10.0 Next Generation Energetic Materials

10.1 Fundamental Points

Materials for Air Force applications in propellants, explosives, and pyrotechnics are critical core technologies having impact on a wide range of munitions including warhead lethality and the kinematic performance of missile systems.

New energetic propellants and explosives are vital enablers of the Air Force's mission. Both the uniqueness and the high performance characteristics required of military systems limit the applicability of commercial technology to the Air Force needs of tomorrow.

10.2 Current Situation and the Future

We will present here a brief summary of the state of the art in energetic materials technology, the issues, and recommendations. This section is followed by a more focused discussion of energetic materials required for the areas of propulsion and explosives. In the individual areas of explosives and propellants, we discuss new advanced materials and discuss concepts that are capable of generating revolutionary advances in warhead lethality, pyrotechnics, and our ability to propel missiles, boosters, and spacecraft.

The U.S. energetic materials area has been narrowly focused on insensitive energetic materials for application to tri-service insensitive munitions (IM) for the past 10 to 20 years. Insensitivity is a critical issue, and programs related to the IM objective must be continued. Our emphasis on IM as the single driving force has pushed us into very narrow development programs and has probably resulted in missing opportunities for improved systems. An expansion of the objectives of energetic material research to focus on performance is needed to recover lost opportunities in the areas of molecular synthesis, formulation chemistry, detonation, combustion chemistry, and combustion physics. Materials design, based in quantum chemistry and solid-state mechanics, is defining revolutionary first principle approaches to energetic materials and offers "leap ahead" as opposed to "catch up" approaches to meeting tomorrow's challenges.

While new materials have been created, few of these new materials have been implemented into a rocket propellant system. There have been no major advances in materials in the propellant industry in the last 40 years, performance has not improved significantly, and the industry is moribund. Meanwhile, the Russians have fielded new strategic missile systems having significantly improved performance (see the discussion on ADN). Another example is the case of U.S. air-to-air missiles having a shorter range and inferior capabilities as compared with the current Russian weapons. Our most advanced propellant materials programs today are the High Energy Density Materials (HEDM) and Integrated High Payoff Rocket Propulsion Technology (IHPRPT) programs. The goals of the HEDM and IHPRPT programs are shown in Figures 10.1 to 10.3.

Under IHPRPT, rocket propulsion capabilities should double by 2010, and the factors of reliability, cost effectiveness, environmental compliance, operational efficiency, and safety are integral to the effort.

The explosives community has maintained a broader technological foundation through aggressive program coordination under Project Reliance and the DoD/ DOE Conventional

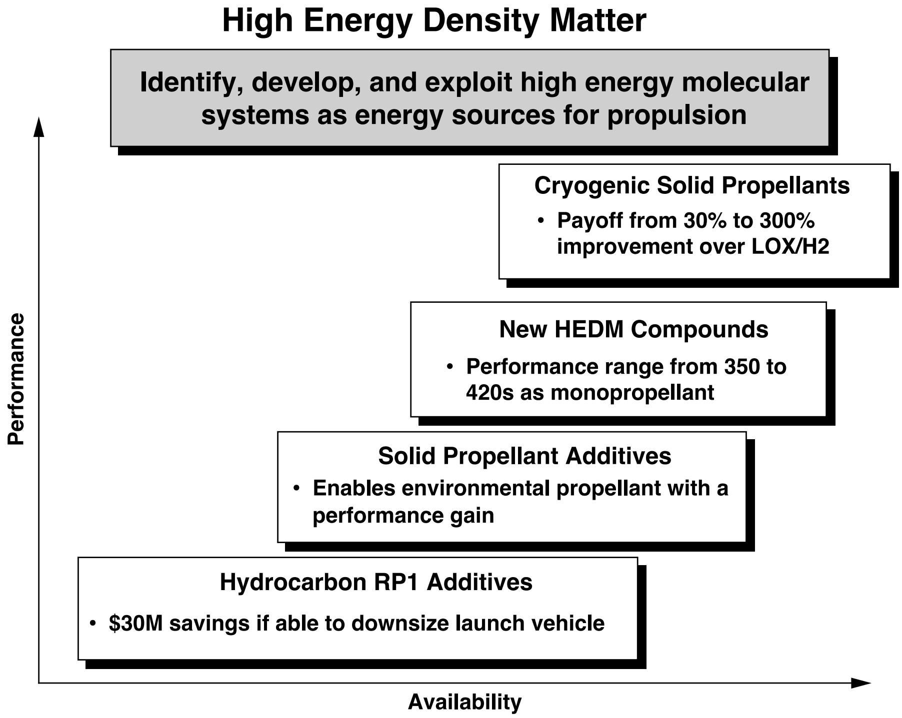

Figure 10.1 HEDM Program Goals

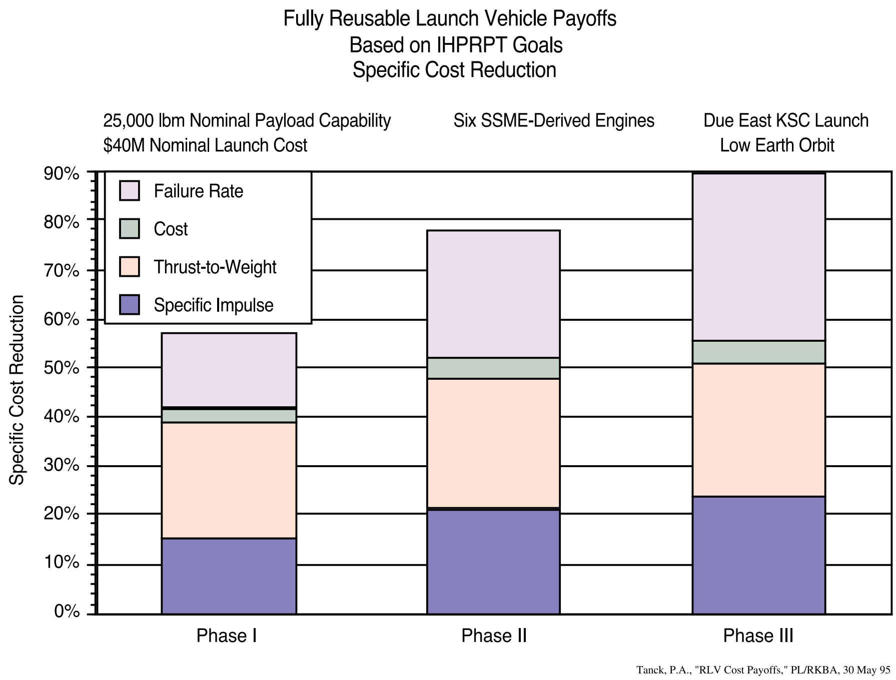

Figure 10.2 IHPRPT Goals for a Fully Reusable Launch Vehicle

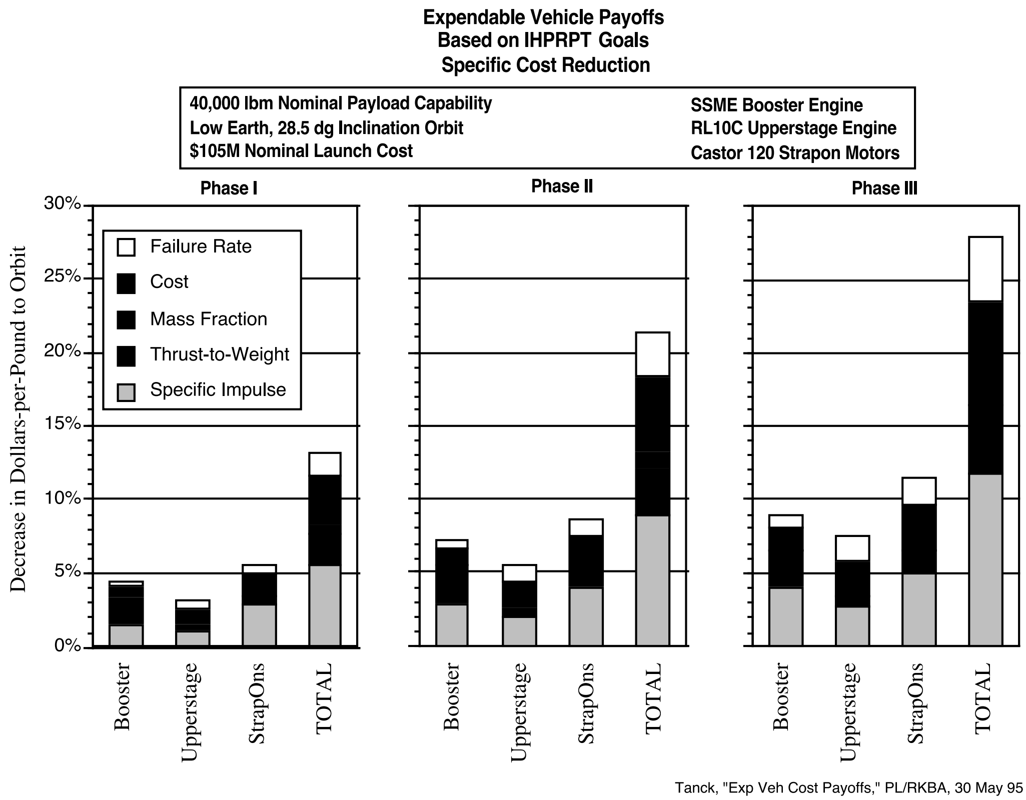

Figure 10.3 IHPRPT Goals for Expendable Launch Vehicles

Munitions MOU. However, even this technology base is being threatened by downsizing activities in both the DoD and DOE. New formulations have transitioned into weapons systems. Significant performance improvements have resulted from this work. LX-14, an explosive formulation developed at Lawrence Livermore National Laboratory containing HMX as the primary HEDM, has been transitioned into the warheads of the Hellfire and TOW-2 missiles. Recent examples of deployments include PBXN 9 as an interim IHE in the Hellfire and TOW upgrades, PBX 110 in the Standard Missile, and AF 108 in the joint service AMRAAM missile warhead. These examples are representative of formulation solutions to today's problems using yesterday's molecules. This is an area that can further profit from the introduction of the new energy storage concepts to improve performance.

These evolutionary advances in explosives are not capable of effectively attacking chemical and biological weapons (CBW). CBWs require specialized explosives and pyrotechnics, materials that are probably available, but not being exploited.

The USAF can achieve significant performance advantages in rocket propulsion, explosives, and pyrotechniques using new energetic materials and developing an understanding of their behavior and properties. Energetic materials are enabling technologies. New weapons based on advanced energetic materials would give the Air Force larger standoff distances, shorter times to target, and higher destructive power in the near term. The safety of platforms depends on having a longer reach; we will have too few platforms in the future to risk losing them. Our adversaries are already projected to win short-range engagements due to improved propellant and explosive materials.

The neglect of developing new propellant systems contributes to the extremely high costs of getting payload to orbit. Simple improvements in the energy density of liquid fuels could enable the use of smaller launch vehicles for similar size payloads. This would have dramatic cost savings (estimated at greater than $30M/launch for a change from Atlas 2 to Delta 2 and greater than $130M for a change from Titan 4 to Atlas 2 AS). Similar improvements can be expected from the solid strap-on boosters.

A whole new generation of improved materials is available and materials are continuing to be invented for use in rocket propulsion and munition applications. These are fundamentally new ingredients for use in propellants and explosives. We are now entering into the fourth generation of conventional energetic materials, perhaps the next revolution in energetic materials.

One can define generations of energetic materials as:

- Generation 1—discovery
  Gunpowder, fireworks, small arms
- Generation 2—formulation for safety
  Commercial explosives (e.g. dynamite,TNT)
  Gun propellant
  High energy propellants (nitroglycerin)
- Generation 3—molecular synthesis for performance
  HMX, RDX, aluminum, and ammonium perchlorate
  State-of-the-art explosives
  State-of-the-art high energy propellants
- Generation 4—combination of physics and chemistry to prepare alternative energy sources (the future)
  ADN, CL-20, TNAZ, PGN, AMMO, BAMO, AlH_3 and maybe other metal hydrides, focused energy, focused application materials, cryogenic materials

Each succeeding generation has significantly enhanced the capability of weapons either by improving performance or safety. The Russians fielded, 20 years ago, weapon systems based on at least one of the fourth-generation materials. First-principle-based design approaches promise to revolutionize many of our most fundamental concepts of energy storage in these systems. Metastable Interstitial Composite and Extended (MICE) solids are examples of these first principle design approaches.

The next 20 years will see significant improvements in conventional weaponry and a fundamental new understanding of energy storage. The new materials will give significant range enhancements along with improved safety. The new explosives can enable reducing the size of warheads to either make smaller rockets or increase the range and/or velocity of existing rockets. The challenge is the identification of the process to ensure early exploitation of these materials to satisfy a wide range of Air Force mission needs.

10.3 Issues

We have recognized several issues that directly relate to the field of energetic materials:

Broad Based Issues

R&D technology base disappearing. The DoD needs to recognize and support the development of those technologies that will have a large impact on future weapon system capabilities.

No clear technology development requirements. The DoD has not provided the requirement or the financial means to maintain a strong technology base effort. The recently initiated IHPRPT program is the first example of a change in that attitude. Without strong leadership and clear directions to pursue technology development, the contractors and government laboratories fall into a mode of chasing near-term, system-oriented goals and having to start all over when that particular system is killed. Since we are falling behind other nations in capabilities in energetic materials, this is a problem.

Safety. Insensitivity of new propellant and explosive formulations has been of importance for the last decade. Significant progress has been made. IM is an enabling technology as it allows for more weapons to be carried or stored in closer confinement. This must remain an emphasis in any development/synthesis program. We need to emphasize finding ways to obtain higher performance while not sacrificing safety.

The bridge from laboratory development to use is fragile at best. There is no good mechanism to get from 6.1 to 6.4 and beyond. This results from a lack of application programs on standby which are ready to use the technology.

Specific Technology Issues

Is chlorine a real bugaboo or not? A decision needs to be made on what are the real environmental issues that have to be addressed. For example, is chlorine emitted by propellants a real issue? If it is, then we need a directed program to bring replacements forward quickly.

Rocket propulsion is not a mature area contrary to popular opinion. If a new system wants to buy its propulsion unit “off the shelf”, it will be buying very old technology. It will not be taking advantage of the results currently available in research laboratories nor will it be taking advantage of the tremendous increases available from more research. The commercial sector will not be the leader in developing this technology. Energetic materials are not commercially developed other than in the mining industry. This area must be funded by the government and, due to the high-risk nature, it must be done with long-term programs.

The chicken or the egg problem. Few new materials are in current systems, because the system program offices don’t demand them. Program managers don’t allow new materials, because they don’t have sufficient information about their properties, and no program office wants to be the first to take the risk of using a new material. Almost all development work on propulsion in this country is dedicated to evolutionary improvements in existing systems, because of this chicken and egg problem. The developers don't want to use new materials because they are not readily available, not demonstrated, and are considered high risk. So in the face of these problems, no risks are taken.

Life cycle cost determined by more than just the initial material cost. The value of energetic materials is generally determined by the initial cost of the material. Explosives and propellants need to be judged on the total system cost and the value of the mission.

Multidisciplinary approach to problem. Energetic materials research is generally accomplished in a small group that is not in close communication with the potential developers and users of the technology. The developers and users need to communicate their needs to the researchers and researchers need to provide feedback on the possibilities of new materials.

10.4 Recommendations—Propellants

The USAF needs an aggressive program of research and development to create a new generation of boosters, interceptors, and spacecraft based on new ingredients and energy storage technologies. We have fallen behind our adversaries in this important area and our platforms are vulnerable to longer range, higher performance weapons from the FSU. New weapons based on higher energy propellants will enable the USAF to control their environment in a cost effective manner. The following items must be done:

- Fund the development of new energetic ingredients.
- Fund the development of new rocket motors based on new oxidizers and binders.
- Encourage unconventional approaches such as thermoplastic elastomers (TPE) and gel based polymer binder development.
- Accelerate the use of energetic fuel additives to RP-1 liquid fuels.
- Increase funding for basic research to solve the burn-rate problems of hybrid boosters.
- Investigate the use of aluminum hydride in rocket systems.
- Expand research into other advanced hybrid concepts and HEDM materials to give 350 to 420 second monopropellants.
- Continue or expand research into cryogenic or other exotic propellants to seek a propulsion breakthrough.

10.5 Recommendations—Explosives

- A window of opportunity exists for the USAF to bring to the field advanced weapons based on recently invented ingredients.
  - Push forward the introduction of new oxidizers (CL-20) and energetic binders into a weapon system.
  - Continue research on new methods of focusing and tuning the energy of explosives and developing new thermites.

- Initiate weaponization investigations of tunable energy thermite systems.
- Fund research into revolutionary concepts for new high explosives to fill the gap between conventional and nuclear weapons.

10.6 Examples of the Contribution of New Materials

Solid Propellants

Calculations tell us that the use of an improved oxidizer (such as ADN) in a propellant system can give up to a 51 percent increase in range of a ground-to-air missile over a conventional AP/Al/binder system. Similar calculations tell us that the uses of ADN in inertial upper stage (IUS) orbit transfer from low earth orbit (LEO) to geosynchronous orbit (GSO) would provide a 8.9 percent increase in payload (452 pounds). Using ADN in the booster and IUS would give a 17.4 percent payload increase (886 pounds). Introduction of a more advanced system using aluminum hydride to replace aluminum and the use of ADN in the IUS would provide a 12.4 percent increase in the LEO to GSO transfer step (631 pound payload increase for a Titan IV). These are dramatic gains in performance, unmatched since the introduction of composite propellants in the 1950s. The dramatic payload gains can be traded off for a smaller launch vehicle, thus decreasing the size of the system and its cost. Significantly, ADN is environmentally benign if disposal is required; it photolytically degrades to nitrate and nitrous oxide, and is chlorine-free.

The use of an energetic binder can have a major impact on the solids loading of a propellant. The reduction in the solids loading is likely to greatly improve the safety of the overall system, possibly taking it from a sensitive 1.1 category propellant to an insensitive 1.3 system. For example, using a BAMO/AMMO binder to replace a convention binder with AP and Al as the other ingredients gives a reduction in solids from 90 percent in the conventional system to 80 percent in the advanced system while having the same energy density. A gap binder system may give similar results.

Liquid Propellants

Improvement in the specific impulse (I_{sp}) of RP1, a hydrocarbon fuel that is unchanged since the 1960s, can save up to $30M per launch. This savings is in part due to the fact that a smaller, higher performance launch vehicle can be employed. Additives have already been identified to do this.

Hybrids

There are several ways HEDM materials may improve hybrids. First, an energetic material may be used to increase the burn rate or grain regression rate which is a major problem with current hybrids. A low rate requires extremely complicated grain designs in order to get adequate mass flow rates. Second, since the solid grain is essentially a rubber matrix as inert as a pencil eraser, it may be the ideal way to incorporate aluminum hydride, the new and very high-energy fuel that the Russians say they can use and one which the U.S. has failed to capitalize on.

10.7 Energetic Materials—Propellants

The current inventory of propellants and other energetic materials were identified 20 to 40 years ago as having the optimum fit to the cost/performance trade-offs of the time. We are currently flying or using systems that use storable propellants selected in the 1950s and 1960s to meet cold war performance, cost availability, toxicity, and environmental needs of the time. The result is old propellant systems that cost more and more as incremental patches are applied to bring out-of-date systems into compliance with current operational restraints. Our society, industrial base, and particularly environmental and health laws continue to evolve and redefine our operability restraints without a concomitant change in the energetic materials we employ.

Yet ingredients have been discovered and made available that are capable of providing revolutionary payoffs for the armed forces. Other new materials are under investigation. Thus, we can correct the situation by employing our best technology in a cost and time effective manner. High payoff items identified as opportunities in rocket propulsion are:

- Near term: Implement major improvements for solid motors by incorporating advances in binders and oxidizer (5 percent to 20 percent improvement in mass to orbit or a 5 percent to 15 percent increase in specific impulse) with a concomitant improvement in liquid systems. TPE's and gels will give environmental and processing advantages.
- Middle term: Develop advanced hybrid systems with improved performance (goal of 350 sec for a strap-on) new oxidizers, TPE binders, gel binders, new fuels like AlH_3.
- Long term: Use cryogenic high energy density materials and materials like metallic hydrogen (specific impulse greater than 1500 sec (i.e. performance 4 times greater than LOX/H_2)) to revolutionize access to space.

Most of our solid propellant systems were developed in the late 1950s with some development continuing into the early 1970s. But no significant new energetic material has been introduced into the propellant area since then. However, many new materials and technologies are now available that we need to employ.

Solid/Gel Rocket Propellants

New propellants are required not only to increase the available energy of a propellant and raise the specific impulse (I_{sp}), but also to meet environmental and toxicity constraints and improved safety. Special requirements for handling and disposal significantly increase the cost of the overall system. New propulsion materials will significantly reduce overall weight and therefore the cost of propulsion systems. They also permit innovative manufacturing techniques which will yield revolutionary rocket engine designs. Finally a better understanding of the chemistry and material properties for propulsion systems will lead to solutions to problems that continue to plague the propulsion industry today.

Solid propellants are used in all application areas of rockets employed by the Air Force, including tactical, strategic, and space boost. Specific examples are:

Solid or composite propellants. A revolution is underway in the types of oxidizers and binders available for use in solid propellants. The combination of the new energetic binders with new oxidizers offers system benefits (I_{sp}, safety, energy density) exceeding anything fielded today. The new materials for propulsion must be viewed from a system view, that is, the effect of the combination of an energetic binder and oxidizer on performance rather than the effect of each individual component. The combination of the energetic binder and new oxidizer can reduce the solids loading in a propellant significantly. In one example, the reduction went from 91 percent to 82 percent while maintaining the same energy density. These changes increase the safety of the system while enhancing performance.

In the oxidizer arena, ADN is the most promising near-term material. The FSU demonstrated ADN-based ICBM boosters in the early 1980s. ADN offers payload increases ranging from 1.5 percent to 19.7 percent, depending on the application. An excellent example of the effect of using advanced oxidizers is in the earth to GSO application. Only the propellant sample in the IUS was changed, the basic booster was untouched. Calculations done at United Technologies show that using an ADN based propellant system gives an increase of 17.4 percent in the payload delivered to GSO. This is a quantum leap in performance. Higher levels of performance can be achieved by improving the energy density of the liquid booster portion of the system.

For tactical systems the I_{sp} can be improved by 5 percent by use of new oxidizers—CL-20, ADN, and others are candidates. The IHPRPT tactical propulsion goals are a good measure of what is desired. IHPRPT has improvements planned over the next 15 years that can only be achieved using advanced materials. Higher levels of performance improvement are possible and should be pursued.

CL-20 looks good for tactical applications both as a propellant application and as an explosive. CL-20 is the closest to scale up of all the potential materials. TNAZ has promise, and HNF is being explored as a possibility in the U.S. and abroad. CL-20, especially in concert with an energetic binder, can be used to give smokeless or minimum-smoke propellants with improved range over current propellants.

Ammonium nitrate (AN) has reappeared as a potential bright spot for low-cost, chlorine-free, smokeless propellants. A method for stabilizing the phase transitions of AN has been patented by the Thiokol Corporation that should overcome many of the problems (low burn rate, phase changes) associated with AN. Thiokol calls this new material phase stabilized ammonium nitrate (PSAN). PSAN can be used in propellant applications as the oxidizer for smokeless formulations. However, the use of PSAN to achieve a chlorine free exhaust carries with it a decrease in energy from the standard ammonium perchlorate propellants.

The new energetic binders allow for energy partitioning in tactical propellants. This means that instead of having all the energy in the oxidizer, the binder system contributes part of the load. The consequence of this is that the energy and oxidizing power of the system is better distributed leading to a better burn in a usually less sensitive system. The recently invented materials include PGN, AMMO, and BAMO.

Because these energetic binders are TPE, they are capable of benign removal from the system, enabling the whole propellant charge to be recycled. This use of energetic TPEs will minimize waste and allow recycling of the propellant charge. Overall we will have improved safety in a better performing, more energetic propellant system.

ADN or CL-20, in combination with an energetic binder system, could start appearing in systems within the next ten years and could be in widespread use in 20 years, having a major impact on Air Force operations.

The forecast is that we could have these energetic materials employed in a tactical system within the next ten years if development is encouraged. A great deal of development needs to be done, yet the potential is there and enough basic research is in the bank to enable a rapid development of the energetic TPEs, a system with the potential for major impact.

Solution propellants. A very recent development is the solution propellant. The advantages of this system are that it is an environmentally clean formulation including no chlorine and has potential for very high process efficiency. These solution propellants are water soluble, so disposal is accomplished by simply washing out the motor with water. They are processed by pouring the liquid or slurry materials into the case and then allowing them to solidify. The development work on this is ongoing at Phillips Laboratory (Propulsion Directorate) and at the Aerojet Corporation.

This technology is a medium-term possibility for system application.

Conventional Liquid Propellants

The Air Force uses storable liquid fuels and oxidizers in some launch systems. Liquid propellants have performance, restart, and throttling advantages over solid propellants and will continue to be attractive for use in future systems. Improvements must be made to reduce the hazards of handling and storage of the materials while maintaining or increasing performance.

Nitrate-based oxidizers (nitrogen tetroxide and IRFNA) and hydrazine-based fuels (A-50, MMH, and UDMH) have good performance and ignitability, but are also very corrosive, volatile, and toxic. These factors drive up the cost of manufacture transport, handling, vehicle design, pad operations, launch safety, launch window, and pad cleanup. The environmental factors alone are becoming a major driver in the need to replace older oxidizers and fuels. Reducing these hazards is required.

Liquid propellant fuels can be improved by an investigation into the use of non-volatile or non-toxic oxidizers and the use of new high energy hydrocarbon fuels. There are current investigations ongoing at Phillips Laboratory (Propulsion Directorate, Edwards AFB) and at the Office of Naval Research (ONR) on new oxidizers and fuels for rockets. Additionally, Wright Laboratory (Propulsion Directorate) is working on endothermic fuels that should be applicable to rocket propulsion. A significant potential is available for crossover between the two programs.

The emphasis at Phillips Laboratory on the creation of strained hydrocarbons that can give improvements of several percent of I_{sp} in the near term. Even small gains of a few percent are enough to save many millions of dollars per launch (estimated at $30M per launch). The materials under investigation as fuel additives include commercial replacements for RP1 such as decane, hexane, and cyclododecane, plus higher-performance synthetic materials such as spirocyclopropanes, triangulanes, cubane, and quadricyclane.

Oxidizers are a more difficult problem, however, viable alternatives are becoming available. ADN is an environmentally benign, high performance oxidizer that can be put into liquid form and used as a monopropellant system (ADN + ammonia, hydrazinium dinitramide + hydrazine, or hydroxylammonium dinitramide + hydroxylamine). Hydrazinium nitroformate (HNF) is a candidate oxidizer, but its toxicity has not yet been determined.

One promising way to improve system performance is the development of monopropellants with significant I_{sp}. A system of dinitramide salts with ammonia, hydrazine or hydroxylamine as the counter ion has been proposed as well as HNF.

There is a significant opportunity to develop new materials for liquid-fuel rocket propulsion having a major impact in the next ten years.

Advanced Fuels for Solids and Liquid Rockets

A major improvement in performance can be achieved by the development of new fuels in rocket propellants. An example of this is the claim by the FSU that they have been able to use

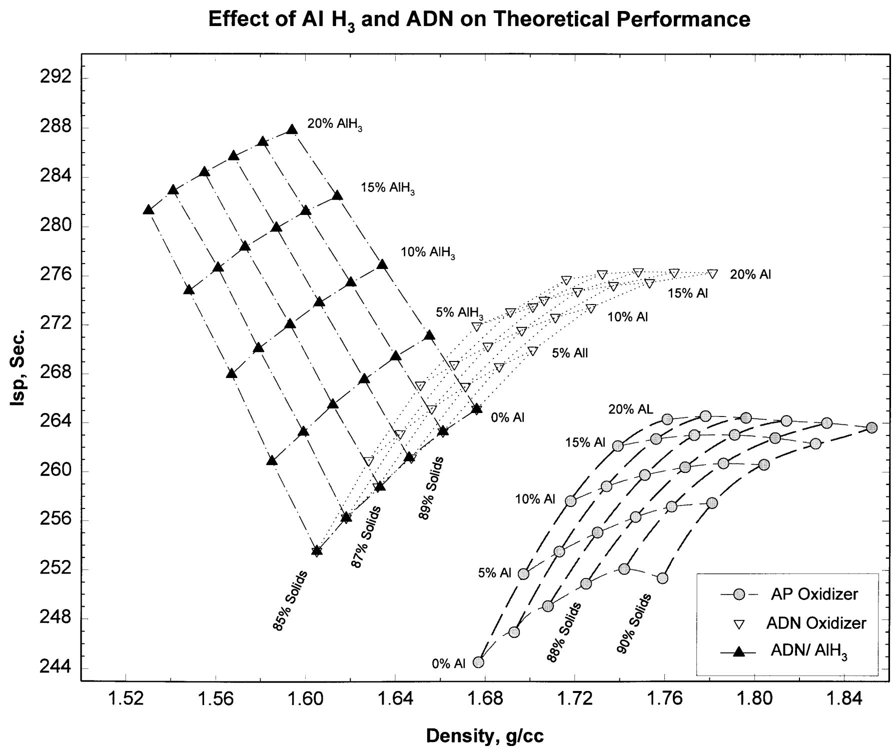

Figure 10.4 Propellants Based on Aluminum Hydride, ADN, and AP

AlH_3 successfully in solid rocket propellants as a replacement for aluminum metal. A major research program in the U.S. in the 1960s failed to accomplish this, but the Russians claim to have a fielded system with ADN as the oxidizer. This combination of AlH_3 and ADN could give as much as a 25 percent improvement in specific impulse in the rocket system. Figure 10.4 below shows a graph of specific impulse versus density comparing an AP-based oxidizer systems with an ADN based oxidizer system and of the combination of ADN with AlH_3 in a propellant formulation. A drawback of the AlH_3 system can be seen in the reduction in density of the overall formulation.

A number of other metal hydrides or other metal fuels can be considered for this application. At a minimum, we need to determine if the FSU statements on AlH_3 are factually correct and determine how they employed AlH_3. Alternatively, we need to initiate a program to study the potential use of AlH_3 as a fuel for solid rocket motors. Interestingly, the best place to employ fuels such as AlH_3 is in hybrid type motors. Here, the fuel is surrounded by only an inert polymer matrix so the concerns about the fuel reacting with oxidizer or other substrates is eliminated. This may be the nearest term use for such exotic materials. This insertion of metals (or the use of otherwise pyrophoric organometallics) into an inert matrix opens up a world of possibilities. Finally, studies are underway to determine if atomic species can be distributed in the matrix. This approach will dramatically increase the energy density if successful.

Strained or high-energy hydrocarbon compounds should be investigated in further depth to determine their utility as fuel additives in hybrids and in liquid fuels. Both hybrids and liquid-fueled rockets need fuel additives to improve the energy content and the combustion efficiency and have great opportunities for early use. One can consider the use of Diels-Alder type materials that decompose to give easily combustible compounds. This approach would be akin to the Russian approach where they first determined the combustion requirements then designed and synthesized hydrocarbon structures to meet their needs. This resulted in improved combustion and engine performance. We could learn from this approach instead of relying on RP1, a fuel developed in the 1950s.

A more dramatic improvement might come from developing methods to decompose the hydrocarbons and generate hydrogen or atomic hydrogen. Molecular or atomic hydrogen have been shown to improve the combustion efficiency in endothermic fuels and should have the same effect in rocket motors.

Hybrid Motors. Hybrid motors have been proposed as a replacement for solid fueled boosters in space launch applications. This is a technology that could have an impact beyond space launch as a way to propel a rocket. Realization of the potential of hybrid systems requires both developmental and fundamental research.

We show in Figure 10.5 the basic hybrid rocket motor design. In a hybrid, a solid fuel core is used with a separate liquid oxidizer tank. The fuels currently used are conventional, readily available hydrocarbon binder systems.

The major problem in hybrids is that the burn rate is approximately an order of magnitude too slow to make the technology viable for use in a standard grain design. Engineering

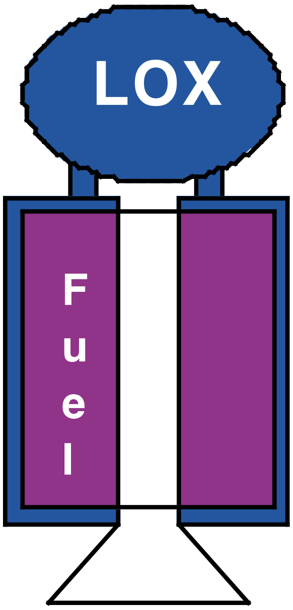

Figure 10.5 Basic Hybrid Rocket Motor Design

solutions require high surface area designs that drastically reduce density thus decreasing performance. Fundamental solutions to burn rate problems can only come about by improving the chemistry. There is no investment in this area, even though the payoff is extremely high.

This technology would profit from the introduction of metal hydrides such as AlH_3 into the matrix to improve the energy density and potentially the combustion rate. Other fuel additives and energetic hydrocarbons can also be profitably incorporated. A higher risk approach would be to introduce atoms or organometallics into the matrix to increase energy density. These new methods represent high risk methods until proven. Proving such approaches and removing the risk requires investment in exploratory research.

In addition to performance improvements, hybrids offer a means to reduce launch support costs. Since the current solid strap-on boosters have to be in place long before the actual launch, special safety practices must be followed on the launch pad. However, the hybrid grain is as inert as an automobile tire and no special safety practices are necessary. This technology has the potential to replace composite propellants and provide safe, inexpensive heavy lift capability within approximately ten years once the fundamental problems are solved.

Monopropellants. Monopropellants find use in applications such as maneuvering thrusters. The major threat here is the toxicity of the propellants and their limited energy density. Several advanced systems are possible based on the new energetic materials (ADN in ammonia is an example), but this area is not generally given much priority.

Exceptionally Energetic Ingredients and Cryogenic Propellants. The proposed goal of a new cryogenic propellant is to increase the specific impulse by 30 percent to 300 percent over LOX/H_2. Most of this effort is ongoing at Phillips Laboratory and through AFOSR. This program is for identification and synthesis of novel cryogenic solids. Both agencies are funding a heavy computational effort to predict species for use in propellant systems.

There are two goals for this program. The near-term goal is to prepare molecules (e.g. solid ethylene) that can react with LOX to give I_{sp} of greater than 350 sec. The long term goal is the preparation of cryogenic solids containing atoms and other highly energetic materials with the ultimate goal of preparing metallic hydrogen. The long term goal is for improvement of specific impulse by 30 percent to 400 percent over LOX/H_2.

The development program has started to show success. A cryogenic motor has been fired at Edwards AFB, using frozen ethylene as the fuel in a prototype hybrid setup. This demonstrates that frozen cryogenic materials can be successfully employed, an important first step. Ultimately, this should lead to using cryogenic solids containing additives in hydrogen or solid oxygen. This is a new type of rocket motor.

The next goal is to demonstrate that cryogenic matrices containing fuel additives and other energy dense ingredients can be burned in the motor. Ultimately, they will employ atomic species in a hydrogen matrix as the fuel to be burned. One potential system, is a H_2 matrix spiked with B_2 to yield a monopropellant having I_{sp} greater than 600 sec. The calculated additive effects of this combination are shown in Figure 10.6 below. There are other similar metal additives to hydrogen that can potentially significantly increase the I_{sp}, but we will not discuss them further.

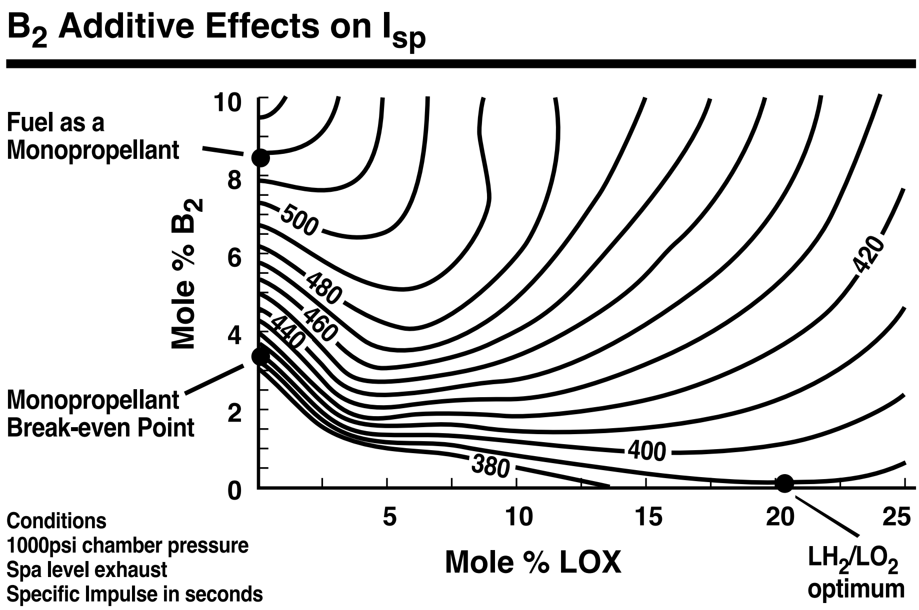

Figure 10.6 Effects of Metal Additives on Specific Impulse

At the highest level, it may be possible to prepare metallic hydrogen. Metallic hydrogen has a calculated I_{sp} of approximately 1600 sec, approximately four times today's systems. This is calculated to be the upper end that is possible for conventional propellant materials.

The cryogenic aspects of this program are clearly a long term, high risk effort, operating on a 30 to 50 year time frame for implementation, unless a dramatic breakthrough takes place. This program is the Air Force's best chance for revolutionary gains in performance, but it carries a very high risk.

10.8 Energetic Materials—Explosives

New higher energy explosives are available, but only minimal usage has been made of these materials. These energetic materials all have the ability to dramatically increase the explosive potential of warheads and bombs, thus increasing the killing potential. These new materials can be especially effective in directed energy explosive warheads proposed for use in the next generation of air-to-air missiles. We foresee in the long term explosive concepts being developed to allow for tuneability of explosive charges, a way to vary the energy output to match the mission requirements. We also need to rethink the design requirements for explosives to match the new needs of moving metal and momentum transfer in smaller warheads. Advanced thermites are available that provide the ability to attack chemical and biological warfare sites with improved probability of destroying the target without release of the agents.

More esoteric concepts can be employed in the long-term. These include using such theoretically possible molecules as polymeric nitrogen or fuels such as metal hydrides to the cryogenic explosives. High-payoff items identified as opportunities are:

- Near term: Achieve major improvements in the capability and reductions in the size of specialized warheads by implementing new materials such as CL-20. New explosives are exceedingly valuable for reducing the size of precision weapons.
- Middle term: Develop technologies to allow tuning of explosive charges (energies between conventional and thermonuclear) implement advanced thermites, nanoformulated explosives to improve yield and control.
- Long term: Pursue more esoteric concepts including using theoretically possible molecules such as polymeric nitrogen (three times the energy density of HMX), such fuels as metal hydrides, or cryogenic explosives.

Advanced Conventional Explosives

A prime contender for near-term application is CL-20, first invented at the Naval Air Warfare Center at China Lake. The U.S. appears to have a significant lead in the synthesis and availability of CL-20. The table below compares the properties of CL-20 with current state-of-the-art compounds HMX and RDX. In all categories of merit CL-20 vastly outperforms current materials. As such CL-20 development should be accelerated for applications where performance is of primary importance.

Table 10.1 Current State of the Art Explosive Compounds

Explosive Ingredient	Density (gm/cc)	ΔH_f (cal/gm)	Detonation Velocity (km/sec)	Detonation Pressure (kbar)
RDX	**1.82**	**66**	**8.85**	**338**
HMX	**1.90**	**60**	**9.11**	**390**
CL-20	**2.04**	**203**	**9.66**	**454**

The properties of CL-20 are such that warheads for penetrators can be half the size of the current generation. This means smaller or faster or longer range missiles and improved capability.

In addition to CL-20, there are several other compounds that are already available or are in the process of being developed. These include TNAZ, TEX, cyclodextrine nitrate, and HTREL, plus new oxidizers such as ADN that are currently available, and the developing area of high nitrogen compounds that have great potential for providing an enhancement over CL-20. Most of these compounds were developed under ONR sponsorship and AFOSR has almost no presence in the synthesis of new, conventional, basic energetic materials. In development efforts, the Air Force, Army, Navy, and DOE are well coordinated and integrated at the 6.2/6.3 level of exploration.

The currently available materials—CL-20, ADN, and TNAZ—could all be brought to field use within ten years, providing a dramatic impact.

Exotic Explosives

At the upper level of possible performance is the new HEDM type extended solid materials. These are proposed materials with a performance of three to five times that of HMX. Should these materials work out they would fill a performance gap above the current conventional materials. Currently proposed materials include compounds such as solid N_2 and other cryogenic explosives. These compounds are referred to as extended solids and are proposed to be prepared by high pressure synthesis possibly involving photochemical processing. New high energy fuels can be prepared using this methodology, including new isomers of BH_3. New fuels can have great impact on the energy density of new fuels, explosives and propellants.

While this research is of high technical risk, the potential payoff is revolutionary and worth investment.

Pyrotechnics

Sophisticated sensor devices have made all areas of the electromagnetic spectrum accessible on the battlefield. Infrared (IR) sensors in particular are critical today. Simple pyrotechnic devices (such as IR flares) have been used for 30 to 40 years used to defeat IR seeker heads in air to air missiles, but seekers are so sophisticated that they can tell the color difference between standard flares and an aircraft, and whether the flare is moving or not (kinematic differences).

The USAF also finds uses for pyrotechnics in other roles. A recent requirement for pyrotechnics is battlefield illumination, particularly in conjunction with night vision goggles in special operations. In the night vision applications the flare emits in a narrow band to allow detection by frequency-specific goggles. Finally, pyrotechnics are excellent compact, very high heat sources that can be used for the destruction of CBW materials.

Pyrotechnics have had steady advances. There are ongoing programs to combine IR frequency selectivity, kinematics, UV opacity and RF properties in one aircraft flare. However, progress is slow as this is not a high priority. Be that as it may, a cheap flare can defeat an expensive missile and save an extremely expensive plane.

The most exciting progress is in development of very high heat source materials called metastable interstitial composites (MIC). The progress has been dramatic in the last two years. The nanomaterials developed having intimate mixtures of an oxidizer and fuel have dramatically increased the heating capability of devices built from these materials. Extreme temperatures with high energy density can be reached in very short times giving us a capability that lies between conventional weapons and thermonuclear devices. This is an area that needs exploitation and can be used to meet the requirements of several specific applications such as the destruction of CBW weapons. Using advanced pyrotechnic devices, the biological agents are capable of being destroyed in place while minimizing the potential exposure to other areas. Chemical agents can be handled in a similar manner.

These materials should be in the field in less than ten years. There is a need to speed their introduction into the inventory.

Story of the Synthesis of ADN and the Lessons Learned

In our panel deliberations, it was our opinion that the story of the discovery of ADN, its potential impact, and the inhibitors to introduction was worthy of inclusion into this report. ADN is an oxidizer, the oxygen source in solid propellants and other munition applications. ADN is recognized as having potential as a revolutionary replacement for ammonium perchlorate in missile systems. ADN is calculated to give higher I_{sp} propellants (5 percent to 20 percent depending on the application) and is environmentally benign.

In the early 1980s, the ONR initiated a search for improved energetic materials. This effort was a long-term research program into new materials, the kind that is effective but hard to maintain. This program led studies on the development of cubane-based explosives, fuels, and oxidizers. While in the process of developing an improved route to dinitramines for application on cubanes, Dr. Jeffrey Bottaro of SRI conceived of and synthesized the dinitramide molecule, the parent of ADN, in late 1989. SRI filed for patents on the composition of matter of the dinitramides in the U.S. and abroad, and these patents have been granted.

Following the publication of the patents in 1991, rumors began circulating that the USSR had employed ADN in some of their systems. These rumors were confirmed when Z. Pak of the LNPO Soyuz presented a paper at the AIAA meeting in 1993 describing some of their work. Later, the development work in the FSU was described in a newspaper article published in 1995.

The situation as we currently believe to be true is that the USSR ran an equivalent of the Manhattan Project to develop ADN for missile applications. The program was very heavily classified and compartmentalized. The Soviet ADN effort was apparently not detected by the U.S. intelligence community. The original inventors were awarded the Lenin Prize in 1976. This program moved ADN from the laboratory to production in seven years, an extremely rapid pace for the introduction of an energetic material.

The USSR operated at least one full-scale plant for the production of ADN for as long as 10 years through 1990. This plant had a capacity of 700 metric tons of ADN per year. This production is believed to have gone into the following families of missiles:

- SS-24 (second generation, first and third stages)
- Topol-M (second generation, second and third stages)
- SS-20-N

The Russians also claim to have used AlH_3 in their missile systems and are rumored to have an ADN/AlH_3 system in operation.

The Russian facility for the production of ADN is mothballed. At least two U.S. groups are trying to buy the ADN technology from the Russians, but have not yet succeeded. Additionally, no one has yet evaluated a propellant sample of the Russian ADN-based propellant.

Several conjectures have been offered as to why the Russians put so much effort into ADN:

- Defeat of U.S. space-based early warning systems—no hydrogen chloride spectra to detect
- Lack of adequate ammonium perchlorate production
- Need for increased boost energy
- Method to violate missile treaties without detection—intermediate range missiles using ADN as the oxidizer would have ICBM-like range
- Fast burn first stage to decrease U.S. reaction time

Despite the evidence that the USSR had succeeded in implementing a revolutionary new ingredient into current systems, there has been minimal funding in the U.S. to verify the tremendous potential. ONR and BMDO have funded basic R&D on the synthesis, ONR has funded some initial propellant work, and Army Missile Command (MICOM) has funded some ADN work. Investigations are underway at Phillips Laboratory on using ADN in gel-type propellants.

The most important reason to present this lesson is that we have run into all the problems inherent in trying to bring a new material into the market. In the ADN case we have an ingredient with a demonstrated utility in the FSU plus a significant amount of calculational work done here in the U.S. Yet a sustained effort to apply the technology to a system in the U.S. does not exist.

Our experience with ADN would indicate that we have a very poor development history for new materials. Propellant developers are reluctant to investigate a new material unless it is available in large quantities, in the right particle size, and in abundant quantity at a very low price. New materials are never available in large quantities and are always expensive until economies of scale are introduced. If large, inexpensive samples of a new materials are not available, developers will do only minimal work on them. This is especially true for propellant makers who require large test samples. Unfortunately, it’s hard to provide materials in quantity before they have been tested and determined to be of value.

New materials are inherently expensive to buy until they go into a system. There is no production capability to allow economies of scale to operate. The early high price tag inhibits timely evaluation and development. The problem will be even greater in the future because we have so few new systems coming along.

We also see that there is a need for a commitment by funding agencies to establish and maintain a research effort that will be adequate to provide the country a strong technology base. This requires developing materials and ingredients without necessarily having an immediate use for the materials, but rather the knowledge that having qualified materials on the shelf will result in the next system being developed using today's technology, not yesterday's.