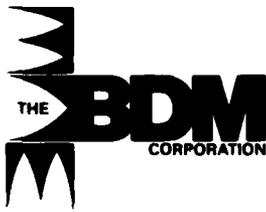
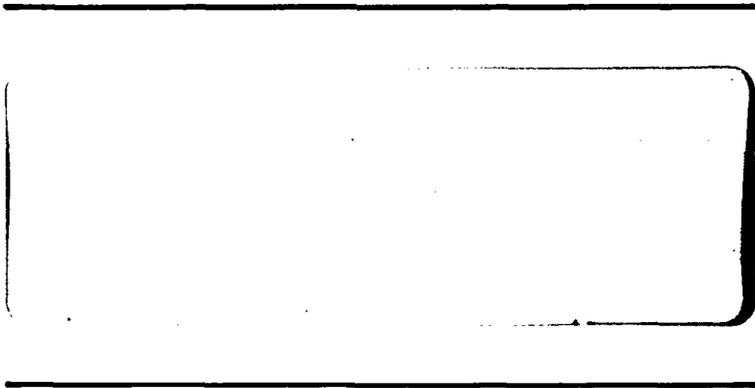


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BDM/M-003-80
15 May 1980

**HIGH DEFLAGRATION RATE (HIDEF)
IGNITER TECHNOLOGY APPLICATIONS
FINAL REPORT**

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↙ into a black powder replacement, especially in large caliber guns.

Potential igniter configurations were also examined.

Finally, the key program requirements, including demonstration testing and materials characterization, are listed. Relative risks, benefits, and payoffs for the various HIDEF technology candidates are summarized.

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EXECUTIVE SUMMARY

The ARRADCOM High Deflagration Rate (HIDEF) Igniter Technology Program will address those key problem areas of ballistic control in modern guns and ammunition that can be traced to igniter functioning. These include action times, temperature dependence, pressure transients in the gun chamber and residue, as well as difficulties in igniting developmental low vulnerability, deterred, and cool burning propellants.

The HIDEF Phase I program objective and subject of this report is to develop a background sufficient to address key issues in structuring an exploratory HIDEF technology program.

In the course of the Phase I HIDEF program, literature, data, and opinion on potential HIDEF candidate materials was gathered from a variety of sources including libraries and government and private laboratories. The objective was to identify those classes of chemical compounds which might be suitable for further development into a black powder replacement, especially in large caliber guns. Candidates identified herein include modified "standard" ignition mixes, selected classes of polyhedral boranes, certain transition metal cyano-complex ions coprecipitated with oxidizer, and several relatively unexplored chemistries such as silanes, hydrides, CuO/Al reactions, fluoroelastomers, and foamed compositions.

Potential igniter configurations were also examined. Black powder, BKNO_3 and Benite can be replaced in standard igniter designs with granulated, pelletized, or extruded HIDEF candidates. The use of HIDEF materials inside a flexible metal cord will allow variations in igniter geometry such as embedded non-central or peripheral placement. Novel approaches such as fluid igniters, telescoping combustable igniter parts, pyrotechnic tape, and coated propellant grains are also discussed.

Finally, the key program requirements, including demonstration testing and materials characterization, are listed. Relative risks, benefits, and payoffs for the various HIDEF technology candidates are summarized.

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A. INTRODUCTION

1. New Demands on Ammunition Ignition Trains

The introduction of new propellants and sophisticated projectiles, ammunition, and cannon into modern gun systems has placed an increased burden on ammunition ignition trains for these weapons. Figure 1 illustrates some of the trends that have emerged in recent years and how they impact the ignition function.

The need for high performance, higher rate-of-fire weapons (both medium and large caliber) has resulted in fundamentally new engineering design approaches to both cannon and ammunition. The guns may have high chamber pressures and longer caliber barrels than previously used. The fire-out-of-battery systems reduce recoil to the weapon chassis. Sliding breech block designs require low residue with noncorrosive properties. Larger propellant charges are being introduced into constant volume chambers, severely reducing the ullage previously available for flow of ignition gases. New, compact charge designs are being introduced to increase volumetric efficiency under armor. "Smart" projectiles have fragile components that cannot tolerate severe pressure transients during the ignition sequence. On top of all this, the basic weapon ballistic dispersions must be minimized to match system accuracies made feasible by computer-driven fire control and gunnery computations.

Concurrently with advances in weapon/ammunition design, a series of major programs sponsored by the Services has produced new families of high efficiency propellants that combine high impetus with low flame temperatures and lowered vulnerabilities. Virtually all of these propellants have one thing in common--they are in general more difficult to ignite in comparison to in-service propellants.

The combinations of demands dictate that the ignition sequence must be faster, more efficient, more controllable in time and geometry, and more reproducible across the temperature range than was previously required.

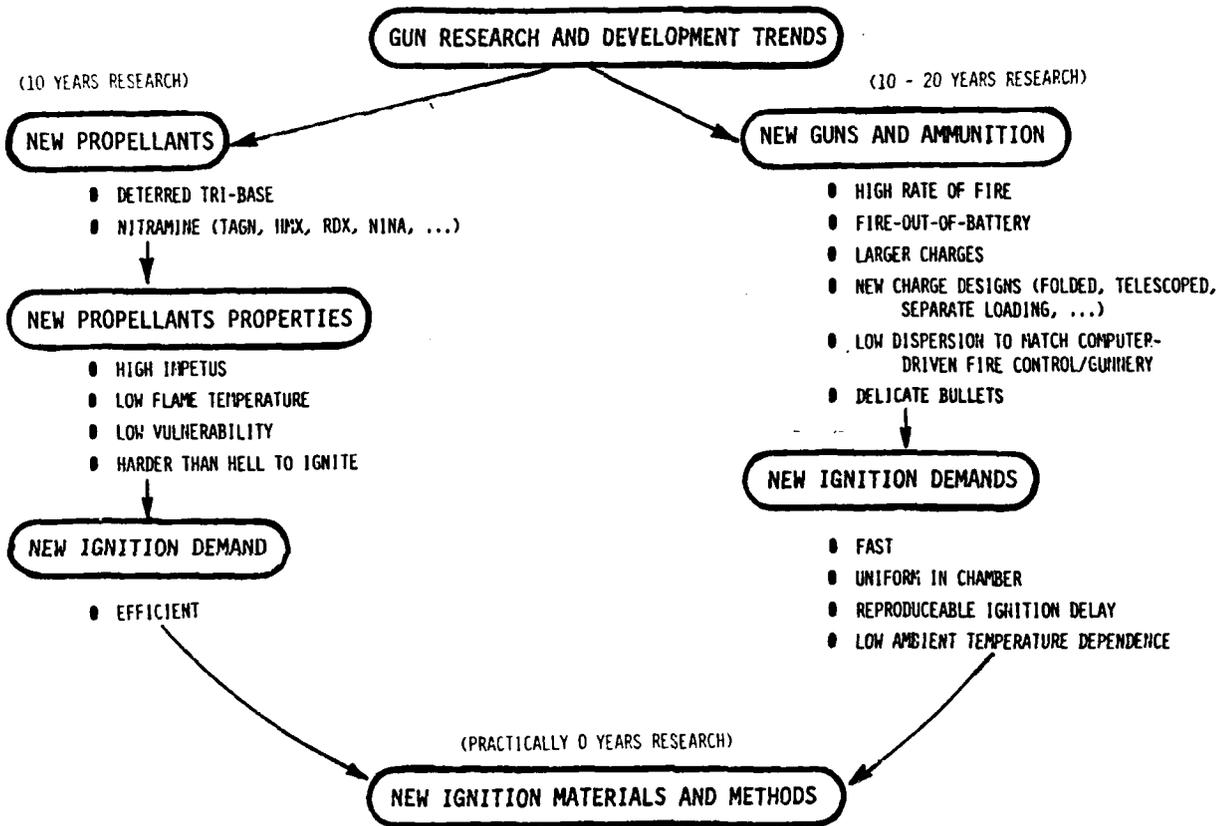


FIGURE 1. NEW GUN IGNITION MATERIALS AND METHODS ARE REQUIRED TO MATCH CURRENT GUN/AMMUNITION/PROPELLANT DEVELOPMENT

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a. Propellant Ignitability

Two distinctive trends are emerging in development of propellants for modern guns:

- Lowered flame temperatures (accompanied by lower molecular weight combustion product gases) to reduce barrel erosion
- Lowered vulnerability.

Chemically, these trends are manifested by lowering the fractions of hot burning constituents such as NG and raising the fractions of cool burning ingredients such as nitro-guanidine (NQ), or heavily deterring the propellant mass. Some of these trends are illustrated in Figure 2.

A corollary to the changing chemistry is that the propellants are increasingly difficult to ignite based on current research on ignitability, including arc-image and TGA/DTA studies. This means there are much greater demands on the efficiency of the ignition train. Additionally, it is surmised that ignition parameters such as flame temperatures, gas/solids ratio, and speed may have to be optimized to a new criteria than that developed for traditional igniter operation.

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	M30	PROPELLANT		LOVA
		M31	EC-NACO	
COMPOSITION				
NC (%N)	28 (12.6)	20 (12.6)	91.4 (12.0)	RDX/HMX 75%
NG	22.5	19	0	} 25%
NQ	47.7	54.7	0	
DETERRENT/ STABILIZER	1.5	7.5	8.6	
IMPETUS (10 ³ FT-LB)	364	334	276	310+
FLAME TEMP., °K	3040	2560	2200	~2170+
GAS M.W.	23.2	21.7	~24.6	19.5
GAS, (MOLE/G)	.0431	.0462	.042	--

FIGURE 2. CURRENT TRENDS IN PROPELLANT DEVELOPMENT ARE RESULTING IN DIFFICULT IGNITABILITIES

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b. Ballistic Control

New engineering design approaches to gun systems and subsystems has resulted in a demand for very carefully controlled internal ballistics. The propellant burning that is manifested in the ballistics depends intimately on the ignition sequence. An example of the type of control desired for the 155mm soft recoil gun being studied by ARRADCOM is shown in Figure 3.

The action time is a critical measure of the control of the internal ballistics of this gun. To match the soft recoil runout, the ignition event must occur at a very precise time after latch release. If ignition occurs too soon, the unbalanced recoil must be absorbed by the carriage. If ignition is delayed, the barrel assembly runs out of travel before sufficient rearward momentum is transferred to the breech. Either case can result in inaccurate external ballistics at launch and possibly damage to the artillery piece. Moreover, the proper control must be maintained across the operating temperature range.

In ARRADCOM and other testing, it can be fairly well demonstrated that the variability in action times can be traced directly to the igniter. This variability will be exaggerated when difficult-to-ignite propellants are introduced into service use.

Similar control in ignition and action time is required for rapid fire guns such as the GAU-8.

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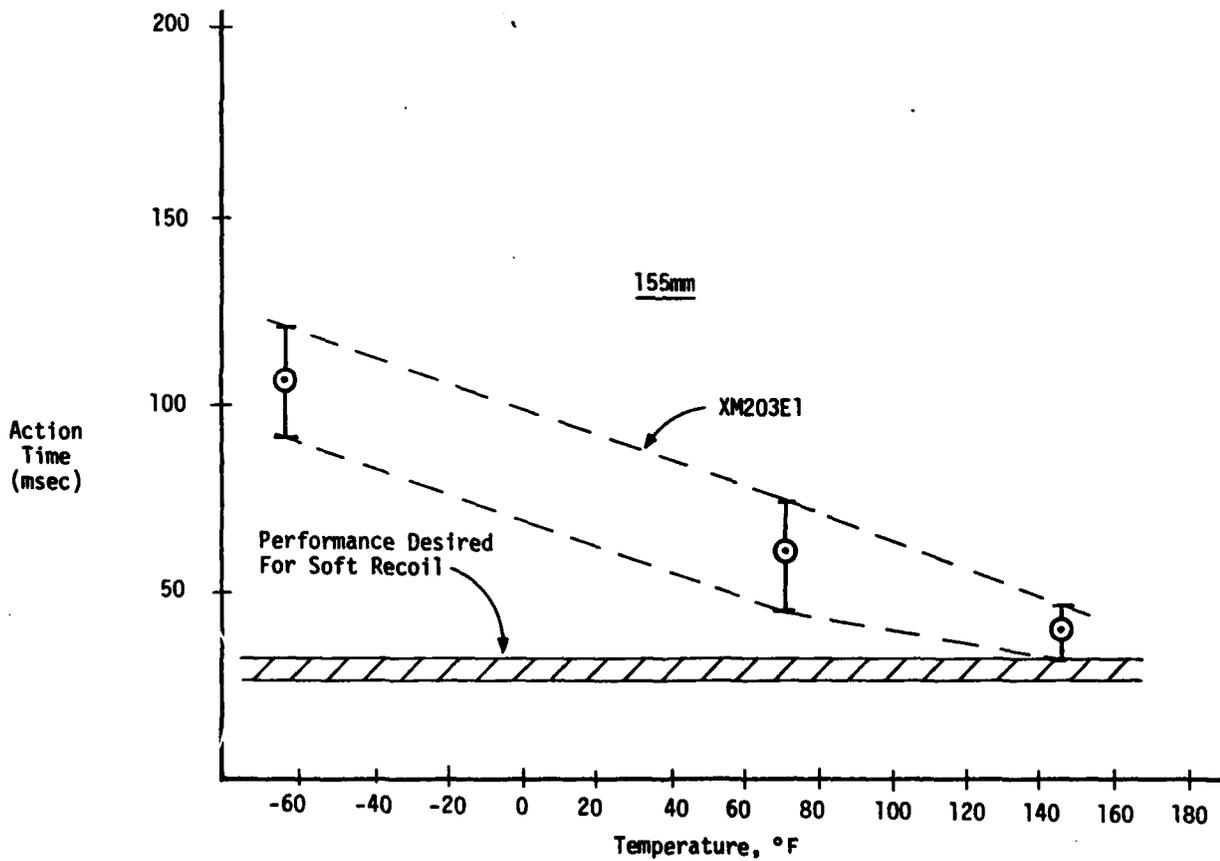


FIGURE 3. MODERN CANNON OPERATION SUCH AS SOFT RECOIL
REQUIRES TIGHT BALLISTIC CONTROL

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2. Limitations of Black Powder Ignitors

At the present time, black powder (BP) is used almost exclusively in the ignition trains of both large and small caliber ammunition. This material, consisting of a mixture of potassium nitrate, sulfur, charcoal, and a graphite glaze, has been in general use in warfare since the 17th century. A relatively modern BP composition was developed in the 16th century, and the BP chemical concept probably predates the birth of Christ.

This material is, in fact, a pyrotechnician's nightmare. There are at least three active ingredients, and it is possible that the glaze may in fact constitute a fourth ingredient. This implies a multi-dimensional surface to describe the combustion stoichiometry. There are some fundamental problems with black powder in that the choice of materials, particularly the charcoal, is dependent on the origin of the constituents. While the processes for combining these constituents has been refined for many years, the introduction of new processing facilities, supposedly intended to produce an identical material, has met with difficulty. The grinding, pressing, and glazing operations are difficult to control.

In addition to the processing difficulties with black powder, there are inherent limitations in the performance of this material as a function of pressure and temperature. Problems associated with black powder in various large caliber ignition trains were recently reviewed by White and coworkers at BRL.¹ Current ignitor problems are associated with symptoms such as pressure waves/breech blows, hangfires, erosion/residue, and ignition delays in cannon firings. These can be traced to igniter configuration and varied ballistic performance of black powder, including lot-to-lot variations. The combustion chemistry and flame spread phenomenon associated with black powder burning is still not fully understood.

Evidence is mounting that the practical utility of black powder is reaching an end as gun systems and their attendant ignition systems become increasingly sophisticated. Therefore, it will be necessary in the next few years to develop suitable black powder replacements which have chemical and performance characteristics more suited to these new applications.

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COMPOSITION: GRANULATED KNO_3 /SULFUR/CHARCOAL + GLAZE

HISTORY: 1st CENTURY BC - CHINESE FIREWORKS ?
400 - 1300 AD - GREEK FIRE. USED AGAINST CHRISTIANS IN THE CRUSADES
1200 - ROGER BACON DESCRIBES BP-LIKE MIXES
1500 - COMPOSITION CLOSE TO MODERN BP
1500 - 1980 - IMPROVEMENTS TO PRODUCTION PROCESSES

PRODUCTION PROCESS:



PROBLEMS: PRODUCTION PROCESS DIFFICULT TO CONTROL
COMBUSTION CHEMISTRY & KINETICS STILL NOT FULLY UNDERSTOOD
RELATIVELY WEAK IGNITOR
UNREPRODUCEABLE IGNITION PERFORMANCE BY MODERN STANDARDS
(IGNITION DELAY, TEMPERATURE DEPENDENCE, ...)
CORROSIVE COMBUSTION PRODUCTS

FIGURE 4. LIMITATIONS OF BLACK POWDER AS A MODERN IGNITION MATERIAL

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3. HIDEF Technology

In recent years, very little research and development has been done on new ignition materials and methods. As was shown in Figure 1, the progress in this field has not matched that in propellant, cannon, or ammunition design. The result is that there is currently a gap in ignition technology that is hindering the introduction of new gun system technologies into service use.

In the limited work that has been done on gun ignition in the last five years, there are some bright spots. Certain types of boranes which exhibit very high deflagration rates and a good balance of gas to hot particles in the combustion products have shown promising ignition performance in both small and large caliber ammunition. Other types of standard and nonstandard ignition compositions can probably be formulated to match these burning characteristics. The candidates should have one attribute that appears important to meet new ignition demands--they should function "fast" with respect to black powder. We call the general class of materials with good ignition characteristics and a high deflagration rate "HIDEF" ignition compounds.

Efforts to date to explore utility of HIDEF materials has been fragmented within the military services. The necessary background research into the range of properties available with these materials, their synthesis in mass production, safety, and compatibility has not been adequately addressed. It was apparent that a technology program was definitely needed to develop and exploit the tactical value of these materials. Toward this end, the Propulsion Technology Branch of the Applied Sciences Division at ARRADCOM's Large Caliber Weapons System Laboratory is structuring a study to address these issues. This program is called the HIDEF Ignitor Technology Program, and its objectives are shown in Figure 5.

In Phase I of the HIDEF program, the objective was to develop a background sufficient to address key issues in structuring an exploratory HIDEF technology program. Literature, data, information, and opinion on HIDEF candidate materials and applications was gathered from a variety of sources including libraries and government and private laboratories. The payoffs in HIDEF application, promising HIDEF candidates, definition of required demonstration and research studies, interfaces with complementary programs, and overall program requirements were then addressed. This final report summarizes Phase I results.

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- DEVELOP A COORDINATED APPROACH TO SURVEY AND EXPLOIT HIDEF TECHNOLOGY AS A BLACK POWDER REPLACEMENT;
- DEMONSTRATE THE UTILITY AND ADVANTAGES OF HIDEF TECHNOLOGY IN TACTICAL SYSTEMS APPLICATIONS;
- PRODUCE A GUIDELINE DATA BASE FOR SPECIFYING HIDEF PERFORMANCE CHARACTERISTICS AND HARDWARE CONFIGURATIONS IN IGNITERS FOR TRANSITION TO SERVICE USE.

FIGURE 5. THE ARRADCOM HIDEF (HIGH DEFLAGRATION RATE) IGNITER TECHNOLOGY PROGRAM OBJECTIVES ADDRESS KEY IGNITION ISSUES

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B. HIDEF IGNITION MATERIALS CANDIDATES REVIEW

1. Summary

In the course of the Phase I HIDEF program, literature, data, and opinion on potential HIDEF candidate materials was gathered from a variety of sources including libraries and government and private laboratories. The objective was to identify those classes of chemical compounds which might be suitable for further development into a black powder replacement, especially in large caliber guns.

Figure 6 summarizes emerging results from Phase I.

Of "standard" ignition mixes with burning rates faster than black powder, certain Zr mixes with both gas producing and gasless oxidizers appear promising for further exploration.

Certain types of polyhedral boranes have known pyrotechnic utility. Compositions based on the anion $B_{10}H_{10}^{-2}$ have exhibited very high deflagration rates and been used in small and large caliber gun igniters with considerable success. However, sensitivity from impact, friction, and electrostatic discharge continues to be a problem with these materials. It is likely that other polyhedral borane families like the $B_{12}H_{12}^{-2}$ salts may have comparable performance with reduced sensitivity.

Coprecipitated compositions of cyano-complexed transition metals and oxidizers have also demonstrated burn rates comparable to polyhedral boranes. The chemistry of these types of compounds appears very promising.

Finally, a number of relatively unexplored approaches to igniter compositions, including higher silanes, fluoroelastomeric binders, and Al/CuO type reactions could be explored.

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- FAST BURNING "STANDARD" IGNITION MIXES
 - GAS PRODUCING
 - MODIFIED GASLESS DELAY MIXES, SUCH AS Zr/OXIDIZER
- POLYHEDRAL BORANES
 - $B_{10}H_{10}^{-2}$ FAMILY
 - $B_{12}H_{12}^{-2}$ FAMILY
- COPRECIPITATED CYANO-METAL COMPLEXES
- NOVEL MATERIALS

FIGURE 6. SUMMARY OF CANDIDATES FOR HIDEF IGNITION MATERIALS

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2. Properties of Igniter Materials

In considering the development of new igniter materials, the designer must consider more than just performance in the gun system, as shown in Figure 7. As sophisticated automated hardware and low vulnerability components are introduced into the inventory, safety and sensitivity characteristics have to be examined. Additionally, there is a growing awareness of toxicity hazards. Costs, in terms of raw materials as well as investment in manufacturing facilities, must be controllable from the outset.

In the HIDEF program, these considerations will be examined early. To guide in material evaluation, the following attributes of an ideal igniter chemistry are listed:

- Simple, reproduceable stoichiometry
- Controllable burn rate (including flame spread, induction, regressive burning of particles)
- Controllable brisance (non-detonating)
- Controllable flame temperature, gas output, gas/solids ratio, and solid product luminosity
- Low pressure and temperature functional dependence
- Low impact, friction, and static sensitivity
- High autoignition temperature and long-term high temperature stability
- Low volatility and hygroscopicity
- Nontoxic and noncorrosive before and after burning
- Affordable and produceable; easy to manufacture, store, and transport
- "Universal" application in small, medium, and large caliber gun igniters.
- "Special" applications in igniter systems requiring advanced performance or configurations.

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- PYRO CHARACTERISTICS (BURN RATE; HEAT & GAS OUTPUT, TEMPERATURE DEPENDENCE, RELATIVE EFFICIENCY, ...)
- SAFETY (IMPACT, FRICTION & STATIC SENSITIVITY, TOXICITY, ...)
- ECONOMICS (REPRODUCEABILITY IN PRODUCTION, COST, STORABILITY, ...)

FIGURE 7. IGNITION MATERIAL PROPERTIES OF INTEREST INCLUDE MORE THAN PERFORMANCE

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3. Meaning of "Burn Rate" of Ignition Materials

It has been recognized for some time that "speed" is useful for igniters, especially when slower, cooler burning propellants are used. The present HIDEF effort concentrates on materials whose "burning rate" is high. Such a material (if efficient) gives a closer approximation to the "instantaneous" ignition of propellant grains assumed in most simpler ballistic models. The term burning rate must be further defined in terms of its constituent phenomenon. For discussion, we assume a bed of granules arranged in a column.

There is a characteristic rate at which the flame front spreads along the column. Black powder rates in a high pressure bayonet primer are typically to 1,000 to over 10,000 in/sec. Ambient rates are about 20 in/sec. Low pressure igniters burn at about 200 in/sec. Polyhedral boranes and cyano-metal complexes which might be HIDEF candidates exhibit columnar propagation rates of 7,000 - 20,000 in/sec; these are consolidated beds of very fine particles. Low order detonations are in the 100,000 - 200,000 in/sec region and high order detonations are in excess of 250,000 in/sec.

These flame spread rates must be distinguished from propagation rates in compacted beds. Flame spread through column of compressed (5000 psi) black powder is about 1.5 in/sec. Typical "standard" ignition materials have compacted rates up to 20 in/sec. The high rates of boranes and cyano-metal complexes are for highly compacted beds; this suggests that the reaction propagation mechanism for these types of materials may be different than the diffusion limited process controlling the "standard" igniter material rates.

Finally, after passage of the flame front stimulus, there is a regressive burning of the actual granules comprising the ignition mix. The characteristic dimension of these granules may be a few millimeters as is the case for Class I black powder to a few microns, as is the case for coprecipitated compositions. Burning of the individual granules might be accompanied by an induction time akin to that accompanying propellant ignition. The rate of regressive granule consumption is manifested by the duration of luminosity of the burning column.

A useful attribute of HIDEF ignition materials would be to exhibit fast linear columnar propagation relatively independent of ambient environment, and additionally, a fast compacted burn rate so that the energy is released quickly into the propellant bed.

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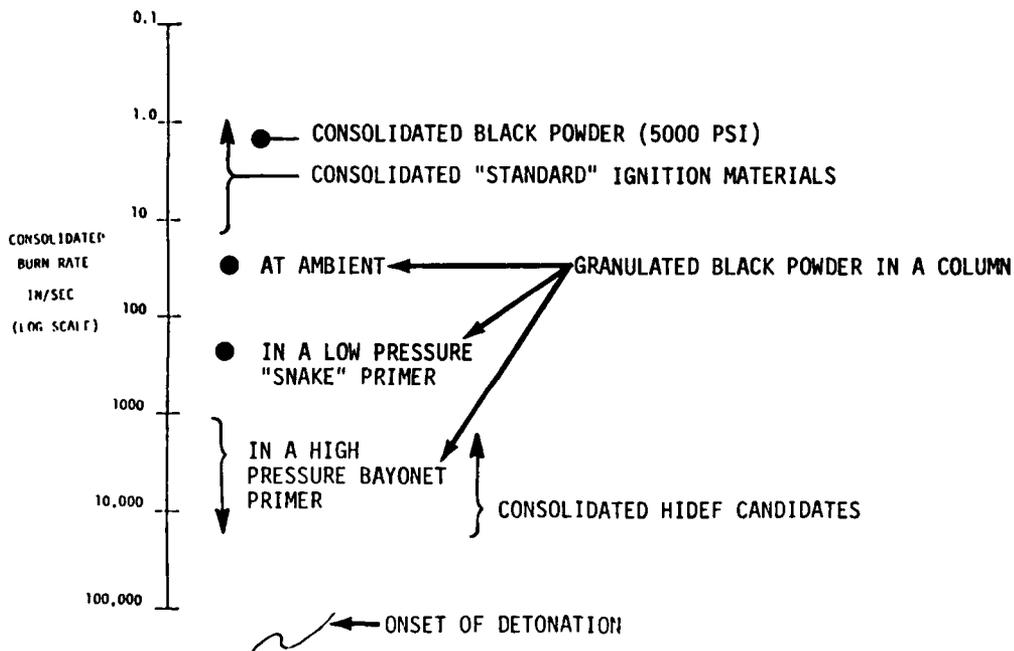


FIGURE 8. "BURN RATE" MUST BE REDEFINED IN TERMS OF THE CONSTITUENT PHENOMENA

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4. Standard Ignition Materials

An obvious approach to developing new ignition systems is to look at ignition mixes that are "standard", i.e., have been characterized and used in the past, possibly for other purposes. Ignition material technology has been fairly well standardized for rocket ignition applications as of the mid 1970's. A handbook of "standard" ignition materials and properties is published² by Bermite. Certain standard materials tried in gun igniter applications have been recently listed by East.³ A list of useful igniter compositions based on barium nitrate oxidizer was also provided by L. Stieffel of the ARRADCOM Small Caliber Lab.

a. Gas Producing Mixes

Figure 9 gives examples of materials which have burning rates faster than black powder, and which are possibly candidates for exploration in the HIDEF program. These were selected on the basis of burn rate, sensitivity, and gas output. The burn rates refer to linear column propagation rates of pellets consolidated at 5000 psi. Also shown on Figure for reference are data for three commonly used gun igniter materials -- black powder, $BKNO_3$, and $ALCLO$.

Three types of ingredients must be ultimately considered: fuels, oxidizer, and moderators. Fuels that are attractive include Zr, Al, Ti, and alloys of these as well as hydrides. The common, stable oxidizer is $KClO_4$. However, for some gun applications, the use of halogen-containing oxidizer may be undesirable, and nitrates of potassium or barium can be considered. One oxidizer known in the literature but unexploited is tetramethylammonium nitrate; this material should give a high gas output. Boron and sulfur are moderators (and fuels). Boron is preferable where noncorrosive combustion products are desired.

A note concerning sensitivity is in order. A major attribute of black powder is the tendency to ignite easily from a flame source, but high resistance to ignition from impact. It is likely that this combination is a result of the processing technique. Some of the faster burning ignition materials in Figure 9 exhibit substantially higher impact sensitivity than black powder.

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COMPOSITION INGREDIENTS	HEAT OF EXPLOSION (cal/g)	FLAME TEMPERATURE °K	GAS/SOLIDS RATIO	BURN' RATE @ 500 psi (in/sec)	COMMENT
Black Powder (KNO ₃ /S/charcoal)	735	2400	52/48	1.5	Reference
BKNO ₃	1550	2520	19/81	1.5	Reference
Al/KClO ₃	2485	3800	3/97	0.9	Reference (Very high pressure exponent)
Al/Zr/Ba(NO ₃) ₂ /KClO ₄	1580		10/90	1.5	Flat pressure exponent
Al/B/ZrNi/KClO ₄	1550		48/52	1.8	Al/KClO ₄ replacement
Black Powder/Mg	1040		28/72	2.3	
Zr/KClO ₄	1260		24/76	2.3	
Al/MoO ₃	1050		44/56	2.5	
B/Mg/KNO ₃ /binder	1750		27/73	3.4	Hygroscopic
TiH ₂ /KClO ₄	1500		43/57	4.0	Violent output
Zr/B/KClO ₄	1390		12/88	5.0	Boron attenuates brisance
Zr/Ba(NO ₃) ₂	1670		15/85	5.5	Excellent stability
Ti/KClO ₄	1730		22/78	10	High pressure exponent
DDHP/KClO ₄	1125		68/32	13	May exhibit DDT

FIGURE 3. SOME CHARACTERISTICS OF STANDARD IGNITION MIXES

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b) Gasless Mixes

Also of interest may be the use of "gasless" delay compositions blended with a suitable high gas producing oxidizer/monopropellant such as tetranitrocarbazole, NC, or nitramines. A wide range of linear burning rates is achieved with gasless delays, as shown in Figure 10. The key unknown to whether the burn rate can be maintained by adding additional active binder, i.e., using the gasless mechanism to control burning rate.

The best fuel to achieve high burn rate appears to be Zr. The burn rate is varied by almost an order of magnitude with common gasless oxidizers. Heat outputs are characteristically low. Sensitivity to impact and friction are very low for the fast burning Zr mixes; however, the Zr/PbO₂ mix is very static sensitive.

An ignition composition based on a gasless reaction to control burn rate might be expected to exhibit a small pressure dependence but a large temperature coefficient.

It is apparent from examination of Figures 9 and 10 that an order of magnitude increase in burn rate over that of black powder can be achieved with "standard" mixes. But there is no indication that propagation in a loose column of granules, as in a gun igniter, would be faster than black powder in a typical primer configuration. This phenomenon must be explored in the HIDEF experimental program.

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COMPOSITION INGREDIENTS	HEAT OF EXPLOSION (cal/g)	BURN RATE @ 500 psi (in/sec)	COMMENT
Ti/BaCrO ₄	865	1.8	Hot particle ignition
Al/CuO	790	1.5	Very low pressure exponent
B/PbCrO ₄	440	2.0	"Soft" ignitor
Mg/Ba(NO ₃) ₂	1515	2.5	Very low pressure exponent
Zr/BaCrO ₄	500	3.0	Excellent storage life
Zr/MoO ₃ /Cr ₂ O ₃	500	4.0	Cr ₂ O ₃ lowers burn rate
Zr/Fe ₂ O ₃	520	4.2	AIA composition
Zr/PbCrO ₄	500	15	
Zr/PbO ₂	250	20	Efficient in lighting large propellant masses. High flame temperature.

FIGURE 10. GASLESS IGNITION MIXES

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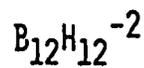
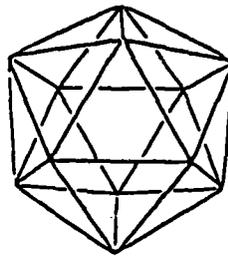
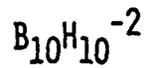
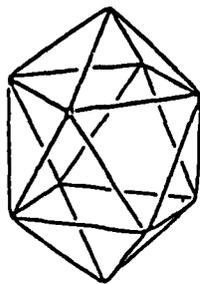
5. Polyhedral Boranes

Of the nonstandard ignition materials explored for gun ignition purposes in the last five years, the most data exists for certain salts of the anion $B_{10}H_{10}^{-2}$ and oxidizer, primarily KNO_3 . This material is from one family of a series polyhedral boranes with a highly symmetric, closo- structure.⁴ The principal ions known to be of pyrotechnic use include $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$, and coupled B_{10} polyhedra such as $B_{20}H_{18}^{-2}$. Certain classes of these materials exhibit columnar burning rates 1 to 4 orders of magnitude faster than black powder.

The polyhedral boranes $B_nH_n^{-2}$ are analogous to planar aromatic systems in organic chemistry. The B_{10} and B_{12} "cage" structures are unusually stable, the B_{12} being somewhat more stable towards substitution reactions than the B_{10} . There is a great deal of similarity in the chemical properties of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ions. Both anions have unusually good kinetic stability in the presence of acids and bases. They are oxidatively and hydrolytically stable, and their alkali-metal salts are stable under vacuum to 600 to 800°C, respectively. The aqueous heat of formation of the $B_{10}H_{10}^{-2}$ ion is reported as +22+5 kcal/mole and that of the $B_{12}H_{12}^{-2}$ ion, +11+10 kcal/mole. This indicates that, depending on the heat of formation of the salt cation and the energy bound in the crystal lattice, certain of these polyhedral borane salts may contain substantial free energy, i.e., exhibit exothermic composition per se. The toxicity of the salts appears to be low; that of the sodium salts of both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ is comparable to sodium chloride. This is in contrast to the high toxicity of decaborane and its usual derivatives.

Because of the significance of such materials to the HIDEF program, a review of the literature on synthesis, properties and pyrotechnic characteristics is given separately in Appendix A to this report. Results of government tests on ignition materials and propellants based on $B_{10}H_{10}^{-2}$ chemistry are also discussed in Appendix A.

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- VERY HIGH HYDROLYTIC AND OXIDATIVE STABILITY
- POSITIVE AQUEOUS HEAT OF FORMATION
- WIDE SUBSTITUTION CHEMISTRY AND CATION VARIETY POSSIBLE
- LOW TOXICITY
- KNOWN PYROTECHNIC UTILITY

FIGURE 11. POLYHEDRAL BORANES OF INTEREST TO THE HIDEF PROGRAM

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a. Polyhedral Boranes of Pyrotechnic Interest

Polyhedral Borane families with known pyrotechnic utility are summarized in Figure 12. Most of the recent experimental work has involved the $B_{10}H_{10}^{-2}$ fuels and mono-propellants, and these results are summarized in subsequent sections.

No systematic exploration of $B_{12}H_{12}^{-2}$ and the B_{20} anions comparable to that done on the B_{10} family has been performed. It is likely, however, based on characterizations that have been done on the B_{10} family, that other polyhedral borane families may offer significant utility in future propellant and pyrotechnic applications. The compound families can be tailored to control physical properties, burning rate, energy output, and gas and particulate combustion products. For example, it is known that in squibs, the B_{12} nitrate double salt functions about 30 times slower than the corresponding B_{10} double salt. This suggests flexibility in burn rates can be achieved by varying the borane family. It is also possible that reduction in sensitivity might be achieved with this family.

Another class of complex salts consisting of complexed ions of cobalt and chromium, polyhedral boranes, and oxidizer have been patented. Representative compounds include:

$[Co(NH_3)_5NO_3]B_{10}H_{10}(NO_3)_2$, $[Co(NH_3)_6]B_{12}H_{12}(NO_3)_4 \cdot 4H_2O$, $[Co(C_{10}H_8N_2)_3]B_{10}H_{10}(ClO_4)$,
 $Cr_2(NH_3)_{10}(NO_3)_4B_{10}H_{10}$. These are believed to be (possibly) detonating materials useful as ignition and primer explosives.

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$B_{10}H_{10}^{-2}$ MONOPROPELLANTS

- SUBSTITUTED GUANIDINE SIMPLE SALTS
- HYDRAZINE AND SUBSTITUTED HYDRAZINE SIMPLE SALTS
- DOUBLE SALTS $Cs_2B_{10}H_{10} \cdot CsNO_3$ AND $(Cs_2B_{10}H_{10})_2Cs_2Cr_2O_7$

$B_{10}H_{10}^{-2}$ HIGH ENERGY FUELS

- AMMONIUM AND SUBSTITUTED AMMONIUM SALTS
- TETRAMETHYLAMMONIUM SALTS
- ALKALI METAL SALTS, ESP. Cs AND K

$B_{12}H_{12}^{-2}$ MONOPROPELLANTS

- $Cs_2B_{12}H_{12} \cdot CsNO_3$

$B_{12}H_{12}^{-2}$ FUELS

- AMMONIUM, TETRAMETHYLAMMONIUM, ALKALI METAL, ...

COMPLEX SALTS

- $[Co(NH_3)_5NO_3] B_{10}H_{10}(NO_3)_2$ AND SIMILAR

HIGHER POLYHEDRAL BORANES

- $B_{20}H_{18}^{-2}$, $B_{20}H_{18}^{-4}$, ...

FIGURE 12. POLYHEDRAL BORANES OF PYROTECHNIC INTEREST

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b. Pyrotechnic Properties and Applications of $B_{10}H_{10}^{-2}$

A substantial body of information exists on certain mixes and coprecipitates incorporating $B_{10}H_{10}^{-2}$ in ignition materials, cords, pressed rods and propellants, some of which are supplied by Teledyne McCormick Selph under the tradename HIVELITE. Some unusual properties claimed or measured for these materials include the following:

- Ultrahigh Deflagration Rates, 10,000 - 20,000 inch/sec and above without transition to detonation (porous configuration)
- Burning characteristics almost independent of ambient temperature
- Very low or even negative pressure exponents
- Chemistry of the compounds can be tailored to achieve a wide range of heat output, gas or particulate products
- Unusually high temperature stability (400°C)

1) Burn Rates

Measured burn rates in government or open literature for various materials are shown in Figure 13. The higher burn rates, 10,000 in/sec and up, place these materials in a unique category of compounds having propagation rates midway between deflagration and detonation.⁵ The non-detonating high burn rates have been confirmed in limited testing at Lawrence Livermore Laboratory,⁶ and at ARRADCOM.

A series of high burn rate propellants were developed by the Interior Ballistics Division of BRL for use in a 40mm hypervelocity travelling charge experimental gun. The compositions are proprietary to Teledyne McCormick Selph. A high burn rate combustor was used to measure consumption rates of pressed pellets. Burning rates on unconfined pellets of eight different compositions are shown in Figure 13. Burning rates for pellets with circumferential confinement were 30 to 130% higher than unconfined pellets of the same material. Experimental measurements of impetus were 50-70% of theoretical.

A series of fast burning propellants were developed and characterized by the Weapons Systems Department of NSWC in support of the 3-inch Lightweight Intermediate Caliber Gun System (LICGS).⁷ These incorporated HIVELITE ignition compositions with nitrocellulose binders. Burn rates for propellant type 1 were 20-50 inches per second with an apparent negative pressure exponent. Propellant type 2 burn rates were 140-250 inches per second with a positive pressure exponent. Similar compositions employing TAGN are described in the patent literature with burn rates up to 500 in/sec.

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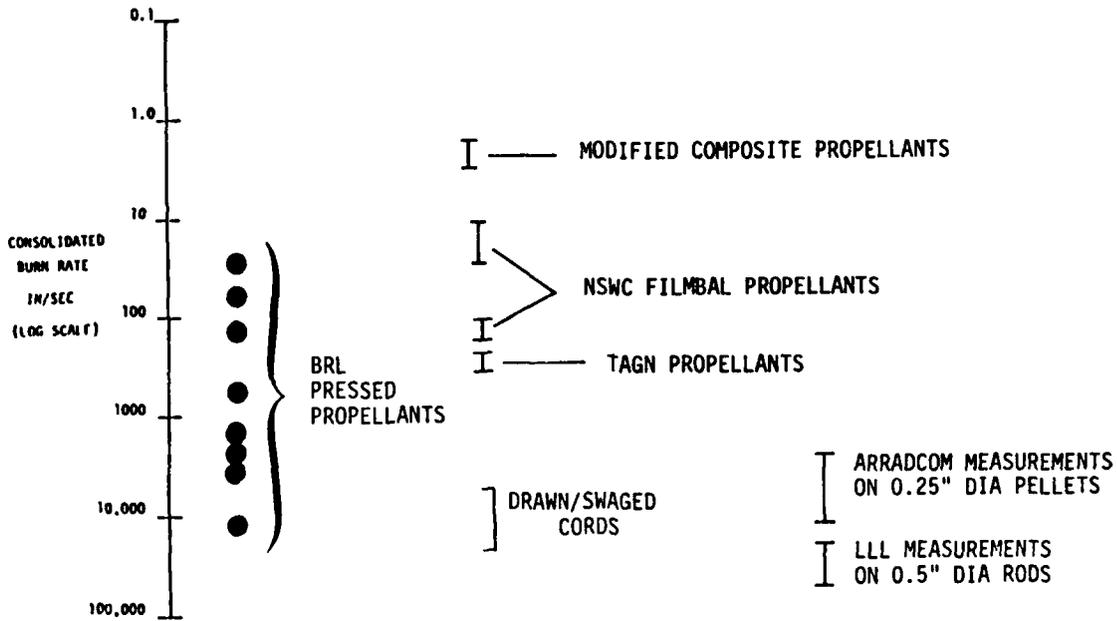


FIGURE 13. PRODUCTS CONTAINING $B_{10}H_{10}^{-2}$ DISPLAY A WIDE RANGE OF BURN RATES

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2) Large Caliber Applications

a) EX 164 Electric Primer

A ignitor that utilizes a fast burning composition is being developed for limited production for the 5"/54 gun at NSWC, culminating an eight year effort to characterize ignition phenomena and develop a high performance igniter.³ The current configuration uses a central HNS lead-jacketed mild detonating cord as the linear propagation element; it is surrounded by pellets of HIVELITE (Teledyne McCormick Selph part no. 300435), as shown in Figure 14.

A standard electric primer for the MK1 MOD1 is used. The flash from the black powder charge in the primer is picked up by a booster assembly (lead azide/PETN) that ignites the MDF cord. The cord is surrounded by pressed pellets about 0.3 in diameter made from a pyrotechnic mix containing cesium decahydrodecaborate ($\text{Cs}_2\text{B}_{10}\text{H}_{10}$) and potassium nitrate with a binder.³ The active ingredients are housed in an extruded nitrocellulose primer tube. The complete assembly is called the Rapid Ignition Propagation (RIP) igniter.

Comparative tests at Dahlgren showed the RIP igniter was superior to igniters with black powder, MDF/black powder, and MDF/ALCLO materials in reducing pressure transients and propellant bed movement in the chamber. The RIP igniter achieved a dramatic reduction in acceleration loads on the projectile base.

b) Large Caliber Soft Recoil Igniter

A program within LCWSL has been under way since 1975 to develop reproducible ignition in the 155mm Large Caliber Soft Recoil System. Two series of test firings were conducted using an XM119 center core igniter configuration that incorporated strands of HIVELITE (metal encapsulated ignition composition based on $\text{B}_{10}\text{H}_{10}^{-2}$, manufactured by Teledyne McCormick Selph) in various geometries. One series of firings indicated that normal ignition delays of 60 msec were reduced to 20-30 msec with very good reproducibility across the temperature range. In parallel test shots, stick propellant in the center core in place of HIVELITE gave 20-30 msec (+1.5 msec deviation) ignition delays. A second series was inconclusive.

The conclusions reached by the experimenters were that reduced ignition delays and uniformly for large caliber soft recoil applications could be accomplished cheaper and easier with methods other than HIVELITES.

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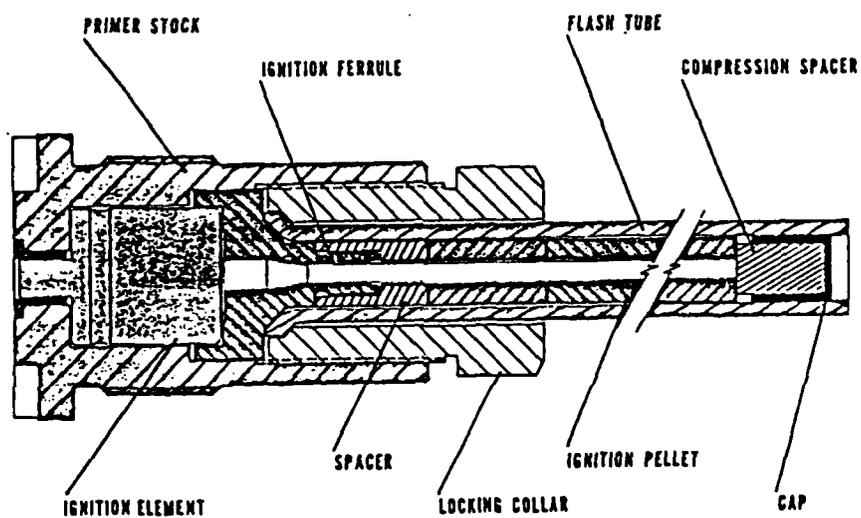


FIGURE 14. THE NAVY'S EX 164 ELECTRIC PRIMER IS AN EXAMPLE OF A LARGE CALIBER IGNITER USING $B_{10}H_{10}^{-2}$ COMPOSITIONS

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3) Small Caliber Applications

a) Telescoped Ammunition Ignition

In a series of tests conducted at Frankford Arsenal,⁸ "AMMOLITE" ignition materials (proprietary Teledyne McCormick Selph compositions identified as #'s 300432 and 300473) were evaluated for use in medium caliber telescoped ammunition. These are described as fine powders with heats of explosion of 717 and 1348 cal/gram respectively and high temperature stability. Characterization tests including hygroscopicity, IR spectra, and DSC were run by ARRADCOM. The 300432 material was found to have relatively high hygroscopicity.

The AMMOLITES were evaluated in comparison to black powder and BKNO_3 in a 25mm telescoping round shot-start test fixture. Principal test data results are shown in Figure 15.

Conclusions from the studies were that the "... tests have shown that the Ammolite materials examined, when used in telescoped ammunition, are capable of providing more consistently reproducible projectile seating action times over the temperature extremes than either black powder or boron/potassium nitrate igniters. Also, the required charge weights for the Ammolites are generally much less than the other igniters tested."

b) Air Force Armament Laboratory (AFATL)

The Ballistics Branch of the Guns, Rockets, and Explosives Division of AFATL has conducted medium (20-40mm) caliber propellant ignition studies. A recent series of tests on ignition of deterred triple base propellant in the GAU-8 round used perforated flash tubes containing various types, configurations, and quantities of ignition materials, including A4 black powder, BKNO_3 , ITLX detonating cords (1/8" dia), HIVELITE part numbers 134024 and 300435 (Teledyne McCormick Selph). The objective of the development testing was to reduce action times on the deterred tri-base GAU-8 round to the order of 3 milliseconds. In 56 firings between Sept 1978 and Feb 1979, only the ITLX (833 mg load) and HIVELITE 134024 (733 mg) gave the desired performance.

In a second series of tests conducted at Eglin, a test fixture was developed to observe and measure luminosity (intensity, duration) in the medium caliber ignition sequence. The general conclusions were that HIVELITE performance was on a par with ALCLO. Both were substantially better than BKNO_3 , which in turn was better than black powder.

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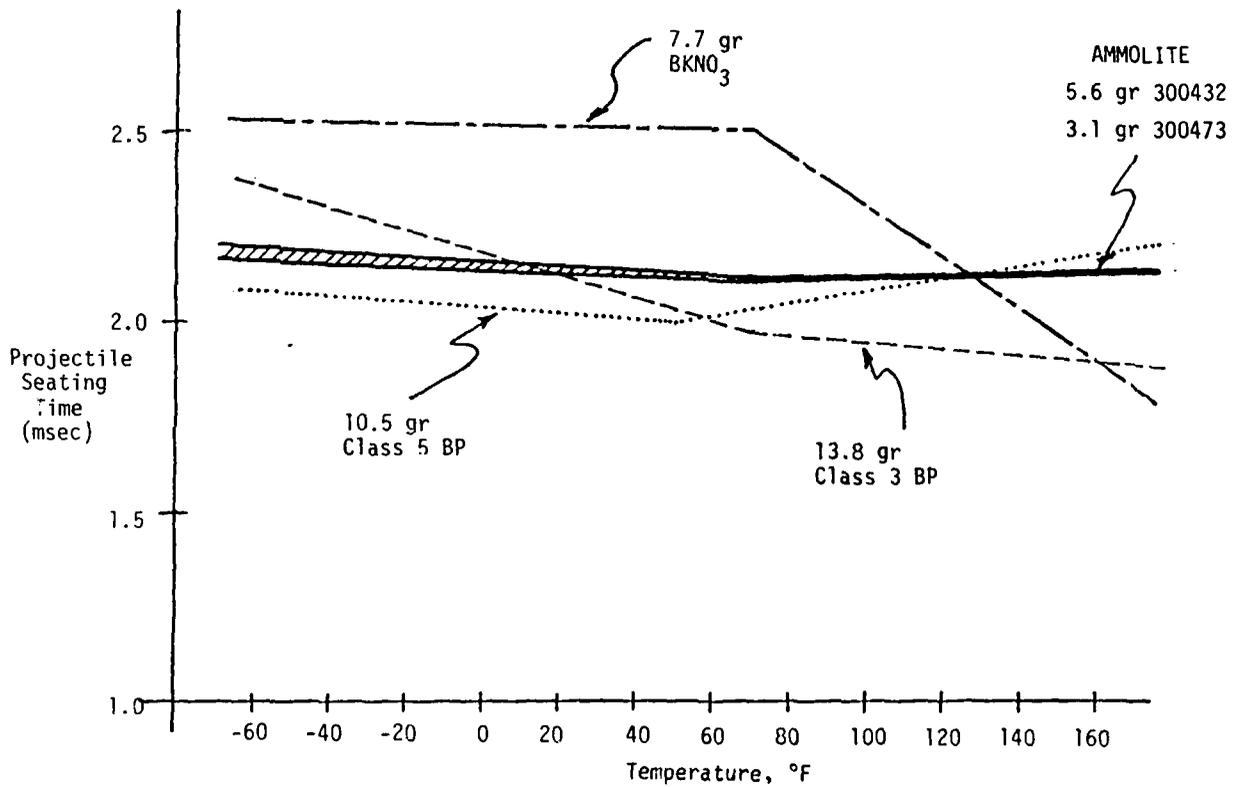


FIGURE 15. FRANKFORD TESTS INDICATE LOW TEMPERATURE DEPENDENCE OF $B_{10}H_{10}^{-2}$ COMPOSITION FUNCTIONING

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4) Sensitivity and Properties Problems Associated with $B_{10}H_{10}^{-2}$ Compositions

During the course of tests on materials using $B_{10}H_{10}^{-2}$ salts as the energetic component, a number of drawbacks have been reported.

As part of the EX 164 primer development, a series of characterization tests on the ignition material HIVELITE 300435 were done at ARRADCOM.⁹ The tests included impact, friction and electrostatic sensitivity; vacuum stability; autoignition temperature; detonation velocity; density; DTA/TGA; physical stability; effect of moisture. No detonation was observed when pressed pellets were ignited. Deflagration rates of about 12,000 in/sec were observed. Thermal stability data (vacuum stability and TGA) did not indicate a particularly stable composition at elevated temperatures (TGA showed a 6% weight loss between 190 and 370°C). The material was exceptionally friction and static sensitive and was also quite impact sensitive, as shown in Figure 16. The composition was hygroscopic and possibly deliquescent at very high humidities (90-99%). It was the conclusion of the experimenters that HIVELITE 300435 must be handled as a sensitive primary explosive.

Possible sensitivity to friction when HIVELITES were blended with double base propellants were also reported by Eglin.¹⁰

It is apparent that any efforts to utilize $B_{10}H_{10}^{-2}$ compositions in an igniter material for general service use must carefully address these sensitivity issues. Most of the tests to date have been on a single material. It is believed that alternate members of this family or alternate processing techniques may produce materials with substantially better properties.

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	HIVELITE 300435	LEAD STYPHNATE	LEAD AZIDE	PETN	BLACK POWDER
P.A. IMPACT 10%, IN	6	3	4	6	16
ELECTROSTATIC SENSITIVITY (Joules), 50% PT	.0009	.00034	.00236	.06	>12.5
P.A. FRICTION PENDULUM (STEEL & FIBRE SHOE)	EXPLODES	DETONATES	DETONATES	UNAFFECTED (FIBRE SHOE) CRACKLES (STEEL SHOE)	UNAFFECTED (FIBRE SHOE) SNAPS (STEEL SHOE)

FIGURE 16. PICATINNY ARSENAL DATA ON ONE COMMONLY USED HIVELITE
SHOWS SENSITIVITY TO ELECTROSTATIC AND FRICTION IGNITION

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c. Polyhedral Borane Availability

At present there are (at least) three producers of basic polyhedral borane and pyrotechnic materials:

- Callery Chemical Company (Division of Mine Safety Appliances Co., Callery, PA). $B_{12}H_{12}^{-2}$ salts. Callery does not manufacture pyrotechnic or explosive materials. Patented and licensed products are indicated in Appendix A.
- Teledyne McCormick Selph (Hollister, CA). $B_{10}H_{10}^{-2}$ salts and pyrotechnic/ignition compositions based on them (some marketed under the tradename HIVELITE). Known patented and some licensed products are indicated in Appendix A.
- R & N Chemical/Roberts Research (Hollister, CA). Certain types of $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$ and pyrotechnic/ignition compositions.

A limiting factor in any future large scale production of polyhedral boranes is the availability of starting materials. The most convenient starting material is decaborane, $B_{10}H_{14}$, which until recently was available only in small (10 lb) quantities at about \$2500/lb from a sole supplier (Callery Chemical Co.). The U.S. Army (MICOM) has recently brought on-line a carborane plant at Callery that uses a continuous vapor phase pyrolysis to convert diborane to decaborane in parallel unit reactors. The present facility is sized for 15,000 lb/year with expansion potential to 30,000 lb/year. The projected cost at the lower production figure is about \$500/lb in FY' 80 dollars.

Using nominal estimates for stoichiometries and conversion efficiencies for a coprecipitated ignition mix consisting of 15% tetramethylammonium decahydrodecaborate and 85% KNO_3 , the boron cost in a pound of mix is about \$35/lb. For a 25% $Cs_2B_{10}H_{10}$ /75% KNO_3 mix the cost is about \$42/lb. Processing and other materials costs estimates indicate that a granulated ignition composition for use as a black powder replacement should be produceable for \$500/lb or less. For a large caliber igniter, about 3 ounces of compound is required, so that the per-pound cost is less than \$10.

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- PRIMARY SYNTHETIC ROUTE OF $B_{10}H_{10}^{-2}$ AND $B_{12}H_{12}^{-2}$ IS THRU DECABORANE, $B_{10}H_{14}$
- ALTERNATE ROUTES FROM DIBORANE, BH_4^- , AND BORAX ARE KNOWN AND COULD BE CHEAPER.
- MICOM CARBORANE PLANT AT CALLERY, PA, HAS PROJECTED $B_{10}H_{14}$ COSTS OF ABOUT \$500/LB
- COPRECIPATED IGNITION MIX BASED ON GOVERNMENT PRODUCED DECABORANE IS ESTIMATED AT \$50/LB OR LESS
- COST OF IGNITION MATERIAL IN A LARGE CALIBER ROUND LESS THAN \$10 ON A BLACK POWDER REPLACEMENT BASIS.

FIGURE 17. COST OF IGNITION MATERIALS BASED ON POLYHEDRAL BORANES ARE NOT UNREASONABLE

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6. Cyano-Metal Complex Igniter Compositions

A family of materials that have demonstrated very high deflagration rates were developed by Fronabarger at Unidynamics (U.S. patent 3,793,100). A composition called CC prepared by coprecipitating potassium perchlorate and potassium cobalticyanide from aqueous solution shows very well defined burn rates in the 10,000 in/sec region in deflagrating cord form (0.055 in dia). CC has been evaluated to determine its basic pyrochemical properties, sensitivity and stability characteristics, and burn rate characteristics:

- (1) The variation in burn rate with temperature from 50°C to +250°C is low, as shown in Figure 18
- (2) The material is relatively insensitive to impact initiation but has high electrostatic sensitivity (5600 ergs, 23% level).

A second material prepared by a similar process was called CI, potassium ferricyanide/potassium perchlorate ($K_3Fe(CN)_6/KClO_4$). Both materials show low impact sensitivity (75 cm, BOM, 10% for CC; 45cm, BOM, 10% for CI), high autoignition temperatures, and moderate heat of explosion (CC: 900 cal/g; CI: 1052 cal/g).

The chemistry described in the forementioned patent is extensive in terms of the combination of complex anions, oxidizing anions, and cations that could be utilized. Of particular interest might be the introduction of non-halogen containing oxidizing anions, such as NO_3 . A concern that must be addressed by varying the chemistry is to reduce the static sensitivity.

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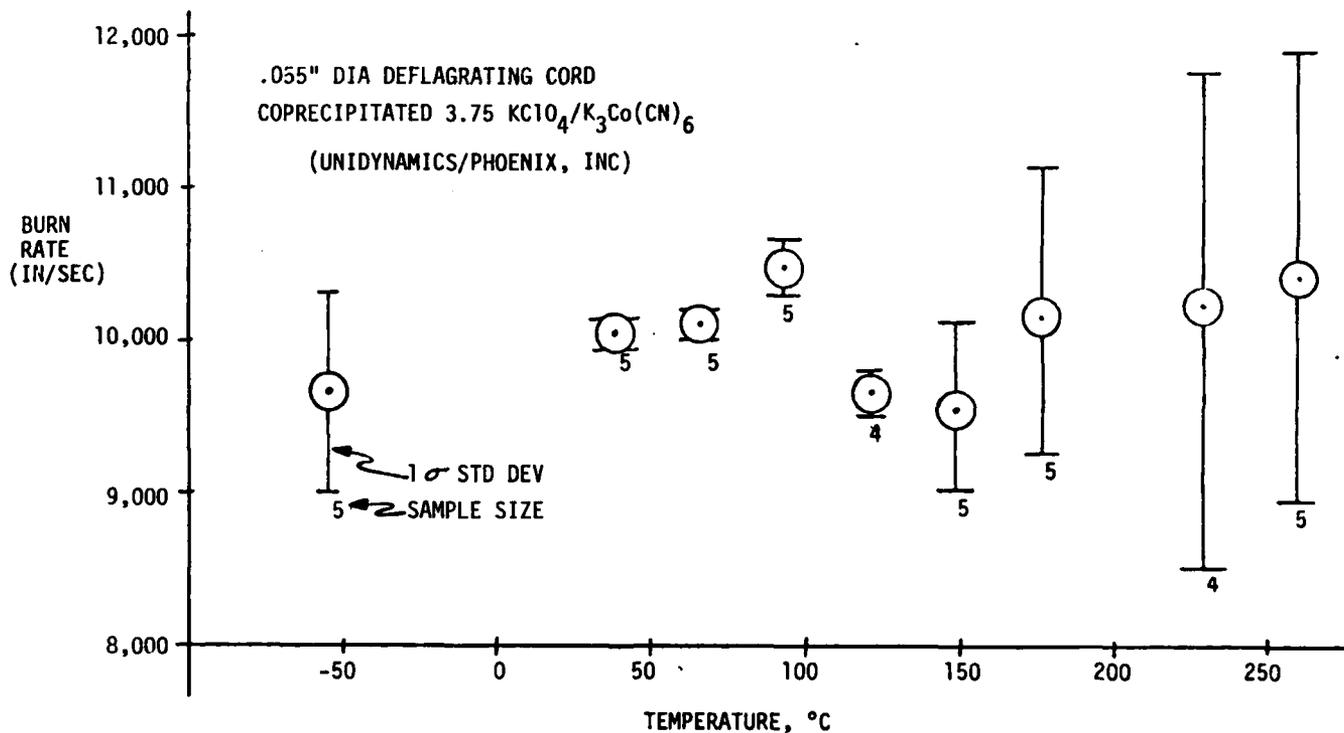


FIGURE 18. CERTAIN COPRECIPITATED TRANSITION METAL CYANO-COMPLEXES EXHIBIT HIGH DEFLAGRATION RATES AND UNIFORM TEMPERATURE DEPENDENCE

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7. Other Novel Ignition Material Approaches

Discussions with various members of the primer and igniter materials community revealed that several other approaches might be feasible to develop HIDEF materials:

- Silanes (analogous to polyhedral boranes), if they could be obtained in stable higher molecular weight structures, could exhibit fast burn rates.
- It may be feasible to combine high burn rate gasless delay mixes with oxidizer in such a way so as to control burn rate.
- Intermetallics per se are probably not feasible as HIDEF compounds, as they have long induction times and are gasless. Perhaps they could be used as burn rate controlling elements. Pyrofuse (palladium/aluminum) burns at about 16 in/sec.
- The CuO/Al reaction may have analogous behavior with Boron, and should be tested.

Other references to interesting materials are found in the literature, including Zr and Ti blends with NC, NG, and $KClO_4$; B/Te/ O_2 /fluoroelastomer (U. S. patent 3,519,505); metal or metal nitride/oxidizer/fluoroelastomer/fluoride (U. S. patent 3,753,811). Other potential classes of materials include various hydrides and foamed compositions.

None of the forementioned pyrotechnic chemistries have been explored in detail, and a "fresh start" approach must be taken toward them.

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- HIGHER SILANES
- CUO/AL TYPE REACTION WITH B SUBSTITUTIONS
- ZR AND TI WITH NC, NG, PROPELLANTS
- B/TEO₂/FLUROELASTOMERS AND RELATED COMPOUNDS
- METAL NITRIDE/OXIDIZER/FLUROELASTOMER/FLUROIDE
- METAL HYDRIDES
- FOAMED COMPOSITIONS

FIGURE 19. ADDITIONAL TYPES OF POTENTIAL HIDEF IGNITER MATERIALS

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C. POTENTIAL HIDEF IGNITER CONFIGURATIONS

1. Summary

In considering applications of HIDEF technology it is necessary to look at configurations as well as materials. Probably the "ideal", although impractical, method of igniting a propellant bed is to permeate the bed with a combustable gas that produces hot particles in the combustion products. Upon ignition this should give a nearly uniform propellant ignition throughout the geometry of the bed. The closest practical analog to this is to coat individual propellant grains with igniter composition, as discussed in Section C.4.

2. Materials Processing Techniques

Assuming the basic HIDEF igniter compositions are initially produced as powders, there are at least four standard processing techniques to package the powder into the igniter hardware, as shown in Figure 20.

The easiest method is to press into pellets, which may be the size of small pills or as large as large caliber propellant grains. Granulation involves one of two methods:

- *Mixing, pressing and corning (like the black powder process)*
- *Mixing wet with a binder, pressing thru a screen, and drying.*

Both materials could be graphite glazed to reduce sensitivity and enhance pouring properties. It is also feasible that powdered or granulated compositions could be extruded into a Benite-like strand, if a suitable formulation were developed.

Finally, powder detonating and deflagrating powders are commonly drawn or swaged into metal encapsulated cords; aluminum and lead are commonly used. In this configuration, some of the igniter energy is expended in rupturing the metal sheath.

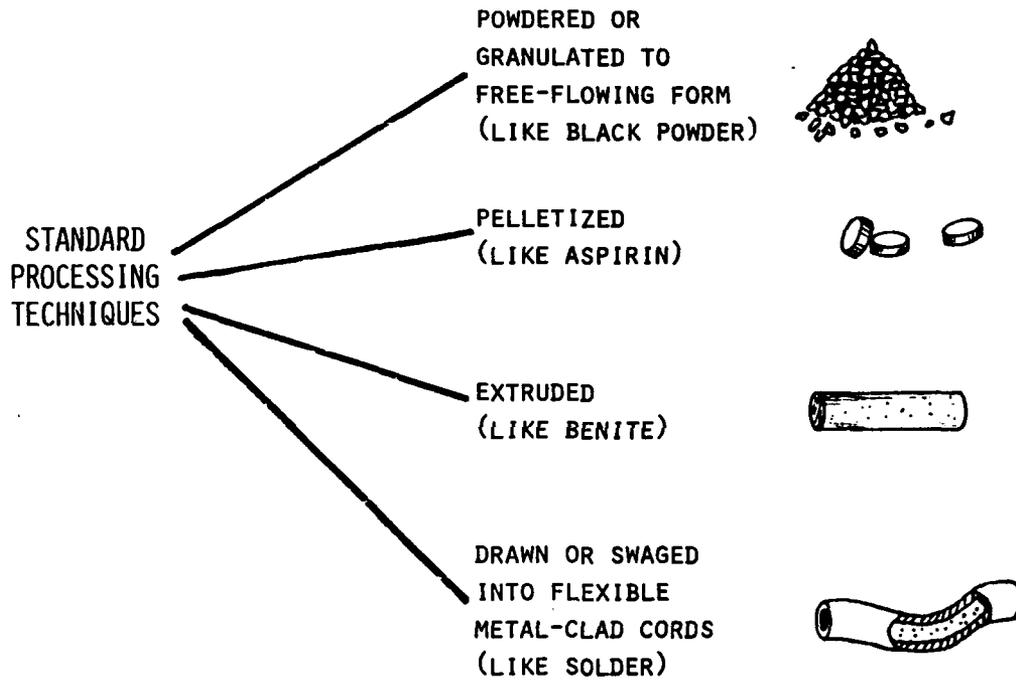


FIGURE 20. STANDARD PROCESSING TECHNIQUES WILL ALLOW HIDEF MATERIALS TO BE PRODUCED IN A VARIETY OF PHYSICAL FORMS

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3. Standard Primer Configurations

Using the granulated, pelletized, or extruded processing techniques, the HIDEF compositions might be used on a direct replacement basis for granulated black powder in sausage bags or bayonet primers, in place of $BKNO_3$ tablets in picollo igniters or in place of Benite or propellant in center core strand igniters.

One configuration of interest to the overall HIDEF program is the use of packets of granules or pellets space longitudinally in a non-continuous distribution along the igniter axis. This method lends itself to the use of telescoping combustable support elements that can be expanded for different zoning solutions. The packet envelope must be of such a design to sequentially transmit the ignition stimulus. The use of a flexible, detonating or deflagrating cord could also be used to connect the packets.

In the center core bag charge igniter, similar to the M203 charge configuration, some consideration must be given to the interface between the base charge (which must pick up the primer flash) and the low pressure center core igniter material. A flexible cord might be a possible solution to this also.

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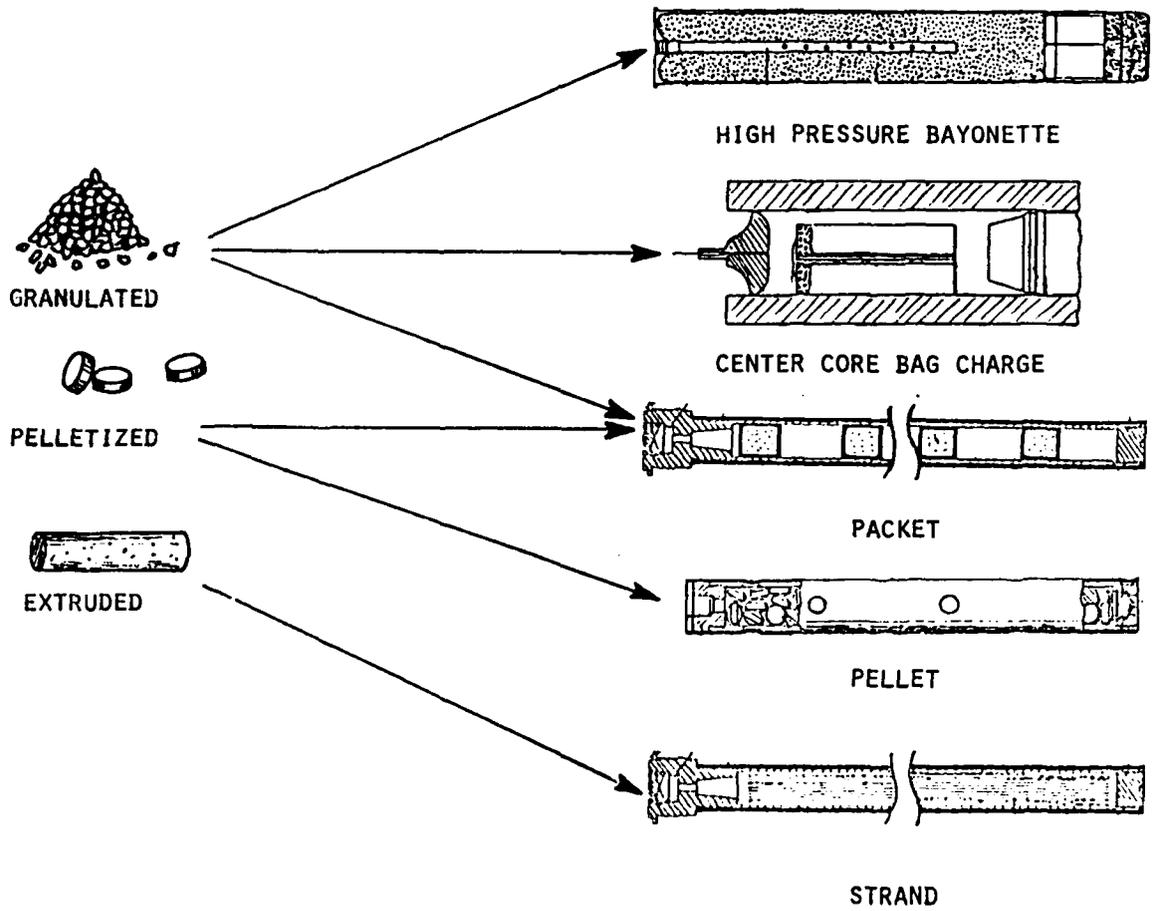


FIGURE 21. HIDEF CAN POSSIBLY BE FORMULATED AS A DIRECT BLACK POWDER, $BKNO_3$, OR BENITE REPLACEMENT

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4. Flexible Linear Arrangement

The use of igniter mix in a flexible linear form, such as cord or tape, allows the ammunition designer expanded latitude in optimizing the igniter design. The industrial methods for metal-encapsulating ignition powders suggest some novel igniter configurations, some of which are shown in Figure 22.

A cheap and effective means of rapidly spreading the ignition stimulus longitudinally is to encapsulate in a single cord a mixture of high explosive and pyrotechnic powders. The stimulus propagates along the cord at a detonation velocity while the pyrotechnic provides a hot radial flame. A more sophisticated version can be made in which the detonating core is surrounded by multiple cores of pure ignition mix; this has the effect of isolating the propellant bed from any direct detonating stimulus.

Flexible cords of the the type described above can be formed into some interesting configurations, as shown in Figure 22. It is possible to achieve embedded ignition that spreads the ignition very uniformly thru the propellant bed. Peripheral ignition (i.e., external, along the propellant bed cylindrical surface) can also be achieved.

One problem that arises with cord-type igniters is the pyrotechnic train that must connect the cord to the primer charge. If a detonating cord is used, the train must normally produce a detonating wave from the primer flash. This involves primary or booster explosives and the attendant mechanical and environmental seals.

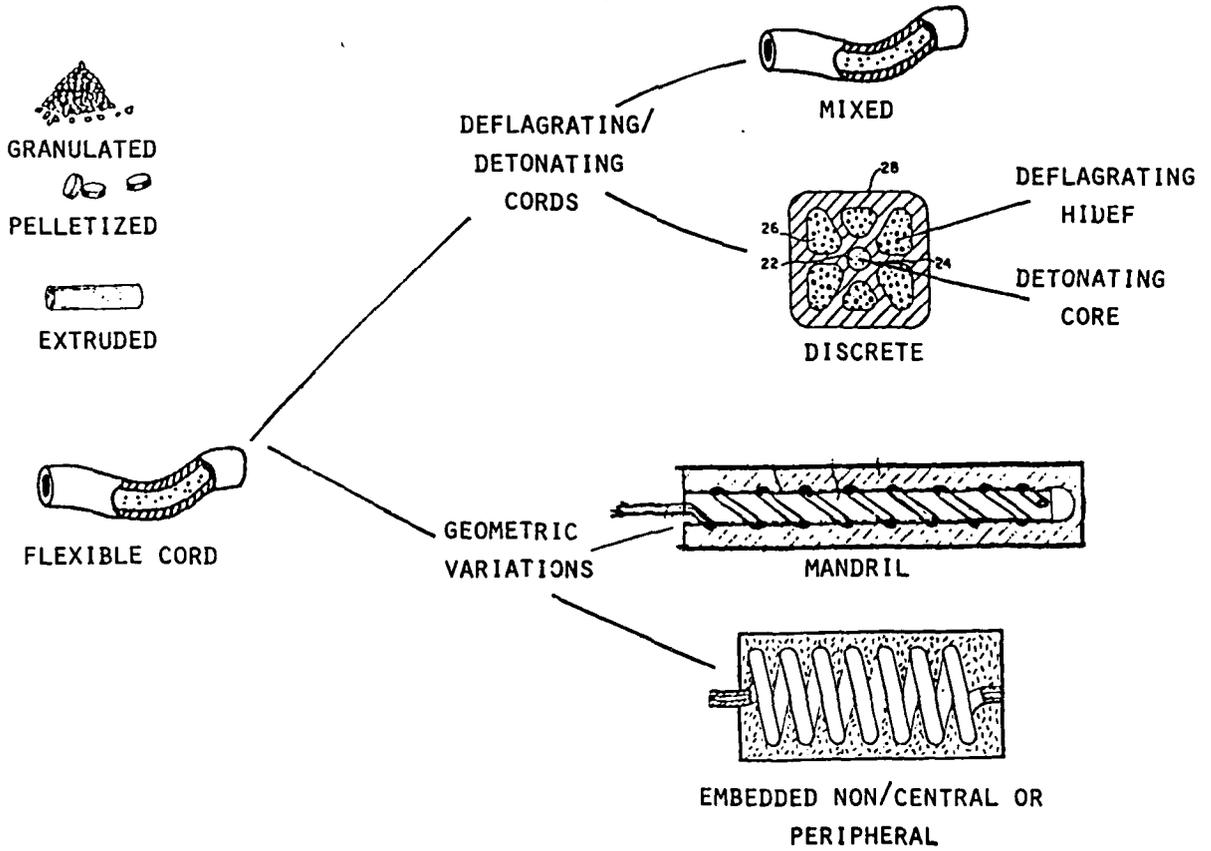


FIGURE 22. FLEXIBLE CORDS GIVE FLEXIBLE IGNITER CONFIGURATIONS

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5. Non-Standard Methods

Several novel approaches which arose during the HIDEF Phase I studies are worthy of mention and summarized in Figure 23.

A fluid igniter consisting of monopropellant or fuel contained in an incompletely perforated center tube that is ruptured, dispersing the fluid into the propellant bed in drop-let or vapor form, followed by ignition (something like a FAE effect) could be examined. Rupture could possibly be by hydrodynamic shock from a booster charge set off by primer flash. The system might be engineered so that a separate igniter cord must function to effect ignition, thus constituting a built-in safe-and-arm possibility. An ignition enhancer, such as a soluble polyhedral borane, might be dissolved in the fluid.

Telescoping combustable center core igniter with incremental charges or flexible ignition cords, or telescoping combustable outer support tubes with attached igniter packets or cords would enable zoning solutions.

A pyrotechnic tape, consisting of ignition composition incorporated into a snake or in cord form attached to a one-sided sticky tape could be used to hold assembled bag charges together. This would accomplish peripheral ignition. It could possibly be used in cased ammunition attached to the inside case wall. Peripheral ignition configurations imply increased vulnerability.

Other approaches that may obviate the need for an ignition train per se involve coating the propellant grains with ignition composition or dispersing the pyrotechnic in a continuous phase of the solid propellant. The technique for coating is similar to that used to coat flash reducer onto the grains; the chemistry of the ignition composition could possibly be adjusted to function also as a flash reducer. A drawback to the coated configuration or any other approach that disperses ignition materials or elements in the propellant bed is an inherent increase in vulnerability of the charge. In a center core igniter train, at least some protection from projectile or fragment impact or rough handling is afforded to the highly ignitable compositions by the propellant bed.

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- FLUID IGNITER
 - RUPTURE VIA MDF CORD
 - CAN CONTAIN DISSOLVED IGNITION ENHANCER

- TELESCOPING COMBUSTABLE PARTS
 - CENTER CORE: AMENABLE TO PACKET CONTAINERS
 - OUTER SUPPORT TUBES: AMENABLE TO FLEXIBLE CORD ATTACHMENT

- TAPE WITH INTEGRAL SNAKE

- COATED PROPELLANT GRAINS

FIGURE 23. NOVEL METHODS FOR IGNITER EMPLACEMENT CAN
ALSO BE EXPLORED

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D. HIDEF TECHNOLOGY DEVELOPMENT OUTLINE

In Phase I of the HIDEF program, preliminary estimates of program risks, payoffs, and requirements were examined. These will be used as starting point for the overall formulation of a comprehensive program to exploit HIDEF technology.

1. Payoffs

The data gathered and analyzed in Phase I suggests a number of payoffs if advanced ignition materials are developed. The principal elements are shown in Figure 24.

First, it appears feasible to develop a direct black powder replacement that can be introduced into service use in Product Improvement Programs (PIP) and advanced ammunition currently being developed around black powder igniters.

For both PIP and new designs, properly formulated HIDEF compositions will result in significantly improved ballistic control. This has already been demonstrated in small and large caliber applications.

Based on the chemical flexibility inherent in the "families" of HIDEF candidates, it is virtually certain that high efficiency materials can be tailored to effectively ignite LOVA, nitramine, heavily deterred, and other difficult-to-ignite materials.

Finally, improved ignition materials and configurations will allow the ammunition designer a much wider license to consider innovative solutions to ammunition packaging efficiencies and performance.

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- DIRECT BLACK POWDER REPLACEMENT POSSIBLE
 - PIP
- CONTROLLED BALLISTICS HAVE BEEN DEMONSTRATED ALREADY
 - REPRODUCEABLE AND CONTROLLABLE ACTION TIMES
 - LOW TEMPERATURE DEPENDENCE
 - REDUCED PRESSURE TRANSIENTS IN CHAMBER
- CAN USE NEW PROPELLANTS
 - EFFICIENT IGNITION OF LOVA, COOL BURNING, AND HEAVILY DETERRED COMPOSITIONS
- AMMUNITION PACKAGING EFFICIENCIES
 - TELESCOPED ROUNDS
 - ZONED CHARGES

FIGURE 24. PHASE I DATA ON HIDEF TECHNOLOGY
DEMONSTRATES HIGH PAYOFF POTENTIAL

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2. HIDEF Candidate Technologies Risks and Benefits

Figure 25 gives estimates of the risks and payoff potential for each of the candidate HIDEF technologies identified during Phase I. These include both materials and igniter configurations.

A payoff potential is considered "high" for HIDEF materials if there is a significant probability that its characteristics might approach the attributes of an ideal igniter mix. For example, the payoff in developing the $B_{10}H_{10}^{-2}$ family is "moderate" because sensitivity properties may be expected to be worse than black powder, whereas the payoff in $B_{12}H_{12}^{-2}$ development is "high" because they are expected to be less sensitive than the B_{10} 's. If no body of information is available on a material or configuration, the technical risk is considered "very high". If materials or configurations are well characterized, the risk is "low".

Payoffs are considered "very high" if a significant advance in the concept of ignition can be effected by the introduction of the candidate technology. The two such concepts listed involve materials processing and configurations that are non-standard and therefore require more development work than the other candidates. Therefore, foamed compositions and fluid igniters qualify as "very high" technical risks also.

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CANDIDATE TECHNOLOGIES	TECHNICAL RISK	PAYOFF POTENTIAL
MATERIALS		
STANDARD IGNITION MIXES	L	M
MODIFIED "GASLESS" IGNITION MIXES	M	M
$B_{10}H_{10}^{-2}$ POLYHEDRAL BORANES	L	M
$B_{12}H_{12}^{-2}$ POLYHEDRAL BORANES	M	H
CYANO METAL COMPLEXES	M	H
SILANES	VH	H
CUO/AL TYPE REACTIONS	M	M
FLUROELASTOMERICS	M	L
METAL/COMPOSITE DOUBLE BASE	M	M
HYDRIDES	M	H
FOAMED COMPOSITIONS	VH	VH
CONFIGURATIONS		
DIRECT BP REPLACEMENT	L	M
BENITE STRAND REPLACEMENT	M	M
TELESCOPING/PACKET/CORD	M	H
FLEXIBLE CORDS	L	H
FLUID IGNITER	VH	VH
TAPE	M	H
COATED PROPELLANT	M	M

L = LOW M = MODERATE H = HIGH VH = VERY HIGH

FIGURE 25. ESTIMATES OF RISK/PAYOFF OF VARIOUS HIDEF CANDIDATE TECHNOLOGIES

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3. Program Requirements

In Phase I, key data and hardware requirements for the overall HIDEF effort were estimated, and are summarized on Figure 26. These are valid for all but the "very high" risk technologies.

The preliminary definition of feasible chemical approaches has been done in Phase I, but must be expanded in Phase II to delineate specific chemical compounds to be synthesized.

The next major step is a demonstration program to synthesize and characterize selected compounds or families of compounds formulated into one or more of the standard processing technique products. Expanded definitions of the characterization requirements are given in Sections D.3.a and b. It was the opinion of a number of members of the pyro community that a key requirement here is to elucidate the burning mechanism (physically and chemically). This is especially true for materials in consolidated columns which exhibit very high flame propagation rates.

The material must be evaluated in test hardware that adequately simulates the ignition event and can be used to obtain parametric data to guide in configuration optimization.

Finally, it is important that a data bank on HIDEF technology formulations, characteristics, applications, and parametric test data be established for use by ordnance and ammunition specialists in government and industry. A summary of key data and applications should be widely disseminated in the community.

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- DEFINITION OF FEASIBLE CHEMICAL APPROACHES
- DEMONSTRATION OF FEASIBLE CHEMICAL APPROACHES
 - ELUCIDATION OF BURNING MECHANISMS
 - SPECIFICATION OF KEY CHARACTERISTICS OF MATERIALS
(SAFETY, TOXICITY, COMPATIBILITY, PHYSICAL PROPERTIES,
PYROTECHNIC BEHAVIOR, AND PRODUCEABILITY)
- APPLICATIONS AND DEMONSTRATION IN IGNITER TEST HARDWARE
- DATA BANK ON HIDEF TECHNOLOGY

FIGURE 26. KEY HIDEF PROGRAM REQUIREMENTS

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a. Sensitivity

Candidate tests and evaluations of HIDEF materials for safety, toxicity, and compatibility are listed in Figure 27.

Standard sensitivity tests as listed were developed primarily to characterize detonating materials. As such, some are not directly applicable to deflagrating compositions, or at a minimum, inadequate comparative data exist to interpret test results with respect to ignition applications. During the Phase II HIDEF efforts, these tests procedures should be thoroughly reviewed with a view toward modifying or supplementing these procedures to more accurately reflect ignition application requirements.

In a first evaluation, anticipated toxicity should be estimated from existing data on chemically equivalent or similar compounds for both virgin ignition material and its resulting combustion products. The combustion product concentrations can be estimated to first order with free energy minimization calculations such as the BLAKE code with expansion to ambient pressure.

Standard compatibility tests between HIDEF materials and representative propellants and igniter support materials should also be done.

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SAFETY

- EXPLOSIVE CLASS
- IMPACT SENSITIVITY
- FRICTION SENSITIVITY
- ELECTROSTATIC SENSITIVITY
- AUTOIGNITION (5-SEC)
- VACUUM THERMAL STABILITY
- CARD GAP

TOXICITY (CHEMICAL EVALUATION BASED ON INGREDIENTS)

- UNBURNED
- COMBUSTION PRODUCTS (DETERMINED FROM FREE ENERGY MINIMIZATION CALCULATIONS)

COMPATIBILITY

- METALS
- DOUBLE BASE/NITRAMINE PROPELLANTS
- SELECTED POLYMERICS

FIGURE 27. CANDIDATE SAFETY CHARACTERIZATION REQUIREMENTS

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b. HIDEF Materials Characterizations

Candidate tests and evaluations of HIDEF materials for physical and pyrotechnic properties and several produceability estimates are listed in Figure 28.

Most of the tests are standard, with the exception of burn rate measurements on very fast deflagrating columns of igniter materials. This will require a special test fixture which is further discussed in the next section.

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PHYSICAL PROPERTIES

- TRUE DENSITY
- BULK DENSITY
- HYGROSCOPICITY
- DTA/TGA

PYROTECHNIC PROPERTIES

- HEAT OF EXPLOSION
- FLAME TEMPERATURE (MEASURED)
- COMBUSTION PRODUCTS (CALCULATED)
(DTA/TGA)
- BURN RATE (BULK, COMPRESSED)
- CLOSED BOMB PRESSURE-TIME HISTORY

PRODUCEABILITY

- BULK PROCESS PROCEDURE OUTLINE
- ESTIMATED COSTS
- RAW MATERIALS AVAILABILITY

FIGURE 23. CANDIDATE CHARACTERIZATIONS OF HIDEF MATERIALS PROPERTIES

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c. Specialized Test Hardware

Preliminary estimates of specialized test hardware and apparatus are listed in Figure 29. These capabilities are beyond what would be expected to be available in a well-equipped pyro lab.

The HIDEF program will eventually require testing of materials in primer/igniter configurations in a laboratory environment. An excellent review of apparatus used for this purpose has recently been given by Fisher.¹¹ Simulators for large caliber igniter studies include set-ups at Calspan, Picatinny, BRL, and the disposable breech instrument at NSWC. Efforts are underway by McClure at NSWC to instrument the disposable breech assembly to measure local gas temperature and heat flux to propellant grains.

In order to study flame spread and burning in a fast igniter column, an apparatus that is akin to a fast strand burner may be required, probably using electrooptical detection techniques. If mechanism studies are to be done, the most direct way of characterizing the intermediate species is thru time resolved spectroscopy. This capability could possibly be integrated with the strand burner.

As the list of candidate HIDEF materials is narrowed, it is useful to analyze combustion products directly from closed bomb tests to supplement thermochemical calculation estimates. This involves a direct transfer of gases to spectrometric and chromatographic analytical instruments. This capability is available only in a few labs.

Finally, it is believed that the use of an electron scanning microscope with microprobe (wavelength dispersive) would be a very valuable tool to examine the physical and chemical microstructure of fine particle size coprecipitates or ignition mixes.

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- LARGE CALIBER INSTRUMENTED TEST FIXTURES
 - BRL 155MM IGNITER SIMULATOR
 - PICATINNY LCWSL 155MM IGNITER SIMULATOR
 - FRANKFORD/BRL VENTED CHAMBER
 - DYNAGUN (CURRENTLY A CHARGE ACCEPTANCE FIXTURE)
 - NSWC DISPOSABLE BREECH GUN TEST FIXTURE
 - BRL DISPOSABLE BREECH GUN TEST FIXTURE

- FLAME SPREAD TEST FIXTURES
 - FLAME SPREAD IN GRANULAR BED
 - "FAST" STRAND BURNER
 - PCRL FLAMESPREAD TESTER

- SPECIALIZED CHEMICAL CHARACTERIZATION
 - BOMB WITH COMBUSTION PRODUCT ANALYSIS CAPABILITY
 - TIME RESOLVED SPECTROSCOPY
 - ELECTRON SCANNING MICROSCOPY WITH MICROPROBE FOR ANALYSIS OF COPRECIPITATES.

FIGURE 29. SPECIALIZED TEST FIXTURES AND INSTRUMENTATION WILL BE REQUIRED TO STUDY HIDEF TECHNOLOGIES

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