alamos National Laboratory as components of DoD and ONR programs, and at SRI International and at the Rocket Propulsion Laboratory, Edwards Air Force Base, by the Defense Advanced Research Projects Agency (DARPA). While a plethora of new molecules has been synthesized, none has yet been prepared in sufficient quantity or purity for extensive evaluation. Theoretical calculations on some target molecules suggest that materials with greater performance than that of HMX, and a higher heat of formation than that of either HMX or CL-20, may exist in this class of energetic materials.<sup>17</sup> Highsmith,<sup>18</sup> Shechter,<sup>19</sup> Hiskey,<sup>20</sup> and Koppes<sup>21</sup> touched on several examples in their presentations to the committee. Many of these compounds, or relatives thereto, were initially discovered and reported in the open literature by scientists in the former Soviet Union.<sup>22-31</sup> To date, no

<sup>16</sup>K. Anderson, J. Homsy, R. Behrens, and S. Bulusu. 1998. Modeling the thermal decomposition of TNAZ and NDNZ. Pp. 239-247 in Proceedings of the Eleventh International Detonation Symposium, August 31–September 4, 1998, Snowmass, Colo.

<sup>17</sup>R.J. Bartlett, University of Florida. 2002. Presentation to the committee. April 18.

<sup>18</sup>T. Highsmith, Thiokol. 2002. Presentation to the committee. April 17.

<sup>19</sup>H. Shechter, OSU. 2001. Synthesis of 1,2,3,4-Tetrazines Di-N-Oxides, Pentazole Derivatives, and Pentazine Poly-N-Oxides. Presentation to the committee. December 13.

<sup>20</sup>M.A. Hiskey, LANL. 2002. Presentation to the committee. April 18.

<sup>21</sup>W. Koppes, NSWG-IH. 2002. Presentation to the committee. April 18.

<sup>22</sup>S.A. Shevelev, I.L. Dallinger, T.K. Shkineva, and B.I. Ugrak. 1993. Nitropyrazoles, 7. Nitro derivatives of bi-, ter-, and quaterpyrazoles. Russian Chemical Bulletin 42:1857-1861.

<sup>23</sup>I.L. Dallinger, T.I. Cherkasovaa, and S.A. Shevelev. 1997. Mendeleev Commun. 58.

<sup>24</sup>S.Sh. Shukurov and M.A. Kukaniev. 1993. A new synthesis of 3-alkyl-6-alkylthio-1,2,4-triazolo [3,4-b] 1,3,4-thiadiazoles, Russian Chemical Bulletin 42:1860-1861.

<sup>25</sup>S.A. Shevelev, V.M. Vinogradov, I.L. Dallinger, B.I. Ugrak, A.A. Fainzilberg, and V.I. Fillipov. 1991. Reaction of NH-Azoles with fluorosulfonyl-N, N-difluorohydroxylamine. Synthesis of N-Fluorosulfonylazoles. English translation of Izv. Akad. Nauk Ser. Khim. 10:2419-2429.

<sup>26</sup>3(5)-Amino-4-nitropyrazole: Convenient synthesis and study of nitration. 1993. Russian Chemical Bulletin 42:1861-1864.

<sup>27</sup>H. Piotrowski, T. Urbanski, and K. Wejrochmatacz. 1971. Reaction of 2, 2-dinitropropane-1,3-diol with 1, 3, 5-trialkylhexahydro-s-triazines. Bull. Acad. Sci. France 359-362.

<sup>28</sup>O.V. Zavarzina, O.A. Takitin, and L.I. Khemlnitskii. 1994. Substitution of the nitro group in chloronitrofurazan by N- and O-trimethyl derivatives. Mendeleev Commun. 135.

<sup>29</sup>I.B. Starchenkov, V.G. Andrianov, and A.F. Mishev. 1998. Chemistry of furazano [3,4-d]pyrazine 6. 1,2,3-triazolo[4,5-d]furazano[3,4-b]pyrazines. Chemistry of Heterocyclic Compounds 34:1081-

evidence exists which suggests that any of these materials reported in the former Soviet Union were moved into military systems. Investment in the category of high nitrogen compounds appears at this time to have the potential for generating significant midterm application. Additionally, new energetic materials efforts over the past 10 to 15 years funded by the DoD Office of Munitions, in partnership with the national laboratories, have resulted in the synthesis of many polycyclic nitrogen-containing heterocyclic materials of potential military application. More recently, DARPA has initiated continuation funding for energetic materials work in this field at SRI International.<sup>32</sup>

### *All-Nitrogen Materials*

In the general area of high-density energetic materials, the syntheses and reduction to practice of all-nitrogen compounds are high-risk endeavors. Theoretical calculations predict that many of the all-nitrogen compounds will have higher positive heats of formation (the calculated heat formation of the unknown compound,  $N_4$ , is 753,120 J/mol, whereas the heat formation of HMX is 75,019 J/mol), higher densities (the calculated density of  $N_4$  is 2.757 g/cm<sup>3</sup>, whereas the density of HMX is 1.905 g/cm<sup>3</sup>), lower combustion signatures, good calculated propellant characteristics, and perhaps lower sensitivities than those of materials in the arsenal.<sup>33</sup> These properties have yet to be verified by experiment.<sup>34</sup> The heat of explosion for these all-nitrogen compounds relies solely on the endothermicity of these molecules, as they have no constituents that will oxidize binder, metal, or fuel to contribute to  $I_{sp}$ , or detonation pressure.

The recently synthesized  $N_5^+$  cation is highly reactive and only relatively stable when associated with a large polyfluoro-element anion.<sup>35</sup> Ideally, based on ionization potential and electron affinity calculations, the imaginary  $N_5^-$  species is a likely candidate to form a stable, high-energy compound when combined with the  $N_5$  cation. The probability of a functionally fielded, all-nitrogen compound is very low, even in the long term. While theorists may predict that a variety of all-nitrogen species should exist, e.g.,  $N_4$ ,  $N_5^-$ ,  $N_7^-$ ,  $N_8$ , and  $N_{10}$ , the synthetic routes to these materials will certainly be a long time in coming. Syntheses of the all-nitrogen compounds should be a far-term goal at best. Nevertheless, this highly innovative research effort should be continued.

It must be noted that all of the new energetic molecules discussed above are essentially legacy molecules that resulted from sustained, concerted multiyear or even multidecade efforts, and that the funding of these materials synthesis programs has essentially dwindled to near zero. These legacy materials are in no way ideal, however, and some degradation and decomposition must be expected. The Advanced Energetics Initiative has begun to address the current funding deficiencies, but it is manifestly clear that a significant infusion of resources—both funding as well as new trained personnel—will be required to reestablish this critical technology base.

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1085.

<sup>30</sup>V.A. Tatakovsky. 1996. The design of stable high nitrogen systems. Pp. 15-36 in Proceedings of the Materials Research Society, Vol. 418: Decomposition, Combustion, and Detonation Chemistry of Energetic Materials, T.B. Brill, T.P. Russell, W.C. Tao, and R.B. Wardle, eds. Warrendale, Pa.: Materials Research Society.

<sup>31</sup>Y. Yongzhong and S.Z. Huang. 1989. Synthesis of polynitrocompounds from nitroguanidine. *Propellants, Explosives, and Pyrotechnics* 14:150-152.

<sup>32</sup>J. Bottaro. 2001. Presentation to the committee. December 14.

<sup>33</sup>R.J. Bartlett, University of Florida. 2002. Presentation to the committee. April 18.

<sup>34</sup>R.J. Bartlett, University of Florida. 2002. Presentation to the committee. April 18.

<sup>35</sup>K.O. Christe, USC. 2001. Presentation to the committee. December 14.

## CURRENT TRANSITION TO APPLICATIONS

Of all the new energetic materials synthesized over the past 20 years or so—and there have been literally hundreds—CL-20 is unique in that it has shifted to significant commercial production. It is now in exploratory and advanced development for a variety of defense applications. CL-20 has also received considerable interest in the Free World, and extensive work on this material has been and is being conducted in Sweden, France, Great Britain, and elsewhere. ATK Thiokol Propulsion markets CL-20 in the United States. BOFORS/Celsius of Sweden and Société National de Poudre et Explosifs of France are also commercial manufacturers of CL-20.

It must be emphasized that the slow transition by CL-20 bodes poorly for other promising materials. The research effort that led to the synthesis of CL-20 spanned a period of approximately 15 years, culminating in its synthesis in 1987. Its transition to commercial production has taken another 15 years; it is currently available commercially from U.S. and foreign vendors. All other energetic materials CHNO/F compounds, that is, high explosives as well as other materials, are in early stages of research and exploratory development and are, at a minimum, 5 to 10 years from potential utilization. Most of these materials will need a similar investment in order to reach their commercial potential, but it is unlikely that they will receive such an investment.<sup>36</sup> The 6.1, 6.2, and 6.3 funding for new energetic materials synthesis has been significantly reduced across the board at all DoD laboratories performing energetic materials research and development.<sup>37</sup>

Although the transition history of CL-20 is long, it is still shorter than the norm for new energetic molecules currently in the U.S. arsenal. An examination of energetic materials fills currently in use in the modern U.S. weapons arsenal reveals that the principal ingredients for explosive and propellant applications remain TNT (a World War I explosive) and the nitramines HMX and RDX (World War II explosives). The same materials are the preponderant ingredients for foreign military applications as well. These highly energetic CHNO compounds are the choice of weapons designers because they are relatively inexpensive and available, and they meet the extensive and stringent list of requirements imposed for performance, safety, reliability, compatibility, lifetime, environmental impact, and life-cycle cost, to list just a few characteristics.<sup>38</sup> Consideration of all of these properties is critical before a promising new material can be moved into production. In order to adequately address them, substantially more time and effort will be needed. Unfortunately, today's funding environment does not support the requisite transition program for potentially viable new energetic molecules.

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<sup>36</sup>The only "material" that does not fall into this category is the thermobaric fill demonstrated by a Defense Threat Reduction Agency effort. This is termed a new material, but it was devised simply through formulation, using currently employed energetic materials to mimic an explosive fill first demonstrated by the former Soviet Union.

<sup>37</sup> It is important to note that the sponsor's principal charge to the committee was to find, if it existed, the "low hanging fruit" generated by the synthesis/energetic materials community. The criteria for this goal were such that if a significant investment was made in the near term—that is 1 to 3 years—a particular material could be brought to maturity for insertion into weapons use. Unfortunately, no low hanging fruit was found to exist in any of the technologies that the committee was charged to examine.

<sup>38</sup> A. Sanderson. 1995. Proceedings of the NIMIC (NATO Insensitive Munitions Information Center) Workshop on What Makes a Useable New Energetic Material. NIMIC TR19950061. Listed online at <http://www.nato.int/related/nimic>.

## FINDINGS AND RECOMMENDATIONS

### FINDINGS

With regard to the research and development of new energetic materials, the committee found that:

- CHNO/F (carbon-hydrogen-nitrogen-oxygen compound with fluorine) compounds will continue to be the central and core energetic ingredients for the vast majority of explosive and propellant formulations for the foreseeable future. As such, this specialized field of synthesis will be a dynamic element of any initiative for meeting the emerging performance goals of future military ordnance.
- One of the greatest barriers to capitalizing on current efforts is the lack of adequate and stable resources (including personnel) for continued synthesis of new materials and for supporting transition development studies of the most promising materials from the laboratory into fielded systems (from 6.1 [basic research] to 6.2 [applied research] and 6.3 [advanced technology development] and beyond).
- Expansion of the scale-up and properties characterization program is imperative to move the most promising materials from 6.1 to the 6.2 and 6.3 levels.
- The anticipated smaller, internally carried ordnance with a concomitant requirement for higher performance will require new explosive formulations with higher energy content. These new critical tactical requirements of the battlefield mandate a strong synthesis program.
- Many of the current synthesis efforts are essentially one-person efforts or are led by very senior scientists. Funding these first-class synthetic chemists at a continuous, high level so that they are able to develop the next generation of energetic materials scientists is of utmost importance. The future of energetic materials syntheses and development rests on this group.
- CL-20 is the only new CHNO explosive compound that is currently available for large-scale synthesis and qualification in new military explosive and propellant formulations.
- The classical organic synthesis of new energetic molecules has low risk, yet a disproportionately high payoff. Performance and property enhancements available from new materials will be the stepping-stones to improved weapons effectiveness.
- Current productivity in the area of organic synthesis has been quite high, in spite of a relatively small annual investment.

### Recommendations

To conclude, energetic materials synthesis has provided the only "low hanging fruit" identified by the committee, and the Department of Defense should invest in the continued discovery, characterization, and development of such materials.

The committee recommends that:

- An investment strategy be implemented that emphasizes not only the development of new energetic materials, but also their characterization and scale-up.
- Investment be made in formulation technology to facilitate the transition of new compounds. It is important that this effort be funded to the point at which a weapons system designer can be assured that these new formulations have sufficiently low risk for implementation because they ensure improved performance against targets.

## 3

## Thermobaric Explosives

### CURRENT FOCUS

Of the topics assigned to the committee to review, only the area known as thermobarics has received national attention in the open media and throughout the DoD/DOE/Defense Threat Reduction Agency (DTRA) community. The committee heard extensive presentations by speakers from Sandia National Laboratories (SNL), Lawrence Livermore National Laboratory, agencies from the United Kingdom and Canada, and DoD agencies.<sup>1-6</sup> While the focus of these groups varies significantly, each of the presentations began with reference to weapons of the former Soviet Union (FSU), fielded in the 1980s, that were deployed by the FSU in Chechnya and which reportedly exhibited highly unusual effects in confined environments. The interest in these reported effects has grown exponentially.

### BACKGROUND AND CURRENT RESEARCH

The Russian military uses the term "thermobaric" to describe a class of munitions that the FSU investigated beginning in the 1960s; fielded FSU systems of this type appeared in the 1980s. This new class of energetic material, closely related to metallized fuel-air explosives, has received extensive attention in recent months. Indeed, the use of a "thermobaric" weapon by the U.S. military in Afghanistan was widely reported by the news media.

The extensive reporting surrounding these events has led to a lack of specificity in the use of the term "thermobaric." Early reports claimed that these energetic materials provide vastly increased performance relative to conventional high explosives. These claims appear to be based on anecdotal evidence from selected tests rather than on scientifically rigorous data.

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<sup>1</sup> R.J. Bartlett, University of Florida. 2002. Presentation to the committee. April 18.

<sup>2</sup> M. Baer, SNL. 2001. Presentation to the committee. December 13.

<sup>3</sup> J. Walton, CIA. 2001. Presentation to the committee. December 13.

<sup>4</sup> A. Kuhl, LLNL. 2001. Presentation to the committee. October 25.

<sup>5</sup> K. Kim, DTRA. 2001. Presentation to the committee. December 13.

<sup>6</sup> A. Kesby, UK DERA. 2001. Presentation to the committee. December 13.

While the Russian military identifies its weapons systems as thermobarics, the Russian scientific community refers to these materials as low-density explosives, or metallized volumetric explosives. Studies of thermobaric systems in the West date to about 1988 and were driven primarily by interest from the intelligence communities and by efforts to exploit foreign technology. A working definition of the term evolved, defining the thermobaric weapon as a single-cycle, fuel-rich explosive system that has a long-duration thermal pulse accompanying and supporting shock output. The term "thermobaric" now appears to be synonymous with fuel-rich or enhanced-blast explosives.

Current thermobaric munitions have been purported to exploit secondary combustion as a source of lethal energy and as effectively providing increased internal blast energy when deployed against soft targets such as buildings and against personnel and equipment inside confined targets, including tunnels and caves. Whether or not the extra combustion energy enhances the lethality of a munition depends on how the extra energy couples with the target. Energy that does not contribute to the detonation (shock) regime may still prove lethal if it can add to the total impulse within 10s of milliseconds inside a building or up to a second within a tunnel.<sup>7</sup> Further, the addition of materials that increase the density of the fireball may improve the coupling between it and the target, which can provide additional effectiveness. While extensive modeling studies are currently under way, few if any of these phenomena are well understood in the context of a thermobaric explosive application. Careful trade-off studies that examine the contributions of these effects are necessary for their successful implementation.

The committee's assessment of the present state of thermobarics research and testing in the United States is that it is relatively immature and not particularly well structured.<sup>8</sup> As discussed further below, the committee believes that this is a result of the following:

- The speed with which the United States attempted to field a thermobaric munition clone for use in Afghanistan;
- The inability and reluctance of the services to field new materials (hence, the redefinition of thermobarics to include Indian Head Explosive 135 [IH-135]);
- The unclear definition of terms;
- The lack of careful analysis and experimentation;
- Inadequate diagnostics that have perpetuated the reliance on anecdotal evidence as opposed to data; and
- Testing against varied types of targets and unclear scale effects.

An advanced concept technology demonstration (ACTD) effort was initiated by the Defense Threat Reduction Agency in 2001. It was to be a 3-year program. Driven by media reports from Chechnya and in the aftermath of September 11, 2001, the DoD and DTRA diverged from the original plan and embarked on an ambitious, 60-day ACTD program to demonstrate a thermobaric weapon in Afghanistan. The materials studied were conventional high explosives that included some of the features seen in Russian thermobaric systems, which utilized fuel-rich, heavily metallized, minimally confined explosive fills.

In contrast to the recent U.S. effort, much of the work done on thermobarics by others outside the United States focused on direct experimentation, some of which was quite sophisticated and dealt directly, although empirically, with the difficulty in measuring the performance of particular explosive devices. In the aforementioned presentations to the committee, evidence showed that the performance of this type of thermobaric explosive is

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<sup>7</sup> H. Shechter, OSU. 2001. Synthesis of 1,2,3,4-Tetrazines Di-N-Oxides, Pentazole Derivatives, and Pentazine Poly-N-Oxides. Presentation to the committee. December 13.

<sup>8</sup> K. Kim, DTRA. 2001. Presentation to the committee. July 31.



highly dependent on test configuration. This raises a serious question regarding the battlefield effectiveness outside of a very specific target set; fortunate placement of a weapon may even be required in order to achieve the expected effect.

## TRANSITION BARRIERS

The impetus to field a thermobaric weapons system has been understandable in light of reports from Afghanistan where the military target mix included some targets that were vulnerable to enhanced blast and increased impulse. However, the committee believes that the accelerated efforts to develop fieldable systems are counterproductive. In particular, the ACTD that led to the BLU-118B expended considerable resources while fielding a munition of, at best, only marginal improvement over its predecessor. The munition's configuration (a heavily confined warhead body) and the material (IH-135) appear to have been selected on the basis of programmatic expediency rather than thoughtful optimization.

Only a longer and broader view will avoid certain disappointment with limited progress in this potentially promising technology area. The Advanced Energetics Initiative has funded work focused on understanding the fundamental physical phenomena of thermobaric explosives. This project is focused on the underpinning physics of thermobaric systems, including studies of detonics, material dispersal, turbulence, pressure- and temperature-dependent ignition of metal combustion, energy release, coupling to targets, and comparison with traditional devices. The work will give priority to understanding known thermobaric systems, even if they are not optimized for deployment by the services. High-fidelity diagnostics development is critical to the success of this effort. Field tests could supplement scientific laboratory-scale experiments. Proposed model development and model validation are a necessity for predictive understanding of thermobaric explosive systems.

## FINDINGS AND RECOMMENDATIONS

### Findings

The committee found the following with regard to current work in the field of thermobaric explosives:

- The implementation of thermobarics may offer the first major shift in explosives application since the introduction of the shaped charge. If the underlying principles can be understood and consistently controlled, a significant new weapons system or series of weapons systems may become available to the warfighter.
- The engagement of formulators early in the development and characterization of potential thermobaric explosive formulations is necessary in order to capitalize on their experience and insight into advantageous material properties. A wealth of experience related to the Fuel-Air Explosives (FAE) programs exists in the services to assist in material selections and possible formulation guides. As with all explosive materials, chemical composition is only a starting point in discussing performance. Many safety and performance properties are related to purity, particle morphology, material density, binder selection, and processing methods. Parametric studies of specific formulations will be needed to characterize the structure and optimize the performance of thermobaric systems. Work on the predictive tools, test methods, and carefully crafted parametric studies on potential formulations is currently making good progress, and further success will ensure an effective and efficient program to weaponize a thermobaric explosive.

## Recommendations

In order to further develop thermobaric weapons systems the committee recommends the following:

- An evaluation and ranking of candidate thermobaric materials should be undertaken. The explosives community typically ranks explosive materials by some figure of merit, typically detonation velocity or pressure. Through decades of scientific study, such detonation properties have been used to predict performance characteristics such as brisance (the rapidity with which an explosive develops its maximum pressure). The TNT-equivalence for blast overpressure has also been used to rank explosives. Because thermobaric materials may not detonate efficiently and their lethal effects may include temperature and impulse, traditional detonation properties and TNT-equivalence are unlikely to provide the necessary figures of merit. A simple, direct measurement tool is needed. One such tool is the "stop sign" reported by Canadian researchers.<sup>9</sup>
- A concerted and focused effort is needed for understanding the phenomenology of enhanced-blast kill mechanisms and what they may offer over conventional munitions in effectiveness. This effort should be conducted to the point at which the major parameters influencing enhanced-blast effectiveness have been identified and incorporated into a model useful for effectiveness calculations and design of weapons.
- Warhead designs should be based on sufficient understanding of mechanisms in order to guide design toward optimal performance.

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<sup>9</sup> D. Frost, McGill University. 2001. Presentation to the committee. April 29.

## 4

## Reactive Materials

### INTRODUCTION

In this report, the term "reactive materials" (RMs) denotes a class of materials that generally combine two or more nonexplosive solids which, upon their ignition, react to release chemical energy in addition to the kinetic energy resulting when the high-speed projectile containing the reactive materials collides with the target.<sup>1</sup> When designed into munitions as part of the fragmentation component, reactive materials potentially have added benefit against soft targets, providing not only destruction similar to that achieved with inert fragments, but also energy release after penetration. The committee was briefed on aspects of this technology by investigators and program sponsors from ONR, the Naval Surface Warfare Center (NSWC)-Dahlgren, NSWC-IH, Eglin Air Force Base, ARDEC, Aerojet, and ATK Thiokol Propulsion.

A reactive fragment initially delivers its energy to a very small area of a target, perforating or penetrating the intended target. However, the reactive fragment must hit a component of the target for the ignition of the reactive materials of the fragment and the initiation of subsequent reactions, either with itself or with parts of the target. Experimental firings against soft targets have shown enhanced blast damage, greatly increased observable external rupture damage, and potentially increased lethality when compared with conventional fragment performance.

In most operational concepts presented to the committee, the performance of the RM fragment relies on initial penetration of the outer skin of the target, followed by impact of the RM fragment with interior solid components of the target to ignite the reactive material. There is also interest in and initial work underway to examine the application of reactive

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<sup>1</sup> M.E. Grudza, D. Jann, C. Forsyth, W. Lacy, W. Hoye, and W.E. Schaeffer. 2001. Explosive Launch Studies for Reactive Material Fragments. Presented at the 4th Joint Classified Bombs/Warheads and Ballistics Symposium, Newport, R.I., June.

<sup>2</sup> J.M. Goldwasser, ONR. 2001. Presentation to the committee. July 31.

<sup>3</sup> W. Hoye, NSWC-Dahlgren. 2001. Presentation to the committee. October.

<sup>4</sup> A.T. Nielsen. 2002. Presentation to the committee during its site visit to ATK Thiokol Propulsion. May.

<sup>5</sup> S. Struck. 2002. Presentation to the committee during its site visit to Eglin Air Force Base. May.

material warheads for hard target attack by replacing standard metal liners with reactive materials in shaped charges or explosively formed penetrators. However, this discussion focuses on the soft target application of reactive materials. Comparisons are made between reactive and inert fragments because of the near-term potential application of reactive fragments as direct replacements for inert fragments in existing fragmentation warheads.

This comparison is shown in Figures 4-1 through 4-4.<sup>6</sup> Figure 4-1 illustrates the damage done by inert fragments to a guidance component of a missile. Figure 4-2 shows the greater damage caused when reactive fragments were employed against an identical guidance component. Similarly, Figure 4-3 exhibits the results of perforation damage from inert fragments on a missile body, and Figure 4-4 shows the effects of reactive fragments against the same target, illustrating the catastrophic destruction of the test object.



FIGURE 4-1 Damage done by inert fragments to the guidance component of a missile.



FIGURE 4-3 Damage done to a missile body by a warhead's inert fragments.



FIGURE 4-2 Damage done by reactive fragments to a guidance component identical to that shown in Figure 4-1.



FIGURE 4-4 Damage done to the same target shown in Figure 4-3 by a warhead's reactive fragments.

<sup>6</sup> Figures 4-1 through 4-4 come from W. Hoye's (ONR) August 25, 2001, presentation to the committee.

Reactive materials can potentially damage targets by means of numerous mechanisms that may have cumulative effects:

- Perforation-increased internal temperature from the chemical reaction of the reactive material fragment,
- Explosion-induced shock/blast waves with enhanced impulse within the target,
- Overpressure,
- Carbon shorting of electronic components, and
- Reaction with and degradation of critical components.

If the cumulative damage caused by the reactive fragments is great enough, the likelihood of immediately discernible kills is increased. Often, when a target is disabled by a conventional fragment, the exterior and structural damage may be limited, making it difficult to ascertain the result of an attack and prompting further attacks on what may be a neutralized target. A goal of reactive fragment development programs is to cause visually ascertainable damage resulting in improved damage assessment by standard means.

Increased lethality is projected to arise from the use of reactive fragments because of a greater probability that sufficient damage will be done to a target with a smaller number of fragments and because there is a greater probability that a critical part of the target will be damaged by the secondary (chemical) reaction of the fragment within the target. The quantification of increased lethality is difficult owing to a number of uncertainties:

- Lack of confidence in the ignition of the reactive fragments;
- Questions regarding the energy transferred from a material of lower density than steel,
- Uncertainty about the overall probabilities of impacting the target, and
- Lack of knowledge about the physical integrity of the reactive fragments during launch.

Energy release from reactive materials is potentially tunable, and other applications, such as reactive casings, shaped charge liners, and explosively formed penetrators, are envisioned. Moreover, a number of reactive systems are potentially useful. Those under consideration include thermites, intermetallics, metal-polymer mixtures, metastable intermolecular composites (MICs), matrix materials, and hydrides.

## FINDINGS AND RECOMMENDATIONS

### Findings

With regard to reactive materials, the committee found that—

- Reactive materials research and characterization are in an early state of exploration and development.
- Most experimental demonstrations of weapon effects from reactive materials have shown more extensive, externally visible target damage when compared with damage caused by inert fragments under similar conditions.
- Higher peak pressures and a detonation-like reaction were achieved in experiments with RM-4. The results in these cases were dramatic.<sup>7</sup>

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<sup>7</sup> R.G. Ames, R.K. Garrett, and L. Brown. 2002. Detonation-like Energy Release from High-Speed Impacts of Polytetrafluoroethylene-Aluminum Projectiles. Presentation at 5th Joint Classified Bombs/ Warheads and Ballistics Symposium, Colorado Springs, June.

### Recommendations

Research on reactive materials is very promising in terms of potential near-term payoff. The research may also have potentially longer-term, broader-based application. The committee recommends the following:

- Many trade-off studies should be conducted before reactive materials can move forward.
- The possibility of more advanced applications (such as liners and cases) should be explored.
- Appropriate analytical tools should be developed and used, along with critical experiments, to determine applicability.
- Other materials such as thermoplastics should be investigated in greater detail with lower processing temperatures to allow the use of other metals.
- Requirements regarding the material properties of reactive materials should be correlated with results in realistic warhead tests including probability of kill.
- Greater emphasis should be given to materials engineering research and deployment methods to improve the lethality of reactive materials against both soft and hard targets.

## 5

## Nanomixtures and Nanocomposites

### INTRODUCTION AND CURRENT RESEARCH ACTIVITIES

Broadly speaking, energetic nanomixtures and composites consist of a support matrix containing submicron particles of metals, metal oxides, and/or organic and inorganic energetic materials. Defense-related applications of nanomixtures and nanocomposites that hold near-term and midterm promise include their use to enhance the performance of conventional explosives, propellants, and pyrotechnics in terms of stability, energy release, and mechanical properties. Nanomixtures and nanocomposites overlap other technology areas addressed in this report, especially that of reactive materials, and possibly thermobarics.

Federal support for nanotechnologies of about \$0.5 billion was provided in FY 2002; of that amount, about 32 percent was earmarked for DoD applications.<sup>1</sup> A small fraction of this DoD support (about 5 percent, or \$8 million) is designated for the nanotechnology of energetic materials.<sup>2</sup> Three DOE laboratories (Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Sandia National Laboratories), the DoD laboratories and centers (mainly ARDEC, Army Research Laboratory [ARL], NSWC, the Naval Air Warfare Center [NAWC], and Eglin Air Force Base), DARPA, and DTRA are each sponsoring or conducting modest-sized research activities devoted to the preparation, characterization, and application of nanometric energetic materials in service-specific settings.

The Army Research Office sponsors the Defense University Initiative in Nanotechnology (DURINT), which is centered at the University of Minnesota. The DURINT program represents a substantial investment in enlisting the academic community to help gain a fundamental understanding of the formation, processing, chemistry, and modeling of energetic nanoparticles and their formulations.

Most of the briefings to the committee about nanotechnologies were mostly at the program level as opposed to the bench level, since most research in this area is still in the discovery phase. The range of ideas presented to the committee was large in relation to the

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<sup>1</sup> David Mann. 2002. Presentation to 38th JANNAF Combustion Subcommittee meeting, Destin, Fla., April 8-10.

<sup>2</sup> R. Doherty, OS&T/IH. 2002. Presentation to the committee. June 6.

tangible successes and quantitative test results available to date. Thus, the practicality of these materials or processes remains to be determined.

The materials and processes discussed in the presentations to the committee were primarily in the following areas:

- Nanometric fuels, which mainly involve the use of aluminum powder sized at less than 50 nm, although other reactive metals and alloys were not excluded;
- Passivation and coating of nanometric metal particles to eliminate, or at least reduce, the rate of aging due to reaction with air and moisture;
- Sol-gel processing as a strategy for synthesizing and/or incorporating nanodimensional organic and inorganic materials in a supporting gel; and
- The use of carbon nanotubes and nanoporous materials as a support or container for energetic materials and reactive gases.

Arguments in favor of the use of nanoscale energetic materials and fuels rely primarily on gains resulting from altered chemical kinetics rather than thermodynamics. For example, 1-nm aluminum reacting with oxygen releases only 1.04 times as much energy as ultrafine aluminum (the micron particle-size range).<sup>3</sup> On the other hand, the rate of energy release of the latter is potentially faster because the balance of the rate-controlling factors shifts as the particle size is reduced. More specifically, the rate of a combustion or explosion process is controlled by the balance of the generally slower mass transport rates and faster chemical reaction rates. This fact frequently makes mass transport a controlling energy release process in conventional munitions and propellants in which micron and larger particle sizes of energetic materials are used. By contrast, the high surface area ( $10^4$  to  $10^6$  times that of the particles used in traditional formulations) and the short diffusion length of nanoscale particles are expected to enhance the role of chemical kinetics. Consequently, an unprecedented degree of control of the energy release rate may be possible by varying the composition on the nanodimensional scale. The burning rate might be accelerated, the delivered specific impulse could be increased by improved combustion efficiency, and the detonation might achieve greater ideality.

Companies such as Technanogy, Nanotechnology, Argonide, and Aveka have begun to provide nanoscale metals in response to commercial applications of nanoscale reactive metals beyond their use in military systems. It is hoped, therefore, that this activity will provide additional research and development beyond that supported by the the Department of Defense, as well a stable source of materials.

### TRANSITION CHALLENGES

The well-touted advantages of nanodimensional fuels and oxidizers appear against the backdrop of several disadvantages. In particular, the problem of aging of formulations containing nanoparticles is aggravated by the high surface area and the resulting higher reactivity of these particles. Oxygen and moisture cause a metal oxide to form on the particle surface, which leads to a loss of energy, lower reactivity, and added dead weight. Processing difficulties have been observed in the experimental development of nanoscale composites because the high surface area leads to problems such as drastically increased viscosity of formulations. Many military energetic material applications require a high degree of quality control of the particle size, surface characteristics, and physical and chemical properties. Meeting these requirements has yet to be demonstrated by nanomaterial manufacturers.

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<sup>3</sup> Michael Zachariah, University of Minnesota. 2001. Presentation to the committee. December 13.



In most of the DOE and DoD laboratories mentioned above, the majority of work on nanoscale energetic materials is directed at nanoscale aluminum fuel. The expectation is that performance enhancements will be achieved by the increased rate and magnitude of the energy release step. A lesser amount of work has been conducted on other reactive metals, such as magnesium and aluminum/magnesium.

An illustration of the type of work being conducted is a substantial program underway at Eglin Air Force Base to incorporate nanoscale Al into formulations. This effort is being bolstered by attempts to passivate the aluminum particles by coating them with a polymer.<sup>4</sup> Eglin Air Force Base has proposed an evaluation protocol for nanostructured materials, but it has been acknowledged that an understanding at the fundamental physical chemistry level will be needed to exploit these materials fully. In particular, the initiation and growth mechanisms, the solid-liquid-gas phase chemistry, and the detailed kinetics of nanoscale energetic materials remain unknown. The DURINT program is attempting to provide some insight into these areas. In general, however, the needed level of characterization of nanomixtures and nanocomposites is very difficult to achieve and may not be available any time soon.

A second major area of effort is being pursued at LLNL, where the incorporation of metal oxides (e.g., ferric oxide) with nanoscale aluminum into polymer support is being sought using sol-gel technology to produce a xerogel.<sup>5</sup> The reaction of aluminum with ferric oxide produces a thermite reaction. The polymer binder and/or added gas-generating materials are able to produce a working fluid when this is desired. The incorporation of nanodimensional organic energetic materials (e.g., RDX and pentaerythritol tetranitrate) and inorganic oxidizers (e.g., ammonium perchlorate) into silicate gels or resorcinol-formaldehyde (RF) gels by the use of sol-gel methods was initially pursued at LLNL, with tantalizing results. Recently this direction has also become a thrust area in the DURINT program, where an attempt is being made to desensitize impact-sensitive materials such as CL-20 by incorporating them on the nanoscale into RF and nitrocellulose gels.

The Army laboratories at ARDEC and ARL have plans to investigate the possible applications and gains that nanoscience might provide for gun propellants and explosives.<sup>6</sup> The possibilities include the use of functionalized carbon nanotubes and nanoporous materials to store hydrogen and oxygen separately, as is envisioned in fuel cell technology, to create an explosive. The energy released in the explosion was estimated to be twice that of HMX. The functionalized carbon nanotube could possibly be filled with nanodimensional energetic material, which is easily and reliably ignited with a plasma source. Such materials might have application in the Electrothermal Chemical (ETC) gun propellant program. It should be noted that efforts in these areas are preliminary basic research programs; transition to fielded systems would be many years away.

## MANUFACTURING AND TRANSITION BARRIERS

In all of the cases discussed above, a central issue in the use of nanotechnologies is the capability of the manufacturing complex to convert the most promising advances into mass production. The procedures for making and formulating nanomaterials of the future are quite different from those for conventional munitions. One problem that nanoenergetic developers may encounter is the challenge of making valid comparisons of these new materials and conventional materials. This barrier probably cannot be surmounted without

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<sup>4</sup> W.H. Wilson, AFRL/Eglin. 2001. Presentation to the committee. July 31.

<sup>5</sup> A xerogel is a solid material with an open porous framework; xerogels have very high interior surface area and a density between 25 and 75 percent of bulk properties.

<sup>6</sup> J.A. Lannon, ARDEC/Picatiny. 2001. Presentation to the committee. July 31.

side-by-side fundamental studies of the physical and chemical properties of the two types of materials.

## FINDINGS AND RECOMMENDATIONS

### Findings

The major findings of the committee on the topic of nanomixtures and nanocomposites are as follows:

- Research on nanotechnology and nanomaterials for military energetic material applications is essentially still in the discovery phase;
- The range of ideas presented to the committee regarding nanomixtures and nanocomposites was large in relation to the tangible successes and quantitative test results available to date;
- The practicality of these materials or processes remains to be determined; and
- Suppliers of nanomaterials have yet to attain reproducible product properties.

The combination of nanotechnologies and nanocomposite materials offers potentially high payoff at moderate to low risk. As a class, these materials offer high energy density and—in nanomaterial form—the capability for high power. This combination appears to generate a different category of explosion, and it does not typically generate gas, thus providing no efficient working fluid. It remains to be demonstrated whether nanomaterials can be combined with gas generators to make them extremely powerful propellants and explosives.

The approach of making composites of various oxidizers and fuels, especially at the nanometer-length scale, appears very powerful in that it might allow formulations scientists and engineers to overcome the diffusion-limited problems of reactivity that have hampered previous efforts. The approach also allows tailoring the sensitivity and performance attributes for increased effectiveness. Applications of nanoscale metal particles into formulations will rest heavily on achieving the long-term passivation of the particle surface without losing the benefits of the faster reaction rate.

### Recommendations

Research efforts focused on nanotechnologies destined for energetic applications have a modest but justifiable level of support. The current research and development program in nanomaterials and nanocomposites is a diverse collection of activities. The Advanced Energetics Initiative should develop a national strategy for focusing the effort on these interesting materials. The committee recommends that this strategy include the following:

- A suite of experiments and test criteria should be developed so that the properties of these various nanomaterials and procedures can be directly compared with those of conventional materials.
- Higher emphasis should be placed on performance testing of nanoaluminum formulations.
- Standard characterization techniques should be developed and implemented for nanomixtures and nanocomposites.
- The passivation process should be studied to ensure the stability of these composite materials.

## 6

## Advanced Gun Propellants

### CURRENT RESEARCH FOCUS

The status of advanced gun propellants was obtained from presentations to the committee given by or discussions held with Army and Navy researchers from ARDEC, ARL, NSWC/IH, and ONR.<sup>1-3</sup> In order to meet the requirements of future warfighting concepts that call for the use of smaller, lighter, more lethal forces with minimal logistics tails, both Army and Navy researchers recognize the need to develop new and improved gun propellants. Medium- and large-caliber guns will continue to play a major role in these concepts, but barrel sizes must be reduced and munitions must be made smaller, lighter, more lethal, and longer-range. For example, to meet the needs of the Army's Future Combat System, the size of the main tank gun, currently at 120 mm, must be significantly reduced, but at the same time muzzle energy must be increased by 25 percent. The Navy will depend more on 5-in. guns that fire extended-range munitions. To reduce the logistics burden further, gun tube wear must be reduced. New energetic materials and geometries must be used if these needs are to be met.

Additionally, health and safety concerns establish needs for environmentally safer, or "green," munitions that are insensitive to harsh handling and less vulnerable to attack. Advances in propellants alone cannot meet all of these needs. There must be synergistic design of the barrels, breaches, recoil systems, munitions, and propellants.

As in the case of new energetic materials research and development, the number of U.S. researchers actively working on the formulation and development of advanced gun propellants is a group of fewer than 25 dedicated individuals. Researchers in this area are concentrated at ARDEC, ARL, NSWC/IH, and a small number of industrial corporations. Significant research and development efforts in high-performance gun propellants are going on throughout the world, most notably in Germany and Switzerland. The efforts of foreign

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<sup>1</sup> A.B. Forch Horst. 2002. Review of Army Advanced Energetic Materials Programs and Facilities, U.S. Army Research Laboratory Weapons and Materials Research Directorate. Aberdeen Proving Ground, Md. May 7.

<sup>2</sup> M.N. Magdinec, J. Pertucci, J. Brough, and D. Cichra. 2002. Discussion of advanced energetic materials at Indian Head. Teleconference with the committee held on May 31.

<sup>3</sup> J.M. Goldwasser, ONR. 2001. Presentation to the committee. July 31

researchers have led to the development of propellants with reported performance advantages over currently fielded U.S. propellants—the performance of the former is relatively flat over a wide temperature range.<sup>4</sup>

The most promising research in progress for Army applications involves the use of new layered propellants that use new energetic ingredients. Navy researchers are likewise very interested in the use of layered propellants to enhance performance, but are also strongly motivated to find ways to reduce barrel erosion and thereby enhance barrel life. Both Army and Navy approaches employ advances in propellant-processing technologies that have matured significantly during the past decades. Additional details of these two research thrusts are discussed below. It should be noted that no significant research in gun propellants is being conducted by the U.S. Air Force.

### CURRENT GUN PROPELLANTS

All those who made presentations on gun propellants noted that over the past 30 years, the basic ingredients in fielded propellants have remained the same. The most important of these ingredients include nitrocellulose, nitroguanidine, nitroglycerin, and other nitrate esters. No propellants using new energetic molecules have been fielded. What has improved during this time period is the processing, formulation, and manufacturing of widely used, legacy molecules. Examples of uses for these materials are shown in Table 6-1.

**TABLE 6-1 Comparison of Formulations (in percentage) for Propellant Materials**

Propellant Material	M1	M14	M30A2	Low-Vulnerability Ammunition (LOVA)
Nitrocellulose	83.11	88.00	27.00	4.00
Nitroglycerine	0	0	22.50	0
Nitroguanidine	0	0	46.25	0
Cyclotrimethylene trinitramine (RDX) + cyclotetramethylenetetranitramine (HMX)	0	0	0	76.00
Dinitrotoluene (DNT)	9.77	7.82	0	0
Dibutylphthalate (DBP) + diphenylamine (DPA)	5.87	2.93	0	0
Diethylene glycol dinitrate (DEGDN)	0	0	0	0
Ethyl centralite	0	0	1.50	0.40
Potassium nitrate	0	0	2.75	0
Other	1.25	1.25	0	19.60

SOURCE: N. Eldredge, Picatinny Arsenal, 2001. Presentation to the committee. December 13.

New, recently fielded U.S. propellants have compositions and performance characteristics very similar to those of the formulations listed in Table 6-1. For example, Propulseur d'Appoint à Poudre (PAP 7993) solid propellant (a joint development between ARDEC and industry) is very similar to M1 but uses an environmentally acceptable plasticizer to replace dinitrotoluene (DNT). While this propellant shows improvement in the environmental area, it does not provide any added performance.

<sup>4</sup> R.L. Simmons and B. Beat-Volgelsanger. 2000. Introduction to NitroChemie EI Gun Propellant. Presentation to 37th JANNAF Combustion Meeting, Monterey, Calif., November. CPIA Publication 701:201-205.

## ADVANCED GUN PROPELLANT RESEARCH

The challenge with respect to propellants research and development is to enhance propellant performance significantly, while taking into account such objectives as reduced gun tube wear, lower flame temperatures of propellants, and "soft launch" capability for smart munitions, among other attributes. Research and development efforts in propellants have focused on performance, increased survivability, reduced vulnerability and sensitivity, and enhanced safety during transport and use. Efforts should continue in these areas. To reduce the size of munitions—thus allowing reductions in casing, barrel, and breach sizes—it is recognized that focusing solely on propellants will not provide an adequate solution. Propellant developers will need to work with gun tube designers to increase the size of the breach relative to smaller gun tubes in order to maintain the volume available within the casing for propellants. Such cooperative efforts among propellant and gun tube designers offer potential for improved systems and should continue.

### Army Research Activities

To improve propellant performance so that it reaches the goal of increasing muzzle energy by 25 percent without increasing barrel wear, ARL and ARDEC are currently exploring energetic formulations based on thermoplastic elastomers (TPEs). These formulations include the use of new, higher-energy fillers (such as CL-20) and nanostructured energetic materials. The primary driver for the use of these new TPE-based propellants has been their excellent performance coupled with relatively low flame temperatures (see Figure 6-1).

In addition to the advantage just noted, TPE propellant may be used in advanced layered geometries. Typical layered geometries are shown in Figure 6-2. When propellants are manufactured in these configurations, a relatively slow burning propellant is used on the outer layers and a faster-burning composition is used in the center core. Propellant geometries are tightly controlled to enable the inner-core propellant to begin burning as the projectile moves down the bore. This allows the pressure to be maintained at a high level for a relatively long duration and often results in a double hump in the pressure time response, as shown in Figure 6-3.

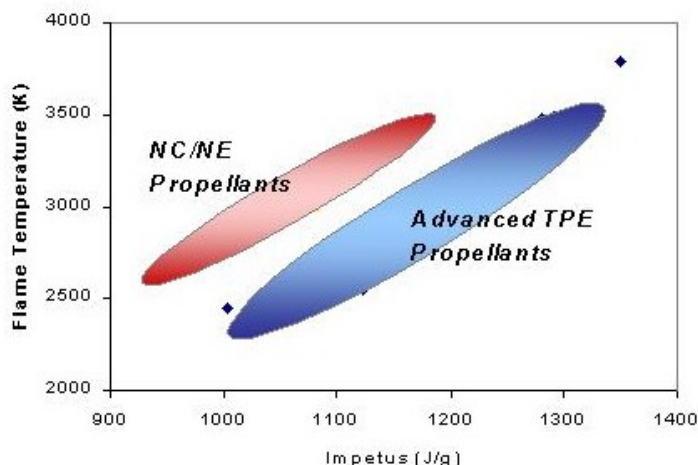


FIGURE 6-1 Calculated impetus and flame temperature for conventional (nitrocellulose [NC] and nitrate esters [NE]) and thermoplastic elastomer (TPE) propellants.

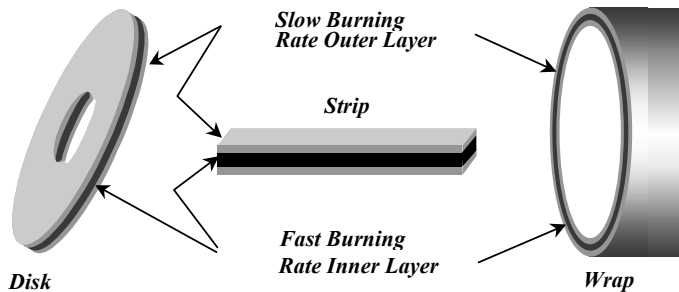


FIGURE 6-2 Typical layered geometries of TPE propellants.

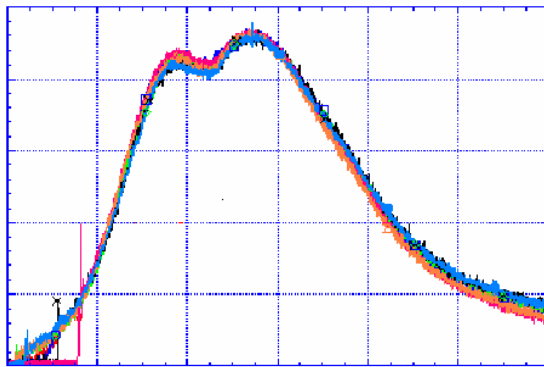


FIGURE 6-3 Pressure time trace from the firing of a 120-mm gun using layered TPE propellant.

The use of these layered propellants results in improved energy transfer to the kinetic energy of the round and hence in higher muzzle energy.<sup>5,6</sup> Despite these promising results, no layered propellants are used in currently fielded systems.

The new propellants under development by the Army have thermochemistry different from that of traditional nitrocellulose-based propellants. The impact of these differences in combustion products on gun bore erosion is not known. To begin evaluation of the erosivity of new propellants, researchers at ARL have been using a subscale erosion tester. It is anticipated that this device will be very useful in determining comparative erosivity of new and current propellants.

At the same time, Army researchers are evaluating tantalum coatings or ceramics on the surface of the barrel bore. To support this effort further, modeling is being done at both the molecular and the macroscopic level to assess thermochemical reactions and surface kinetics, respectively; the results are being validated with experimentation.

The advanced layered propellants under development by the Army have exhibited problems with sensitivity. ARL and ARDEC have initiated a collaborative advanced technology directive focused on insensitive high-energy munitions.

A key test in assessing the vulnerability of propellants is the pendulum test developed at ARL. In this test, a shaped charge jet attenuated through a conditioning plate of rolled homogeneous armor challenges a propellant sample (see Figure 6-4). The violence of the reaction is then compared with a baseline such as JA2 (a nitrocellulose gun propellant

<sup>5</sup> Joseph A. Lannon, RDC/Picatiny. 2001. Presentation to the committee. July 31.

<sup>6</sup> N. Eldredge, Picatiny Arsenal. 2001. Presentation to the committee. December 13.

developed in Germany). According to recent results reported to the committee, a high-energy layered propellant can be similar in reaction violence to the baseline JA2 if the geometry of the layered propellant is chosen properly.<sup>7</sup> The sensitivity of the test result to geometry was large, and more work would have to be done in this area.

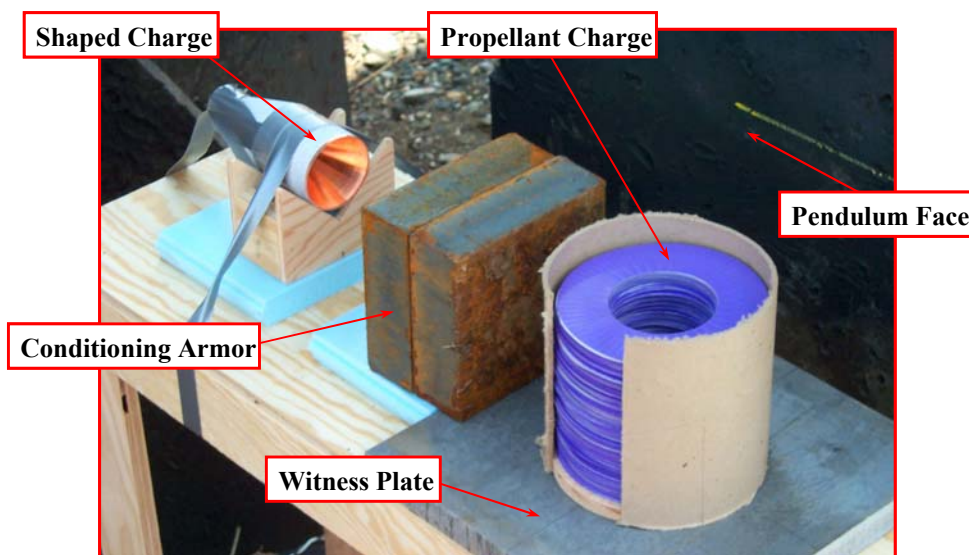


FIGURE 6-4 Typical test setup for a pendulum test used to evaluate advanced layered propellant.

Chemical propulsion research in the Army is not all internal. A significant amount of research is solicited from academia, national laboratories, and industry. Eleven universities are addressing topics including the theory of energetic reactions, heat and shock pulses on energetic materials, high-temperature energetic kinetics, and seven others. Research in the physics and chemistry of propulsion will further validate molecular and macroscopic modeling.

In a parallel and complementary effort, the Army's Electrothermal Chemical (ETC) gun program has been a prolonged technological effort to produce a gun in which electrical energy is used to augment and control the release of the chemical energy of the propellant. The muzzle energy comes entirely from the chemical energy, rather than from the electrical energy. Significant performance enhancements using ETC technology with existing or advanced propellants have been demonstrated. The ETC effort should continue to work on the development of high-energy propellants possessing acceptable vulnerability characteristics. The present program is focusing on the identification of gun propellants with the desired properties and on the extension of ETC technology to medium-caliber guns. Reduction to a fielded system remains many years away.

### Navy Research Activities

As with the Army, the Navy has some very strong points, as well as some shortcomings in its propellant programs. Research in Navy propellant design has suggested areas in which the Navy proposes to continue work. For example, a layered gun propellant approach came out of Navy research in ETC propulsion design. In collaboration with the Army, the Navy is

<sup>7</sup> P.C. Braithwaite. 2002. Update on Advanced Gun Propellant Efforts, presentation to the committee during its visit to ATK Thiokol Propulsion, Brigham City, Utah, May 22.

looking at low-CO-content propellants with high-nitrogen compounds such as 1,5-diazido-3-nitrazapentane (DANPE). The theoretical advantage of using materials such as DANPE is illustrated in Table 6-2. These numbers are especially impressive when compared with those for current propellants such as JA2, which has similar flame temperatures and an impetus of 1151 J/g.

**TABLE 6-2 Theoretical Benefits of Systems Using DANPE**

Ingredients	Impetus (J/g)	$T_v$ (K)	Gas MW
TNAZ + DANPE (40/60)	1439	3490	20.16
RDX + DANPE (55/45)	1425	3497	20.40
CL-20 + DANPE (40/60)	1419	3527	20.67

NOTE: The acronyms are spelled out in Appendix C.

SOURCE: R.L. Simmons. 1996. Guidelines to Higher Energy Gun Propellants. Paper 22 in Proceedings of the 27th International Conference of Institute of Chemical Technology, Karlsruhe, Germany. June 25-28.

The Navy is also evaluating new energetic ingredients such as Field Operating Activity (FOA) Organic Explosive 7 (FOX-7), FOA Organic Explosive 12 (FOX-12), dihydrazinotetrazine (HzTz), triaminoguanidinium azobitrazolate, and bis-aminotetrazolyl-tetrazine (BTATz) as new ways of tailoring propellant burning rates to meet the demands of layered propellants.<sup>8,9</sup> As with the Army propellants, the first layer provides a relatively cool burn, while the second layer releases much higher energy. This approach maintains a stable gun pressure that increases muzzle energy, as described above, but at the same time it is predicted not to increase tube wear significantly. More research is needed to see what happens at the boundary layer of these two materials, especially when they are made of dissimilar compounds.

The Navy has also had success in using energetic thermoplastic binders to develop green propellants.<sup>10</sup> These binders are costly, so the Navy is looking at twin screw continuous extrusion processes to compensate for the higher material costs by reducing manufacturing costs. Using this technology, Navy researchers at NSWC-IH have successfully processed sufficient TPE-based propellants through a twin screw extruder to support a series of 5-in. gun firings.

Figure 6-5 shows the extrusion of a slab material through a twin screw extruder (TSE). In this case a single material is being extruded. Research is currently being pursued at NSWC-IH to explore the possibility of using two separate TSEs to extrude layered propellant in a single operation.<sup>11</sup> It should be noted that this technology has been successfully used in the food processing industry for several years. Whether it will be possible to manufacture layered gun propellants effectively and efficiently using this technology remains to be demonstrated.

<sup>8</sup> R.J. Cramer. 1998. Advanced Gun Propellants. Presentation at 35th JANNAF Combustion Meeting, Tucson, Ariz., December 7-11.

<sup>9</sup> C. Walsh. 2001. Advanced Gun Propellant Formulations. Presentation at Energetics for Naval Gun Ammunition Technical Exchange Workshop, Waldorf, Md., October 23.

<sup>10</sup> J.M. Goldwasser, ONR. 2001. Presentation to the committee. July 31.

<sup>11</sup> C. Walsh and C. Knott. 2002. Advanced Gun Propellant Formulations. Presentation at the 2002 National Defense Industrial Association Guns and Ammunition Symposium, Panama City, Fla., April 15-16.





FIGURE 6-5 Slab extrusion using a twin screw extruder.

## FINDINGS AND RECOMMENDATIONS

New technologies offer promise in advancing the state of the art in propellants. However, it is the opinion of the committee that reduced, unstable funding has significantly affected these efforts. Limited 6.2 funding in this area reduces the ability to exploit advances in basic research, and most 6.3 funding is being used to better package old technologies. As a result of this lack of funding and focus, the workforce and the facilities for gun propellants continue to age. If this trend persists, technological innovations will be severely hampered and the recruitment of the brighter minds in the field will be difficult. Specific technical recommendations of the committee are as follows:

- The development of high-energy layered propellants with a focus on vulnerability and producibility should be continued.
- The exploration of high-nitrogen compounds as novel gun propellant ingredients in a variety of configurations should be pursued, with a requirement for an early demonstration.
- System-level efforts should be continued at a modest level for barrel wear, chamber design, and modeling.<sup>12</sup>

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<sup>12</sup> The Army and the Navy have numerous codes that model these systems. However, the committee is not able to specify a particular modeling technique. The perception of the committee is that with the improvements in modeling turbulent flow and erosion phenomena, the continuation of modeling efforts is warranted.

## Exotic Physics

The committee was tasked to review a limited set of more far-term, exotic materials that to date have not been seriously considered by the weapons development community as viable candidate energetic materials. This chapter addresses such materials.

### CURRENT RESEARCH EFFORTS

The committee heard presentations and did a literature search concerning two approaches for storing energy at extremely high densities in antimatter, specifically, as positrons in a Penning trap<sup>1</sup> or possibly as positronium in a standing wave laser trap.<sup>2</sup>

A positron, the antimatter electron, releases 1 MeV on recombination with an electron. This is about  $10^5$  times the energy of TNT on a per-molecule basis. Theoretical calculations indicate that practical devices may have to store about  $10^{22}$  positrons per liter, which is  $10^9$  times greater than concentrations that have been stored to date and exceeds by many orders of magnitude current positron storage capabilities. Extreme technological challenges must be overcome before practical devices based on this or other exotic material will be ready for even exploratory development. These challenges include vastly increased production rates for positrons as well as the development of confinement technologies.

The committee also received several presentations on nuclear shape/spin isomers as potential high-density storage media. The second metastable isomer of hafnium,  $178m2$  Hf, is typical of a limited number of nuclear isomers under consideration as energetic materials. It has been calculated that each atom of  $178m2$  Hf stores 2.5 MeV, which is about  $3 \times 10^5$  times the energy/molecule of solid TNT. Preliminary experiments, which are under serious debate, suggest that a 10 keV photon might trigger a  $178m2$  hafnium atom to release this energy; however, the efficiency of the triggering process is unknown and may be too small for practical applications. Many significant uncertainties exist about the relevant fundamentals of isomer selection, production, separation, and triggering and radiation handling. The

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<sup>1</sup> K.W. Edwards, Eglin Air Force Base. 2001. Presentation to the committee. December 14.

<sup>2</sup> J. Ackerman, J. Schertzer, and P. Schmelcher. 1997. Long-lived states of positronium in crossed electric and magnetic fields. *Phys. Rev. Lett.* 78:199-202.

committee has no special expertise in these technology areas. However, the technology of nuclear isomers as energetic materials was reviewed earlier by the JASON Committee, which suggested that this line of research was of exceedingly high risk.<sup>3</sup> The JASON report concluded that—

Before committing resources to such an experimental effort, there must be an adequate existence proof in the form of approximate, order of magnitude, estimates to justify investigating this effect. Without such a defensible order of magnitude estimate of how the reaction rate will be increased to useful values, this approach seems to have no merit at the present time.

## FINDINGS AND RECOMMENDATIONS

With respect to exotic physics, the committee found that—

- The use of both antimatter and nuclear isomers for storing energy for rapid release is at a very early, exploratory predevelopment stage. Moving these technologies to development and to engineering practice is far in the future.
- The payoffs of successful reduction to practice may be very high for technologies based on exotic physics; however, the technical risks are extremely high.
- Military applications for devices based on exotic approaches need much further elaboration.

With respect to pursuing the development of exotic physics, the committee recommends that—

- The Department of Defense should continue only small investments in well-focused research projects in the area of exotic physics in order to determine whether these technologies might mature toward proof-of-principle demonstrations. Because of the early stages of research, high costs, and high risks, heavy investments in these technologies seem to be premature at this time. The horizons for their practical applications are many decades away.

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<sup>3</sup> DoD JASON Committee. 1997. High Energy Density Explosives. JSR-97-110.

## Major Conclusions and Recommendations

The central conclusion reached in this study is that the introduction of improved materials into the defense systems and weapons inventory is necessary, looks overwhelmingly difficult, and requires sustained, long-term efforts. Today's small, fragmented, suboptimal effort in energetic materials research and development puts a critical U.S. national technology area at risk. Resources across the entire spectrum of energetic materials research and development are severely limited, but particularly so in the funding for scale-up and advanced development studies of potential new materials.

Funding for the nation's energetic materials technology effort is shrinking.<sup>1</sup> Without the opportunity for the current workforce to train the next generation of expert scientists and engineers, much corporate knowledge may be lost. This knowledge is key to maintaining the current weapon stockpiles safely, to ensuring their performance, and to developing the next generation of energetic materials.

Resources required for scale-up and characterization of new materials are so limited that it has proven nearly impossible to advance a new energetic material through the required extensive characterization and qualification that must be performed to bring the material to a level of maturity that will allow a system developer to consider the material as a low- or moderate-risk candidate. In addition, transition funding for promising new materials and formulations is essentially nonexistent. Concomitant with the decrease in research and development resources, the committee found that the industrial base for production of energetic materials has continued to erode, as observed also in a manufacturing study by the Department of Commerce,<sup>2</sup> which concluded that energetic materials technology development is in rapid decline and that the nation's energetic materials technology base is at risk unless significant new resources are committed to this vital technology and top-level national leadership is committed to sustaining this capability.

Revolutionary, orders-of-magnitude increases in performance as measured by increased energy density or increased power are unlikely to occur in the near future. Yet,

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<sup>1</sup> U.S. Department of Commerce, Bureau of Export Administration, Office of Strategic Industries and Economic Security. 2001. National Security Assessment of High Performance Explosives and High Performance Components Industries. Executive summary available at <http://www.bxa.doc.gov/defenseindustrialbaseprograms/OSIES/DefMarketResearchRpts/ExplosiveComponentsIndustries.html>. Accessed September 2003.

<sup>2</sup> Department of Commerce. See note 1 above.

incremental improvements in performance provide great leverage when coupled to other systems-specific improvements. Potential payoffs accrue in improved survivability and in increased range and increased lethality of weapons.

The scarce resources available to the energetic materials technology effort are too often focused on short-term responses. The driving force behind such short-term efforts is perceived technology capability gaps, which may be attributable to hyperbole in news accounts of foreign weapons effects, as well as overly dramatized intelligence reports of foreign capabilities.<sup>3</sup>

The current defense focus is on limited theater actions, with an emphasis on deployment of precision strike weapons that are smaller, cheaper, and at the same time more lethal against all target classes. An extensive technology effort from the energetic materials community will be required to meet the explosive and propellant requirements of these new systems. To ensure that such an effort is effective, it is important to couple it closely to efforts of the services to improve target lethality and weapons effects.

Current funding for the services often focuses on near-term individual service requirements, and the resulting competition for scarce resources inhibits cooperative efforts aimed toward more global national requirements. To overcome these barriers and competition for scarce resources, a major restructuring of the programmatic control and funding of energetic materials research and development is required in order to rebuild a robust and productive national effort in energetic materials technology.

**1. The committee recommends that the Department of Defense redirect attention and resources to focus on strategies for reducing transition barriers to scale-up.**

This effort should be closely coupled to the ongoing efforts of the services to improve target lethality and weapons effects. Such an approach would ensure an extensive technology effort from the energetic materials community and would help provide for an adequate supply of well-trained scientists and engineers to meet the nation's future defense requirements.

**2. The committee recommends that the Department of Defense consider centralizing its management of energetic materials research and development in order to achieve a longer-term, cross-service perspective.**

One possible approach to such a restructuring might include establishing an Energetic Materials Technology Office in the Office of the Secretary of Defense (OSD). Similar to the Office of Munitions, such an office would require a unique program element funding line with the charter and authority to lead a national, coordinated energetic materials technology thrust effectively. A clear benefit of this approach would be a robust and productive national effort in energetic materials technology.

The recently initiated Advanced Energetics Initiative might be the cornerstone of this national effort. However, any approach to achieving this suggested office would require establishing broad oversight and coordination responsibility as well as authority over all the energetic materials programs of the Department of Defense and a charter to develop cooperative engagement with and coordination of industrial and academic programs at the National Laboratories focused on energetic materials.

The overarching issue remains one of priority. Energetic materials are a key component of the nation's defense strategies. A coordinated and sustained effort in research, technology transition, and production technologies is needed to maintain the contribution of these materials to U.S. national defense.

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<sup>3</sup> Examples can be found at [http://news.bbc.co.uk/1/hi/world/south\\_asia/1854371.stm](http://news.bbc.co.uk/1/hi/world/south_asia/1854371.stm) and <http://www.commondreams.org/headlines02/0303-06.htm>. Accessed November 2003.

## APPENDIXES

## Appendix A

### Biographical Sketches of Committee Members

**Ronald L. Atkins** (*Chair*) was director of the Energetic Materials Center (EMC) at Lawrence Livermore National Laboratory (LLNL) from 1993 to 1999. His responsibilities included the development of a program plan to address the energetic materials research, development, technology, and evaluation requirements of LLNL and the Department of Energy (DOE); the implementation of joint programs addressing conventional weapons energetic materials needs of the DoD; and leading the High Explosives Working Group. In 1999 Dr. Atkins served on an international panel chartered to review the Swedish Defense Ministry's FOA 2 Division, which conducts the energetic materials research and development program for the Swedish government. From fall 1999 through spring 2000, Dr. Atkins served as a member with a team of scientists and engineers that assisted Lockheed Martin Corporation in its start-up activities as Lockheed Martin, and two British firms took over the contract to operate the Atomic Weapons Establishment (AWE) of the United Kingdom. His role was to examine the energetic materials research and development program at AWE, Aldermaston, and to recommend future programs and structure of the U.K. programs in supporting their nuclear weapons program. Prior to joining LLNL, Dr. Atkins was employed at the Naval Weapons Center at China Lake, California. He was part of the Chemistry Division, Research Department, for many years, as a research chemist (1973-1980), branch head of the Energetic Materials Branch (1980-1985), and head of the Chemistry Division (1985-1989). From 1989-1993, Dr. Atkins served as deputy program manager, Standoff Weapons Program Office, Attack Weapons Department, Naval Air Warfare Weapons Division at China Lake, Calif., where he contributed to the management of the Tomahawk Cruise Missile Project and was direct supervisor of the Tomahawk Baseline Improvement Project. Until his transition to the Attack Weapons Department, Dr. Atkins was very active in the American Chemical Society (ACS), and served for 3 years as chair of the Mojave Desert Section. He has also been involved in Sigma Xi and the Research Society of America, for which he served 2 years as chair of his local chapter. Dr. Atkins received a B.S. degree in chemistry from the University of Wyoming in 1966, an M.S. in organic chemistry from the University of Wyoming in 1968, and a Ph.D. with highest honors in organic chemistry from the University of New Hampshire in 1971.

**David E. Bender** is vice president of operations at Aerojet. In this position he is responsible for the company's design, development, manufacture, and testing of advanced energetic subsystems that include divert and attitude control systems (DACS), variable thrust axial propulsion systems, armament systems, and advanced energetics. Before assuming his current position, Mr. Bender was responsible for the company's tactical propulsion and warhead development product sector. Mr. Bender began his career with Aerojet at the Aerojet Ordnance Company in 1982 and was active in explosively formed penetrator (EFP) warhead design and demonstrated finned aerostable EFPs for programs such as Select Armor Defeating Artillery Munitions and Wide Area Side Penetrator Mine as well as Long Rod EFPs for programs such as Tube-Launched, Optically-Tracked, Wire-Guided Weapons System 2B and Advanced Anti-Tank Weapons System-Medium. He has also served in positions at Aerojet responsible for Predator engineering and manufacturing development and the Multipurpose Individual Munition/Short Range Assault Weapon Technology Demonstration programs. Mr. Bender has more than 21 years of experience in warhead and propulsion

technology as well as program management. He has authored or coauthored more than 15 technical publications and holds a patent for finned EFP formation methods. He has served as co-chair for multiple National Defense Industrial Association Ballistics conferences as well as for the International Symposium on Ballistics. He has received the Neill Griffiths Memorial at the 2001 International Symposium on Ballistics. He holds a bachelor's degree in mechanical engineering from California State University at Long Beach and a master's degree in business management from the Peter Drucker Center at the Claremont Graduate University, and he has completed the Engineering Management Short Course Program at the University of California at Los Angeles.

**Thomas B. Brill** is a professor of chemistry and biochemistry at the University of Delaware. His research is aimed at gaining fundamental insights into chemical processes at extreme conditions. Examples are the pyrolysis processes that occur on the surface of a burning material and the hydrothermolysis processes that occur in water at very high temperature and pressure. His areas of expertise include infrared and Raman spectroscopy, solid-state effects, thermal decomposition, explosions, supercritical water, and combustion. Since receiving a B.S. in chemistry (with honors) from the University of Montana and a Ph.D. in chemistry from the University of Minnesota, Minneapolis, Dr. Brill has served on the faculty of the University of Delaware in three departments: chemistry and biochemistry, chemical engineering, and art conservation. He has also been a visiting professor at Zhongshan University, Guangzhou, China (1990), and at the University of Oregon (1977). He is a member of the American Chemical Society, Sigma Xi, the Combustion Institute, the Materials Research Society, and the Society of Applied Spectroscopy.

**Philip M. Howe** is currently program manager of Nuclear Weapons Surety, where he is responsible for managing the surety program at Los Alamos National Laboratory (LANL). This involves design, implementation, and supervision of analyses, studies, and research on use control technologies, weapons safety, and explosives safety. Previously, he led LANL programs on explosives research, core explosives science, and explosives surety. He has also worked in the Advanced Technology Assessment Center group at LANL. Prior to joining LANL in 1990, Dr. Howe was director, Antiarmor Munitions Technology Office, Army Materiel Command (1987-1990) and chief, Explosives Effects Branch, Terminal Ballistics Division, U.S. Army Ballistic Research Laboratory (1975-1987). Dr. Howe holds a B.S. (with distinction) in chemistry from Worcester Polytechnic Institute, an M.A. in physical chemistry from Johns Hopkins University, and a Ph.D. in physical chemistry from Johns Hopkins. Dr. Howe's honors and awards include the following: R&D Achievement Award, Invention Awards 1979, 1980, and 1981; elected Ballistics Research Laboratories fellow (1982); Secretary of the Army fellowship (1985-1986); member, Los Alamos Neutron Science Center (LANSCE) Users Group Committee, LANL, (1997-1998); and member, LANSCE Advisory Committee, LANL, (1999 to the present). He is a member of the Materials Research Society, Sigma Xi, Phi Lambda Upsilon, the editorial board of the *Journal of Energetic Materials*, and the organizing committee for the Seventh and Eighth Symposium (International) on Detonation.

**Malcolm F. Nicol** is executive director of the High Pressure Sciences and Engineering Center and visiting professor of chemistry and physics at the University of Nevada at Las Vegas. Dr. Nicol holds a B.A. cum laude degree in chemistry from Amherst College and a Ph.D. in chemistry from the University of California, Berkeley. For most of his postdoctoral career, Dr. Nicol was with the Department of Chemistry and Biochemistry at the University of California, Los Angeles (UCLA), where he retired as professor of physical chemistry. He served on many high-level committees, including the following: Academic Senate Budget and Planning (chair at UCLA and systemwide), Undergraduate Curricula (chair), Educational Policy



(chair), and UC President's Council on the (DOE Defense Programs) National Laboratories. He also has been Gastprofessor Experimentalphysik at the Universitat G.H. Paderborn (1979); associate editor (1980-1990) and senior editor of the *Journal of Physical Chemistry* (1991-1998); chemist at the Lawrence Livermore National Laboratory (1985-1989); and visiting professor at the Materials and Structures Laboratory of the Tokyo Institute of Technology, Nagatsuta (1996-1997). Dr. Nicol's research interests include spectroscopy and the structure and bonding of solids and macromolecules under extreme conditions. His projects include the polymerization of CO, HCN, and other compounds; the search for new phases of materials at high temperatures and pressures; and the study of high explosives (RDX, HMX, triaminotrinitrobenzene, and hexanitrostilbene) and their decomposition products at high temperature and high pressure to learn how they work and to prevent accidents. Dr. Nicol has authored and coauthored over 150 publications and has given more than 50 invited and 125 contributed presentations at professional meetings. His honors and awards include the following: Alfred P. Sloan Foundation fellow, 1973-1977; Gordon Research Conference, Physics and Chemistry at High Pressures, co-chair, 1982; and the Herbert Newby McCoy Award in 1984. Dr. Nicol is a member of the American Chemical Society, Sigma Xi, and the American Geophysical Union and is a fellow of the American Association for the Advancement of Science and of the American Physical Society.

**Jimmie C. Oxley** has been a professor of chemistry at the University of Rhode Island since 1995. She was an associate professor in the Chemistry Department at the New Mexico Institute of Mining and Technology (NMIMT) from 1983 to 1995. She was one of the founding investigators in the Research Center for Energetic Materials (RCEM), a center supported by the National Science Foundation (NSF), industry, government and military laboratories. Dr. Oxley is also the founder and head of the NMIMT thermal hazards group and developer of the NMIMT Ph.D. program in explosives chemistry. Her primary research interests are the thermal decomposition of energetic materials, ammonium nitrate chemistry, and improvised explosive devices. Her other research interests include the development of better small-scale predictive tests, hazard analysis, explosive detection, and the characterization and prevention of terrorist bombings. Among the materials that Dr. Oxley studies are military explosives, such as nitramines, nitroarenes, and nitrate esters; improvised explosives, such as triacetone triperoxide and hexamethylenetriperoxidetriamine; energetic salts, such as ammonium nitrate and perchlorate; and reactive chemicals, such as peroxides, hydrazines, and hydroxylamines. Dr. Oxley is the author of more than 40 papers on the subject of energetic materials and presenter of as many invited lectures. She served as deputy director of the Gordon Research Conferences from 1995 to 1998, and as vice-chair (1994) and chair (1996) of the Energetic Materials Gordon Research Conference. Dr. Oxley cofounded the Conference on Life Cycles of Energetic Materials. She has also organized numerous national symposia for the North American Thermal Analysis Society (NATAS), Eastern Analytical, and American Defense Preparedness Association (ADPA). She was elected a NATAS fellow in 1995. She also organizes special explosives workshops for government and industrial labs. Dr. Oxley is a visiting scientist at Los Alamos National Laboratory and a board member of the International Calorimetry Conference, NATAS and ADPA Energetic Materials Technology group. Dr. Oxley received her B.S. degree in 1971 from the University of California, San Diego; M.S. degree in bioinorganic chemistry from California State University, Northridge; and Ph.D. in organometallic chemistry in 1983 from the University of British Columbia. She has served previously on four National Research Council committees, including most recently the Committee on Commercial Aviation Security and the Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons-Phase I.

**Anita M. Renlund** is a senior scientist in the Explosive Projects/Diagnostics Department at Sandia National Laboratories. She holds a B.S. in general chemistry from Stanford University (1974) and a Ph.D. in chemistry from the University of Utah (1977). Dr. Renlund joined Sandia in 1981 and has worked in the Explosive Technologies Group since that time. She is recognized internationally as an expert in the field of energetic materials (EMs), with specific emphasis on initiation and shock-induced chemistry of EMs. This area includes laser initiation of explosives, explosive response to abnormal environments, and the dismantlement of explosive systems. She currently directs research efforts in advanced energetic materials for highly miniaturized explosive components and hazards assessments of explosive ordnance.

**Albert A. Sciarretta** is president of CNS Technologies, Inc., consultants in research and development, modeling and simulation, management, and support of advanced information technologies and systems. CNS's clients include the Defense Modeling and Simulation Office, the office of the Deputy Under Secretary of Defense for Science and Technology, and the Joint Personnel Recovery Agency. He previously was manager of advanced information technologies at Quantum Research International, Inc. and program area manager of advanced information technologies for the MITRE Corporation. While at MITRE, he managed all of MITRE's support to DARPA, his division's information systems independent research and development efforts, and some efforts involving Army command, control, communications, computers, and intelligence technologies. He has experience in developing technology plans for modeling and simulation, combating terrorism, personnel recovery, DUSD (S&T)'s Smart Sensor Web initiative, and advanced concept technology demonstrations. Mr. Sciarretta has a B.S. degree in general engineering from the U.S. Military Academy and M.S. degrees in mechanical engineering and in operations research from Stanford University. He has worked on National Research Council studies as a member of the NRC staff.

**Jean'ne M. Shreeve** is a professor of chemistry at the University of Idaho. She has also served as the head of the Chemistry Department (1973-1987) and as vice president for research and graduate studies from (1987-1999). Dr. Shreeve received a B.A. degree in chemistry from the University of Montana, an M.S. degree in analytical chemistry from the University of Minnesota, and a Ph.D. degree in inorganic chemistry from the University of Washington, Seattle. She also received an honorary D.Sc. from the University of Montana in 1982. Her expertise involves the synthesis, characterization, and applications of fluorine-containing compounds. Dr. Shreeve has an extensive background in studies relating to fluoride chemistry and high-temperature fluids. She has published more than 340 technical papers dealing with the chemistry of fluorine and its compounds in refereed journals. Dr. Shreeve's extensive list of honors and awards includes the Garvan Medal, the Harry and Carole Mosher Award, and the Fluorine Award from the American Chemical Society (ACS). She is a fellow and was a board member of the American Association for the Advancement of Science (AAAS) and a member of the ACS, Royal Society of Chemistry, and American Institute of Chemists. Dr. Shreeve has been active in the ACS since 1964, including participation at the national level on the board of directors, Budget and Finance Committee, Development Advisory Committee, and Committee on Science; in the AAAS, she has served as chair of the Chemistry Section and on the board of directors and Committee on Nominations. Dr. Shreeve was a committee member for the National Research Council study on Idaho National Engineering and Environmental Laboratory High Level Waste Alternate Treatments (1998-1999). She was recently appointed as chair of the President's Committee for the Medal of Science.

**Robert B. Wardle** is manager of the Propellants, Explosives, and Pyrotechnics Research Department at ATK Thiokol Propulsion. He received B.S. and Ph.D. degrees in chemistry from the California Institute of Technology in 1981 and 1986, respectively. His research programs are on the synthesis and evaluation of new ingredients for application in propellants, explosives, and pyrotechnics and have included chemical process development and optimization for commercial synthesis of new ingredients. Dr. Wardle holds 37 patents in the areas of energetic materials, propellants, gas generants, and explosives and is the author or coauthor of more than 110 technical publications. In 1996, he chaired the American Defense Preparedness Association (ADPA) Energetic Materials meeting, and in 1997 he organized a CL-20 symposium. He has also chaired numerous meeting sessions for ADPA, Joint Army-Navy-NASA-Air Force (JANNAF), and Fraunhofer Institute of Chemical Technology conferences.

## Appendix B

### Meeting Presentations and Site Visits

#### Meeting One July 31- August 1, 2001 National Research Council

*Introduction and Overview*  
George Ullrich, DoD  
Starnes Walker, DTRA

*Energetics Survey*  
Milt Finger, LLNL

*Navy Programs*  
Judah Goldwasser, ONR

*Army Programs*  
Joseph Lannon, RDC/Picatinny

*Air Force Programs*  
Michael Berman, AFOSR  
Bill Wilson, AFRL/Eglin

*Intelligence Perspective*  
Fred Ambrose/DIA

*DARPA Programs*  
Don Woodbury, DARPA  
Art Morrish, DARPA

*DTRA Programs*  
Kibong Kim, DTRA

*LLNL Programs*  
Randall Simpsons, LLNL

*LANL Programs*  
Wayne Danen, LANL

*Sandia Programs*  
Mel Baer, SNL

#### Meeting Two October 25-26, 2001 National Research Council

*Reactive Materials*  
Walter Hoye, NSWC Dahlgren

*Status of OSD AEI*  
Ruth Doherty, OS&T/IH

*Lessons Learned from the AND Saga*  
Bob Wardle, Thiokol

*CL-20 Status Report*  
Lou Cannizzo, Thiokol

*Nuclear Isomers and X-Ray Driven Gamma Emission*  
Jeff Carroll, Youngstown

*Controlled Energy Release in Explosions*  
Allen Kuhl, LLNL

*Energetic Materials Technology*  
Chris Beiter, NGIC

*IHPRPT Program Review*  
Gil Graff, ONR

*Manufacturing Perspective:  
Nanoenergetic Powders*  
Kevin Walter, Technanogy

*Review DoD Requirements Pull vs.  
Technology Push*  
Al Sciarretta

**Meeting Three**  
**December 13-15, 2001**  
**Arnold and Mabel Beckman Center**

*AEWG Update*  
 Ruth Doherty, OSD

*Overview of DURINT Program*  
 Michael Zachariah, University of  
 Minnesota

*UK Perspective*  
 Adam Cumming, UK-DSTL

*Novel Energetic Materials in the Former  
 Soviet Union*  
 Kibong Kim and Mike Seizew, DTRA

*Army Gun Propellant Requirements*  
 Nora Eldredge, Picatinny Arsenal  
 Paul Braithwaite, Thiokol

*Nanostructured Energetics*  
 Randy Simpson, LLNL

*The Metallization of Energetic Systems*  
 Robert Geisler, Geisler Enterprises

*Nuclear Isomers*  
 Fred Ambrose, ITIC

*Survey and Prospects of High-Nitrogen  
 Compounds*  
 Harold Shechter, OSU

*High Energy Density All-/High-Nitrogen  
 Compounds*  
 Karl Christe, USC

*Advanced Heterocyclic Nitrogen  
 Compounds*  
 Jeff Bottaro, SRI

*Overview of Thermobaric Explosives*  
 Mel Baer, Sandia National Laboratories

*Thermobaric Systems*  
 John Walton, CIA

*Positronic Energy Conversion*  
 Ken Edwards, Eglin AFB

**Meeting Four**  
**April 18-19, 2002**  
**National Research Council**

*Speculation on High Nitrogen Molecules*  
 Rodney Bartlett, University of Florida

*Experimental and Computational Study of  
 Molecular and Lattice Symmetries of  
 Energetic Materials at High Pressure*  
 Su Peiris, NSWC-IH

*Synthesis of Insensitive Energetics*  
 Bill Koppes, NSWC-IH

*High Velocity Combustion in the Solid  
 Phase*  
 Vladimir Hlavacek, SUNY Buffalo

*The Effect of Ultrafine Aluminum Powder  
 on the Performance of Explosives*  
 Patrick Brousseau, DRE Valcartier, Canada

*New Ingredients: An Industrial Perspective*  
 Tom Highsmith, Thiokol

*Sol-Gel Processing to Produce Energetic  
 Nanocomposites*  
 Joe Satcher, LLNL

*Detonations in Heterogeneous Explosives*  
 David Frost, McGill University

*The Chemistry of Thermal Explosion and  
 Detonation in HMX and TATB*  
 Bryan Henson, LANL

*The Use of FOX-7 as a Propellant Additive*  
 Chuck Wight, University of Utah

*Synthesis of New Energetic Materials*  
 Mike Hiskey, LANL

*Overview of MIC Working Group*  
 Steve Son, LANL

*UK Approach to Novel Explosives*  
 Andy Kesby UK DERA

*Update on AE IPT*  
 Ruth Doherty, DoD

**Meeting Five**  
**June 5-7, 2002**  
**J. Erik Johnson Center**

*Nuclear Isomers as Potential Energy Sources*

Dave Sparrow, IDA

*OSD Advanced Energetics Initiative*  
Ruth Doherty, OSD

**Site Visits**

*December 15, 2001*  
Technanogy, Irvine, Calif.

*May 5, 2002*  
Naval Surface Warfare Center-Indian Head, Md.

*May 7, 2002*  
Army Research Laboratory-Aberdeen Proving Ground, Md.

*May 8, 2002*  
Naval Surface Warfare Center-Dahlgren, Va.

*May 9, 2002*  
Naval Weapons Station Yorktown, Va.

*May 14, 2002*  
Holston Army Ammunition Plant, Tenn.

*May 15, 2002*  
Argonide Nanomaterials Technologies  
Sanford, Fla.

*May 16, 2002*  
Eglin Air Force Base, Fla.

*May 21, 2002*  
Aerojet  
Rancho Cordova, Calif.

*May 22, 2002*  
Thiokol  
Brigham City, Utah



## Appendix C

### Acronyms and Abbreviations

ACTD	advanced concept technology demonstration
ADN	ammoniumdinitramid
AEI	Advanced Energetics Initiative
APFSDS	Armor Piercing Fragmenting Discarding Sabot
ARDEC	Armament Research, Development, and Engineering Center
ARL	Army Research Laboratory
BLU	Bomb Live Unit
BMED	Board on Manufacturing and Engineering Design
BOFORS	a Swedish defense systems company wholly owned by United Defense
BTATz	bis-aminotetrazolyl-tetrazine
CHNO	carbon-hydrogen-nitrogen-oxygen compound
CHNO/F	carbon-hydrogen-nitrogen-oxygen compound with fluorine
CL-20	hexanitrohexaazaisowurtzitane
DANPE	1,5-diazido-3-nitrazapentane
DARPA	Defense Advanced Research Projects Agency
DATH	diazidotrinitroheptane
DBP	dibutylphthalate
DEGDN	diethylene glycol dinitrate
DNT	dinitrotoluene
DoD	Department of Defense
DOE	Department of Energy
DTRA	Defense Threat Reduction Agency
DPA	diphenylamine
DURINT	Defense University Initiative in Nanotechnology
ETC	electrothermal chemical
FAE	Fuel-Air Explosives
FOA	Field Operating Activity
FOX-7	FOA Organic Explosive 7
FOX-12	FOA Organic Explosive 12
FSU	former Soviet Union
HMX	cyclotetramethylenetetranitramine
HNB	hexanitrobenzene
HNFX	gem-difluoronitramine substituted HMX analog
H <sub>z</sub> T <sub>z</sub>	dihydrazinotetrazine
IH-135	Indian Head Explosive 135
IPT	Integrated Product Team



JA2	nitrocellulose gun propellant developed in Germany
JASON	think tank that meets in July, August, September, October, or November
JANNAF	Joint Army, Navy, NASA, Air Force
LLNL	Lawrence Livermore National Laboratory
LOVA	Low Vulnerability Ammunition
LX-19	Livermore Explosive Formulation 19
MIC	metastable intermolecular composites
NASA	National Aeronautics and Space Administration
NATO	North Atlantic Treaty Organization
NAWC	Naval Air Warfare Center
NAWC-WD	Naval Air Warfare Center – Weapons Division
NC	nitrocellulose
NE	nitrate esters
NF <sub>2</sub>	difluoramine
NIMIC	NATO Insensitive Munitions Information Center
NSWC	Naval Surface Warfare Center
NSWC-IH	Naval Surface Warfare Center/Indian Head
NWC	Naval Weapons Center
ONC	octanitrocubane
ONR	Office of Naval Research
OSD	Office of the Secretary of Defense
PAP	Propulseur d'Appoint à Poudre
RDX	cyclotrimethylene trinitramine
RF	resorcinol-formaldehyde
RM	reactive material
RM-4	Reactive Material 4
SNPE	Société National de Poudre et Explosifs (French industrial group)
SNL	Sandia National Laboratories
TNAZ	3,3,1-trinitroazetidine
TNT	2,4,6-trinitrotoluene
TPE	thermoplastic elastomers
TSE	twin screw extruder