TITLE: Relative Erosivity of Nitramine Gun Propellants with Thermoplastic/Elastomer Binder Systems

# RELATIVE EROSIVITY OF NITRAMINE GUN PROPELLANTS WITH THERMOPLASTIC/ELASTOMER BINDER SYSTEMS

**Charles S. Leveritt, Paul J. Conroy, and Andrew W. Johnson**

*U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005*

Current and future gun propellant development programs are necessarily moving toward compositions possessing ever-higher impetus and flame temperature. A common goal is impetus above 1250 J/g, resulting in flame temperature above 3400 K. Propellants showing the most promise are composite in nature, consisting of an energetic solid in an energetic thermoplastic elastomer (ETPE). Oxidizers are typically CL-20 or RDX. Normally, such systems could be expected to provide some gun tube erosion problems. Erosivity characterizations have been conducted in a blowout chamber, which has been fabricated from the breech and chamber of a 37-mm gun. Relative erosivity is determined by observing the mean mass loss from a contoured nozzle resulting from a series of test firings. In general, the RDX/ETPE and CL-20/ETPE propellants that have been evaluated in this program are considerably less erosive than conventional propellants of similar flame temperature.

## INTRODUCTION

In the quest for ever-increasing muzzle energy, propellants showing the most promise are composite in nature, consisting of an energetic solid in an energetic thermoplastic elastomer (ETPE). Oxidizers are typically RDX or CL-20. The ETPE's are most commonly selected from a family of oxytane polymers. The polymers can be tailored for nitrate ester, azido, or nitratoamine functionality. Systems in common use are BAMO-AMMO, BAMO/BAMO-AMMO, and BAMO-NMMO. Coolants such as NQ, TEX, or TATB are sometimes incorporated, but are limited so as not to degrade impetus.

Prior to this study, no wear and erosion data existed for propellants of this type. In addition to the more energetic thermochemistry, charge designs possess uncommonly high loading density and high mass generation rates, contributing to the potential wear and erosion problem. The propellant thermochemistry coupled with the high performance charge design was expected to provide severe tube wear and erosion problems.

RDX and CL-20 based propellants with oxetane ETPE binder systems have been characterized and compared to triple-base (M30), double-base (M8 & JA-2), and a more recent nitramine composite propellant (M43). Comparison propellants were initially chosen on the basis of similarity in gun chamber flame temperature. The compositions of the comparison propellants are shown in Table 1; compositions of the oxetane propellants are presented in Table 2.

The propellants identified as TGD-002 and TGD-009 were formulated to meet the requirements of the Electrothermal Chemical (ETC) Gun firing demonstration program that was completed some time ago [1,2]. The charge design for this program utilized traditional "fast-core" propellant increments consisting of an inner layer of a relatively fast burning propellant, TGD-002, to which was bonded two outside layers of TGD-009 [3]. This design provided an increased loading density as well as high progressivity, since the inner layer burns at about three times the rate of the outer layers. The TGD-019 propellant was developed more recently as a possible replacement for JA-2, has a slightly more energetic binder system than TGD-009, and is not cooled with TEX [4].

Table 1. **COMPOSITION OF STANDARD PROPELLANTS**

| | M8 | M30 | JA-2 | M43 |
|---|---|---|---|---|
| Nitrocellulose | 52.15 | 28.0 | 59.02 | 4.00 |
| (% Nitrogen) | (13.25) | (12.60) | (12.98) | (12.60) |
| Nitroglycerine | 43.00 | 22.5 | 14.78 | |
| Nitroguanidine | | 47.7 | | |
| Ethyl centralite | 0.60 | 1.50 | | 0.40 |
| Potassium nitrate | 1.25 | | | |
| Diethylphthalate | 3.00 | | | |
| Cryolite | | 0.30 | | |
| RDX | | | | 76.00 |
| Cellulose acetate/butyrate | | | | 12.00 |
| Bis (dinitropropyl) acetal | | | | 3.80 |
| Bis (dinitropropyl) formal | | | | 3.80 |
| Diethyleneglycol dinitrate | | | 24.60 | |
| Akardite 2 | | | 0.70 | |
| Barium oxide | | | 0.05 | |
| Graphite | | | 0.05 | |

Table 2. **COMPOSITION OF OXETANE PROPELLANTS**

| | TGD-002 | TGD-009 | TGD-019 |
|---|---|---|---|
| CL-20 | 78.0 | | |
| RDX | | 58.0 | 76.0 |
| TEX | | 18.0 | |
| BAMO | 14.3 | 6.0 | 6.0 |
| AMMO | 7.7 | 18.0 | |
| GAP | | | 18.0 |

The RDX/ETPE and CL-20/ETPE propellants that have been characterized provide thermochemistry that is considerably more fuel-rich than any of the comparison propellants. In Table 3, the calculated thermochemistry of the propellants is displayed. For the test chamber conditions, properties have been calculated using the BLAKE code [5]. For the test apparatus described in the experimental method below, these conditions apply up until the time that the shear disk fails and are calculated at a standard reference loading density of 0.2 g/cc. When the shear disk fails and flow through the nozzle is established, the NASA-Lewis code, Chemical Equilibrium with Applications (CEA), is used [6,7]. Conditions in the nozzle are calculated for each propellant test series using the actual pressure at which the shear disk failed. The propellant identified as TGD-9/2/9 is the complete "fast-core" propellant assembly consisting of a two mm thick layer of TGD-002, to which has been bonded two outer layers of 0.3 mm thick TGD-009. Since the available TGD-9/2/9 propellant had been designed to meet the ballistic requirements of a 120-mm gun, action time is slow when fired in a 37-mm gun chamber, leading to some heat loss in the experiment. Since the intent of this program is to fairly evaluate propellant thermochemistry, charges identified as Propellant 009+002 were prepared. The Propellant 009+002 charges possess separate weights of TGD-002 and TGD-009 identical to those of the TGD-9/2/9 assemblies; the TGD-002 and TGD-009 are not bonded in the 009+002 propellant so that combustion is simultaneous and action time is reduced acceptably.

Table 3. **SUMMARY OF THERMOCHEMICAL PROPERTIES**

| | **CHAMBER** | | | **NOZZLE** | | | |
|---|---|---|---|---|---|---|---|
| | **Temp(K)** | **F(J/g)** | | **Temp(K)** | **$CO/CO_2$** | **$H_2/H_2O$** | **$N_2$** |
| **M30** | 3022 | 1078 | | 2176 | 3.14 | 0.61 | 0.28 |
| **TGD-009** | 2570 | 1070 | | 1886 | 21.31 | 5.16 | 0.26 |
| **M43** | 3004 | 1155 | | 2129 | 7.70 | 1.54 | 0.24 |
| | | | | | | | |
| **M8** | 3746 | 1169 | | 2898 | 1.51 | 0.21 | 0.14 |
| **TGD-002** | 3722 | 1356 | | 2645 | 14.98 | 2.31 | 0.32 |
| | | | | | | | |
| **JA-2** | 3390 | 1139 | | 2520 | 2.53 | 0.41 | 0.12 |
| **TGD-019** | 3262 | 1294 | | 2293 | 15.34 | 2.77 | 0.29 |
| **TGD-9/2/9** | 3413 | 1292 | | 2395 | 19.22 | 3.30 | 0.30 |
| **009+002** | 3413 | 1292 | | 2395 | 19.22 | 3.30 | 0.30 |

## EXPERIMENTAL METHODS AND RESULTS

A classic method to determine relative propellant erosivity is to measure the mass loss from a nozzle exposed to flow from the combustion gases of the propellant. The erosivity experiments described in this program were conducted in a blowout chamber, which has been fabricated from the breech and chamber of a 37-mm gun. A schematic of the fixture is shown in Figure 1. The gun tube has been shortened considerably and has been provided with a bored cavity on the muzzle end to accept a nozzle and shear disk assembly. The nozzle is made of AISI 4340 gun steel and is located approximately 30 millimeters downstream from the mouth of the cartridge case. Mild-steel shear disks are placed downstream of the nozzle. The shear disks are held against the back of the nozzle by a "short barrel" tailpipe insert having an internal diameter of 12.7 millimeters. This erosivity apparatus has been in use at the US Army Ballistic Research Laboratory (BRL) and subsequently the US Army Research Laboratory (ARL) since the Second World War [8,9].

37-mm Blow-Out Gun

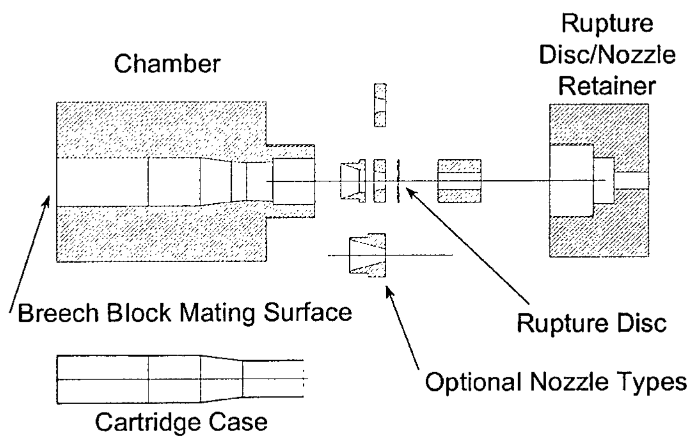


Figure 1. Test Fixture Schematic

In this fixture, the throat diameter of the nozzle is chosen to be 12.5 millimeters so that choked flow is established at the nozzle in preference to the tailpipe. With these nozzle and tailpipe dimensions, two 1.6 millimeter thick shear disks provide a rupture pressure in the nominal range of 260-270 MPa. Shear disk performance can be a study in classical shear dynamics, with relatively quick propellants providing a somewhat higher failure pressure and slow propellants the opposite. Propellant charge masses were adjusted to give a closed bomb pressure of 306 MPa to insure shear disk rupture.

Wear for each propellant was determined by conducting a repetitive series of five to six tests and then averaging the results. Following each shot, the steel nozzle was cleaned with soap and water, dried, and weighed on a balance with a sensitivity of 0.1 milligram. Pressure versus time in the chamber was measured as a record of shear disk failure pressure and to assure that no anomalous ballistic behavior had occurred. In all cases the propellants were ignited with the standard M1B1A2 percussion primer/igniter containing 6.5 grams of black powder. Averages and one standard deviation for shear disk failure pressures and nozzle mass loss (wear) are presented in Table 4.

Table 4. **SUMMARY OF EROSIVITY DATA**

| | **NOZZLE CONDITIONS** | | | | **DISK BURST (MPA)** | **WEAR (mg)** |
|---|---|---|---|---|---|---|
| | **Temp(K)** | **$CO/CO_2$** | **$N_2$** | | | |
| **M30** | 2176 | 3.14 | 0.28 | | 274 +/- 0.8 | 21.1 +/- 5.5 |
| **TGD-009** | 1886 | 21.31 | 0.24 | | 251 +/- 6.2 | 21.4 +/- 2.6 |
| **M43** | 2129 | 7.70 | 0.24 | | 274 +/- 5.5 | 26.8 +/- 7.8 |
| | | | | | | |
| **M8** | 2898 | 1.51 | 0.14 | | --- | 240.5 +/-5.0(*) |
| **TGD-002** | 2645 | 14.98 | 0.32 | | 261 +/- 3.2 | 193.3 +/-3.2 |
| | | | | | | |
| **JA-2** | 2529 | 2.53 | 0.12 | | 254 +/- 9.1 | 250.6 +/-8.4 |
| **TGD-019** | 2293 | 15.34 | 0.29 | | 269 +/- 11.3 | 40.0 +/- 6.0 |
| **TGD-9/2/9** | 2395 | 19.22 | 0.30 | | 260 +/- 8.0 | 79.9 +/- 5.1 |
| **009+002** | 2395 | 19.22 | 0.30 | | 261 +/- 4.0 | 104.3 +/-7.1 |

Note: (*) signifies data for **M8** obtained from [10]; not repeated in this program.

## DISCUSSION

The RDX/ETPE and CL-20/ETPE propellants that have been characterized and compared to more traditional propellants in this evaluation provide thermochemistry that is considerably more fuel-rich than any of the comparison propellants. The propellant TGD-009 possesses the lowest chamber and nozzle temperatures of all propellants studied; yet the erosivity is equivalent to the comparison propellants, M30 and M43. In a previous investigation, it had been predicted that, due to the production of much more CO and $H_2$, M43 would be about 25% more erosive than M30 despite the equivalent flame temperature [11]. The predominant erosion mechanism proposed at that time stated that carburization leading to iron carbide formation would be an important contributing factor for much of the material lost from the gun steel. The M43 erosivity increase has finally been experimentally confirmed in this program. Given the benign chamber and nozzle temperature of TGD-009, the unexpected erosivity equivalency to M30 in the more fuel rich TGD-009 experiment appears to be a more extreme case of the carburization erosion mechanism.

The higher temperature TGD-002 and TGD-019 propellants are similarly high in CO and $H_2$, but are strikingly different from their respective comparison propellants, M8 and JA-2, in nitrogen content. Ponec suggests that the surface disassociation of CO on an iron surface is spoiled by nitrogen intrusion that produces a nitriding of the surface [12]. This leads to the possibility that increasing the nitrogen content of the propellant products may diminish the CO disassociation and thereby the erosivity. We have discovered in this program that for TGD-002 and TGD-019, with similar flame temperatures to the conventional relatively clean burning double-base comparison propellants, erosivity has in fact been greatly reduced. Complicating matters is the fact that these advanced propellants have a much higher $CO/CO_2$ ratio than that of the double-base propellants which should exacerbate the carburization mechanism. Fortunately, Ponec's explanation may be applied to these new propellants because their nitrogen content is approximately three times that of the conventional propellants. Diatomic nitrogen as a product is probably preferred over carbon monoxide, if lower molecular weight is desired for increased impetus, even though the molecular weight of each is the same.

The M242 Bushmaster barrel has the option of nitriding or chrome plating. If it is chrome plated, access for erosion is through the cracks to the substrate [13]. Considering Ponec's hypothesis, nitriding barrels before they are chrome plated may increase the service life by mitigating the erosion at the base of the cracks. It is not believed that the nitrided material chemical process for erosion mitigation was previously understood, other than that it increased the surface hardness.

The strong reducing environment presented to the combustion chamber and nozzle in our erosivity test fixture can apparently be beneficial, at least over the range studied. In general, the RDX/ETPE and CL-20/ETPE propellants that possess a large excess of nitrogen in the products are considerably less erosive than conventional propellants of similar flame temperature.

## REFERENCES


1. P. Braithwaite, G. Dixon, I. Wallace, R. Wardle, J. Northrup, W. Waesche, "Development of Fast and Slow Burning Rate TPE Propellants for ETC Gun Systems", 49th JANNAF Propulsion Meeting, Tucson, Arizona, December 1999.

2. P. Braithwaite, R. Stuart, J. Northrup, "Closed Bomb Characterization of TGD-002 and TGD-009 Propellants", 36th JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee and Airbreathing Propulsion Subcommittee Joint Meeting, Cocoa Beach, Florida, October 1999.

3. F. W. Robbins, B. F. Raley, A. A. Koszoru, J. R. Hewitt, "High Loading Density Gun Charge Configurations of Slab Propellant – Loading and Gun Firing Experiments", 30th JANNAF Combustion Subcommittee Meeting, Monterey, CA, November 1993.

4. P. C. Braithwaite, "Development of an Improved Thermoplastic Elastomer (TPE) Gun Propellant," Contract Final Report, TR12255, February 2001, Thiokol Propulsion, Brigham City, UT.

5. E. Freedman, "BLAKE - A Thermodynamics Code Based on TIGER: Users' Guide to the Revised Program", ARL-CR-422, July 1998, US Army Research Laboratory, Aberdeen Proving Ground, MD.

6. Gordon, S., and McBride, B.J., 1976, Computer Program for Calculating Complex Chemical Equilibria, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations, NASA SP—273.

7. Gordon, S., and McBride, B.J., 1994, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, Part I: Analysis, NASA RP—I 311.

8. J. R. Ward, R. W. Geene, "Erosivity of a Nitramine Propellant with a Flame Temperature Comparable to M30 Propellant", ARBRL-MR-02926, June 1979, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD.

9. R. P. Kaste, I. C. Stobie, J. R. Ward, B. D. Bensinger, “Relative Erosivity of Nitramine, Triple-Base, and Double-Base Propellants”, ARBRL-MR-02339, July 1981, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD.

10. J. R. Ward, R. P. Kaste, I. C. Stobie, B. D. Bensinger, “Role of Surface Oxide on Gun Barrel Wear”, ARBRL-TR-02437, November 1982, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD.

11. P.J. Conroy, P. Weinacht, M. J. Nusca, "Extended Range 5” Navy Gun, Theoretical Thermal and Erosion Investigations”, Proceedings of 35th JANNAF Combustion Subcommittee Meeting, Tucson, AZ, December 1998.

12. Ponec, V., van Barneveld, W. A., "The Role of Chemisorption in Fischer-Tropsch Synthesis," Journal of Industrial Engineering Chemical Product Research and Development, Vol. 18, No. 4, 1979.

13. Conroy, P.J., Weinacht, P., Nusca, M. J., "Gun Tube Coatings in Distress," Proceedings of 36th JANNAF Combustion Subcommittee Meeting, Cocoa Beach, FL, October 1999.