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**SERDP PP-1363: “Environmentally Friendly
Advanced Gun Propellants”
Final Technical Report**

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2 PROJECT BACKGROUND

Current medium caliber ammunition employs environmentally unfriendly materials that make safe disposal of propellants difficult. In the next 5 years, medium caliber munitions will require 7,700 lb per year of diphenylamine (DPA) and 2,000 lb per year of Barium Nitrate. Statement of Need, PPSON-03-08, requested proposals to reduce or eliminate environmentally unfriendly materials (specifically diphenylamine and barium nitrate) used in medium caliber propellants. The energetic thermoplastic elastomer (ETPE) based propellants investigated in this project would be excellent replacement candidates, since they do not require oxidizing agents such as barium nitrate nor do they require stabilizing additives such as DPA.

3 OBJECTIVE

The primary objective of this effort is to identify a suitable replacement for medium caliber ammunition propellants that is environmentally more acceptable, has good safety properties, provides an increased level of performance, and maintains a reasonably low cost. This program is designed to develop an ETPE based gun propellant that meets these criteria. This program will provide three deliverables: first, the manufacture of a down selected ETPE based propellant formulation and the manufacture of twelve rounds of each 25 mm and 30 mm ammunition employing this ETPE based propellant; second, test data: 25 mm gun firing performance in reference to M-793 ammunition and 30 mm gun firing performance in reference to GAU8A ammunition; and third, reports documenting refinement and analysis of two ETPE based gun propellants.

4 BENEFIT

ETPE propellants offer potential advantages over typical nitrocellulose (NC) based propellants in that they may be manufactured into advanced geometries, do not have plasticizer migration issues, are immune to moisture problems, and may be warmed and re-extruded into new geometries. ETPE propellants may be recycled, minimizing propellant waste. Demilitarization work on ETPE propellants has suggested that propellant ingredients are largely recovered. ETPE based propellants do not require

oxidizing agents (Barium Nitrate) or stabilizing additives (DPA). Success of ETPE propellants from 25 mm and 30 mm applications can result in transfer of this technology to other medium caliber systems with minimal modification. Two common medium caliber systems are the M242, 25 mm “Bushmaster” chain gun used in the Bradley fighting vehicle and the 30 mm, GAU-8/A Gatling gun used in the A-10 Thunderbolt.

5 TECHNICAL APPROACH

5.1 ETPE introduction.

BAMO-AMMO and BAMO-GAP are ETPEs investigated for use in gun propellants.^{1,2} BAMO-AMMO contains hard poly (3,3-bisazidomethyloxetane) segments linked with soft poly (3-azidomethyl-3-methyloxetane) segments, while BAMO-GAP contains BAMO segments linked with soft (glycidyl azide polymer) segments. Figure 1 illustrates the chemical structure of BAMO-AMMO. The properties of ETPEs can be modified by varying the ratio of hard to soft segments within the polymer. BAMO-AMMO (25% BAMO), lot # 598-98-069 and BAMO-GAP (25% BAMO), lot # 591-03-137 were the ETPEs used in this investigation.

Advantages of ETPE gun propellants were discussed in the early 1980’s. Early calculations indicated ETPE propellants had performance advantages compared to NC propellants. Feasibility studies were performed in coordination with the Army Research Lab (ARL) and others. Recent efforts have demonstrated ETPE propellants on a larger scale. More than 5,000 lbs of ETPEs have been manufactured by ATK Thiokol, Inc since 1998. The research and development of new ETPEs is an on going process at ATK Thiokol.

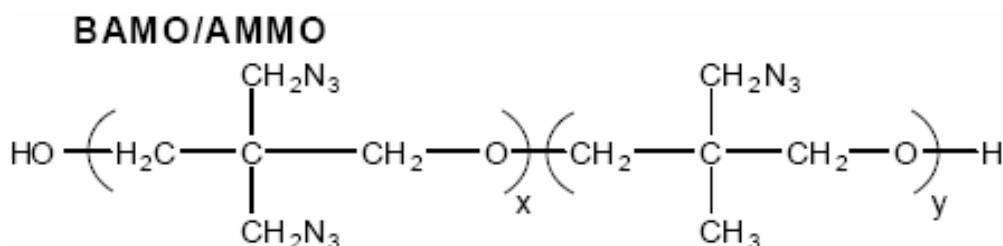


Figure 1: Chemical structure of the energetic thermoplastic elastomer, BAMO-AMMO.

5.2 Experimental approach.

This program was organized into three tasks. Task 1 was to establish a grain design that was predicted to meet or exceed the required ballistic performance. Task 1 also involved a preliminary ETPE toxicology study. Task 2 was focused on propellant formulation tailoring on the quarter-pint (80 g) and one-pint (275 g) scales. Task 3 involved the down-selected propellant manufacture, delivery, and gun testing.

6 PROJECT ACCOMPLISHMENTS

6.1 Task 1: Grain Design.

The interior gun ballistics calculations were performed using the LPGB computer code.³ This program was developed to provide an integrated calculational method for performing gun interior ballistic performance comparisons and optimizations on gun systems using co-layered propellants, but can also be used to analyze the ballistics of deterred and standard propellant geometries. Within LPGB the industry standard BLAKE thermochemistry code and IBHVG2 gun interior ballistics code are imbedded and integrated with a gun database and with iteration, optimization, and graphics modules. A separate charge increments geometry model is used along with a charge dimensioning methodology developed specifically for co-layered propellants. This PC based program is run via a Windows GUI. To develop performance predictions for the 25 and 30 mm systems, optimizing simulations were run given pressure targets less than the nominal requirements and a fixed charge mass corresponding to loading densities of 0.81 and 0.85 g/cc for the 30 mm and 25 mm guns, respectively. A 100% burn fraction was required and the optimization goal was muzzle velocities greater than the nominal specification.

As seen in **Table I**, both TGD propellant candidates are predicted to meet the ballistic requirements of 25 mm and 30 mm ammunition. Calculated TGD-043 was composed of 70.75% RDX, 14.625% BAMO-AMMO, 14.625% BAMO-GAP. Calculated TGD-044 was composed of 75% RDX, 25% BAMO-AMMO. The RP propellants are primarily composed of nitrocellulose. The TGD propellants would offer a potential 22 % reduction in propellant for 25 mm and a potential 16 % reduction in propellant for 30 mm.

Table I: Calculated ballistic performance of TGD-043 and TGD-044.

Propellant:	RP-36	RP-1315	TGD-043	TGD-044
Caliber (mm)	25	30	25 / 30	25 / 30
Density (g/cc)	1.5871	1.6290	1.5920	1.5901
Impetus (J/g)	926	999	1177	1175
Flame Temperature (°K)	2506	2888	2800	2800
Ballistic Energy (J/g)	3502	4067	4259	4268
25 mm Charge (g)	98.5		77	77
30 mm Charge (g)		145	122	122

As shown in **Table II**, both TGD propellants are predicted to produce maximum pressures and muzzle velocities within the criteria set by military specifications MIL-C-71140 (25 mm) and MIL-P-3984J (30 mm).

Table II: Calculated maximum pressure and muzzle velocity for TGD-043 and TGD-044.

Caliber (mm)		Max Press. (MPa)	Muzzle Vel. (m/s)
25	MIL-C-71140	< 402	1075 - 1125
25	TGD-043	316	1100
25	TGD-044	312	1100
30	MIL-P-3984J	< 423	1008 - 1032
30	TGD-043	377	1020
30	TGD-044	373	1020

Extensive calculations of were required to select a propellant grain that was predicted to meet or exceed ballistic performance, represented a realistic processing format, and could be loaded into the ammo case. The initial approach was to explore a single perforation, cylinder grain similar to the medium caliber propellants currently fielded. Single perf grains have advantages in that they are relatively easy to manufacture and are easy to load quickly into the ammunition case. Calculations of single perf grains were based on a non-deterred system because organic deterrents for ETPE-based propellants have not been established at this time. The development of a deterrent specific for ETPEs was beyond the scope of time and funding allocated for this SEED effort.

Calculations demonstrated that ballistic performance would not be achievable with a (non-deterred) single perf, cylinder grain in the 30 mm. The calculated single perf, cylinder grains for the 25 mm were approaching the limits of realistic extrusion geometries and only marginally supported the required performance. In addition, 7 perf, cylinder grains and 0.3-inch by 0.3-inch square grains were calculated, but neither was predicted to meet ballistic performance.

Since calculations suggested that a single perf grain would not be practical without an established deterrent, a rolled sheet grain was then investigated. The rolled sheet was calculated to yield an acceptable performance. This type of grain had an advantage of easy manufacture and handling. Sheet grains of the required geometries were manufactured. The ETPE propellant surface is slightly tacky and the grain needed to be rolled tightly to fit through the opening of the ammo case. Unfortunately, the rolled-sheet

remained tightly coiled after loading into ammo case. The tight coil would greatly reduce the available surface area for flame spread and reduce ballistic performance.

The focus at this point in the investigation was turned to the development of a deterred system accomplished via a co-layering technique. A co-layered ribbon grain composed of a slower burning outer layer and a fast burning inner layer was then calculated. This grain provided a deterred system and is predicted by IBHVG2 to meet or exceed ballistic requirements for both 25 mm and 30 mm. Though the calculated grain thickness for this system was very thin, it was not outside of the previous processing experience with ETPE based propellants. Co-layered ribbons were manufactured in the desired geometries, but their manufacture was much more labor intensive than would have been required for a single perf, cylinder grain or a rolled-sheet grain.

6.1.1 Single perforation cylinder grain.

Table III: Single perf cylinder grain calculations.

TGD-	Cal. (mm)	Geometry	O.D. (in)	Perf Diam. (in)	Length (in)	Web (in)	Muz. Vel. (m/s)
43	25	sing, perf	0.085	0.043	0.255	0.021	1100
43	30	sing, perf	0.110	0.054	0.330	0.028	993
44	25	sing, perf	0.060	0.029	0.180	0.016	1101
44	30	sing, perf	0.080	0.040	0.240	0.020	995

The required muzzle velocities are 1075 – 1125 m/s for 25 mm and 1008 – 1032 m/s for 30 mm rounds. As shown in **Table III**, the optimized, predicted muzzle velocity for a non-deterred single perf grain in the 25 mm round was in the middle of the velocity range required by military specification. Actual muzzle velocities may be lower than predicted. For the predicted, 25 mm grains, the perforation diameter was about 50% of the outer diameter of the grain. The optimized, predicted muzzle velocity for a non-deterred single perf grain in the 30 mm round was clearly lower than required.

6.1.2 Rolled sheet grain.

Table IV: Rolled sheet grain calculations.

TGD	Caliber (mm)	Geometry	Length (in)	Diam. (in)	Thickness (in)	Grain Mass (g)	Muzzle Velocity (m/s)
43	25	Rolled Sheet	50.28	4.00	0.013	68.2	1094
43	30	Rolled Sheet	46.98	5.00	0.020	122.6	1012
44	25	Rolled Sheet	51.57	4.00	0.013	69.9	1102
44	30	Rolled Sheet	48.05	5.00	0.020	125.2	1015

As shown in **Table IV**, the optimized, predicted muzzle velocities for the rolled sheets were within the ranges required for 25 mm and 30 mm. As illustrated in Figures 2 – 6, sheet grains were manufactured and rolled into a tight coil to fit through the ammo case. Once inside the case, the sheet would not unroll due to the tackiness of the propellant and the large surface area that was in contact. To ensure adequate flame spread, the sheet would need to uniformly uncoil in the case. Once inside the ammo case, manipulation (uncoiling) of the grain was not possible, thereby limiting the utility of this approach.



Figure 2: TGD-044 sheet grain shown flat.



Figure 3: TGD-043 rolled sheet grain for 25 mm.



Figure 4: TGD-043 rolled sheet grain in 25 mm case.

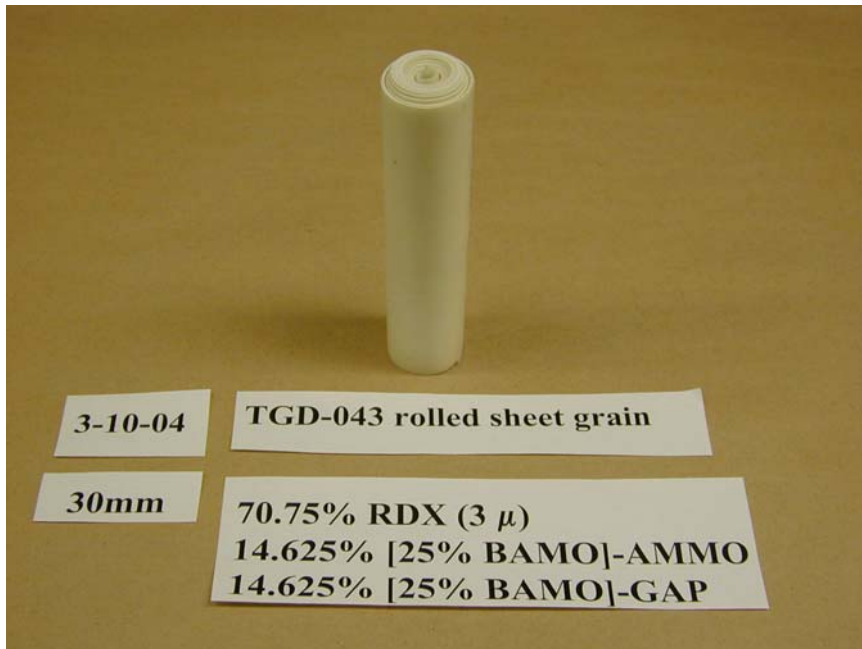


Figure 5: TGD-043 rolled sheet grain for 30 mm.

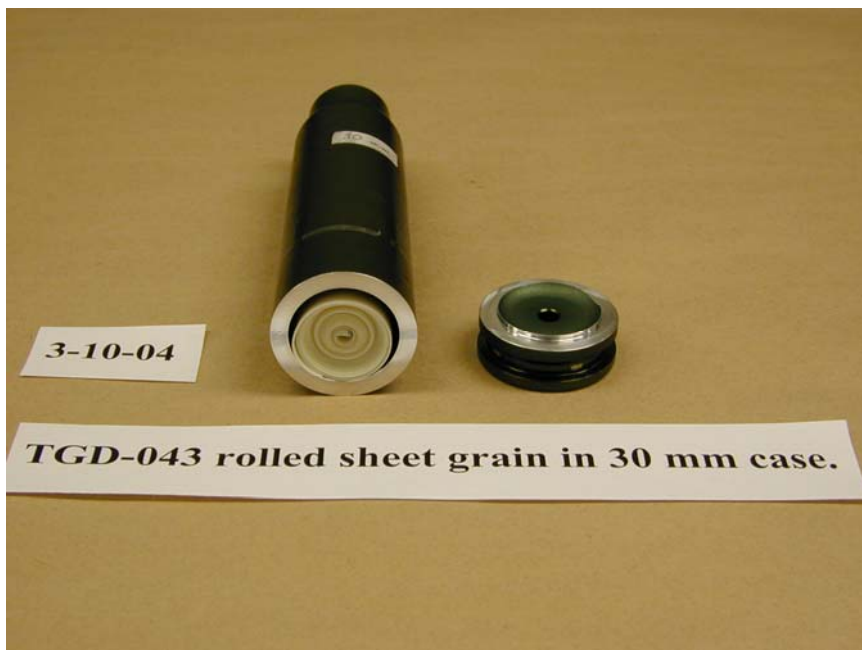


Figure 6: TGD-043 rolled sheet grain in 30 mm case.

6.1.3 Co-layered ribbon grain.

As shown in **Table V**, IBHVG2 calculations were run to establish the optimum grain geometry for a co-layered, deterrent ribbon. The deterrent is achieved in these grains by having a slower burning outer layer on both sides of the ribbon. The loading of the co-layered ribbons into the ammunition cases is illustrated in Figures 11 – 14. The loading of the cases was straight forward, but time consuming once greater than 80% of the charge had been loaded into the case. In lab trials, loading the ammo case required roughly 20 to 30 minutes per round.

Table V: Co-layered ribbon grain calculations.

TGD.	Cal. (mm)	Grain	Width (in)	length (in)	Inner Thickness (in)	Outer Thickness (in)	Total Mass (g)	Muzzle Velocity (m/s)
43	25	co-layered ribbon	0.191	3.5	0.013	0.004	77	1100
43	30	co-layered ribbon	0.191	4.6	0.015	0.005	122	1020
44	25	co-layered ribbon	0.191	3.5	0.012	0.004	77	1100
44	30	co-layered ribbon	0.191	4.6	0.014	0.005	122	1020



Figure 7: TGD-043 co-layered ribbon grains.

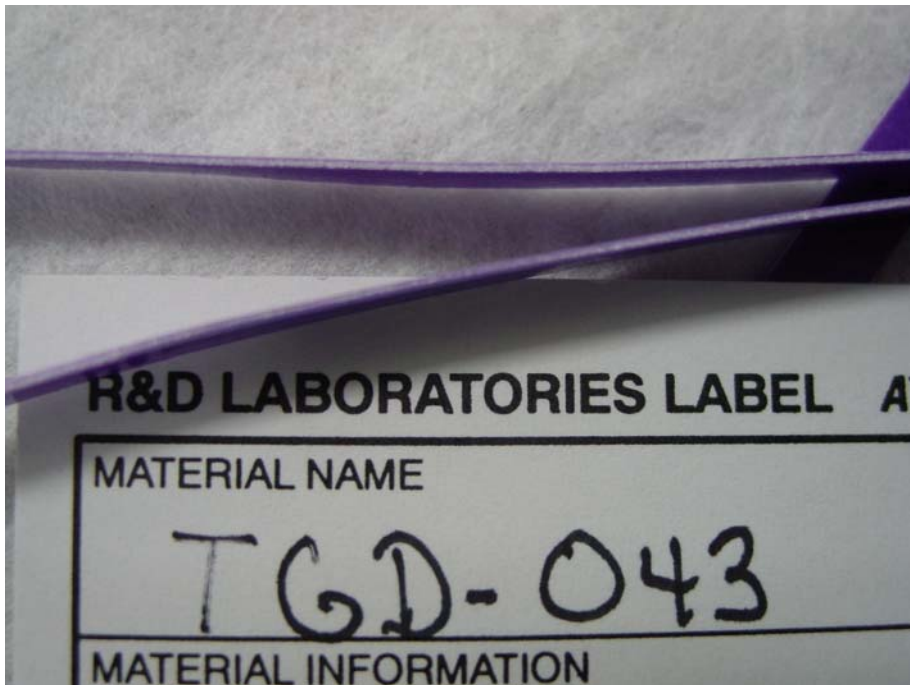


Figure 8: TGD-043 co-layered ribbons, side view.



Figure 9: TGD-044 co-layered ribbon grains.

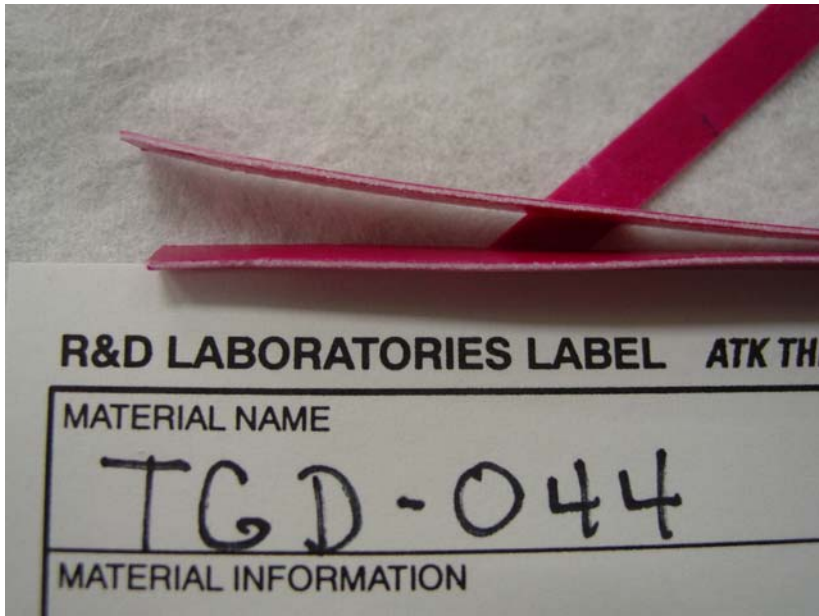


Figure 10: TGD-044 co-layered ribbons, side view.



Figure 11: TGD-044 co-layered ribbon grains in 25 mm case, breech end.



Figure 12: TGD-044 co-layered ribbon grains in 25 mm case, projectile end.

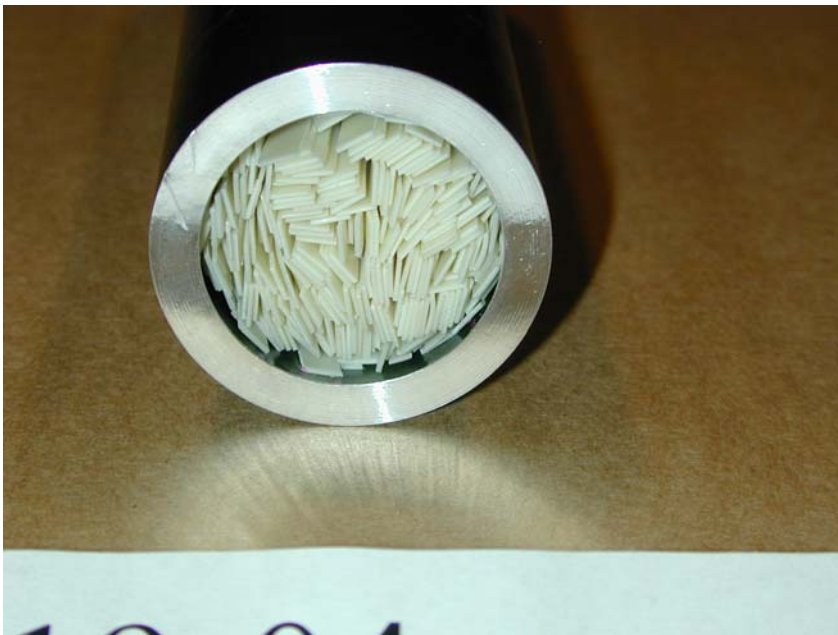


Figure 13: TGD-043 ribbon grains in 30 mm case, breech end.



Figure 14: TGD-043 ribbon grains in 30 mm case, projectile end.

6.2 Task 1: ETPE Toxicology Study

Nelson Laboratories of Salt Lake City conducted a toxicology study on the BAMO-GAP (25% BAMO) and BAMO-AMMO (25% BAMO) ETPEs. NAMSA, Inc. of Irvine, CA is a subcontractor for Nelson Labs. The toxicology study included 3 tests: Cytotoxicity – Agar Overlay (USP), Irritation – Primary skin irritation (ISO), and Systemic Toxicity – USP / ISO systemic injection. All tests were conducted in accordance with the provisions of the FDA Good Laboratory Practice Regulations, 21 CFR 58. To the best of our knowledge, this is the first analysis of ETPE toxicology and there have been no adverse reaction reports involving ETPEs.

6.2.1 Cytotoxicity – Agar Overlay.

ETPE as used in this paragraph is defined as BAMO-AMMO or BAMO-GAP. Nelson Laboratories conducted cytotoxicity analysis. Test was used to evaluate cytotoxicity of diffusible components from the ETPE on cell culture monolayers. Cell Line: Mouse Heteroploid Connective Tissue. Incubation Time: 24 -26 hrs. Incubation Temp: 37 +/- 1 °C. An agar layer was added over cell monolayers to act as a cushion to protect cells from mechanical damage. Samples are then placed on top of the agar layer, and the cells incubated. Cytotoxicity is scored as the degree of cellular damage or cytopathic effects. Scale: 0 (none), 1 (slight), 2 (mild), 3 (moderate), 4 (severe).

BAMO-AMMO Reactivity: 1(slight). Acceptance Criteria: Reactivity score of 2 (mild) or less.

BAMO-GAP Reactivity: 3 (moderate). USP acceptance criteria: Reactivity score of 2 (mild) or less.

6.2.2 Irritation: Intracutaneous Reactivity

ETPE as used in this paragraph is defined as BAMO-AMMO or BAMO-GAP. NAMSA conducted irritation analysis. Test was used to determine whether leachables extracted from the ETPE would cause local dermal irritant effects following injection into rabbit skin. The ETPE was extracted in 0.9% sodium chloride USP solution (SC) and sesame oil, NF (SO). 2 grams of the ETPE was covered with 10 ml of the vehicle. The ETPE was extracted in SC and SO at 37 °C for 72 hrs. Vials were agitated manually. A 0.2 ml dose of the ETPE extract was injected by the intracutaneous route into five separate sites on the right side of the back of each rabbit (male, New Zealand White). Similarly, the corresponding reagent control was injected on the left side of the back of each rabbit. One rabbit was used for each extract. Injection sites were observed immediately after injection. Observations for erythema and edema were conducted at 24, 48, and 72 hrs. Under conditions of this study, there was no evidence of significant irritation from the extracts injected intracutaneously into rabbits.

6.2.3 Systemic Toxicity: IOS/USP Systemic Injection

ETPE as used in this paragraph is defined as BAMO-AMMO or BAMO-GAP. NAMSA conducted systemic toxicity analysis. Test was used to determine whether leachables extracted from the ETPE would cause acute systemic toxicity following injection into mice. The ETPE was extracted in 0.9% sodium chloride USP solution (SC) and sesame oil, NF (SO). 2 grams of the ETPE was covered with 10 ml of the vehicle. The ETPE was extracted in SC and SO at 37 °C for 72 hrs. Vials were agitated manually. A single dose of the ETPE extract was injected into each of five mice (male, albino) per extract by either the intravenous or intraperitoneal route. Similarly, five mice were dosed with each corresponding blank vehicle. The animals were observed immediately and at 4, 24, 48, and 72 hrs after systemic injection. Under conditions of this study, there was no mortality or evidence of systemic toxicity from the extracts.

6.3 Task 2: Propellant Formulation Tailoring

TGD-043 was composed of RDX, BAMO-AMMO, and BAMO-GAP. TGD-044 was composed of RDX and BAMO-AMMO. All ETPEs used in this investigation contained 25% hard block (BAMO) and 75% soft block. The RDX particle size was 89-micron for the inner layer and 3-micron for the outer layer of the co-layered ribbon grains. The safety and compatibility of all ingredients and processing solvents was established prior to formulation development.

A standard propellant mix cycle is described as follows. All of the ETPE was dissolved in a 50% of total propellant weight equivalent of chloroform by stirring in a vertical mixer at 115 °F. (Ethyl acetate has also been found to be an effective processing medium for ETPE propellants.) With stirring, the RDX was added to the ETPE solution

in one-quarter weight increments at 5 to 10 minute intervals. Once thoroughly mixed, the mix temperature was increased to 150 °F and vacuum applied. At the end of mix, the propellant was white or slightly yellow and had the consistency of cookie dough. Total mix cycle was 90 to 120 minutes. Quarter-pint mixes were 80 grams and one-pint mixes were 275 grams. All mixes were conducted remotely by trained operators per safety protocol.

6.3.1 Quarter-pint mixes.

Quarter-pint mixes of the propellant formulations were conducted to establish the mix cycle and provide material for initial safety analysis. The mixes were RAM extruded to determine extrusion parameters and to provide material for Russian deflagration to detonation testing (DDT).

6.3.2 One-pint mixes.

ETPE based propellant manufactured in one-pint mixes were RAM extruded into 0.5-inch diameter cords. A small section of the cord was subject to density measurement by immersion in water. Densities were required to be greater than 98.5% of the theoretical maximum density before further processing was conducted. Once density was verified, the cords were rolled down to sheets of 0.100-inch thickness. Sheets were used to manufacture tiles (1-inch X 1-inch) for burn rate analysis (closed bomb testing) and to produce samples for dynamic mechanical analysis. **Table VI** illustrates the RAM extrusion parameters common to these propellants.

Table VI: TGD propellants: RAM extrusion data.

TGD	Cord Diam. (in)	Temp (°F)	Pressure (lbs)
43	0.5	160 - 170	335 - 420
44	0.5	160 - 170	600 - 700

6.3.3 Safety analysis.

Samples of the gun propellants commonly used in medium caliber ammunition were provided to ATK Thiokol by Radford Army Ammunition Plant for this program. Both RP propellants are composed primarily of nitrocellulose (single based) and employ a deterred, single perforation cylinder grain geometry. The data illustrated in **Table VII** suggest that the TGD propellants are less sensitive on ABL and Thiokol impact tests and are slightly less sensitive to thermal initiation. The TGD-044 co-layered ribbon grains displayed safety properties similar to the TGD propellants from the pint mixes. Interim hazard classifications were granted for TGD-043 and TGD-044.

Table VII: Safety data comparison of TGD-043, TGD-044, RP-36, and RP-1315.

	RP-36	RP-1315	TGD-043	TGD-044	044 ribbons
ABL impact (cm)	13	6.9	21	33	26
ABL friction (lbs @ 8 ft/sec)	800	800	800	800	800
ESD unconfined (J)	> 8	> 8	> 8	> 8	> 8
SBAT onset (°F)	255	249	307	313	315
TC impact (in)	15.7	11	31.6	28.6	25.1
TC friction (lbs)	> 64	> 64	> 64	> 64	
BOE impact @ 4 inch (of 10)	9 no-go	8 no-go	10 no-go	9 no-go	7 no-go
Russian DDT @ 500 psi			No Go	No Go	

6.3.4 RDX particle size distribution comparison.

One effective way to modify the burn rate of an ETPE propellant is to adjust the particle size of the filler, in this case, RDX. In general, as the particle size of RDX increases, the burn rate of the corresponding propellant will increase. The particle size distributions of RDX lots chosen for the inner and outer layers of the co-layered ribbon propellant grains were based on previous experience with this family of ETPE propellants. The chosen ratio of particle sizes (50 percentile at 89-micron versus 3-micron) produced the desired burn rate ratio (1.8 to 1.0). Particle size distribution of 89-micron RDX is shown in Figure 15 and the 3-micron RDX is shown in Figure 16.

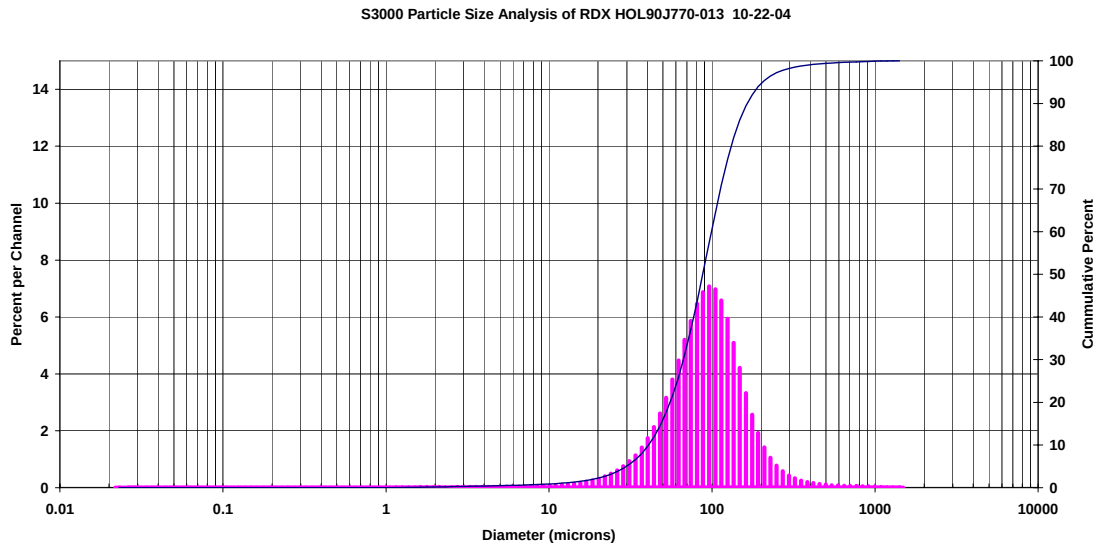


Figure 15: RDX, lot HOL90J770 particle size distribution (inner layer).

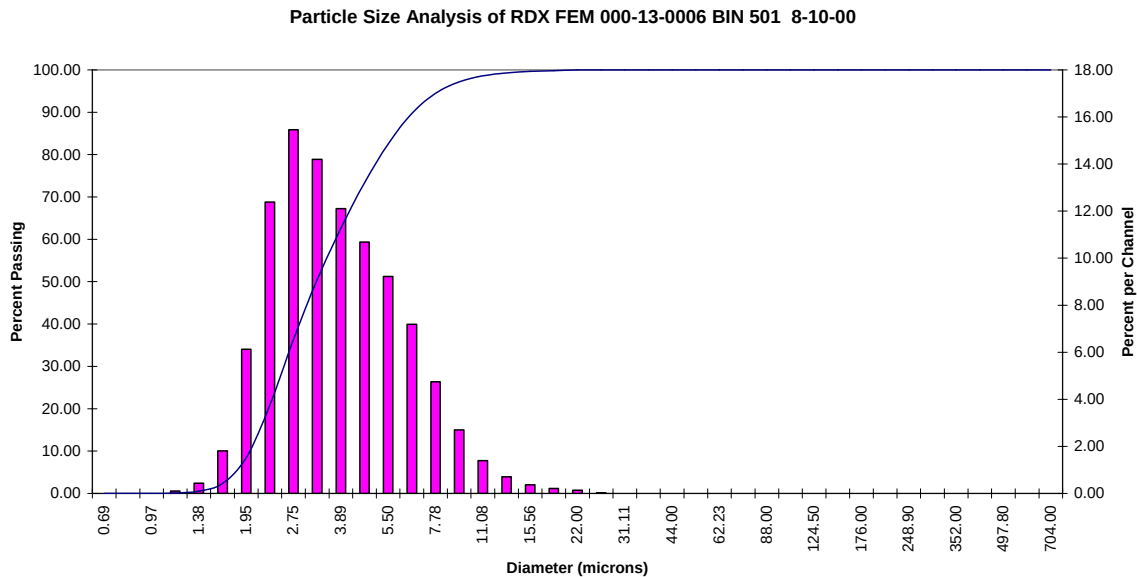


Figure 16: RDX, lot FEM 000-13-0006 particle size distribution (outer layer).

6.3.5 Co-layered grain, burn rate (closed bomb) analysis.

Burn rate analysis was conducted in a closed bomb (200 cc, Harwood Engineering, Model # E3590). Samples for testing were composed of 60 grams of propellant and each data set was fired in duplicate. None of the propellant samples were bagged inside the bomb. This may have contributed to poor flame spread for the ball powder, RP propellants. The igniter was 1.5 grams of DuPont Class 7, black powder and an electric match. Inner and outer layer propellant samples were composed of 1-inch by 1-inch by 0.1-inch tiles that had densities of 99% theoretical maximum density or better. Co-layered ribbon samples were composed of grains in the 25 mm grain geometry. As shown in **Figure 17** and **Figure 18**, the co-layered ribbon grains of the TGD propellants behaved as expected based on the measured burn rates of their individual layers. These data suggest grains should perform as a deterred system during gun firing.

As shown in **Figure 19** and **Figure 20**, the burn rates of the RP propellants were compared to the TGD propellants. These data suggest that the RP-36 has an identical burn rate, while the RP-1315 exhibits a faster burn rate compared to the TGD propellants. As mentioned, the RP ball powders were not bagged for closed bomb testing.

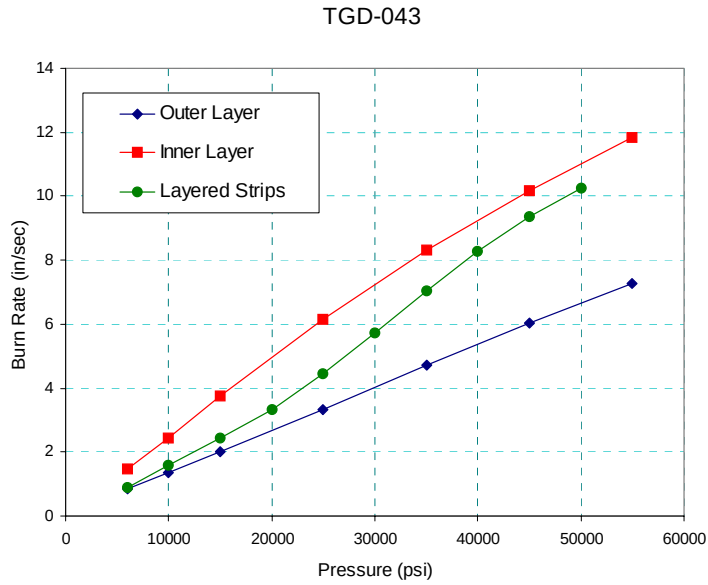


Figure 17: Ambient temperature, burn rate comparison of TGD-043's inner layer, outer layer, and co-layered ribbon.

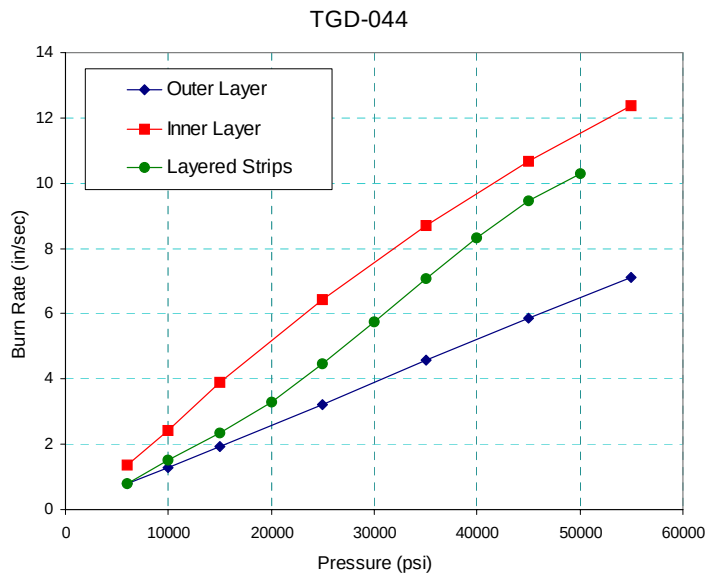


Figure 18: Ambient temperature, burn rate comparison of TGD-044's inner layer, outer layer, and co-layered ribbon.

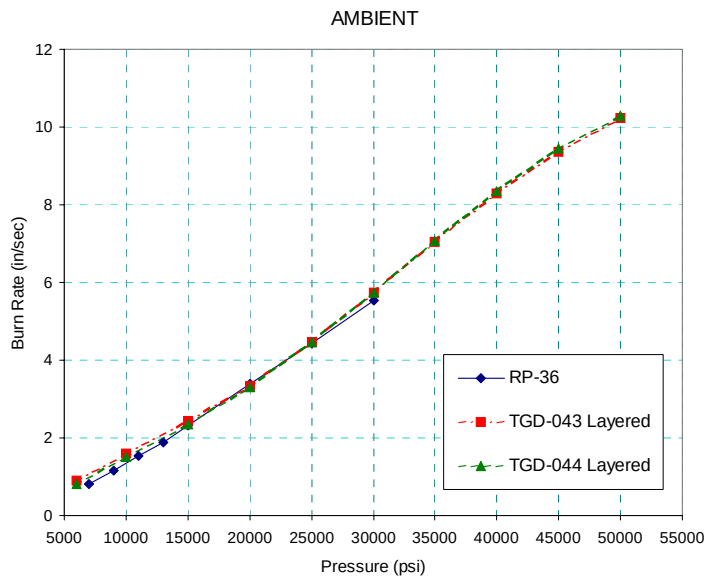


Figure 19: Ambient temperature, burn rate comparison of RP-36 (25 mm, NC propellant) with TGD-043 and TGD-044 co-layered ribbons.

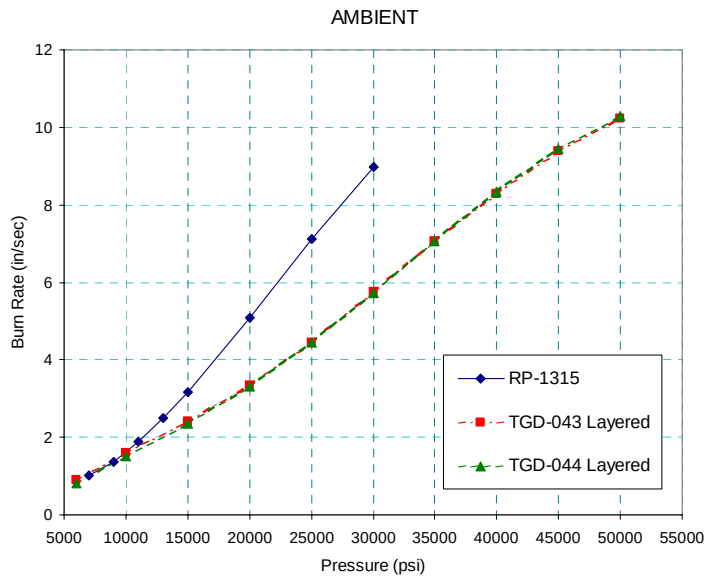


Figure 20: Ambient temperature, burn rate comparison of RP-1315 (30 mm, NC propellant) with TGD-043 and TGD-044 co-layered ribbons.

6.3.6 Burn rate temperature dependence.

Closed bomb testing was also performed on both of the RP propellants at -30 and 50 °C, as shown in Figures 21 and 22. Both RP propellants exhibit minimal temperature dependence, with a higher burn rate at higher temperatures. The opposite effect was observed with the TGD propellant, where a significantly higher burn rate was observed at cooler temperature, as shown in Figure 23. It is believed that the unexpected temperature dependence is due to brittle fracture of the TGD grains. The TGD strips were observed to be significantly more brittle at cooler temperatures. Fracture would expose additional surface area, increasing the burn rate. The strong dependence of mechanical properties on temperature is undesirable, but can be mitigated by selecting grain geometries that are less susceptible to fracture.

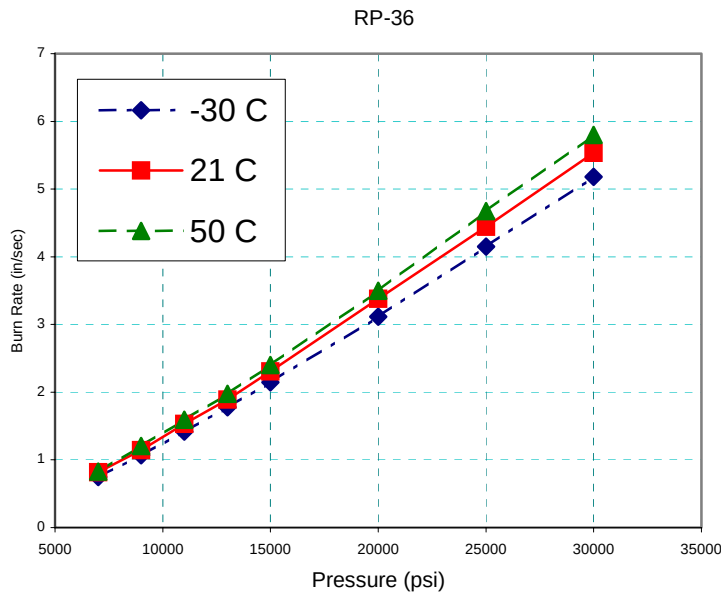


Figure 21: Temperature dependence of RP-36 burn rate.

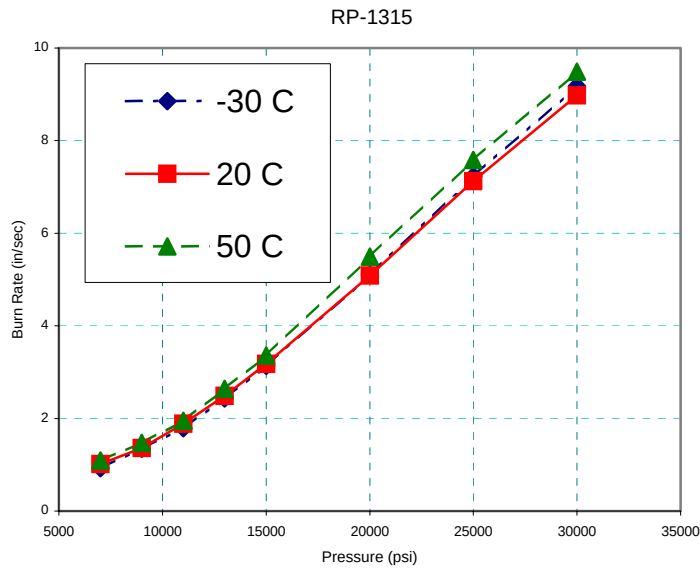


Figure 22: Temperature dependence of RP-1315 burn rate.

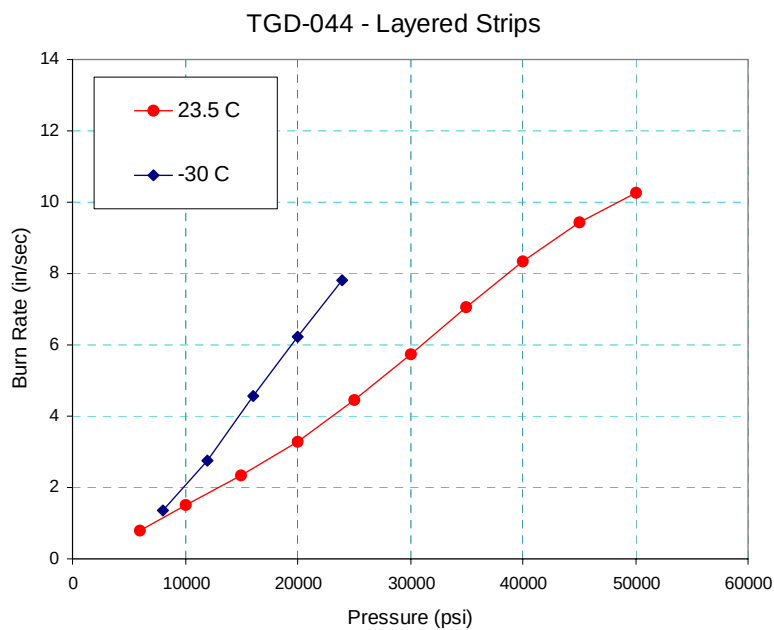


Figure 23: Temperature dependence of TGD-044 burn rate.

6.3.7 Mechanical Property analysis.

As seen in **Figure 24** and **Figure 25**, the mechanical properties of TGD-043 and TGD-044 were determined by dynamic mechanical analysis. TGD-043 was found to exhibit a glass transition temperature of -21°C and a softening temperature of 78°C .

TGD-044 was found to exhibit a glass transition temperature of $-32\text{ }^{\circ}\text{C}$ and a softening temperature of $77\text{ }^{\circ}\text{C}$.

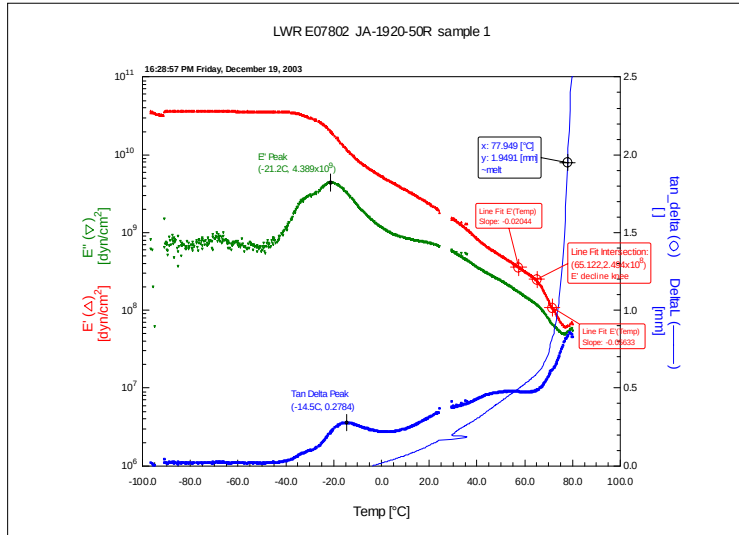


Figure 24: Dynamic mechanical analysis of TGD-043.

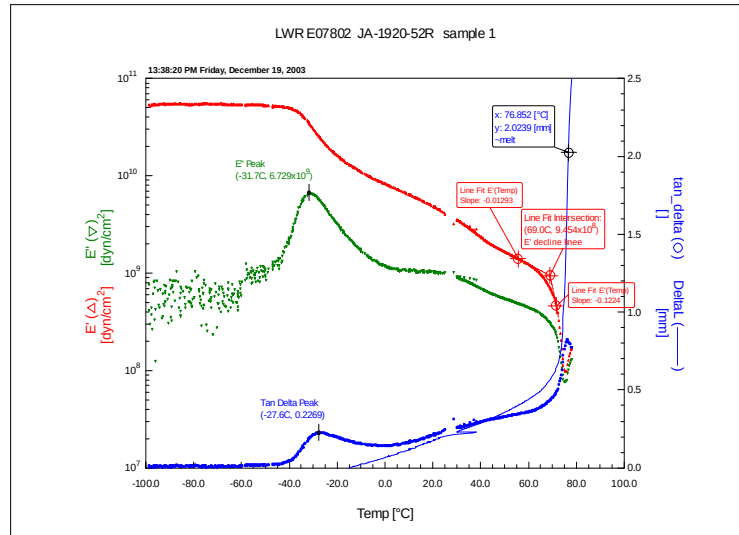


Figure 25: Dynamic mechanical analysis of TGD-044.

6.4 Task 3: Propellant Manufacture

Grains of both propellants were successfully manufactured with the desired grain dimensions. Approximately 0.4 lbs of TGD-043 and 0.7 lbs of TGD-044 co-layered ribbon grains were manufactured to support burn rate analysis and ammunition case loading. Organic dyes were used to color the TGD-043 grains purple and the TGD-044 grains red to help visually distinguish the propellants. An 8-lb delivery quantity of the TGD-044 grains was manufactured to support gun firing tests.

6.5 Task 3: Propellant gun testing

TGD-043 and TGD-044 have almost identical characteristics (ballistic energy, flame temperature, impetus, density, grain geometry, glass transition temperature, softening temperature). Closed bomb testing illustrated that TGD-043 and TGD-044 exhibit nearly identical burn rates at ambient temperature. Both candidates have similar safety properties and potential manufacturing costs. TGD-044 has a slight advantage in that trial loading of ammo cases illustrated that TGD-044 grains were more rigid and could be loaded more readily into a case.

The gun firing performance of TGD-044 will serve as an excellent starting point for the follow-on effort funded by the Environmental Security Technology Certification Program (ESTCP) that is scheduled to begin in 2005.

6.5.1 Calculated off-load performance.

The IBVHG2 calculated off-load performance of TGD-044 was used to guide the charge establishment sequence during testing.

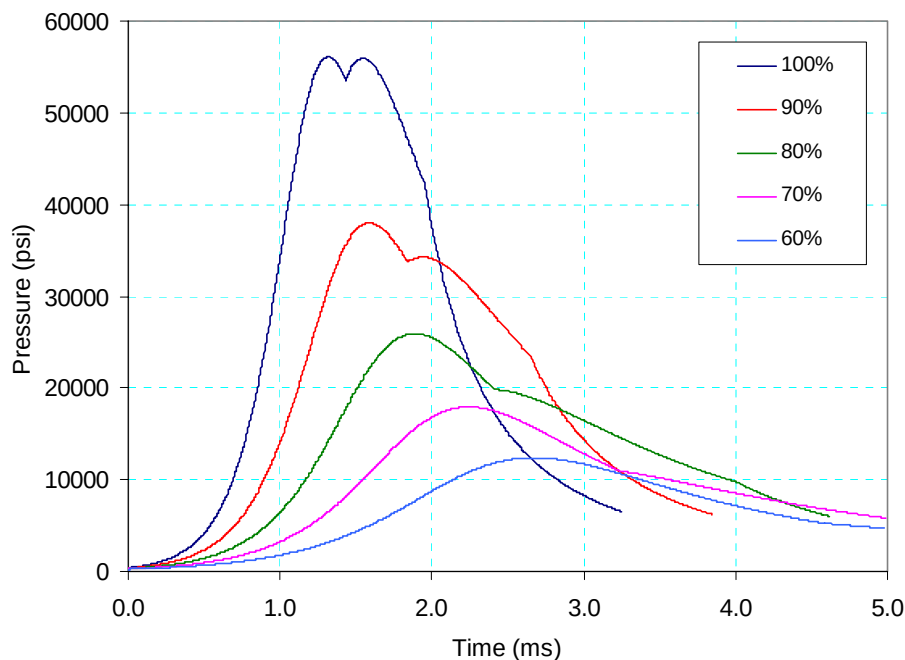


Figure 26: Calculated off-load performance of TGD-044 in 25 mm.

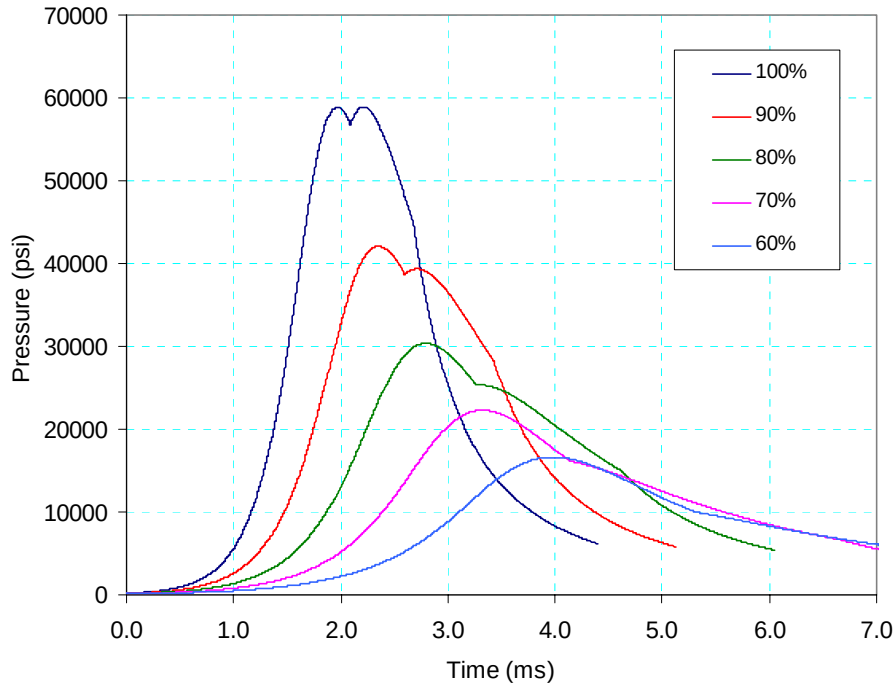


Figure 27: Calculated off-load performance of TGD-044 in 30 mm.

6.5.2 Gun firing matrix.

TGD-044 propellant was subject to charge establishment in a 25 mm gun and in a 30 mm gun at ambient temperature (70 °F). Gun testing was conducted in two phases over two days: charge establishment and charge verification. Each day half of the twelve M-793 rounds (25 mm) and twelve GUA8 rounds (30 mm) were fired as references. After barrel warming and reference rounds were fired, charge establishment was conducted by firing cases loaded with 60%, 70%, 80%, 90%, and 100% of the IBHVG2 calculated optimum charge (100% calculated to be 77 g in 25 mm, and 122 g in 30 mm). Ballistic consistency was determined by firing 11 rounds loaded to 100% of the theoretical optimum charge. The maximum amount of propellant that could practically be loaded (in the configuration shown in Figures 11-14) was determined to be 100% and 110% of the theoretical optimum charge for the 25 mm and 30 mm rounds, respectively. Therefore, on the second day, two additional 30 mm rounds were loaded to 105% and 110% of the theoretical optimum charge and fired after the 100% rounds.

6.5.3 Summary of PVAT data.

Firing of the TGD-044 propellant in the 25 mm rounds (see Table VIII) was considered successful, while the 30 mm data demonstrated a need for further refinement of the grain geometry and primer design. The 25 mm muzzle velocities were approximately 18% lower than expected and the 100% charge was slightly lower than the military specification for this round. The maximum chamber pressures were significantly lower than expected, averaging 45% lower than ballistic predictions. The low pressures

observed make the ETPE propellant an attractive alternative to the NC-based propellants. These results suggest that with minimal refinement of the grain geometry, the TGD-044 formulation will be an ideal substitute for RP-36. Observed actions times were slightly longer than the reference rounds, with a slightly larger spread, but well within the military specifications for the M-793 ammunition.

Table VIII: Gun firing PVAT data for TGD-044, RP-36, and RP-1315 loaded rounds.

25 mm M-793	Average action time (ms)	Average muzzle velocity (m/s)	Average maximum chamber pressure (MPa)
RP-36 REFERENCE			
(10 ROUNDS),	3.89	1100	365
Standard Deviation	1.3%	0.3%	2.1%
TGD-044			
(12 rounds),	4.58	904	202
Standard Deviation	4.8%	5.6%	2.8%
30 mm GAU8	Action time (ms)	Average muzzle velocity (ft/s)	Average maximum case pressure (kpsi)
RP-1315 Reference			
(11 rounds),	4.14	3405	51.9
Standard Deviation	2.1%	0.3%	1.3%
TGD-044			
(11 rounds),	13.14	2822	26.2
Standard Deviation	66.2%	2.8%	6.7%

The 30 mm rounds behaved similarly with respect to muzzle velocities and maximum pressure, but exhibited erratic action times ranging from 7 ms to over 200 ms. All recorded action times were longer than the military specification. The contrasting results observed between the 25 and 30 mm rounds are most likely due to poor flame spreading in the 30 mm round. The 30 mm round employs a flash tube in addition to the primer, which has been designed for granular NC-based propellant geometries. The extension of the flash tube into the case may not be ideal for the strip geometry. Comparison of cases assembled with percussion caps, with and without the flash tube, is suggested for future GAU8 testing of new propellant geometries.

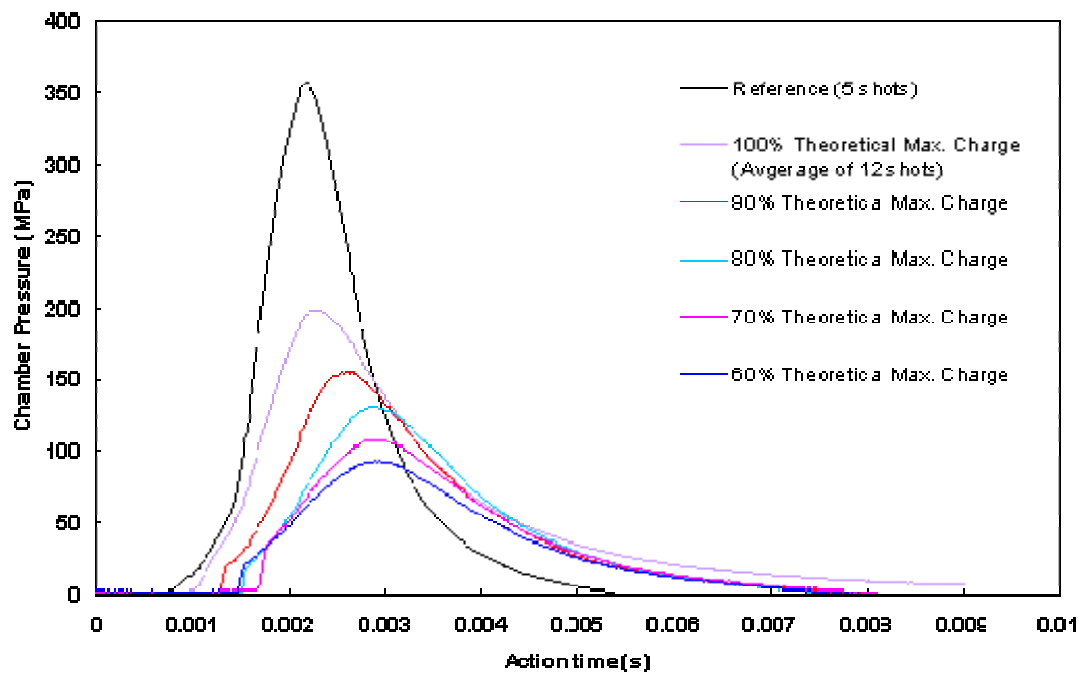


Figure 28: Pressure trace data for TGD-044 and RP-36 firing in 25 mm M-793.

Ballistics simulations with IBHVG2 were performed to support hypothesis explaining differences between the previous ballistic predictions and actual PVAT data. The pressure traces for the 25 mm rounds achieved lower maximum pressures and also did not have the “double-peak” shape that was expected to be characteristic of the co-layered propellant. Variability of layer thicknesses is known to be an unavoidable attribute of the rolling process. Simulations of propellant with thinner high energy and thicker low energy layers were performed, where measurements were comparable to measured cross-sections at discrete locations in rolled sheets. Experimental pressure traces were approximately reproduced with this simulation.

Blocking of propellant surface area was observed due to the high volume fraction loading of the cases. A fraction of the TGD-044 strip grains aligned inside the case, creating a potential for surface blocking during the initial stages of the ballistic cycle. Surface blocking issues were modeled, though the limitations of IBHVG2 required a simplistic approach to mimic this complex phenomenon. Pressure traces for this model did not predict the low observed pressures, but did predict the absence of the second peak. Consideration of blocking and variability of layer thicknesses will be key in designing an improved ETPE grain geometry in follow-on work.

7 RESULTS AND DISCUSSION

Overall the TGD-044 formulation remains a very good candidate for medium caliber propellant replacement, particularly for the 25 mm M-793. As shown, its processing, safety, environmental, and calculated ballistic properties are favorable. A co-layered

ribbon grain geometry may or may not ultimately be the ideal grain configuration for this formulation. It would be favorable to develop a grain that requires a less time consuming manufacturing process and could be more readily loaded into the ammunition case.

There are still propellant parameters to be adjusted to optimize the TGD-044 formulation for medium caliber performance. These parameters will be further investigated during the follow-on effort funded by ESTCP. The parameters that may be investigated include, but are not limited to, items such as; ETPE mechanical properties at high and low temperatures, RDX particle size and corresponding influence on burn rate, grain geometry, igniter design for 25 mm and 30 mm rounds, and development of a deterrent that is specific for ETPE propellants.

The development of a deterrent for ETPE propellants would provide the capability of a greater variety of grain geometries. The chemical structures of ETPEs are significantly different from nitrocellulose. Thus, commonly known deterrent technology may not be applicable to the ETPE family. The deterrents are applied to the NC grains by tumbling the grains with a solvent in a barrel for a pre-determined amount of time at a pre-determined temperature. This technology has been well established for fielded NC propellants and will be considered as candidate technologies for deterring ETPE propellants.

Issues to address in the development of a new deterrent for ETPEs are not trivial. First, the compound must be identified. Potential deterrents must be non-toxic, readily available, compatible with all ingredients, and low cost. The amount of deterrent to be applied that produces the desired burn rate reduction must be determined. An experimental method must be developed that uniformly applies the deterrent to the grain and does not significantly alter grain geometry. Answers to these issues would give the propellant formulator a substantial tool for the optimization of ETPE propellants.

8 SUMMARY

As shown in this report, two ETPE based gun propellants have been developed for medium caliber ammunition. The ETPE propellants under investigation have several potential advantages compared to the currently fielded nitrocellulose based propellants. They would eliminate toxic and carcinogenic ingredients such as diphenylamine and barium nitrate. They employ a lower cost, available filler, RDX. The TGD-044 formulation was down-selected for gun firing analysis. The TGD-044 formulation was predicted to meet or exceed ballistic performance for medium caliber and exhibit excellent safety properties. Firing of 25mm M-793 and 30mm GAU8 rounds showed that TGD-044 is an excellent candidate for the 25mm rounds, but will require further optimization of the grain geometry for use in the 30mm GAU8. The 25mm results suggest that TGD-044 in the current configuration may be suitable for use in the 30mm round, Lightweight 30. A favorable ETPE toxicology is suggested by the preliminary study conducted during this program. These advantages combined emphasize the need to bring ETPE propellant technology to maturity.

9 REFERENCES.

- 1) T. G. Manning, S. Moy, K. Klingaman, A. Aprea, N. M. DeVries, R. J. Lieb, M. G. Leadore, P. C. Braithwaite, G. W. Dixon, "High Energy Thermoplastic Elastomer Laminated Propellant Development," 34th JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee and Airbreathing Propulsion Subcommittee Joint Meeting, West Palm Beach, Florida, November 1997.
- 2) L. E. Harris, T. Manning, K. Klingaman, R.B. Wardle, P.C. Braithwaite, G. W. Dixon, T. Stephens, S. Prickett, "Thermoplastic Elastomer (TPE) Gun Propellant," 1998 NDIA Insensitive Munitions & Energetic Materials Technology Symposium, San Diego, California, November 1998.
- 3) Rozanski, J., "LPGB: A calculational method for simulating and optimizing the performance of co-layered gun propellants", 2002 JANNAF 38th Combustion Subcommittee Mtg., Destin, Florida, April 2002.

10 PUBLICATIONS.

The work conducted during this investigation has not yet been submitted for technical publication.

11 ACRONYM LIST

AMMO	poly(3-azidomethyl-3-methyloxetane)
ARL	Army Research Laboratory
ATK	Alliant TechSystems
BAMO	poly (3,3-bisazidomethyloxetane)
BLAKE	thermochemistry modeling code
DDT	Russian deflagration to detonation test
DPA	diphenylamine
ESD	Electrostatic discharge
ESTCP	Environmental Security Technology Certification Program
ETPE	energetic thermoplastic elastomer
FDA	Food and Drug Administration
GAP	poly(glycidyl azide)
IBHVG2	Internal Ballistics of High Velocity Guns, version 2
ISO	International Standards Organization
LPGB	IBHVG2 code for layered gun propellants
NC	nitrocellulose
Perf	perforated, perforation
PVAT	Pressure, Volume, Action Time
RDX	cyclotrimethylene trinitramine
RP-####	nitrocellulose-based propellant
SC	sodium chloride
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SO	sesame oil
TGD-###	ATK Thiokol gun propellant formulation
USP	United States Pharmacopeia