

LA-UR-17-24143

Approved for public release; distribution is unlimited.

Title: Final report for SERDP WP-2209 Replacement melt-castable formulations for Composition B

Author(s): Leonard, Philip
Francois, Elizabeth Green

Intended for: Report

Issued: 2017-05-19

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Final report for SERDP WP-2209
Replacement melt-castable formulations for
Composition B

Elizabeth Francois; Philip Leonard, M-7
Los Alamos National Laboratory

With technical contributions from Philip Samuels, ARDEC

Contents

List of Tables	ii
List of Figures	ii
List of Acronyms	ii
Keywords	iii
Acknowledgements	iii
Abstract	1
Objective	1
Background	2
Limitations of Melt-casting	2
Comp B. an Excellent Melt Castable explosive.....	3
Materials and Methods.....	4
General	4
Performance measurements	4
Synthesis of Nitrate Salts	4
Synthesis of LLM-201	5
Results and Discussion	5
Rationale for exclusion and down-selection	5
Chemical reaction of the materials in the melt	5
Thermal degradation of materials	6
Sublimation and condensation of explosive material	7
Down-selection criteria.....	7
Preferred alternative formulations and their properties	7
AAD/HMX 50-50 (AH-55)	7
PAX-PrNQ.....	10
LLM-201/HMX 50-50 (LH-55).....	12
PDX.....	13
Conclusion and Implications for Future Research/Implementation	15
Literature Cited	15
Appendix A.....	16
Synthesis of 3-Amino-1,2,4-triazole Nitrate.....	16
Synthesis of LLM-201	16
Water Sorption of AAD	17

Viscometry of AAD, AH-55.....	17
LSGT on PAX-PrNQ.....	19
Irreversible Growth Test Method.....	19
Exudation Test Method.....	19

List of Tables

Table 1, Comparison of melt-cast formulations	5
Table 2, Comparative sensitivity of low melt components and formulations	10
Table 3, Irreversible growth testing	11
Table 4, Exudation testing	11

List of Figures

Figure 1, Melt casting from a kettle into heated cylinders.	2
Figure 2, Melt casting a high-viscosity mixture (left) and low viscosity mixture (right)...	3
Figure 3, Melting of PDX (center) compared to the binder system (left) and DAAF (right).	6
Figure 4, components of the eutectic AAD	8
Figure 5, water absorption of AAD as a function of RH	8
Figure 6, Viscosity of AAD and AH-55 as a function of shear rate.....	9
Figure 7, Pin data and high speed videography of detonating AH-55 column.....	9
Figure 8, structure of PrNQ	10
Figure 9, PAX-PrNQ LSGT at left, exudation test results (right)	11
Figure 10, Ingredient structures in LH-55	12
Figure 11, Structure of diaminofurazan	13
Figure 12, detonation velocity based on pin timing (left) and shot construction (right). .	14

List of Acronyms

AOOA	3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine
ACOF	3-Amino-4-carboximidamidofurazan
ARDEC	Army Development, Research and Engineering Center, Picatinny NJ
AN	Ammonium Nitrate
ANU	Ammonium Nitrate + Urea
BNFF	Bis(NitroFurazanyl)Furoxan
Comp B	Composition B
CONUS	Continental United States
DAAF	Diaminoazoxyfurazan
DH ₅₀	Drop Hammer 50% Probability
DSC	Differential Scanning Calorimetry
Dv	Detonation Velocity
EmimAc	Ethyl imidazolium Acetate
ERL	Impact testing as implemented at ARDEC
ESD	Electrostatic Discharge

GPa	GigaPascal
HE	High Explosive
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
IHE	Insensitive High Explosive
IR	Infrared Spectroscopy
JIMTP	Joint Insensitive Munitions Technical Program
JMP	Joint Munitions Program
Km/s	Kilometer/second
LANL	Los Alamos National Laboratory
LANS	Los Alamos National Security
LLM-201	3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine
NMR	Nuclear Magnetic Resonance
NTMT	1-N-trinitromethyl-1,2,4-triazole
OB	Oxygen Balance
P _{C-J}	C-J Pressure
PDV	Photo Doppler Velocimetry
PHC	Public Health Command
PrNQ	N-propyl-N'-nitroguanidine
QSAR	Quantitative Structure Activity Relationships
RDX	1,3,5-trinitro-1,3,5,7-triazacyclooctane
RH	Relative Humidity
TGA	Thermogravimetric Analysis
TLC	Thin Layer Chromtography
TMD	Theoretical Maximum Density
TNAZ	1,3,3-Trinitroazetadine
TNT	TriNitroToluene
UXO	Unexploded Ordinance
WWII	World War Two

Keywords

High explosive
Composition B
Eutectic
Melt casting
Detonation

Acknowledgements

The Authors would like to gratefully acknowledge the efforts of the LANL analytical team, particularly Jose Archuleta, Hongzhoa Tian, and Mary Sandstrom. We would like to thank Gabriel Avilucea, and Ken Windler for synthesis support. We would also like to thank Alan deHope and Phil Pagoria at LLNL for donating material, time, and advice.

Abstract

Objective. Composition B is a melt-castable explosive formulation incorporating TNT and RDX. Both of these components have undesirable environmental impacts from production and use. The desired outcome of this work was the selection of an explosive material to replace Comp-B that would preserve the beneficial attributes of that explosive without the negative environmental ramifications.

Technical Approach. This project combined synthesis of energetic materials, thermal testing, sensitivity testing, melt casting, and performance testing. Due to the large number of candidate energetic ingredients, the only practical path forward was to begin with compatibility testing at small scale, down-select for sensitivity testing, and then further down-select for performance testing. Thermal stability of mixtures was initially measured using DSC or TGA, however in the interest of conserving time and money a simple optical melting point apparatus was employed. Sensitivity testing at LANL involves type 12B drop hammer, BAM friction testing, and ESD testing. ARDEC additionally performed gap testing on selected materials. Performance measurements focused on detonation velocity, critical diameter, and detonation pressure.

Results. During this project we investigated a number of energetic materials both old and new and determined that most of them were unsuitable due to safety or sensitivity reasons. Unsuccessful coformulants include TNAZ and BNFF for volatility reasons, and DAAF due to thermal compatibility issues. The powerful explosive HMX became a focus of the work in later stages as it conferred excellent power while being commonly available in well-regulated particle size lots and is chemically compatible in the melt with many coformulants. Ultimately three preferred formulations emerged from this work: a formulation tested on large scale by ARDEC involving PrNQ and HMX; a formulation tested at ARDEC and LANL using a nitrate salt eutectic and HMX; a formulation tested at LANL using LLM-201 and HMX.

Conclusions. Several candidate materials were identified by this project however cost to produce is a significant barrier. HSAAP manufactures approximately 9 million pounds of RDX per year compared to only 1 million pounds of HMX at roughly twice the cost per pound. Switching from RDX to HMX would benefit the environment and performance of the munition but at cost and with a limit to scale. The explosive formulations manufactured on the highest scale are actually mining explosives such as ammonium nitrate based blasting media and these do not have adequate power for military use. Existing military production capacity in the United States is insufficient, with contracts going to Polish producers of TNT, and the variety of HE available from CONUS sources places a severe limitation on the production of new formulations.

Objective

The objective of this project was to replace Comp-B with a melt-castable explosive formulation benefitting from new materials made available to the explosive chemist over the last 50 years. One molecule studied intensely was DAAF which has a green synthesis, good insensitivity to handling insults, and respectable performance. Melt-castable

materials were chosen on the basis of melting point, benign environmental properties, long-term sustainability, acceptable storage stability, and detonation performance.

Background

Melt casting has been an essential method for the filling of naval and other artillery shells for well over a century. Early nitroaromatic explosives like picric acid and TNT were highly amenable to the technique of melt-casting, which has the benefit of rapid production times in high volumes of shells. Once the infrastructure and expertise was developed, continuation of melt-casting for the bulk of shell production was an obvious decision. Melt casting has drawbacks, as mentioned below, but other forms of shell-filling including pressing and HE machining, or extrusion and cast-cure, have their own difficulties and drawbacks. Nevertheless, HE parts which require high-tolerance tend to be pressed and machined, which the Air Force uses extrusion and cast-cure for both rocket motors and large main-charges. In short, although other methods are feasible, melt-casting remains a key method for producing shells of moderate internal conformance in high volume.



Figure 1, Melt casting from a kettle into heated cylinders.

Limitations of Melt-casting

The most significant drawback of the melt cast process is the attention to detail required to successfully cast a solid form. This requires careful temperature monitoring and control for the elimination of voids. Obviously control of temperature is also critical to HE safety as severely overheating the explosive being cast will cause chemical degradation, fire, or an even more violent reaction. For this reason steam heat is the preferred method of applying heat at scale since the temperature of the material being heated cannot severely exceed 100 °C. Careful cooling is equally important in melt casting as premature cooling will lead to solidification and void formation. Voids are detrimental for two reasons; they rob energy from the component at the same time that the voids sensitize the material. At ARDEC, special racks apply steam heat in a controlled manner to the piece being casted affording the proper heat-flow and cooling geometry to make properly casted parts.

One of the earliest melt-cast HE was picric acid. Both British and American naval shells were loaded with molten picric acid and then allowed to solidify. Although it was known

that picric acid was incompatible with steel, leading to the formation of the primary high explosive iron picrate, it was believed that a coating of wax could insulate the material from the container. Numerous detonations proved that thermal cycling melted the wax, exposing the metal to the corrosive explosive. These incidents were illustrative of the importance of assessing material compatibility. Moving from picric acid to the TNT eliminated the chemical incompatibility but reduced the power of the fill. To compensate for the reduction in brisance more powerful explosive components were added to the TNT forming a melt-castable flux.

Viscosity imposes another important limitation on melt casting. Because the liquid HE must flow easily into the mold body, there is an absolute limitation to how viscous the material can be in the melt. Most melt-cast formulations are a combination of a liquid phase and a solid phase, constituting a flux of the solid in the liquid. Particle size of the solid must be chosen such that the material being cast can flow into the mold in a conformal manner but maintain suspension such that the part maintains a uniform composition throughout. For solid HE which are prepared to Mil Spec in a variety of particle sizes the appropriate mixture of particle sizes can be chosen to modify the viscosity of the flux. For this reason RDX and HMX, as well as other common military HE which have defined grades, are highly amenable to melt-cast formulation.



Figure 2, Melt casting a high-viscosity mixture (left) and low viscosity mixture (right).

Comp B. an Excellent Melt Castable explosive

It should be apparent from the foregoing discussion that a good melt castable explosive formulation needs to accomplish several important characteristics:

- High thermal stability in the melt
- Good chemical stability with the mold
- Good viscosity in the melt
- Proper suspension qualities for uniform part formation
- Adequate power for the desired performance effects
- Economical preparation of components
- Adequately high melting point to avoid accidental environmental melting

At the time of WWII when materials needed to be transformed into ordnance expediently, melt casting with TNT-based formulations became an immediate necessity. TNT naturally lends itself to utilization as a melt-cast energetic. Unlike its predecessor picric acid, TNT does not corrode metal to make dangerous salts; it has a high enough melting point to stay solidified even in adversely hot environments. TNT also has a low viscosity in the melt; therefore addition of solids with proper particle size could reach 75% by mass and still result in a flowable mixture.

Several formulations of TNT and RDX were made, tested and utilized extensively. Composition B refers to a mixture of 60% RDX and 40% TNT where the RDX is Class 3. [1] A similar formulation added wax to the TNT, and is sometimes referred to as Composition B2. According to the ARDEC Encyclopedia of Explosives and Related Items this was done to improve wetting of the RDX and help maintain suspension. As an inert component the wax reduces both the density and energy density of the formulation, but only slightly. The accepted performance data and characteristics of Comp B with and without wax are given in table 1.

Materials and Methods

General

The synthesis of energetic materials followed normal wet-chemistry techniques employing reagents from Fisher Scientific and Aldrich chemical company as they were available. Proton and Carbon NMR were acquired on a Bruker Avance 400 console using a broad-band multinuclear probe and analyzed using Topspin© software. FTIR spectra were acquired on a Nicolet iQ system using Omnic© software. Melting point determination was accomplished using a Stanford research EZmelt system. Sensitivity testing were performed as follows: the Type 12B drop hammer employs a 2.5 kg weight dropped from up to 320 cm with an average impact value determined using a Neyer D-optimal statistical method; BAM friction testing is performed using the standard method of the Bureau of Mines; ESD testing is performed using an ABL apparatus operating at 10,000 V. Impact testing conducted at ARDEC using the ERL impactor is functionally equivalent to the Type 12B test,

Performance measurements

Performance measurements made using rate stick/plate dent methodology with piezo pins normal to the surface of the stick to measure velocity through time between failure. Detonation pressure was measured by assessing dent depth in a calibrated piece of steel compared to explosives of known performance. In certain cases rate sticks were also analyzed by use of high-speed camera to record the progress of the detonation front over time.

Synthesis of Nitrate Salts

Nitrate salts of energetic heterocycles were made by stirring 10 mmol of the appropriate heterocycle in 100 ml of water at room temperature while adding 10 mmol of 2M nitric acid dropwise over 5 minutes. The reaction mixture was concentrated on a rotovaporator until a precipitate formed. After cooling the aqueous mixture was filtered using a Buchner apparatus and the solid dried in air.

Synthesis of LLM-201

Specific conditions and quantities may be found in appendix A. In general, the starting material 3-Amino-4-carboximidofurazan is condensed with cyanogen bromide in ethanol and the product is collected through filtration to give AOOA. The product is oxidized with hydrogen peroxide in sulfuric acid to yield LLM-201.

Results and Discussion

Table 1, Comparison of melt-cast formulations

	Comp B	Comp B (wax)	201/HMX	AAD/HMX	PAX-PrNQ	PDX
Dv	7900	7820	8250	7997	7760	7600
Pcj	33	33	29	35		
Critical dia.	<0.5	<0.5	<0.5	0.5	0.5	1
Density	1.71	1.68	1.75	1.7	1.65	1.65
Dh 50	33.9	45	50	37.4	>100	195.4
BAM	360	360	270	258	>360	>360
ESD	0.125	0.125	0.125	0.125	0.063	0.125
Exudation	Slight	Slight	Unk	Slight	Slight	UNK
Castability	Easily poured	Easily poured	Easily poured	Easily poured	Difficult	Difficult
Env. Impact	Severe	Severe	Unk	Moderate	Unk	Poor

Rationale for exclusion and down-selection

Early in this project it became apparent why so many compounds which were promising on paper were disused in practice. Adding energy to an energetic system is inherently dangerous for reasons other than the hazard of explosion, these include:

- Chemical reaction of the materials in the melt
- Thermal degradation at low temperature
- Sublimation and condensation of explosive material on equipment and exposure to workers

Chemical reaction of the materials in the melt

In performing scoping reactions with DAAF against low-melting energetics it was found that DAAF has chemical compatibility issues with most chemical motifs in the melt. These reactions result in bubbling, off-gassing, and in many cases expulsion of material. By comparison, the thermal degradation of DAAF as a single component occurs at 250 °C in the form of a rapid transformation to gaseous products. Even with nitroarenes like TNT, which are generally thought of as being quite chemically inert,

DAAF suffers from significant incompatibility. Thermal incompatibility is usually measured, either by DSC or an alternate thermal measurement, as a reduction in the decomposition onset compared to the pure materials. DAAF is by no means unique, in fact, RDX and TNT show a minor material incompatibility, although the reduction in thermal onset is small, ~ 20 °C.

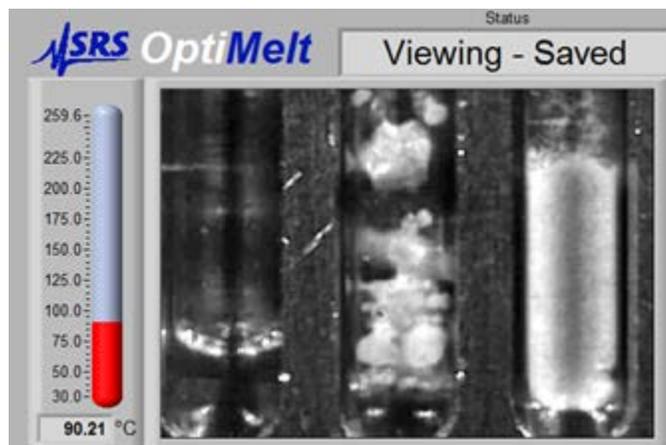


Figure 3, Melting of PDX (center) compared to the binder system (left) and DAAF (right).

DAAF was found to be compatible with HMX as well as a waxed-based low melt system developed by ARDEC. This composition, PDX, was scaled up and tested and will be discussed in more detail in a previous section.

Of the materials we focused on in this study ATAN was the other component that had extreme thermal incompatibility issues, effectively eliminating it from consideration as the eutectic by itself was inadequate in performance and critical diameter to be utilized.

Critical diameter was also a crucial problem in exploiting TKX-50. Although this material is beneficial from the standpoint of explosive performance and environmental impact the critical diameter was assessed by ARDEC at over an inch. Consequently filing small charges such as a hand-grenade would result in degraded performance at best and complete failure at worst.

Thermal degradation of materials

The trinitromethyl triazoles (NTMTs) were greeted with enthusiasm when they were first reported due to useful melting points, excellent oxygen balance, and high densities. Unfortunately single-component thermal stabilities below 150 °C make them unusable as melt-castable materials since the safe operating window for casting these materials is below the accepted operation limit of 50 °C. In general you want the onset of decomposition for a mixture to be cast to be at least 50 °C above your maximum casting temperature, otherwise the likelihood of thermal runaway is high. In addition, thermal stability up to 150 °C is advisable to safeguard against adverse environmental conditions, such as a munition being left in the sun in a hot environment. A similar problem attends the low-melting methylene dinitramine (MEDINA).

Sublimation and condensation of explosive material

Sublimation is a particular hazard when melt casting as it can expose both equipment and personnel to chemical explosive vapor. For the worker this could be an acute health hazard as material breathed into the lungs tends to result in rapid dosing. For equipment, especially motorized equipment, explosive material can condense on moving parts causing an explosion hazard when the piece is actuated. The third issue attendant with sublimation is the difficulty in compositional accuracy when casting as the subliming material is continuously evaporating. Even in a cast piece it should be expected that a material with a high vapor pressure will migrate within the device resulting in a reliability issues and potential hazard. This has long been a problem for TNAZ – an otherwise highly energetic low-melting explosive. Attempts to reduce the volatility of TNAZ by eutectic formation with the precursor DNAZ failed and we similarly could not find a mixture to stabilize it. The same problem attends the nitrofurazan BNFF, one of the only compounds DAAF was found to be stable with in the melt.

Down-selection criteria

In order of importance, the criteria considered critical were as follows:

- 1) Safety, this includes both worker safety in formulating the material and handling the product.
- 2) Castability, realizing that the investment in existing infrastructure was pivotal new formulations must be amenable to current techniques.
- 3) Performance, in considering the history of the IMX formulations and the difficulty in creating ordnance for them equivalent performance is crucial.
- 4) Environmental impact, although no less important than any of the preceding considerations it was the most difficult for us to appraise. This includes synthesis impact and the environmental fate of the formulation.
- 5) Cost to manufacture, this includes a consideration of starting materials and the number of steps to produce.

Preferred alternative formulations and their properties

Four final candidates were considered as potential replacements for Comp B, a short description of their constituents follows.

AAD/HMX 50-50 (AH-55)

This formulation is a mixture of the nitrate salt eutectic of ammonium nitrate, aminotriazole nitrate, and diaminotriazole nitrate (AAD) with the explosive HMX. The closest literature comparator to this eutectic is probably DEMN although AAD benefits from a higher heat of formation and density. These qualities give AAD higher performance while the heterocyclic nature of the compounds also assures their thermal stability. This formulation is, by weight, 50% HMX class II, 25% Ammonium nitrate, 12.5% 3-amino-1,2,4-triazole nitrate, and 12.5% 3,5-diamino-1,2,4-triazole nitrate.

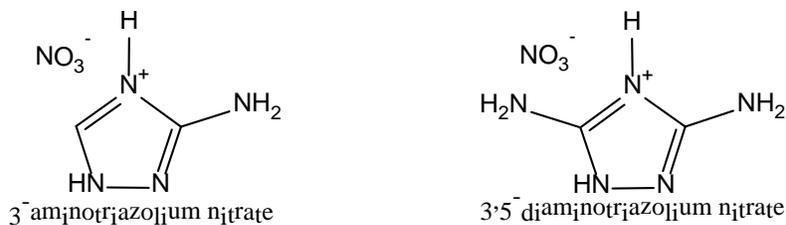


Figure 4, components of the eutectic AAD

Safety. AH-55 is slightly less sensitive to impact than Comp B while both have low sensitivity to friction and ESD. Thermally AH-55 has equivalent temperature stability and at small scale, has a type II cook-off result, outgassing and decomposing harmlessly when overheated. These qualities make AH-55 safe to handle at large scale. As three of the components of this formulation have significant water solubility it should be mentioned that from an EOD standpoint having a formulation that can be made safe by application of water has some advantages. Water can also be a detriment to this formulation as nitrate salts tend to absorb water. In the case of AAD this sorption was studied by ARDEC and determined to be an issue only above a relative humidity of 50%. Proper sealing and storage should be able to mitigate water absorption, however under the most demanding applications during due to water intrusion is a potentiality.

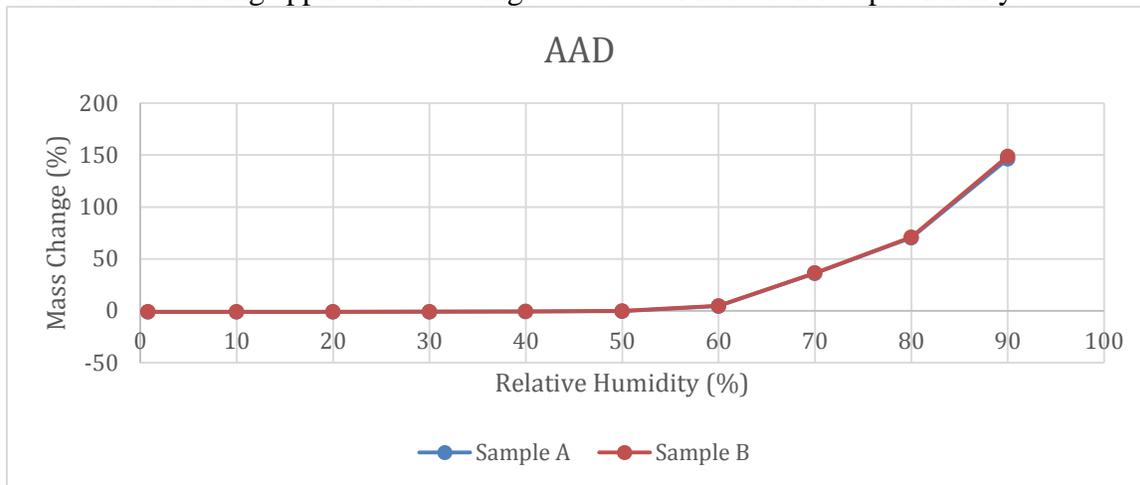


Figure 5, water absorption of AAD as a function of RH

Castability. Viscosity measurements conducted at ARDEC indicate that AAD is a shear thinning fluid with a viscosity similar to that of TNT in the melt. Qualitatively we found pouring molten AH-55 into cylinders was no more difficult than Comp B. AAD does require a higher temperature to melt than TNT, however, ARDEC was still able to melt and cast using standard equipment. ARDEC performed viscometry on AAD and AH-55 that showed this mixture is a shear thinning fluid.

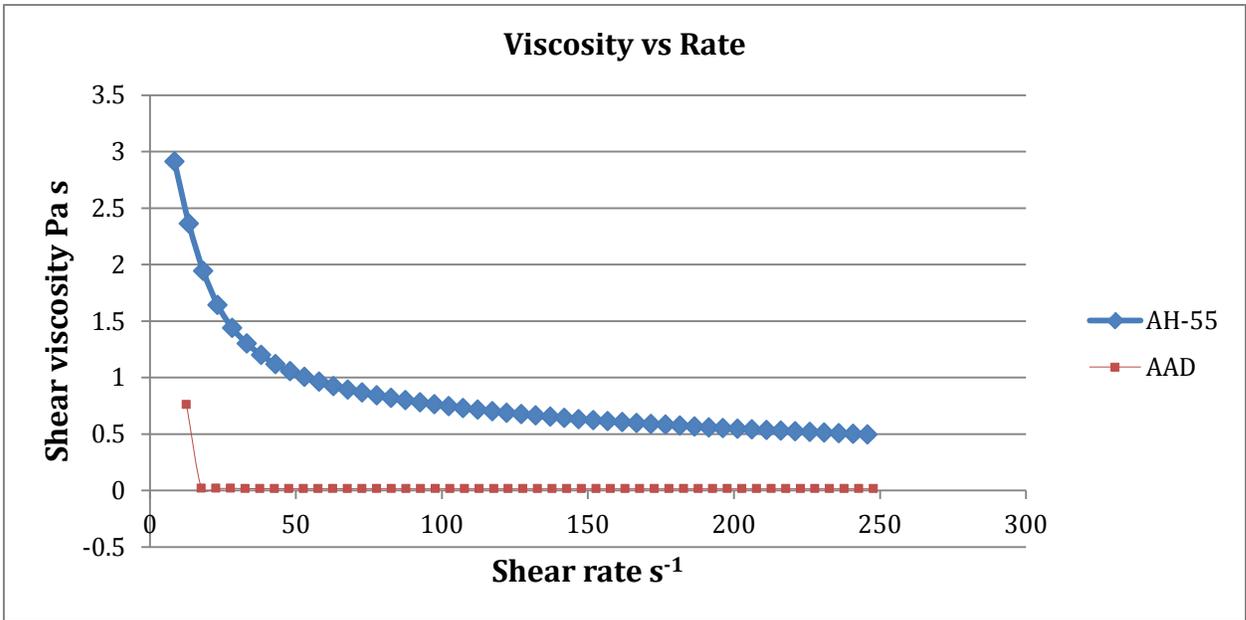


Figure 6, Viscosity of AAD and AH-55 as a function of shear rate

Data from cylindrical shots shows no evidence of settling of the material, a phenomenon which should manifest as an increase in velocity as the shockwave moves toward the bottom of the shot.

Performance. AH-55 is a very close mimic to Comp B with a density 1% higher and a detonation velocity 1.2% faster than Comp B. For the purposes of making fragment-generating ordnance, this formulation should be nearly identical in performance but would have to be validated through system-level testing.

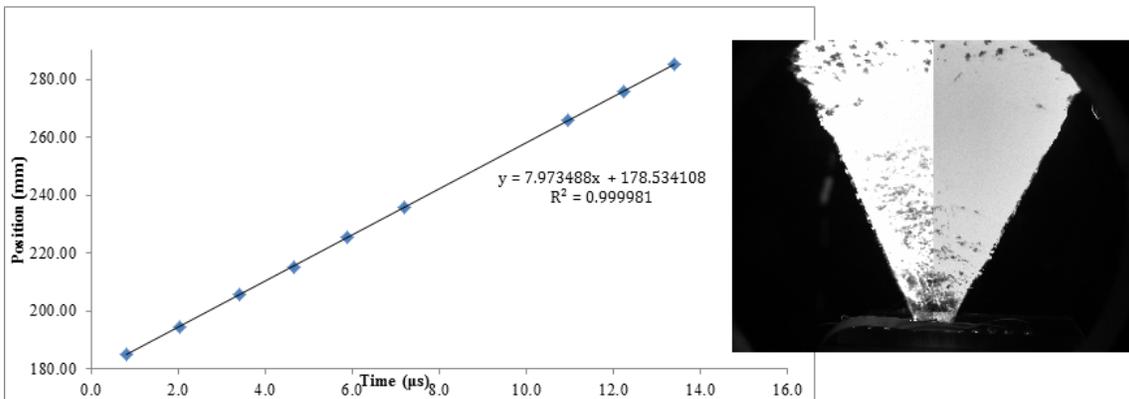


Figure 7, Pin data and high speed videography of detonating AH-55 column

characterized in terms of environmental effect. [2] Although HMX suffers from some of the same drawbacks as its smaller congener RDX, low water solubility and significantly different physical properties have thus far made it less problematic. The second major component, ammonium nitrate, is a common fertilizer and is well understood. As a salt 3-amino-1,2,4-triazole nitrate is not well studied but in the environment it is expected to

return to 3-amino-1,2,4-triazole. This compound is a common general herbicide that interrupts the photosynthetic pathway of green plants, [3] the impact of this compound on aquatic species is still being elucidated. [4] The final minor component 3,5-diamino-1,2,4-triazole nitrate is the salt of a disused anti-cancer drug and has little impact on mammals although the effect on microorganisms appears to be poorly studied. [5]

Cost to manufacture. Cost to manufacture for AAD is expected to be low. HMX and AN are already fully commercialized. The precursors to the nitrate salts are readily available. Although 3,5-diamino-1,2,4-triazole is somewhat expensive currently this is most likely because it is not manufactured at scale for any other purpose. Reactions used to make the nitrate salts are trivial and can be accomplished at any scale by simple neutralization of dilute nitric acid with the heterocyclic amine.

PAX-PrNQ

Utilizing a design of experiments which capitalized on their extensive knowledge in melt-casting ARDEC developed a custom formulation using propyl nitroguanidine (PrNQ) as the low-melt component with HMX as the dominant HE. This formulation has a relatively high solids loading to overcome the low density of PrNQ. As a result of both poor oxygen balance and density PrNQ is not considered an explosive. The formulation is 65% HMX (10% FEM), 29% PrNQ, 4% Aluminum powder, 1.8 % carnauba wax, 0.2% Tween 80.

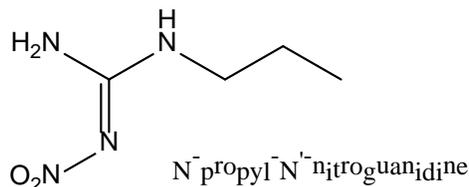


Figure 8, structure of PrNQ

Safety. As a single component PrNQ is compatible with a variety of HE including HMX, RDX, TKX-50, and NTO. Because of the outstanding safety qualities of PrNQ, the mixture of this material with HMX is also quite safe to handle. As can be seen from the table below PrNQ is less sensitive than TNT to impact and much less sensitive than Comp B formulation. PAX-PrNQ performed well in the LSGT test at 175 cards compared to an average of 210 for Comp. B.

Table 2, Comparative sensitivity of low melt components and formulations

	Comp B	PrNQ	PAX-PrNQ	TNT
ERL impact	33.9	>100	>100	88.3
BAM	300	>360	>360	220
ESD	0.25	0.25	0.063	0.25

The thermal degradation of this material was not explored however vacuum stability measurements with various materials were generally promising.

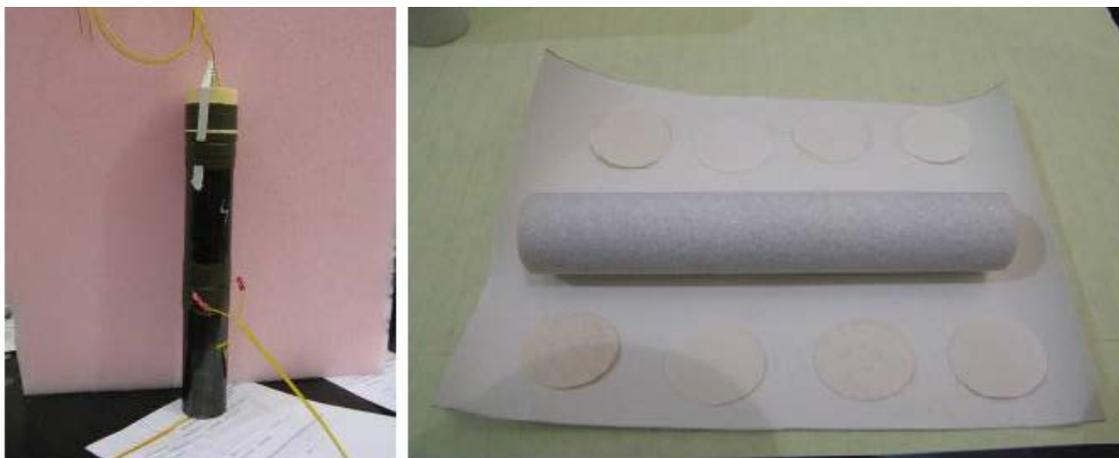


Figure 9, PAX-PrNQ LSGT at left, exudation test results (right)

Castability. ARDEC performed a litany of tests on PrNQ in evaluation of the material as a melt cast component. Of these tests exudation and irreversible growth were two important concerns. The growth test is intended to determine if temperature cycling causes irreversible dimensional changes which might lead to instabilities in the charge or its casing. PrNQ exhibits fairly large increase in volume after temperature cycling but it should be noted that it is only about 65% of DNAN – the low melting component in IMX formulations.

Table 3, Irreversible growth testing

Vol change	Comp B	TNT	Rec. TNT	PrNQ
Ave %	8.46	3.10	3.52	10.63

Despite the fact that the irreversible growth was above the 1% advisory limit ARDEC is confident that PrNQ formulations are amenable to casting into munitions since a similar problem was successfully overcome with the IMX formulations.

Subsequent to irreversible growth ARDEC went on to measure Exudation in PrNQ based formulations. The samples were wrapped with filter paper and placed inside the aluminum test fixtures and then placed in the test chamber for thermal cycling.

Table 4, Exudation testing

Exudation	Comp B	TNT	DNAN	PrNQ
wt %	0.69	0.67	0.068	0.051

The average exudation for PrNQ based on weight loss of the cylinders was 0.051% which is significantly less than other low melt energetics.

The PAX-PrNQ formulation is significantly more viscous than Comp B but still flows adequately for loading.

Performance. PAX-PrNQ has a detonation velocity of 7.76 km/s at a density of 1.64 compared to 7.82 km/s at a density of 1.71 for Comp B (wax). This is good velocity for such a low density however detonation pressure suffers as a result being measured at only

85% of that of Comp B in the same series of tests. This indicates that due to nearly equivalent brisance the same number of fragments could be expected but they would probably be accelerated to significantly lower velocities. By comparison IMX-104 achieves only 7.38 km/s and a detonation pressure equivalent to PAX-PrNQ. Considerable redesign of cases for IMX-104 has been necessitated by its inferior shattering power and Gurney energy.

Environmental impact. All of the components of this formulation are of known environmental quality with the exception of PrNQ. Encouragingly the toxicity of NQ is low and propyl NQ should be even lower due to decreased water solubility. If possible residual funding from this study should be used to fund Microtox assays on PrNQ if they are not currently underway.

Cost to manufacture. All of the components of this formulation are manufactured on large scale with the exception of PrNQ. The reactions to make PrNQ from low-cost starting materials are facile, therefore once economies of scale are considered, the ultimate cost of this material should be low.

LLM-201/HMX 50-50 (LH-55)

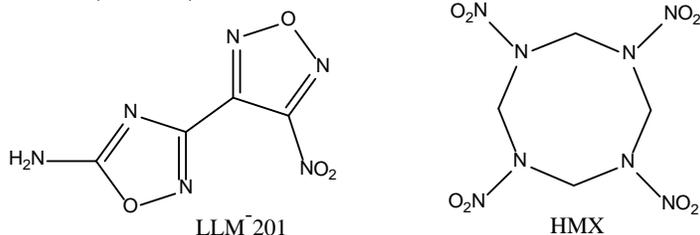


Figure 10, Ingredient structures in LH-55

LLM-201 is a low melt energetic developed at Lawrence Livermore by Phil Pagoria and coworkers. This heterocyclic amine benefits from good density, and reasonable oxygen balance and has a useable melting point. Like most low-melt components sensitivity to external stimuli is low for LLM-201 although it is expected to have a smaller critical diameter than AAD. The performance of LLM-201 by itself is not sufficient to afford a replacement for Comp B. However formulation with HMX can easily exceed Comp B in energy and explosive effect. The composition is 50% LLM-201, 50% HMX class-II.

Safety. The LH-55 formulation benefits from the low sensitivity of LLM-201 itself, consequently, even though it is more brisant the impact sensitivity is lower than AH-55 despite an equivalent amount of HMX.

Castability. LLM-201 has a low viscosity in the melt and the relatively low solids loading makes casting facile although settling may be an issue on larger charges. Due to limitations in material this formulation was cast at a maximum of 20 g.

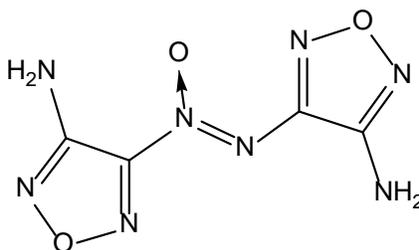
Performance. LH-55 has very high performance as a result of the intrinsic advantage of using a monomolecular low melting explosive for the molten phase. In order to achieve detonability at lower charge diameters an adequate amount of HMX is indispensable. Subsequent testing demonstrated that a formulation of 25% HMX in LLM-201 did not perform adequately achieving only 7.0 km/s. this is likely due to the 12 mm rate stick being close to the critical diameter for that mixture as subsequent tests demonstrated higher performance.

Environmental impact. The environmental fate of LLM-201 is unknown and would have to be appraised before adoption of this material could be promoted. Residual funding from this study should be used to fund Microtox assays on LLM-201 if adequate funds remain.

Cost to manufacture. The synthesis of LLM-201 proceeds from the relatively inexpensive starting material malononitrile, however, it requires six steps over four “pots” which is a significant investment of time and material. The benefit of the LLM-201 synthesis is that oxidation to the nitro compound is the final step, all previous operations can be treated as non-HE producing.

PDX

Using a mixture of liquid lecithin and carnauba wax developed at ARDEC for the formulation PAX-195 we substituted a size-comparative HE charge of HMX and DAAF. By utilizing large-particle sizes in HMX we overcame the diminutive particle sizes in DAAF. The formulation is 61% HMX, 23% DAAF, 12% wax, 4% lecithin.



Diaminoazoxyfurazan (DAAF)

Figure 11, Structure of diaminofurazan

Safety. PDX is a very safe material to handle with a high drop-height impact rating, very low sensitivity to friction, good thermal stability, and a fairly typical electric arc response. Unlike other mixtures with DAAF, PDX performed well in the vacuum stability analysis and should therefore be stable to store. In terms of comparative sensitivity measures many researchers give Drop Hammer Impact (DHI) the most credence, although this test combines impact with friction through extrusion and other insults. With a DHI value of 195.4 cm PDX is the least sensitive explosive of the four selected to those combined insults.

Castability. Because it has a high solids loading at 83% PDX flows with difficulty however it is not beyond the ability of casting methods at ARDEC. Other facilities may have greater difficulty. One benefit of high solids loading is that once the mixture reaches temperature it cools slowly, improving the quality of the final part. Exudation tests were not performed for PDX as they are expected to be similar with PAX-195 which shared the same binder system but used RDX as the crystalline explosive component.

Performance. A casting of PDX was made into a 12.9 mm rate stick with a density of 1.58-1.61 g/cc. The performance of PDX was measured using piezoelectric pins yielding a detonation velocity of 7.92 +/- 0.01 km/s.

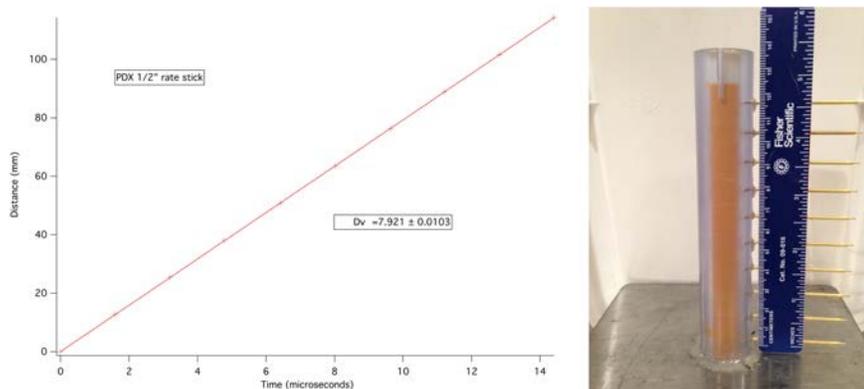


Figure 12, detonation velocity based on pin timing (left) and shot construction (right).

This value is extremely close to the historically reported velocity of Comp B however CJ pressure is hampered by the lower density. According to theory expected CJ pressure should be 25.66 Gpa. However a plate dent returned from the same experiment gave a CJ pressure of only 19.8 Gpa. We believe the experimental value is anomalously low although it is inevitable that the true value will be lower than that of Comp B with a commensurate reduction in Gurney energy and particle velocity.

Environmental impact. The environmental concerns of HMX are discussed above and it has a similar presence in PDX as it does in AH-55. The binder system in PDX is environmentally inert being composed mainly of carnauba wax and liquid lecithin, both of which are natural products. Unfortunately DAAF is implicated in high aqueous cytotoxicity having a significantly lower LC₅₀ against *V. fischeri* bacteria than RDX. [6]

Cost to manufacture. One of the benefits of DAAF is the short and efficient synthesis process used to manufacture it from the starting diamine, diaminofurazan (DAF). This process has been scaled up to good effect at NSWC-IH. The oxidation process benefits from using benign reagents and water as a solvent. Production of DAF is somewhat more problematic as the conventional scheme utilizes a pressure reactor with basic water as the medium at 150 °C. Alternate high boiling solvents can be utilized but liberating DAAF from them can be difficult. Stopped-flow methods for continuous production of DAF

have been studied by Nalas Engineering, however, the pressure reactor method is still the most effective.

Conclusion and Implications for Future Research/Implementation

The formulation AH-55 is the closest surrogate for Comp B due to overall strength in all important characteristics. Due to the fact that AH-55 has equivalent density and power to Comp B, very few modifications to the weapon systems need to be considered. From an environmental standpoint the constituents have been studied in the open literature without demonstrating significant impact. The processes used to make the components of AH-55 are either already performed at large scale, or are trivial to scale-up. The formulation has a reasonable, but still significant critical diameter, which often correlates to shock stability and the handling safety is as good as or better than Comp B. Overall, the current data suggests AH-55 is a good “drop in” replacement for Comp B.

Despite the advantages given above, in some important ways LH-55 is superior. The performance of LH-55 outstrips that of AH-55 and the handling safety is also better, a somewhat rare situation. The increased brisance and detonation pressure of the explosive could either be harnessed to increase system performance, or be reduced by reformulation with less HMX. In either case, LH-55 has more “trade space” for improving application in a device. This formulation also benefits from a lower critical diameter, although the impact on shock sensitivity is unknown. LLM-201 was brought into consideration too late in the effort to receive the toxicological attention it deserves, this should be rectified with future investment. The main drawback of LH-55 is cost to manufacture as it is unlikely that LLM-201 will ever be cost-equivalent to TNT or the other low-melting materials considered in this effort. Consequently LH-55 should be considered a “premium option” for replacing Comp B.

ARDEC invested great effort into formulations involving PrNQ and the results are impressive. The PAX-PrNQ formulation studied above is economical and practical but falls just short of Comp B in performance. While this does not eliminate that formulation from consideration it could limit the potential application to larger systems where increased scale benefits the performance. Nevertheless, many practical aspects of PrNQ such as exudation and expansion counterbalance its low density and performance, therefore it was valuable to assess and may find use after its environmental effects are more fully explored.

The least beneficial formulation which achieved performance testing was PDX. Several issues confront this formulation, including a high critical diameter, low CJ pressure and density, and potential environmental impacts. Production of DAF, the precursor to DAAF is also a difficulty which would have to be overcome to ensure uninterrupted production.

We endorse the formulations AH-55, LH-55, and PAX-PrNQ for further consideration and recommend further study of the environmental impacts of LLM-201 and PrNQ as part of that effort.

Literature Cited

- [1] B. T. Fedoroff and O. E. Sheffield, *Encyclopedia of Explosives and related items*, vol. C, Picatinny, NJ: ARDEC, 1966, pp. C477-C484.

- [2] J. Hawari, "Biodegradation of RDX and HMX," in *Biodegradation of nitroaromatic compounds and explosives*, New York, Lewis, 2000, pp. 277-298.
- [3] J. L. Hilton, P. C. Kearney and B. N. Ames, "Mode of action of the Herbicide 3-amino-1,2,4-triazole (Amitrole)," *Archives of Biochemistry and Biophysics*, vol. 112, pp. 544-547, 1965.
- [4] W. Li, J. Zha, P. A. Spear, Z. Li, L. Yang and Z. Wang, "Changes of thyroid hormone levels and related gene expression in Chinese rare minnow (*Gobiocypris rarus*) during 3-amino-1,2,4-triazole exposure and recovery," *Aquatic Toxicology*, vol. 92, pp. 50-57, 2009.
- [5] E. J. DaSilva, L. E. Henricksson and E. Henriksson, "Effects of pesticides on blue-green algae and nitrogen fixation," *Archives of Environmental Contamination*, vol. 3, no. 2, pp. 193-204, 1975.
- [6] L. R. Williams and W. S. Eck, "Toxicology assessment of dimainoazoxyfurazan (DAAF)," Aberdeen, 2013.

Appendix A

Synthesis of 3-Amino-1,2,4-triazole Nitrate

A 100 ml beaker is charged with a magnetic stir bar and 40 ml 1M nitric acid solution. 3-amino-1,2,4-triazole (3g) is added portion-wise with stirring. Cooling the mixture in ice causes a precipitate to form which is isolated by filtration and washed with ice water.

¹H NMR (D₂O): 7.94, s

¹³C NMR (D₂O): 138.60, 150.42

Synthesis of 3,5-diamino-1,2,4-triazole nitrate

A 60 ml beaker is charged with a magnetic stir bar and 27 ml 1M nitric acid solution. 3,5-diamino-1,2,4-triazole (3g) is added portion-wise with stirring. Cooling the mixture in ice causes a precipitate to form which is isolated by filtration.

¹³C NMR (D₂O): 150.38

Synthesis of LLM-201

Work Performed By:

Gabriel Avilucea, M-7 LANL

Procedure:

A 100 ml RBF is placed in an ice bath with temperature monitoring. To the flask is added 16 ml H₂SO₄ and the solvent is allowed to cool. In a dropwise fashion 8 ml H₂O₂ is added while maintaining the temperature below 20 °C. The resulting solution is allowed to equilibrate for 10 minutes after which pulverized AOOA is added slowly while keeping the temperature at 20 °C or below. When the addition is complete the temperature is increased to 15 °C and a Vigreux column is attached to the RBF. The reaction is stirred overnight.

After stirring for a minimum of 12 hours the reaction mixture is poured into 200 mL of ice water. The mixture is neutralized with sodium carbonate or bicarbonate to a pH of 4 –

7. The mixture is extracted with 3 portions of ethyl acetate in 50 ml fractions using a separatory funnel. The extract is evaporated to dryness.

¹H NMR (DMSO-d₆): 8.48, s

¹³C NMR (DMSO-d₆): 141.11, 156.62, 159.90, 172.72

Water Sorption of AAD

Work Performed By:

Explosives Research Branch

POC: Kelley Caflin

The Quantachrome Aquadyne DVS instrument is used to measure adsorption and desorption isotherms of water vapor. The weight of samples were constantly monitored and recorded as the relative humidity is automatically varied by the blending of dry carrier gas with a saturated gas stream. Information gained through use of this instrument includes: Equilibrium moisture content, hysteresis working range and hydrophobicity/phobicity.

Parameters:

Step	RH %	Chamber Temperature (°C)	Minimum Time (Min)	Maximum Time (min)	Cut off A (%/min)	Cut off B (%/min)	Minimum Flow Rate (sccm)	Maximum Flow Rate (sccm)
1	0	60	120	720	0.001	0.001	30	200
2	10	22	30	2880	0.001	0.001	30	200
3	20	22	30	2880	0.001	0.001	30	200
4	30	22	30	2880	0.001	0.001	30	200
5	40	22	30	2880	0.001	0.001	30	200
6	50	22	30	2880	0.001	0.001	30	200
7	60	22	30	2880	0.001	0.001	30	200
8	70	22	30	2880	0.001	0.001	30	200
9	80	22	30	2880	0.001	0.001	30	200
10	90	22	30	5760	0.001	0.001	30	200
11	80	22	30	5760	0.001	0.001	30	200
12	70	22	30	5760	0.001	0.001	30	200
13	60	22	30	5760	0.001	0.001	30	200
14	50	22	30	5760	0.001	0.001	30	200
15	40	22	30	5760	0.001	0.001	30	200
16	30	22	30	5760	0.001	0.001	30	200
17	20	22	30	5760	0.001	0.001	30	200
18	10	22	30	5760	0.001	0.001	30	200
19	0	22	30	5760	0.001	0.001	30	200

Viscometry of AAD, AH-55

Samples: AH-55 (50% AAD- 50% HMX); AAD

Instrument: Rotational Viscometer, Gap Size - 1.20 mm, Temperature – 135 °C

AH-55			AAD	
Shear rate(s-Å ¹)	Shear viscosity(Pa s)		Shear rate(s-Å ¹)	Shear viscosity(Pa s)
4.706	2.7165		2.7245	2.4336
8.44	3.0605		7.672	0.028525
13.38	2.334		12.605	0.39026
18.32	1.885		17.67	0.018705
23.26	1.6115		22.67	0.01722
28.2	1.424		27.67	0.017525
33.2	1.288		32.67	0.016445
38.17	1.1855		37.67	0.015585
43.11	1.105		42.68	0.015375
48.05	1.0435		47.68	0.015145
52.99	0.9908		52.68	0.01501
57.94	0.94565		57.68	0.01482
62.88	0.9071		62.68	0.0147
67.82	0.8747		67.68	0.015105
72.76	0.84715		72.715	0.01457
77.7	0.82165		77.715	0.01457
82.64	0.79925		82.715	0.01456
87.58	0.77825		87.715	0.01451
92.52	0.7601		92.715	0.01451
97.46	0.74175		97.735	0.014525
102.4	0.72475		102.8	0.01449
107.3	0.70915		107.8	0.014535
112.3	0.69405		112.8	0.01441
117.25	0.68005		117.8	0.01442
122.2	0.6668		122.8	0.01445
127.15	0.65455		127.8	0.014455
132.1	0.6427		132.8	0.01448
137.1	0.63185		137.8	0.0145
142	0.62185		142.8	0.014495
146.9	0.6114		147.8	0.014455
151.9	0.6018		152.8	0.014435
156.8	0.5933		157.8	0.01447
161.8	0.58465		162.8	0.01446
166.7	0.5763		167.8	0.01448
171.6	0.5691		172.8	0.01447
176.6	0.5622		177.8	0.0145
181.5	0.55485		182.8	0.01451
186.5	0.54785		187.8	0.01452

191.4	0.54055		192.8	0.014545
196.3	0.534		197.8	0.01454
201.3	0.52775		202.8	0.01456
206.2	0.5221		207.8	0.014575
211.2	0.5163		212.8	0.01464
216.1	0.511		217.8	0.014665
221	0.50555		222.8	0.014655
226	0.50025		227.8	0.01466
230.9	0.495		232.8	0.01465
235.9	0.49025		237.8	0.01476
240.8	0.48575		242.8	0.01465
245.8	0.48125		247.8	0.01465

LSGT on PAX-PrNQ

Density: 1.65 g/cc Shot #: 10-914

50% point = N - 1 = 1.750" = 175 cards

Shot	Tube #	Gap (in.)	Result (GO/NOGO)
1	11	1.500	GO
2	14	2.000	NO-GO
3	5	1.750	GO
4	9	1.870	NO-GO
5	19	1.820	NO-GO
6	8	1.780	NO-GO
7	10	1.760	GO
8	6	1.770	NO-GO
9	12	1.770	NO-GO
10	4	1.760	NO-GO
11	7	1.750	NO-GO
12	16	1.750	NO-GO

Irreversible Growth Test Method

Performed by: ARDEC

Sample: PrNQ

Test Description: 30 temp cycles between -65°F & 160°F, 3 hrs at each temp.

AOP-7, Edition 2, Rev.1 Method 202.01.010

Exudation Test Method

Performed by: ARDEC

Sample: PrNQ

Test Description: Cycle -65°F - 160°F, 3 hrs at each temperature.

AOP-7, 202.01.010; 30, "Exudation".