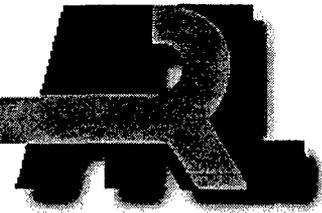


ARMY RESEARCH LABORATORY



# Insensitive High Energy Propellants for Advanced Gun Concepts

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# **Army Research Laboratory**

Aberdeen Proving Ground, MD 21005-5066

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## **Insensitive High Energy Propellants for Advanced Gun Concepts**

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## Abstract

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In recent years, substantial improvements in the performance of solid propellant guns have resulted from the development of higher energy propellants, higher loading density propellant charge configurations, and propellant geometries and concepts that have provided the progressively increasing gas generation rates required to efficiently use available increases in total energy. Unfortunately, these same features also typically lead to increases in ammunition vulnerability to enemy threats. Coupled with the current interest in much lighter fighting vehicles, the need for ammunition with reduced rather than increased sensitivity is obvious. This report describes the development of a new approach in the U.S. Army to address propellant energy/performance and sensitivity/vulnerability as a single set of critical design requirements, to be addressed concurrently from the very beginning of the new energetic material research and development cycle. Some elements of this work were presented in abbreviated form at the 19th International Symposium on Ballistics in Interlaken, Switzerland in May 2001 [1].

## ACKNOWLEDGMENTS

The development and execution of a major new thrust such as the Insensitive High Energy Munitions (IHEM) Program involve the contributions of many people at the U.S. Army Research Laboratory (ARL). Acknowledgment is made to Drs. Arpad Juhasz, Thomas Minor, and William Oberle for contributions through the years to high progressivity/high density and in electro-thermal-chemical gun propulsion concepts. The work of Mr. Jerry Watson provided the background for shaped charge jet vulnerability response plot in Figure 11. Dr. Rob Lieb performs mechanical property measurements and interprets their significance. He also performs the microscopic examination of the non-ignited shear-punch samples. Many people are instrumental in conducting the small-scale vulnerability experiments at ARL. Dr. Reed Skaggs is in charge of our battlefield information coordination efforts, Mr. Al Bines and Mr. Bill Sunderland conduct the electric flyer experiments, and Dr. Larry Vande Kieft and Mr. Oliver Blake run the hot fragment conductive ignition and shear-punch experiment. We thank Dr. Frederick Beyer and Dr. Nora Beck-Tan (formerly of ARL) for their contributions in polymer characterization, and Dr. Brad Forch for his insights to the potential of nanoenergetic materials. Acknowledgment is also made to Dr. David Mann of ARL's Army Research Office and Dr. Dave Downs of the Tank-Automotive and Armaments Command - Armament Research, Development, and Engineering Center for support and critical contributions bringing about the necessary close coordination of the IHEM concept with their respective programs, yielding a fully integrated effort in this important new area. Finally, appreciation is expressed to Dr. Ingo May, former Director of ARL's Weapons and Materials Research Directorate, for long-time support and encouragement of advanced gun propulsion research and to the people pursuing it.

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# INSENSITIVE HIGH ENERGY PROPELLANTS FOR ADVANCED GUN CONCEPTS

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## 1. Background: The Quest for Higher Performance

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The quest for higher interior ballistic performance for any gun system, while encumbered with many possible subtleties and variations in approach, ultimately resolves two simple challenges: providing more energy to the propulsion package and transferring this energy efficiently to the launch vehicle. In terms of the conventional gun approach, this translates into (a) the development of new propellant formulations with higher specific energies, (b) propellant grain and charge configurations that allow increases in overall charge loading density (which for advanced kinetic energy rounds with long rod penetrators extending well back into the charge may be problematic), and (c) techniques for programming this energy release so that the maximum desirable system pressure is reached as early as possible and is nearly maintained as long as possible, preferably until the moment of propellant burnout.

Complete success in both of these challenges would result in the classic "holy grail" for interior ballistic researchers: *a flat pressure-travel curve for the maximum duration allowable by the available propellant charge mass*, as shown in Figure 1 [2]. (We note that maintaining breech pressure at the maximum level does not provide a similarly constant projectile base pressure [the subject of numerous other studies], but we will assume this to be a worthy goal in any case.) Thus, the piezometric efficiency (i.e., the ratio of mean pressure to peak breech pressure) is maximized, *consistent with the available charge mass and the requirement of maintaining operation at maximum allowable breech pressure*. Thermodynamic efficiency (i.e., the ratio of the projectile kinetic energy at the muzzle to the available chemical energy of the propellant charge) is also maximized, since the charge is totally transformed to combustion products at the earliest possible point in the interior ballistic cycle, thus maximizing the work done by expansion of the gases on the projectile.

Today's high performance tank guns already benefit from extremely well-designed propelling charges. While piezometric efficiencies typically fall in the 50% range (low because the charge is consumed relatively early in the cycle), and thermodynamic efficiencies fall in the even less impressive 25% range (owing primarily to the ever-increasing proportion of the total energy release allocated to the kinetic energy of the propelling gases themselves with the high charge-to-mass ratios), a perhaps more useful measure of efficiency is the ballistic ratio [3], which we redefine here as the ratio of the actual muzzle kinetic energy (MKE)

obtained from a system to the MKE that would be obtained if the same total charge mass were burned at constant pressure. Using this measure of efficiency, today's high performance tank guns actually operate at the 90% level—a pretty tough number to beat! Clearly, the charge design community has done an excellent job in extracting performance from a given energy source, the implication being that we should focus on increasing the energy in the system without reducing the efficiency of its use.

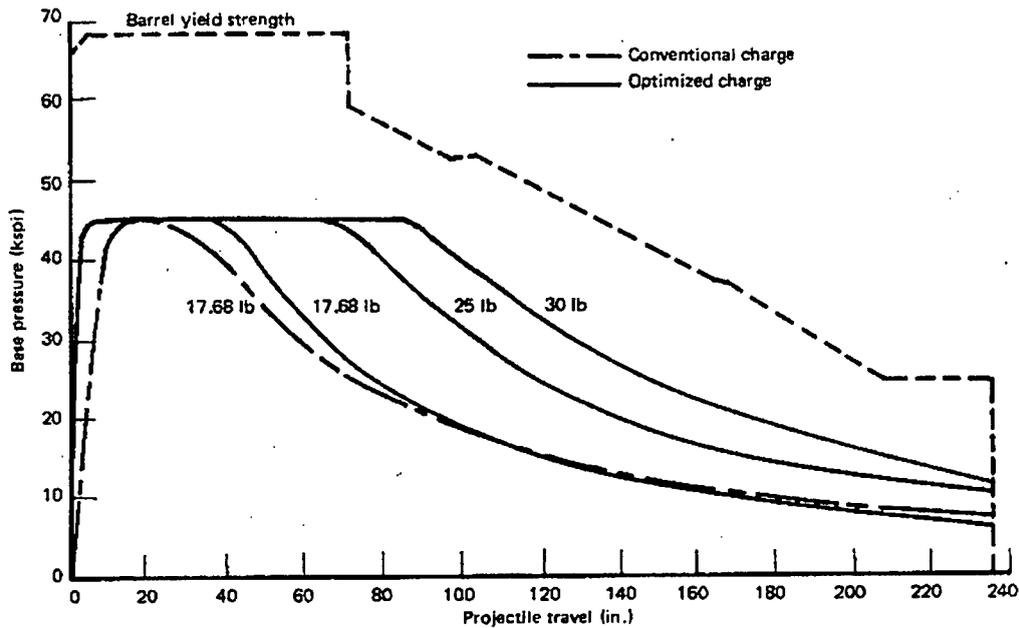


Figure 1. Typical and Ideal (flat) Pressure-Travel Curve, Along With Nominal Barrel Strength Curve for a Navy 5-inch/54-Caliber Barrel [2].

We must point out that numerous credible efforts have been undertaken in recent decades to pursue alternatives to the conventional solid propellant gun approach: traveling charges (to maintain nearly constant projectile base pressures and to reduce losses to propelling gas kinetic energy) [4], propellant-lined gun tubes (to program gas generation rates and to reduce gas kinetic energy losses) [5], propellants with very high burning rates (to allow greater flexibility in propellant geometries for higher loading densities and progressivities) [6], combustion-light gas guns (for lower molecular weight propelling gases for reduced pressure gradients and gas kinetic energy losses) [7], and in-bore ram accelerators (again to eliminate the pressure gradient and losses to gas kinetic energy) [8], to name but a few. None of these concepts, however, has been adapted for use in tactical applications, and it is the intent of this report to limit itself to efforts that provide substantial performance improvement from conventional guns. Nonetheless, the overall philosophy espoused by the approach described herein can be seen to be applicable to virtually all propulsion approaches (gun, missile, combinations thereof, and

beyond) that employ chemically energetic materials as the major source of energy to accelerate the payload.

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## 2. Recent Improvements in Gun Performance

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For more than the past 100 years, virtually all of the world's production gun propellants have been based, at least in part, on the use of nitrocellulose (NC), first discovered in 1845 by Schonbein and then successfully solvated in the 1880's to allow extrusion into strips, cords, or tubes for ballistic control. The resulting "smokeless" propellant, as it replaced the rather dirty-burning black powder used for possibly hundreds of years, is not surprisingly attributed to different individuals, depending on national history, but most often to Vieille in France, and Duttonhofer in Germany [9]. In any case, as successful as NC-base and the higher energy double-base propellants (employing both NC and nitroglycerine [NG] or related energetic plasticizers) have been through the years, this family of propellants exhibits at least two major limitations. First, the nitration level of the NC is limited to below 14%, with higher energy levels dependent on the use of less desirable ingredients such as NG. Second, the solvent production process used to eliminate porosity and improve workability of the material ultimately limits available grain geometries (because of requirements for and results of the drying process) and, perhaps of increasing importance, is environmentally unattractive and essentially irreversible.

Thus, propellant developmental efforts over the past few decades have addressed the use of new materials that could raise energy density without unacceptable increases in flame temperature or sensitivity/vulnerability. The literature abounds with studies of the use of the crystalline, cyclic nitramines RDX (hexahydro-1,3,5-trinitro-1,3,5-7-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) to address these goals, with a recurring problem of high burning rate exponents and performance irreproducibility. However, by the 1980's, work done jointly by the U.S. Navy and Army led to the first service-qualified nitramine-based gun propellant for low-vulnerability ammunition (LOVA) [10]. Subsequently, alternate high energy density ingredients such as CL20 (2,4,6,8,10,12-hexanitrohexaazaisowurtzitane) [11], TNAZ (3,3-trinitroazetidene), and ADN (ammonium dinitramide) have been identified and evaluated in possible new advanced gun propellants. CL20, in particular, is highly attractive as an energetic filler in composite gun propellants because of its high heat of formation (+100 kcal/mole) and density (2.04 g/cc), as well as a significant positive impact on propellant burning rates [12].

Concurrently, new binders were being developed to replace the workhorse NC of the past. Thermoplastic elastomers (TPEs), materials that can be processed like typical thermoplastics but behave at gun operating temperatures like elastomers, offer the opportunity for ready inclusion of energetic fillers, such as RDX and

CL20, while maintaining good physical properties and providing the option for reprocessing. TPEs typically incorporate two polymers, an amorphous soft block and a crystalline hard block, the copolymer yielding the combination of physical behaviors described previously. Moreover, TPEs can be energetic or basically inert. Early LOVA formulations were based on energetic fillers (e.g., RDX) in nonenergetic TPE binders. The quest for higher performance has led to a concentration on the use of energetic TPEs (or ETPEs, such as the oxetanes BAMO (3,3-bis [azidomethyl] oxetane) and AMMO (3-azidomethyl-3-methyloxetane) [12].

The resulting use of these new materials (at least to the gun propellant community) has led to substantial increases in specific energy; increases in material density have resulted in even greater increases in volumetric energy. Figure 2 displays impetus<sup>1</sup> values associated with propellants developed over the past half century. Figure 3 displays an accompanying benefit of more recent formulations: lower flame temperatures for a given impetus, a result of lower mean molecular weights (MMW) of the combustion products (impetus being proportional to the flame temperature divided by the MMW).

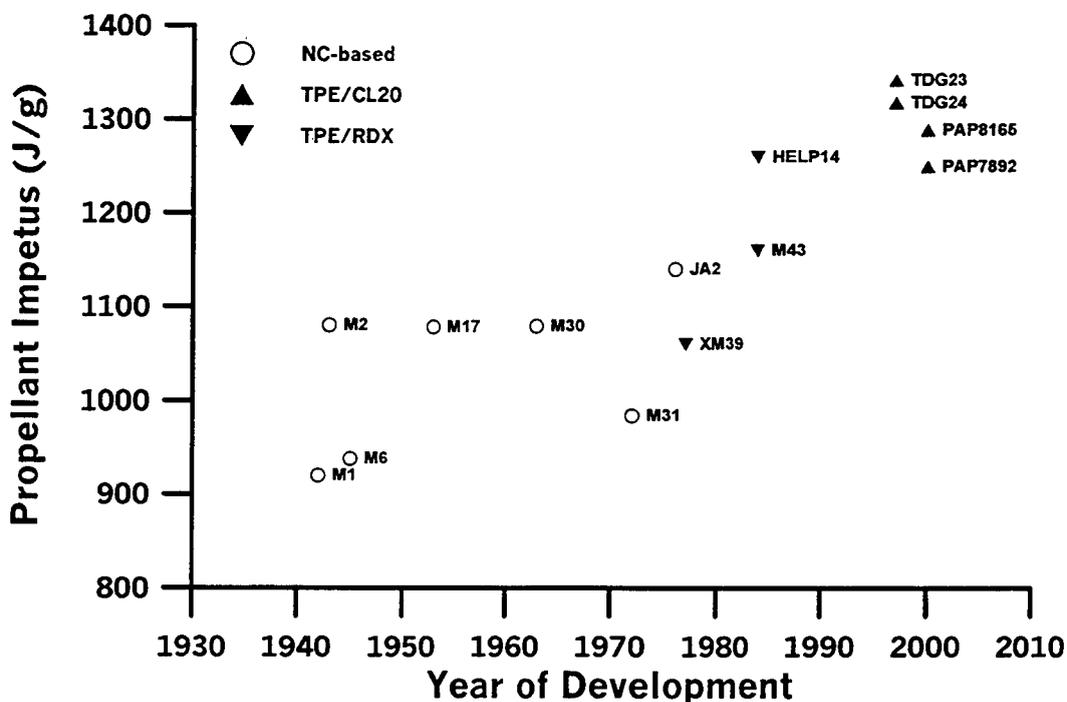


Figure 2. Impetus Values and Approximate Time of Development for Various Gun Propellants (impetus values calculated with the BLAKE<sup>2</sup> code [13]).

<sup>1</sup>Impetus is energy times  $(\gamma-1)$ , in which  $\gamma$  is the ratio of specific heats ( $c_p/c_v$ ) and is the measure more frequently used in the ballistics community.

<sup>2</sup>Not an acronym

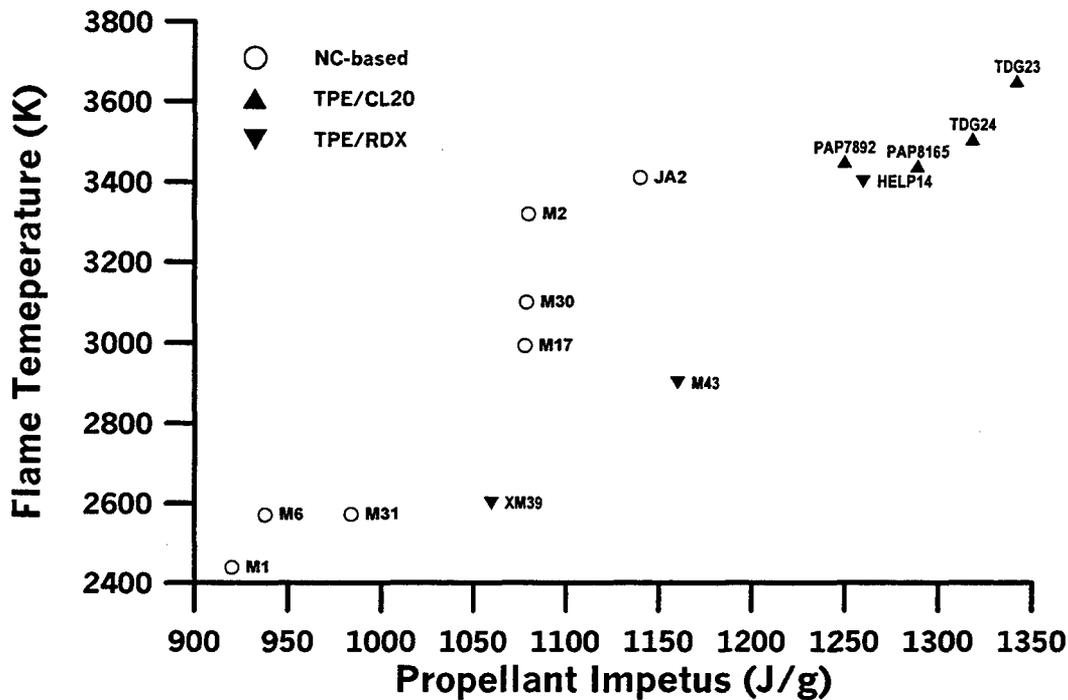


Figure 3. Flame Temperatures Versus Impetus Values for Various Gun Propellants (impetus values calculated with the BLAKE code [13]).

However, increases in available stored energy in the propellant charge are useful only if they can be released in accordance with a strict program that provides rapid pressurization to the peak allowable system pressure, followed by a progressively increasing rate that essentially mimics the increasing in-bore velocity of the projectile (see Figure 4) [2]. The use of multi-perforated grains has been the traditional way of providing progressively increasing burning surfaces as a function of burn distance, as shown in Figure 5, but randomly loaded granular propellant has a maximum loading density of only about 0.85 g/cc with conventional chemistries. Stick propellants pack better, but gas production within the long perforations leads to choked flow, over-pressurization, and fracture of the sticks. Propellant designers have long solved this problem for single-perforated sticks with longitudinal slots; in the past decade, kerfs or partial cuts have been employed to lead to controlled fracture and venting of multi-perforated sticks [14].

Recent approaches to increased progressivity have been based on decoupling gas production rates before and after peak pressure in the gun, that is, to provide a discontinuous increase in burning surface or rates once the projectile has started moving rapidly and is outrunning the gasification rate of conventional grain geometries. Programmed splitting sticks initially burn as simple cylinders until just after peak pressure, when the flame front reaches an array of embedded slits and envelops a much larger burning surface [15]. Most recent has been the use of layered propellants, whereby a discontinuous increase in propellant chemistry

leads to much faster burning rates once peak pressure has passed [16]. This latter concept is not new by any means but has been made practical by the use of TPE propellants, which allow adjacent layers of materials with different burning rates to coexist with adequate chemical stability to maintain the desired differential. In addition, the use of layered materials to obtain the desired progressivity facilitates the use of nonstandard overall charge geometries that can significantly increase overall loading densities by as much as 40%. Figures 6 and 7 provide a schematic of several of these concepts and their influence on progressivity.

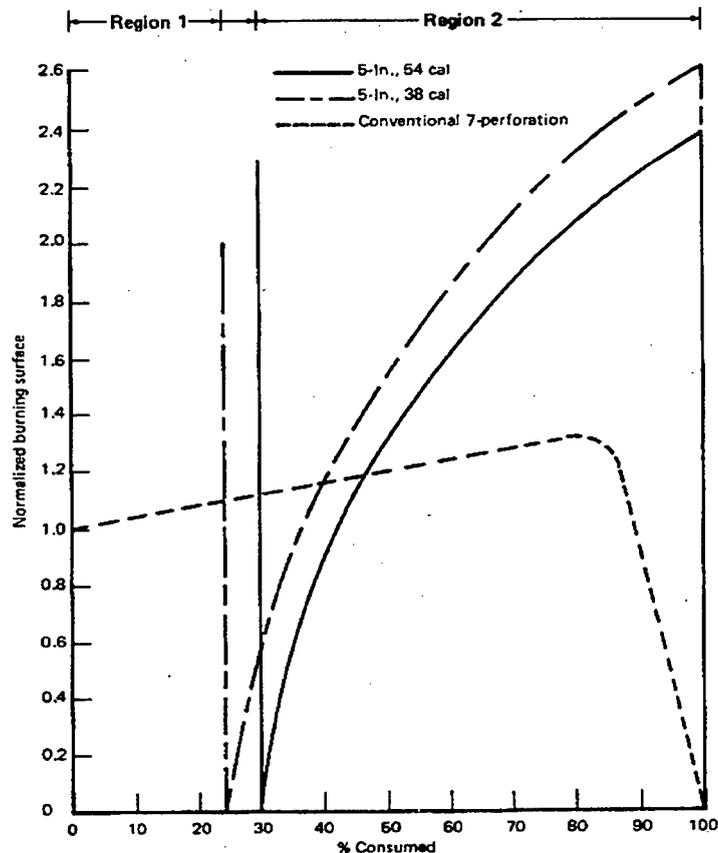


Figure 4. Ideal Grain Surface Versus Burn Distance Profiles Calculated for Navy 5-inch/38-Caliber and 5-inch/54-Caliber Guns [2].

Thus, it would appear that we have attained all features necessary for substantial increases in performance from conventional guns: higher propellant specific energies, higher loading densities for even greater volumetric increases in available energy, and new concepts to program the release of this increased energy consistent with the pressure limits and envelope of the projectile and launcher. Unfortunately, as mentioned earlier, these same features that increase the total energy of the propulsion package also typically increase its sensitivity and vulnerability to unintended initiation, with potentially catastrophic results. Moreover, the safe and reproducible ignition of high-loading-density charges has always presented problems [17]; achieving this ignition with loading densities

that exceed 1.3 g/cc is virtually impossible with classical means. Added to these primary challenges are the many secondary performance issues (e.g., gun tube erosion, flash, blast), increasingly important environmental issues, and the ever-present concern about life cycle costs.

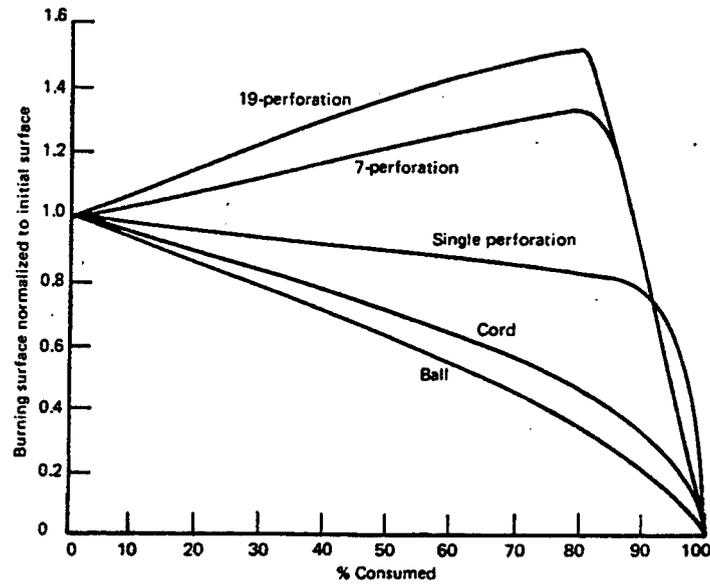


Figure 5. Traditional Grain Approaches to Progressive Release of Combustion Gases [2].

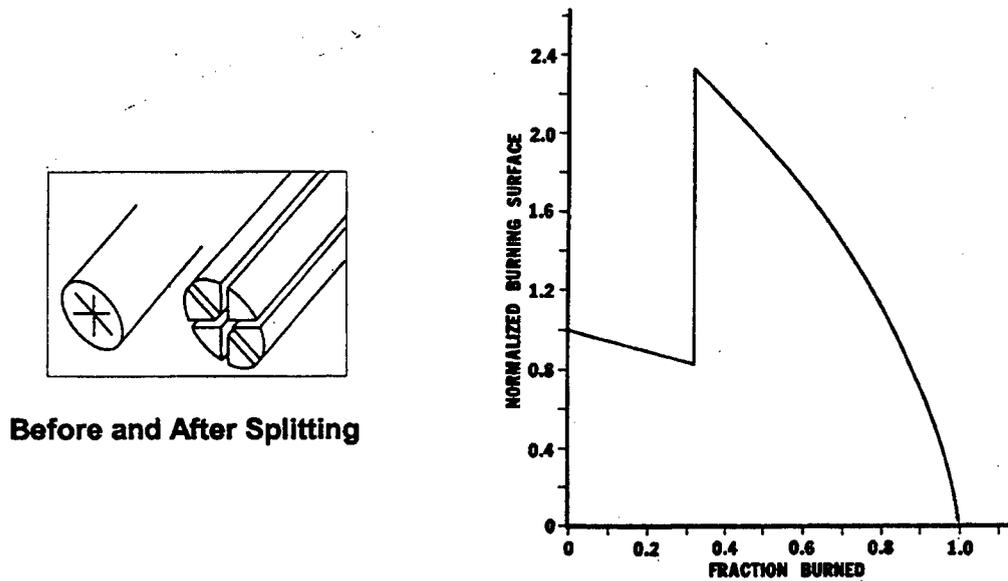


Figure 6. Programmed Splitting Stick Propellant and Associated Surface Profile [15].

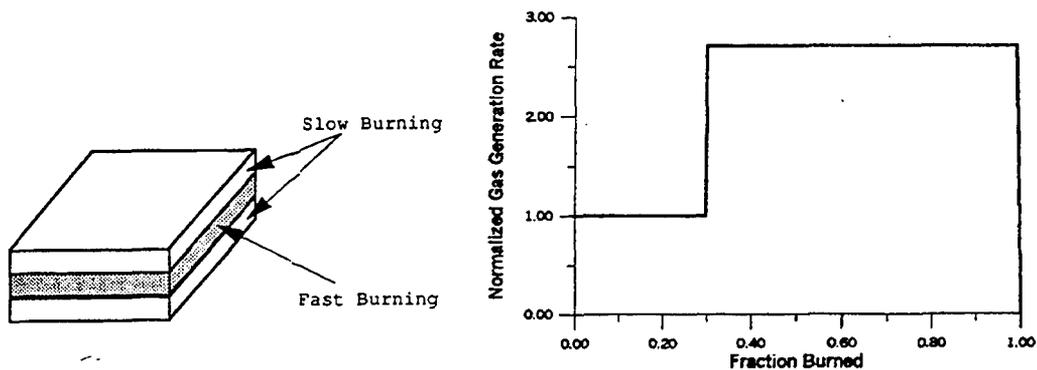


Figure 7. Layered Propellant and Associated Gas Production Profile.

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### 3. Introduction of the Insensitive High Energy Munitions (IHEM) Program

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Current research in gun propulsion within the United States is driven by emerging requirements for lightweight combat vehicles of the future, whose missions will likely include both direct and indirect fire. For propellants, required improvements in system lethality and survivability translate into the need for more energy and less sensitivity. In response to this apparent program direction and to the technical challenges outlined previously, the U.S. Army Research Laboratory (ARL) at Aberdeen Proving Ground, Maryland, has restructured its energetic materials research program, combining major portions of its propellants and survivability programs into a new thrust area, IHEM. Under this program, both the performance and survivability attributes of new energetic materials are treated as a single, essential set of characteristics, even at the earliest phases of research.

Our program focuses on two levels of new insensitive high energy propellant (IHEP) families: (1) modification of current developmental, high energy gun propellants to make them system acceptable, and (2) longer term research into a much wider range of new propellant formulations and approaches, making aggressive use of advanced modeling techniques, limited "smart testing," and close coordination with the overall national effort into new and novel energetics. We address first the nearer term effort, focused on the current generation of developmental propellants employing energetic fillers such as RDX or CL20 in ETPE binders such as BAMO-AMMO block copolymers. Such propellants have been shown to provide the substantial, required increases in specific impetus (>1300 J/g) and the chemical stability and range in burning rates needed to facilitate the use of layered propellants. As such, they can also be configured to offer loading densities as high as 1.4 g/cc. Successful, safe, and reproducible

ignition of charges so assembled, however, has required plasma ignition, as used for electro-thermal-chemical (ETC) propulsion concepts. Apparently, the high plasma temperatures ( $>10000\text{K}$ ) coupled with the high mobility of the lightweight plasma particles successfully penetrate the extremely low permeability of slabs or disks in layered propellants to achieve nearly uniform ignition and freedom from deleterious pressure waves. Benefits in terms of ignition benefits (reduction in delays and extremely reproducible ignition event) and performance (compensation for temperature effects and substantial increases in MKE from the high loading densities of high energy propellant charges) [18,19] can be attributed to the use of plasma ignition with this family of propellants, sometimes called "ETC-friendly" propellants. The remaining challenge for such formulations is to achieve the required modifications in the chemistry and physical product that will achieve required reductions in sensitivity and vulnerability to render them system acceptable.

This challenge is being addressed through the use of a family of new experimental screening devices capable of evaluating performance, sensitivity, and erosivity characteristics with the smallest possible quantities of the rather expensive (at the research stage) candidate materials. Smart testing of carefully selected and manufactured samples, which evaluates the influence of formulation, particle sizes, additives, and processing, is then coupled with an extensive range of modeling techniques to evaluate an otherwise prohibitively costly solution space to attain required propellant characteristics.

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#### 4. Recent Approaches to Performance Screening

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This report does not include a review of classical theoretical and experimental techniques typically employed during the propellant development cycle; however, we briefly mention a number of recent experimental techniques specifically developed to support the evaluation of new candidate formulations when cost or scarcity necessitates experimentation with very small quantities of material. The first of these is the micro-closed bomb (see Figure 7), with an internal volume of about  $25\text{ cm}^3$  rather than the usual  $200\text{ cm}^3$ , thereby allowing burning rate determinations at normal loading densities of less than  $10\text{ g}$  of propellant. Comparability of results has been demonstrated [20], as shown in Figure 8.

Another consideration for advanced charge design is the potential for new high-energy formulations to lead to unacceptable gun tube erosion. Recently, an existing erosivity measurement fixture was refurbished and is being used to provide a relative ranking of gun propellant erosivities, with particular attention on factors beyond the obvious influence of flame temperature (e.g., concentrations of  $\text{CO}$  and  $\text{N}_2$ ) [21].

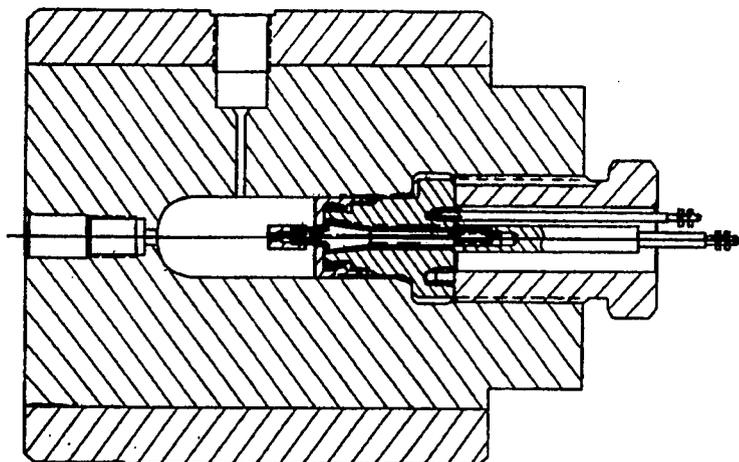


Figure 7. The 25-cm<sup>3</sup>, 800-MPa Micro-Closed Bomb [20].

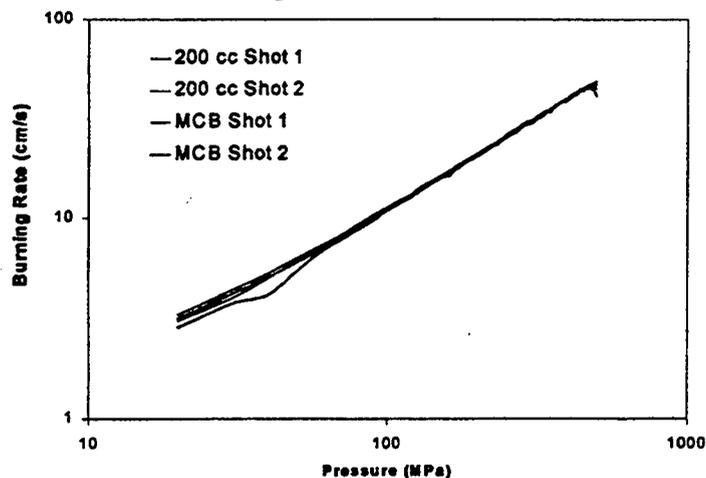


Figure 8. Comparison of Results for JA2 Propellant at 0.34-g/cc Loading Density, Obtained With the Micro-Closed Bomb and a Conventional 200-cm<sup>3</sup> Closed Bomb [20].

Of course, reliable ballistic performance is an absolute requirement for new propellant systems, and evaluation of ballistic parameters with small quantities of available materials presents a significant challenge. It is imperative that any potential problems with these propellants and configurations (temperature sensitivity, delamination, grain fracture, ignition delay) be identified in a scaled interior ballistic environment before they are applied to large caliber systems. To that end, ARL has developed a suite of medium caliber diagnostic devices, capable of exposing relatively small quantities (30 grams to 200 grams) of novel propellant formulations to the interior ballistic environment so that the propellant's temperature sensitivity, material integrity, and ease of ignition and flame-spreading properties are revealed. These fixtures include a 30-mm gun and a short gun/interrupted burner [22].

Although the function of each experimental fixture is different, they were all designed to use identical charge packaging components to ensure consistent performance throughout ballistic evaluation. Case wall thickness can be varied to adjust the chamber volume as required. Foam liners can be used to maintain uniform exposure of the propellant bed to the ignition stimulus when the propellant does not fill the cartridge. The goal is to evaluate candidate propellants without contaminating the propellant performance with ignition anomalies, and a simple, repeatable, uniform ignition system was designed and validated in an igniter fixture.

A diagram of the 30-mm experimental gun fixture (actually 29.2 mm [1.15 inches]) used in these experiments is shown in Figure 9. It consists of a simple screw breech chamber with a 38-mm inside diameter threaded to a 2.667-meter-long gun tube. Peak chamber pressures as great as 450 MPa can be accommodated in this fixture. Instrumentation includes multiple pressure transducers, microwave interferometer (displacement and velocity), velocity screens, and a flash detector. Charges may be temperature conditioned to investigate the temperature sensitivity of the propellant undergoing study.

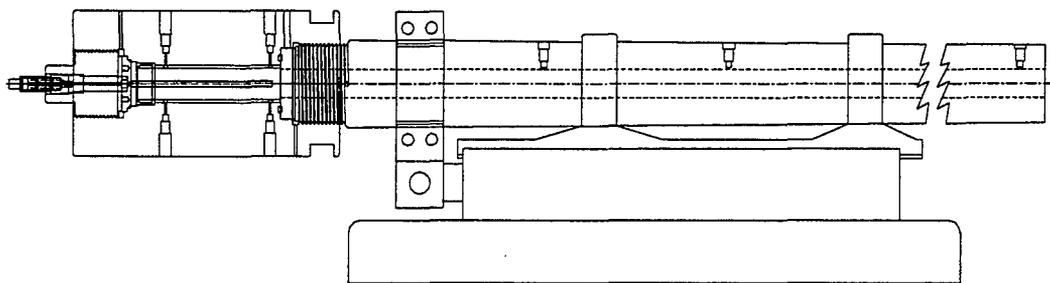


Figure 9. Experimental Gun Fixture (30 mm) for Propellant Performance Screening [22].

A short gun fixture/interrupted burner (see Figure 10) that allows investigation of the same charge and ignition systems as the gun and igniter fixtures is also available. It consists of a chamber and a barrel with 15.24 cm (6 in.) of projectile travel. This fixture can function as an interrupted burner, allowing study of partially consumed propellant samples. Careful control of the ignition stimulus and venting pressures allows studies of surface regression, grain perforation, augmented burning, and propellant damage attributable to the igniter stimulus. Venting pressure can be controlled through variations in projectile mass, charge mass, and chamber volume. Ignition stimulus can be varied through changes in the simple center core igniter system.

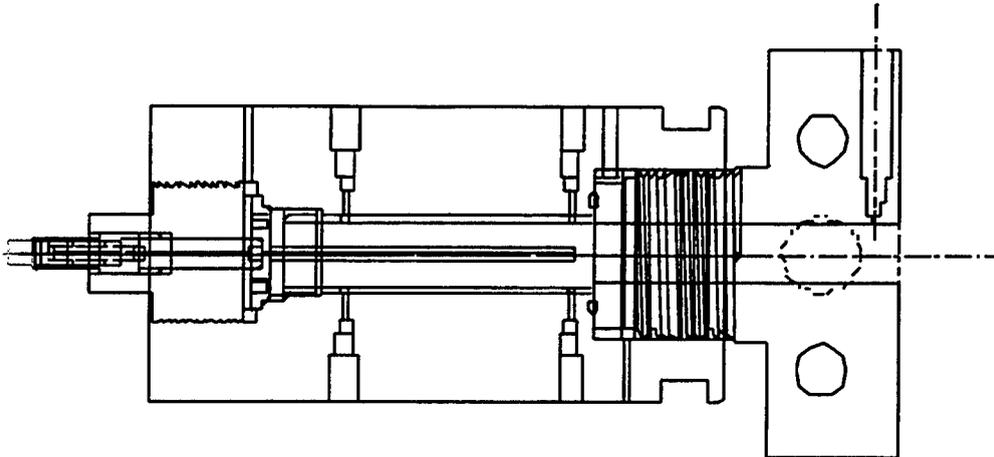


Figure 10. Short Gun/Interrupted Burner for Propellant Performance Screening [22].

The simple design of these fixtures allows for reconfiguration to meet the needs of different ignition systems and propelling charge designs. The moderate propellant requirements allow for statistically significant numbers of experiments with limited amounts of novel propellant formulations.

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## 5. Recent Approaches to Vulnerability Screening

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The coupling of performance and sensitivity requirements for new propellants places an increased burden on the propellant formulator. New ingredients with higher energy and decreased sensitivity are required. Processes to produce reasonable quantities of any novel formulations are expensive and time consuming, so it is advantageous for the researcher to evaluate the usefulness of a formulation or ingredient with minimal amounts of material. Overall system survivability depends largely on system limits and characteristics—a situation that is likely to present even greater challenges as we move to lightweight fighting systems. However, vulnerability is most often also a function of the propelling charge susceptibility to initiation/detonation, typically a function of sensitivity of the propellant, its mechanical properties, and various configural features of the propellant and charge. Emphasis must therefore be placed on identifying and measuring the key sensitivity properties and geometrical relationships that drive the relationship between propellant sensitivity and charge vulnerability. Our goal is to achieve this via meaningful experiments we develop that employ minimal quantities of very expensive materials, at least early in the development cycle.

Threats to a propulsion charge result in ignition stimuli that are either thermal or mechanical, with the latter being further divided into shock or non-shock stimuli. Ballistically, the thermal stimulus arises from spall or small fragment particles

becoming embedded in the charge after they have undergone some plastic heating during the ballistic event. A correlation exists between the temperature of a fragment required to ignite the propellant and its propensity to ignite when impacted by a spall particle or small fragment [23, 24]. ARL continues to use the hot fragment conductive ignition (HFCI) experiment as a measuring device for sensitivity to the spall and fragment threat. This experiment consists of dropping a heated fragment on a propellant sample and watching for sustained combustion. It is a basic experiment, but in concert with other chemical information, it provides keys to propellant development. As an example, the decomposition properties of the binder for a composite propellant were shown to play an important role in determining ignition temperatures [25] and sensitivity to thermal threats.

For the mechanical ignition stimulus, the threat can be a shaped charge jet (SCJ), explosively formed penetrator, or kinetic energy projectile with the response of the propulsion charge being either a detonative or non-detonative event. Either response can be catastrophic. A generic response chart is shown in Figure 11 for the SCJ threat. The curve labeled "rapid deflagration" shows that as the stimulus increases, in terms of either jet diameter or velocity, the energy output from the charge increases in a monotonic fashion. At the stimulus level labeled "2," the output will be unacceptable to the system of interest. The curve labeled "shock-induced detonation" shows that at some other stimulus level labeled "1," the full propulsion charge may detonate. Which trend a propulsion charge follows, the slope of the rapid deflagration curve, and the critical stimulus value for detonation are functions of both charge design and basic propellant sensitivity parameters. ARL is using several screening techniques to measure the latter with small amounts of advanced formulations.

Three important sensitivity parameters are shock sensitivity, sensitivity to a non-shock mechanical load, and propellant mechanical properties. From a ballistic vulnerability perspective, the most important mechanical property of a propellant is its failure behavior under a load. A correlation exists between the failure modulus<sup>3</sup> of a propellant and the response to an SCJ [27]. In general, because of increased burning surface area during the event, brittle propellant behavior will lead to a stronger reaction than ductile behavior. At ARL, a servo-hydraulic machine is used to measure the failure response of a propellant at various temperatures [28]. Experiments are conducted at different temperatures and strain rates. Time-temperature superposition is then used to simulate the high strain rates associated with SCJ impact [29]. Figure 12 shows two generic mechanical behavior curves for gun propellants. The propellant with the strongly negative failure modulus would be expected to have an increased output, compared to the propellant that exhibits work hardening after mechanical failure.

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<sup>3</sup>The failure modulus is the slope of the stress-strain curve in the near linear region between the strain at maximum stress and twice that value. If no maximum stress occurs in the region of failure, the failure modulus is measured between the strain at failure and three times that value [26].

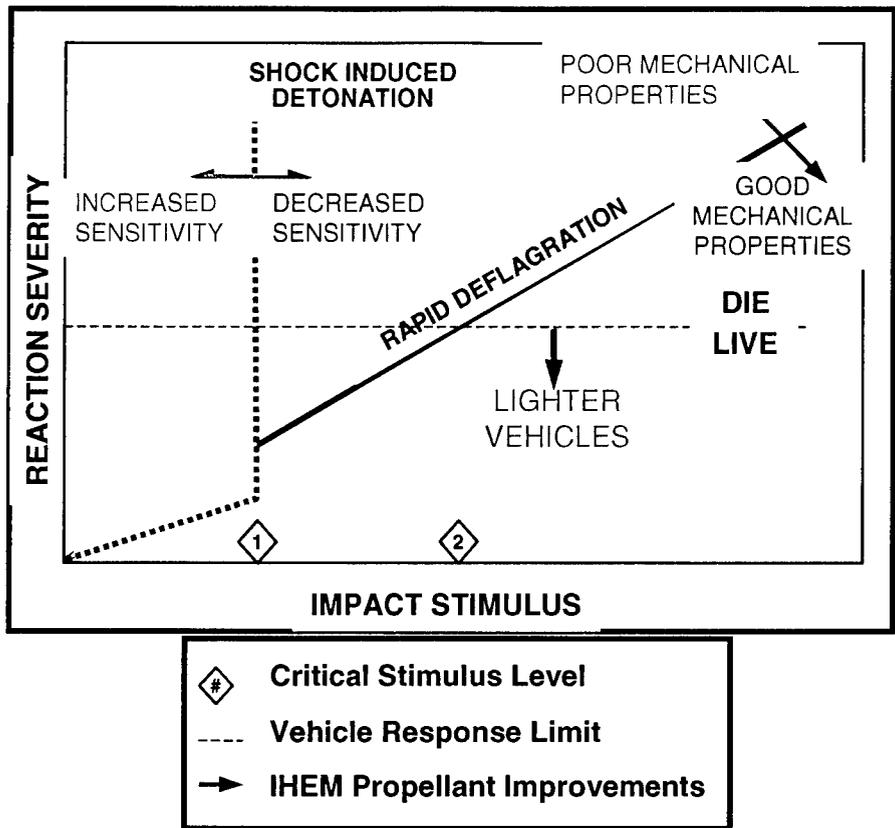


Figure 11. Response of a Propulsion Charge to an SCJ Stimulus.

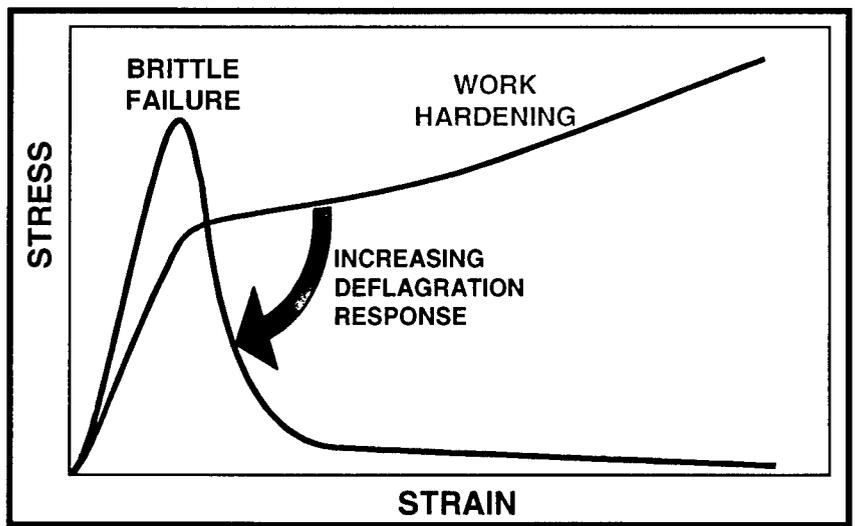


Figure 12. Mechanical Behavior of Several Propellants (concept from Lieb et al. [28]).

Material rankings for shock and shear sensitivity are known to vary [30]. Thus, both must be measured. ARL is using two experiments to evaluate propellant sensitivity to non-shock mechanical loading. One is the ballistic impact chamber

(BIC) invented by Coffey and DeVost of the U.S. Navy [31]. Figure 13 shows that the BIC is a drop-weight impact machine that encloses the propellant in a semi-closed volume. Sample sizes employed at ARL are typically 50 to 100 mg. Unlike standard drop-weight experiments, the propellant is forced to ignite. The pressure in the volume is recorded as a function of time after initiation, with typical outputs for propellants shown in Figure 14 [32]. The total area under the pressure curve is a measure of the propellant's energy, and the initial pressure rise rate provides an indication of the reaction from the hot spots, both of which relate to the vulnerability response of a propulsion charge. Skaggs et al. [32] attempted several correlations of BIC data with large-scale vulnerability data, but to date, no clear correlation exists. Any correlation is clouded by factors such as mechanical properties and flame-spreading issues, which are more influential in full-scale charge response than in the BIC. However, a well-conducted drop-weight impact experiment provides a pressure/shear/strain rate environment that can be representative of some hazard scenarios and is more readily simulated than an actual impact event (e.g., [33]). Thus, ARL continues striving for a methodology that relates small-scale instrumented drop-weight data to charge vulnerability.

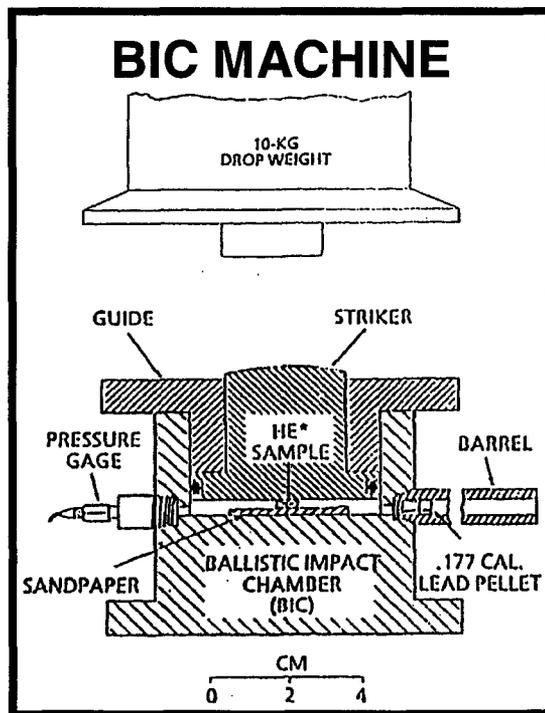


Figure 13. The Ballistic Impact Chamber [31].

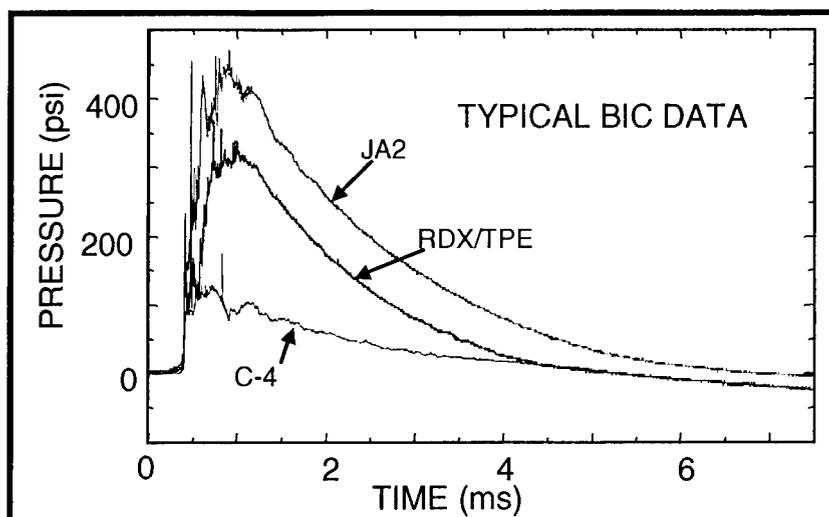


Figure 14. Typical Pressure Records From a BIC Experiment on Propellant [32].

In addition to measuring non-shock sensitivity with the BIC, ARL has developed a "shear-punch" sensitivity experiment to provide insight into the non-shock initiation process [34]. The apparatus is a modified split Hopkinson pressure bar (SHPB) that punches a core out of a sample. Figure 15 shows a schematic of the experiment. The duration, rate of shear, and pressure on the shear plane can be independently varied. Figure 16 shows typical input and output bar strain records and a schematic of sample with a global representation of the shear force. The measured reflected and transmitted strain pulses in the SHPB permit one to evaluate properties of the shear plane during deformation.

Beyond establishing initiation thresholds, several measurements are possible with samples that do not ignite. The most basic is the dent depth and "punch-out" distance in the sample as a function of the load. Some preliminary data for JA2 propellant and an inert, polycarbonate sample are shown in Figure 17. The different curves are an artifact of different mechanical properties of the materials and seals that are used with the JA2 in order to prevent extrusion between the end plate and expendable sections. In combination with the strain records, these displacements provide insight into the stress/strain and shear failure behavior of the samples.

Samples sheared at rates below the reaction threshold are also analyzed with microscopy. This provides information about the shear patterns in the sample and evidence of when decomposition starts. Figure 18 shows an optical image of a 200-micron-thick slice of JA2 taken along the axis of the sample. Evidence of decomposition can be seen on the output bar side of the sample along the shear region. This indicates that the sample is near the ignition threshold in this experiment.

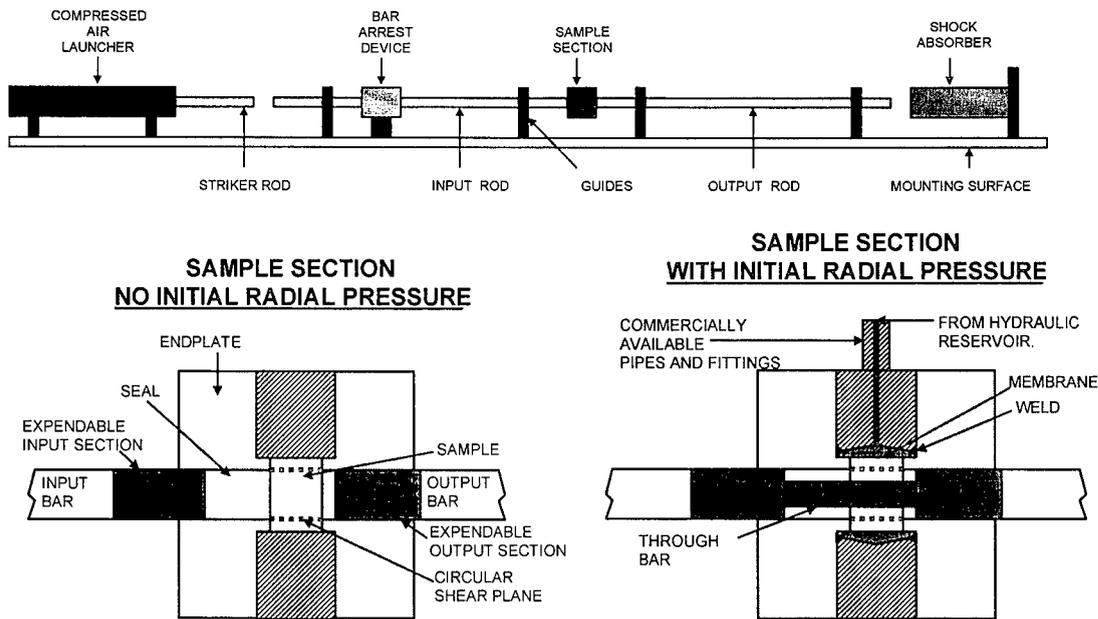


Figure 15. Modified Split Hopkinson Pressure Bar for Measurement of Shear Sensitivity [34].

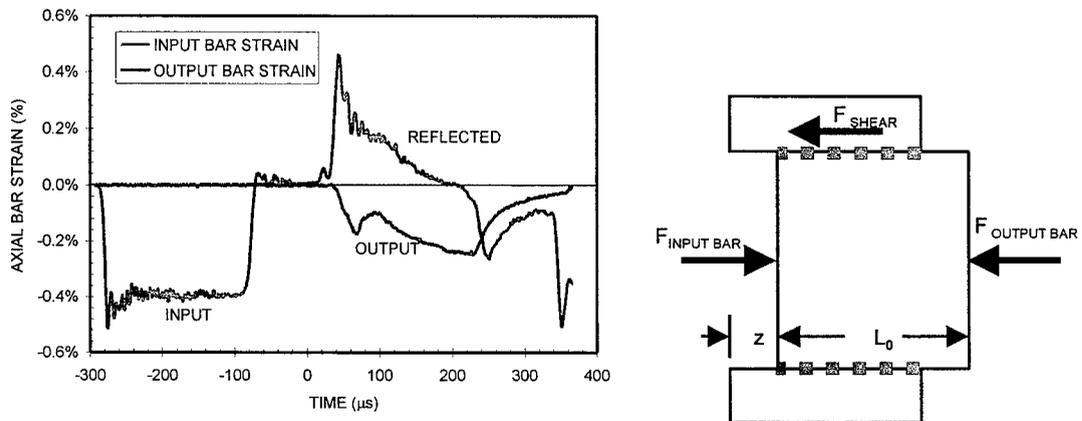


Figure 16. Typical Strain Records on Input and Output Bars and Basic Idealized Sample Cross Section Showing Shear Force.

ARL is also developing a small-scale sensitivity experiment for measuring shock sensitivity [34]. Two measures of shock sensitivity are relevant to vulnerability. One is the low pressure long duration (10 to 100 kBar,  $>1 \mu\text{s}$ ) shock sensitivity, which determines the minimum stimulus level required to detonate a propellant charge. The second is the high pressure short duration ( $>100 \text{ kBar}$ ,  $< 1 \mu\text{s}$ ) shock sensitivity, which could influence how the detonation propagates from grain to grain within a propellant charge and should be related to critical diameter or thickness. Sensitivity rankings for materials occasionally change with pressure and duration since different hot spots may be activated for each. Data from Moulard, Kury, and Delclos [35] indicate for an RDX-polyurethane-graphite

system that low pressure shock sensitivity, as measured by projectile impact, increases with RDX particle size, whereas high pressure short duration sensitivity, as indicated by critical diameter, decreases with particle size.

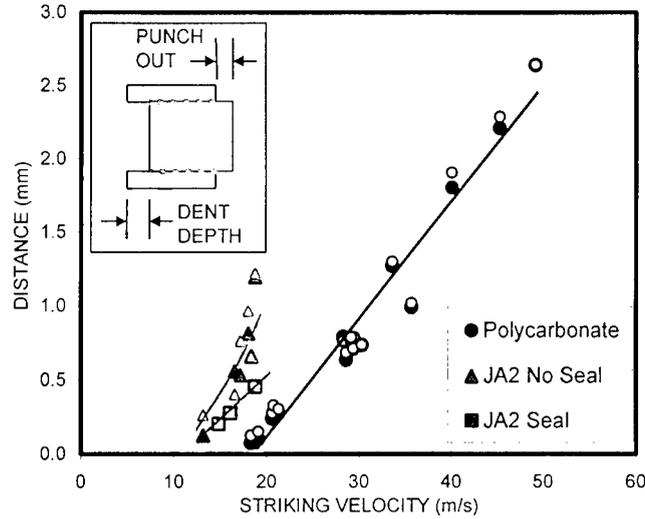


Figure 17. Punch-out and Dent Depths for Polycarbonate and JA2 Propellant Samples (open markers indicated punch-out distance; closed markers indicated measured dent depth).

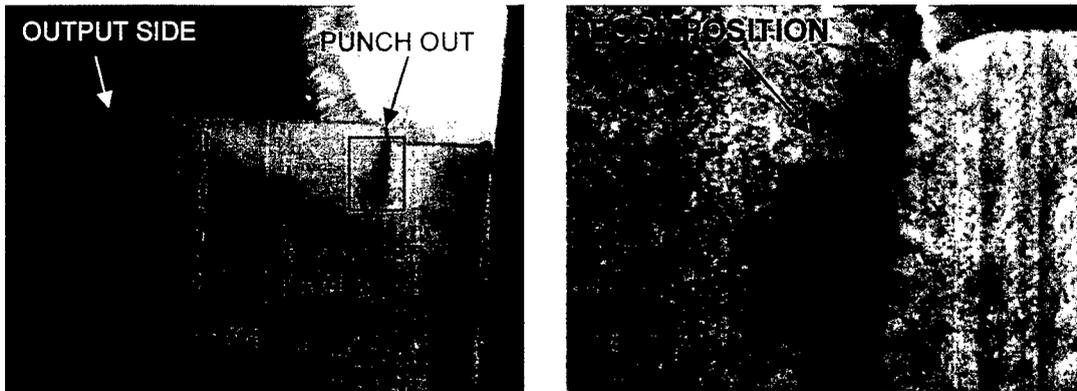


Figure 18. Photograph Showing Evidence of Decomposition Along the Shear Region on the Output Side of a JA2 Sample.

If a propellant can be made insensitive enough to high pressure short duration shocks, then it should be possible to prevent the full charge from detonating even if the material in the SCJ impact region detonates. This would be done by making the individual propellant sections of dimensions that are below some threshold multiple of their critical dimensions for detonation. That multiple appears to be a function of grain geometry and the contact area between the grains.

ARL is evaluating the high pressure short duration shock sensitivity of advanced propellants using the electric flyer shown in Figure 19. The basic setup consists of a high voltage high energy capacitor that is rapidly discharged across a thin metal foil. The ohmic heating vaporizes the foil. The energy dumped into the vapor propels a thin flyer plate into a small sample of propellant at velocities of several millimeters per microsecond. The chart in Figure 20 shows a go/no-go plot for some propellants and explosives. A 0.006-inch-thick Mylar<sup>®</sup> flyer was used for these experiments. Flyer thickness, flyer material, and discharge voltage can all be varied to change the shock delivered to the sample. The present setup uses several "piezo-pins" to indicate time of arrival for impact and when the shock reaches the rear of the sample. The difference is a measure of when the detonation initiates in the sample.

Sample mass is typically 200 mg, which allows evaluation with very small sample quantities. This is beneficial when one is using high-cost difficult-to-produce ingredients. Unfortunately, it also means that sample dimensions are occasionally less than the detonation failure dimensions for the material. However, by increasing flyer thickness and flyer shock impedance, we are attempting to produce an overdriven detonation in the sample, thus permitting sensitivity evaluation for samples with failure dimensions larger than those of the sample. Attempts are being made to simulate the electric flyer experiment with the CTH<sup>4</sup> hydrocode [36]. The objective is to use the electric flyer data to recalibrate the history variable reactive burn (HVRB) model in CTH for high pressure short duration shocks, such as those associated with detonation failure. It may be possible then to use this recalibrated reactive model to simulate aspects of larger scale charge vulnerability problems with the CTH code.

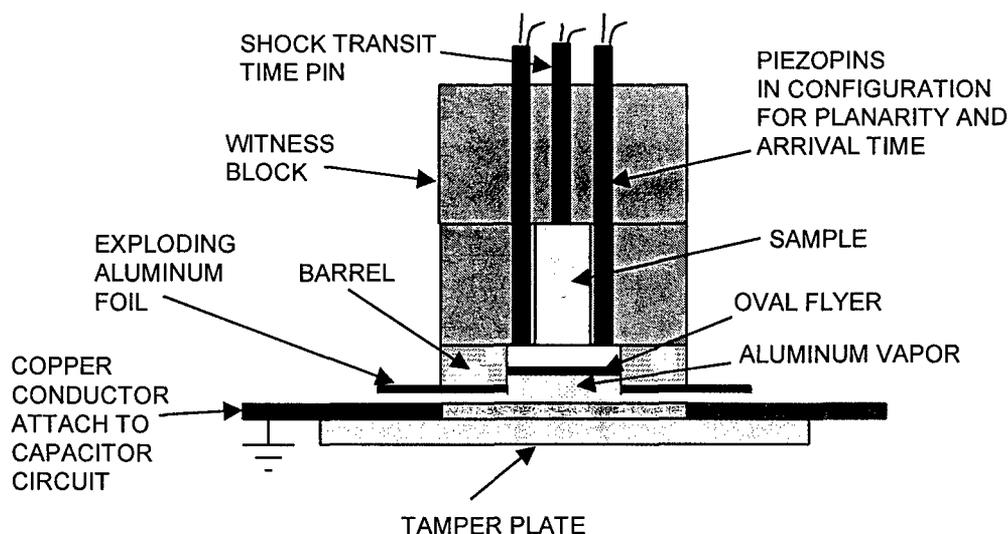


Figure 19. Schematic of Electric Flyer Plate Experimental Apparatus to Measure High Pressure Shock Sensitivity.

<sup>4</sup>Not an acronym

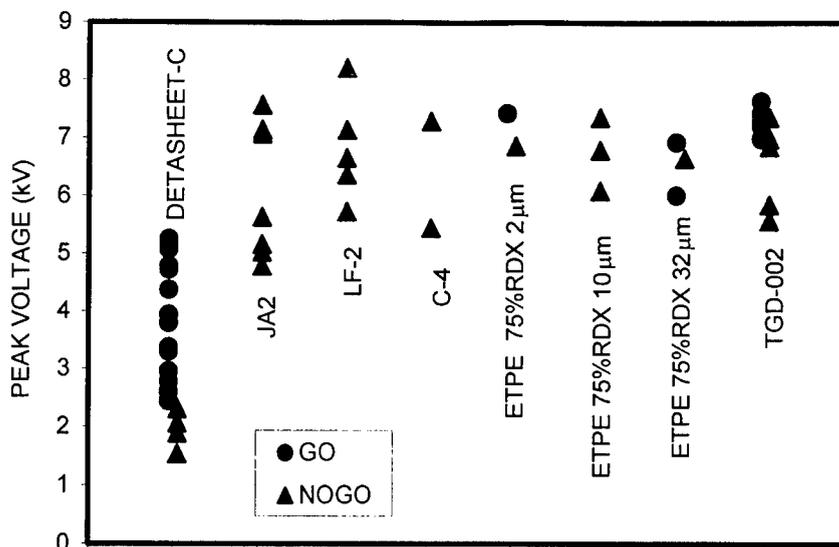


Figure 20. Go/No-Go Data as a Function of Voltage Across the Foil for Selected Propellants and Explosives.

The combination of the HFCl, mechanical properties, BIC, shear-punch, and electric flyer experiments provides ARL with a suite of small-scale propellant evaluation tools that can provide insight into vulnerability for advance propulsion charges. We can evaluate the sensitivity to both thermal and mechanical ballistic threats by measuring the key propellant properties that influence charge vulnerability. Once these properties are measured, they provide insight to propellant developers who are designing new ingredients and engineering new formulations. These properties are also delivered to charge and system developers. When combined with performance parameters, the sensitivity parameters can be used to make design decisions that reduce system vulnerability while permitting increased ballistic performance.

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## 6. The Search for Advanced IHEP Concepts

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Our longer term effort addresses new approaches to the development of advanced IHEPs for the future, including the use of new highly energetic molecules (e.g., high nitrogen materials), the use of nanomaterials for improved combustion efficiency and higher burning rates, and new propellant physical matrices, including nanocomposites for improved mechanical properties. Moreover, the potential for initiation-specific materials is being explored in an effort to identify new high-energy propellant formulations and matrixes that are difficult to ignite or initiate (i.e., low sensitivity/vulnerability) except by specific, intended stimuli. Earlier research with limited success addressed the use of laser ignition, even the use of staged laser stimuli, to provide reliable ignition of

otherwise difficult-to-ignite materials [37]. More recent work addresses the use of plasma ignition, now demonstrated to be an enabler for the use of very-high-loading density charges but yet to be shown able to similarly enable the use of new IHEM formulations that might be categorized as "ignition-specific" materials.

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## 7. The Growing Role for Theoretical Chemistry

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The identification of opportunities for new IHEPs is being addressed via a multidisciplinary approach that involves predictive modeling and simulation and complementary laboratory experimentation. Theoretical chemistry calculations are being used to provide further understanding of the mechanisms that control the energy and sensitivity/vulnerability of new energetic materials. Such information can be used to design new IHEPs with specific performance properties. These properties may include initiation specificity, burning rate and control of energy release, flame temperature, mechanical and rheological properties, sensitivity, and erosivity.

In this section, we describe our recent efforts in developing a set of computational tools that can be used to rapidly predict properties associated with performance and with vulnerability of energetic materials. The tools are based on quantum mechanical (QM) calculations and describe relationships between the QM properties of an isolated molecule with its behavior on the macro-scale. The predictive methods all use quantum mechanical predictions of the electrostatic potential that surrounds an isolated molecule.

The first computational tool developed is used to predict heats of formation of energetic materials in the gas, liquid, and solid states [38]. This quantity is used to assess detonation properties or potential performance of the material during idealized gun firing conditions. Predicted gas-phase heats of formation for 35 molecules using this computational tool have a root mean square (rms) deviation from experiment of 3.1 kcal/mol. Predicted liquid and solid phase heats of formation for 24 and 44 energetic materials have rms deviations from experiment of 3.3 and 9.0 kcal/mol, respectively. Figure 21 shows predictions of heat of formation for these and additional molecules, compared with experimental values and values compiled in the Cheetah 2.0 reactant library [39].

The heats of formation predicted with these methods can be used to predict heats of detonation of pure and explosive formulations [40]. The methodology is based on a simple scheme to calculate detonation properties as proposed by Kamlet and Jacobs [41] and can be implemented from knowledge of heats of formation. We combined our method of predicting heats of formation of explosives with the Kamlet-Jacobs method for calculating heats of detonation, and we applied this

tool to pure explosive and explosive formulations for which experimental data were available. We also compared our results against predictions made with the thermo-chemical code Cheetah 2.0. For pure explosives, the quantum mechanically based results have an rms deviation from experiment of 0.138 kcal/g, whereas the Cheetah predictions have an rms deviation from experiment of 0.133 kcal/g. For explosive formulations, the QM predictions are in reasonable agreement with experimental values, with an rms deviation of 0.058 kcal/g. Although the Cheetah calculations have a stronger theoretical basis for predicting detonation properties, this methodology has the advantage that neither heats of formation nor densities need to be measured or estimated to calculate the heat of detonation of an explosive. A comparison of predicted heats of detonation with measured values is given in Figure 22.

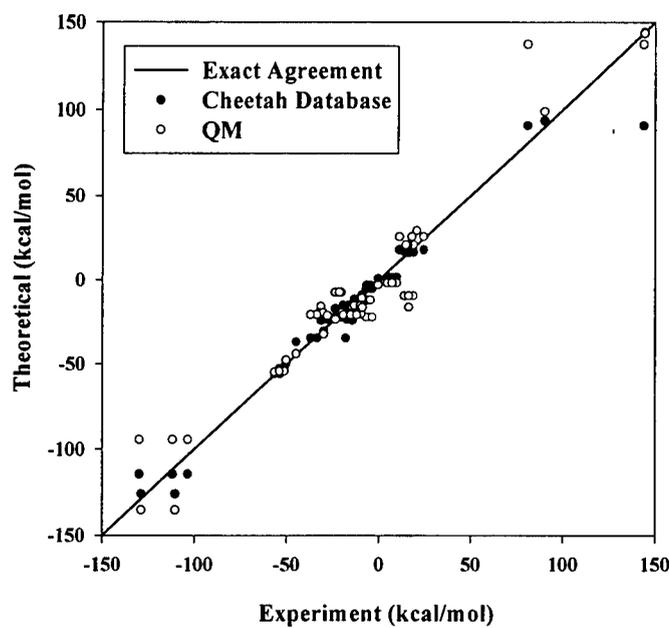


Figure 21. Solid Phase Heats of Formation for Explosives Contained in the Cheetah 2.0 Reactant Library (filled circles) and Predicted With the QM Methods Described Herein (hollow circles) Versus Experimental Values (solid line denotes exact agreement [38]).

Finally, we describe our efforts to establish functional relationships between statistical properties of the electrostatic potentials for a set of energetic molecules and their impact sensitivities. The process involves calculating the electron density distribution associated with an isolated molecule and then determining the electrostatic potential (i.e., the response of this distribution to a charge) at that point on the isosurface. Figure 23 depicts such a set of calculations for an epsilon polymorph CL20 molecule, with resulting values reflected by gradations in color.

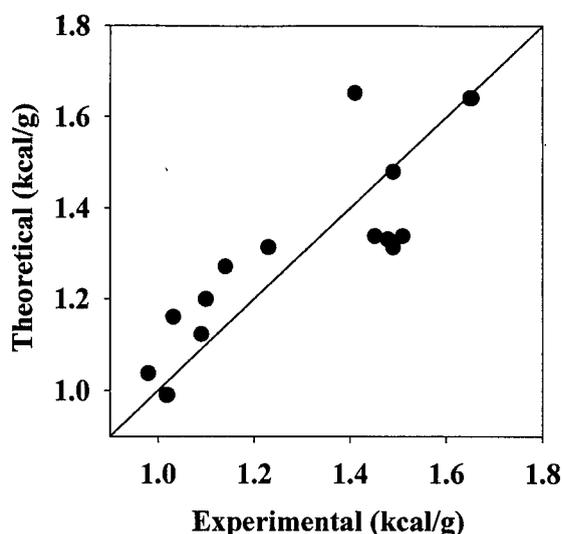


Figure 22. Predicted Versus Experimental Heats of Detonation (solid line denotes exact agreement [40]).

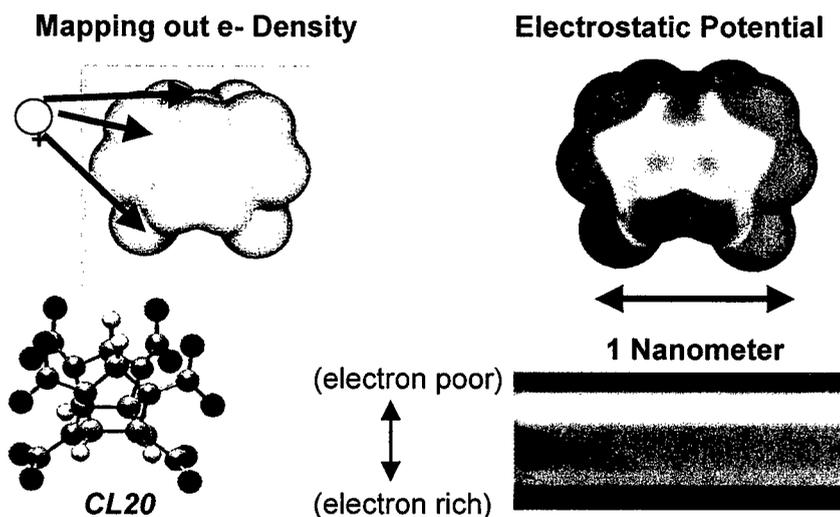


Figure 23. Process for Determining the Electrostatic Potential for Isolated CL20 Molecule.

Impact sensitivities are often described as the results of drop-weight impact experiments, with the results quoted as  $h_{50\%}$ . We have performed QM calculations on 34 polynitroaromatic and benzofuroxan molecules for which such measurements have been performed [42] and we have established a functional relationship between their  $h_{50\%}$  values and properties of the electrostatic potentials and the heats of detonation of the molecules. The predicted values (shown in Figure 24) are in good agreement with experimental values for materials ranging from the highly sensitive hexanitrobenzene to the highly

insensitive explosive TATB (triaminotrinitrobenzene). Rms deviation of the predictions from the experimental values is 19 cm.

Impact sensitivities for 11 additional energetic molecules were calculated and compared to the experiment in order to determine the predictive capability of the computational tool. These molecules were not used in establishing the correlation and include PETN (tetranitrate pentaerythritol), RDX, HMX,  $\beta$ - and  $\epsilon$ -polymorphs of CL20, HNS (2,2',4,4',6,6'-hexanitrostilbene), methyl picrate, styphnic acid, NTO (3-nitro-1,2,4-triazole-5-one), NQ (nitroguanidine), and FOX-7 (1,1-diamino-2,2-dinitro-ethylene). For these materials, there is excellent agreement between the predicted and measured values, with an rms deviation of 22 cm from the experiment.

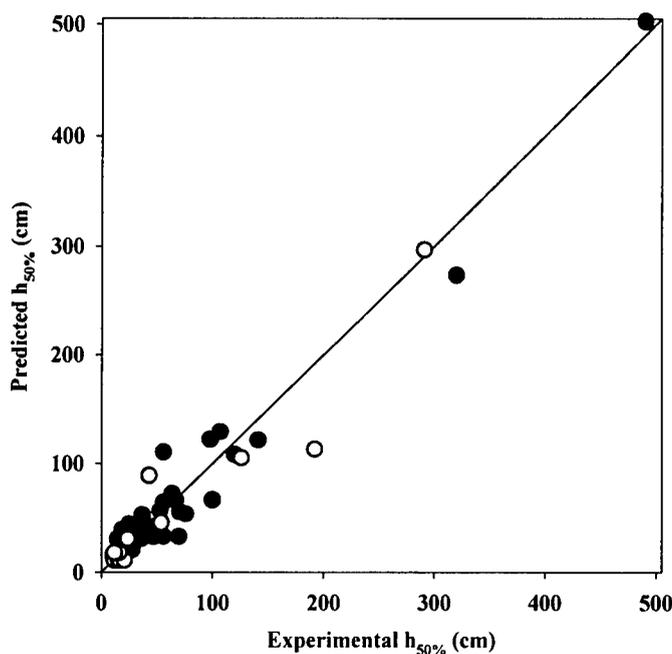


Figure 24. Predicted Versus Experimental  $h_{50\%}$  Values for Explosives (solid circles denote 34 explosives whose values were measured by Wilson et al. [42], and hollow circles denote 11 molecules used to assess the predictive quality of the model; solid line denotes exact agreement).

The quantum mechanical calculations characterizing properties of energetic molecules related to performance and impact sensitivities of explosives have resulted in accurate computational tools that will predict these properties without the need for synthesis and measurement of the actual material. It is hoped that this methodology can be extended to predict other properties of interest to the materials designer in order to provide him with a powerful suite of predictive screening tools.

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## 8. Nanotechnology<sup>5</sup> for Energetic Materials

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In addition to the use of new modeling tools to speed the development of new insensitive high energy materials, new approaches to the modification of existing materials will expedite research and development to optimize the best candidate materials and greatly reduce testing and evaluation. Nanomaterials, including nanocomposites [43], nanotubes [44] and caged nanostructures [45] are being investigated for modification of energetic materials to achieve improved mechanical properties, ignition, ballistic and vulnerability responses. Research to date has focused on nanocomposites, primarily inorganic silicates containing naturally occurring sodium and potassium ions that are exchanged for organic cations with a high affinity for the host polymer. This interaction serves as the basis for the two-dimensional dispersion of modified silicates and enables much greater modification of properties at low levels than is achieved with micro-scale unidirectional fibers, which have an inherently lower surface-to-volume ratio. Typically, only 2 to 5 weight percent of the binder has been sufficient to improve material characteristics of commercial polymers [46]. For composite propellants, which contain more than 50% solids crystal fill, a nominal 1% incorporation of the nanomaterial would be sufficient to provide significant property changes with minimal intrusion.

Property improvements achieved in commercial nanopolymer systems include increased modulus and diffusion resistance and (because the silicate layers flow well at mixing temperatures) reduced processing viscosity. These properties would also benefit development of ETPE-based propellants. For example, improved dynamic compressive failure response is desired to ensure that the ETPEs have structural integrity over the entire temperature range of operation required for weapon systems. The modulus of the ETPEs can be improved by increasing the molecular weight of the hard block, although a concomitant increase in processing viscosity is suffered. Since nano-composites offer the potential for simultaneously improving modulus and reducing processing viscosity, options for the design of ETPE polymers are increased. At low operating temperatures, the glass transition ( $T_g$ ) can result in undesirable brittle fracture. The addition of a small amount (3% to 5% of the binder level) of an energetic plasticizer can suppress the  $T_g$  to desired temperatures below operational limits without plasticizer weeping. Nonetheless, plasticizer migration is a concern for layers with a dissimilar type or level of plasticizers or if the binders in the two layers have a different affinity for the plasticizer. However, any small difference in affinity that oxetane-based ETPEs of different chemical composition are apt to have for a single plasticizer or level could most likely be controlled by the diffusion barrier properties of the nanocomposite

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<sup>5</sup> Nanotechnology involves basic research on structures that have at least one dimension of about 1 to several hundred nanometers.

additives. In the ETPE application, an appropriate selection of organic molecules is being sought to ensure a high affinity for the oxetane binders. Dispersion of montmorillonite clay substituted with a commercial surfactant (known as Cloisite clay, Nanoclay, <http://www.nanoclay.com>) was achieved in a BAMO/NMMO ETPE binder, as evidenced by x-ray diffraction data in which the spacing between the clay layers has increased when precipitated from solution into the binder (see Figure 25).

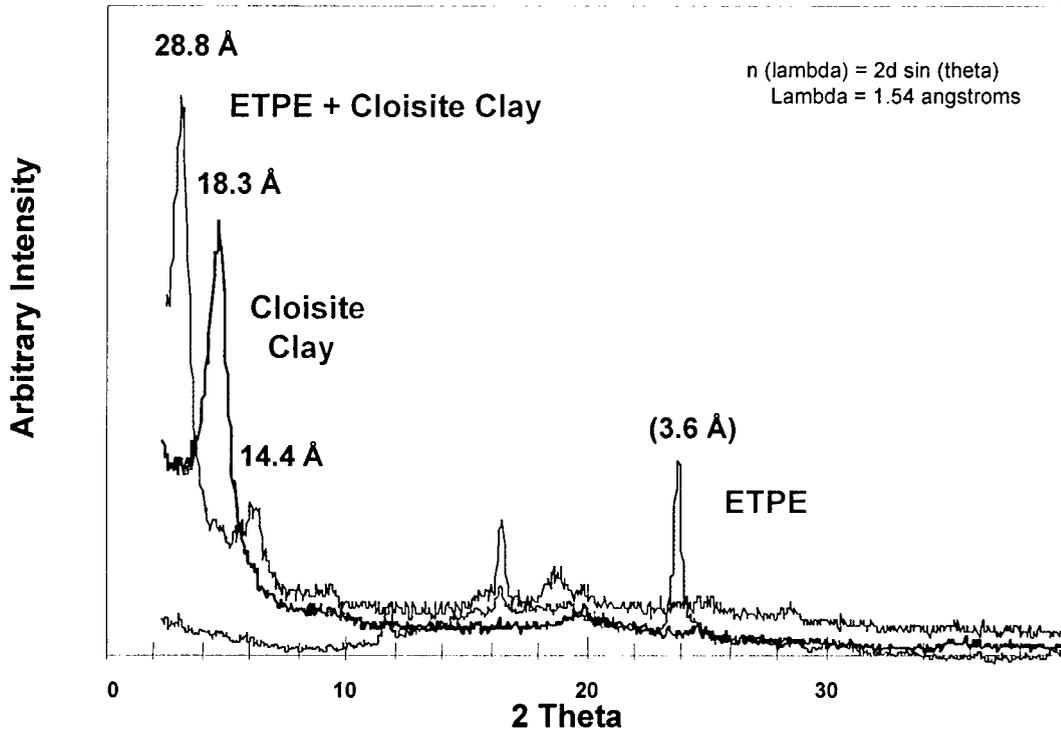


Figure 25. X-Ray Diffraction Data for Cloisite Nanosilicate Clay Dispersed in a BAMO/NMMO ETPE Binder.

Nanotechnological approaches are also being pursued for tailoring ETPE-based propellants for plasma ignition and burning rate modification to facilitate improved performance and vulnerability response of very high loading density charges. Under a program to investigate plasma-propellant interactions, chemical species (e.g., chromophoric linkages) that promote plasma initiation and burning rate modification, will be identified and targeted as candidates for nanocomposite modification of the propellants. Since the radiation output of plasmas is intense, a low level of the modified nanosilicate is expected to be sufficient to render the ETPEs sensitive and specific to plasma output and reduce vulnerability to ignition by sources other than a high temperature plasma. Analogous modifications for laser-specific initiation are also feasible.

Improved vulnerability response for the advanced propellant configurations is also intrinsically coupled to the initiation and decomposition of the energetic

crystals that comprise as much as 80% of the propellant formulations. Shock, impact, mechanical properties, and thermal sensitivity are fundamental aspects of energetic materials that influence propellant vulnerability. A basic understanding of these phenomena is being pursued through modeling and carefully designed small-scale vulnerability experiments, in which changes in propellant crystal morphology and chemistry in response to initiation stimuli in small-scale experiments makes it possible to begin to understand vulnerability properties of energetic materials at a fundamental level. Research is being pursued to exploit recent advances in nanoscale characterization, i.e., high resolution imaging and chemical analysis methodologies, to help researchers understand the very earliest processes that occur for propellant samples in response to initiation stimuli, such as high rate impact, shock and plasma interactions [47]. Such a basic understanding will lead to increased survivability and the development of design rules for energetic materials and will be used to validate and refine molecular models being developed to relate vulnerability to molecular structures of crystals, initial reaction sites, crystal dislocations, and crystal phase and polymorph transformations.

Advanced (although currently notional) applications of nanomaterials include the high reactivity of fuel oxidizers in nanoscale materials, in which intimate contact of fuel and oxidizer is assured through a unique geometry and promises extremely high heat release rates and extraordinary combustion efficiency. The unique properties of nanotube and fullerene structures offer further potential for confining energetic crystals in a nanomatrix and for unprecedented reactivity and stability, which are usually diametrically opposed properties [48]. Moreover, derivitization of these compounds with energetic functional groups would improve performance and facilitate dispersion into a polymer matrix. Strained ring compounds, including all-nitrogen species, offer potential for high-energy storage within intra-molecular bonds. The potential for engineering nano-modified energetic materials with increased performance and reduced vulnerability is vast, and realization of that potential is facilitated by recent advances in nano-scale synthesis and characterization, molecular dynamics simulations, and well-designed small-scale experimentation for elucidating fundamental performance and vulnerability mechanisms.

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## 9. Outlook: IHEPS and 21st Century Weapon Systems

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We have described a program that addresses the need for IHEPs in terms of various levels of new technology. Both performance and sensitivity attributes are considered from the earliest stages of research. In all cases, advanced modeling techniques lead the way; smart, selective experimentation on small quantities of new materials follows; full scale and ballistic evaluation follows for highly attractive candidates. Primary efforts to render RDX- and CL20-filled ETPE

propellants acceptable for weapon system use are being complemented by longer term research that addresses totally new approaches to providing even higher energy levels with acceptable system survivability characteristics. Such efforts, in concert with related efforts across the community, are designed to provide the revolutionary advances likely to be required by lightweight, highly mobile weapon systems of the 21st century.

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