

High Impetus Cool Burning Gun Propellants

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ABSTRACT

This study explores the possibility of reducing the flame temperature (T_f) without decrease in impetus of RDX-NC matrix-based high energy gun propellants by partial replacement of RDX with triaminoguanidine nitrate (TAGN). Compositions containing TAGN as an energetic oxidiser with varying percentage of RDX have been formulated. Glycidyl azide polymer was incorporated as an energetic plasticiser to achieve the higher level of impetus. Performance in terms of ballistic parameters (theoretical/experimental) sensitivity, thermal characteristics, stability and mechanical properties was evaluated and compared with the basic composition containing RDX as a single oxidiser. Experimental data indicates that the partial replacement of RDX by TAGN in gun propellant compositions decreases T_f significantly with only marginal decrease in impetus.

1. INTRODUCTION

Conventional gun propellants based on NC, NG and picrite have reached best level in terms of energy. In order to meet the requirements of tank gun ammunition, propellants of higher impetus with lower flame temperature (T_f) are required to achieve the higher muzzle velocity (MV) and minimise the gun barrel erosion.

The impetus or force constant F is given by the equation:

$$F = nRT_f = \frac{RT_f}{M}$$

where

n = Number of moles of combustion gases evolved per gram of propellant

R = Universal gas constant

T_f = Flame temperature of propellant

M = Average molecular weight of combustion gases

From the above equation, it is clear that high impetus can be obtained by increasing T_f and/or decreasing M , i.e. increase the gas output.

Extensive research is being carried out all over the world in this direction by increasing the number of moles of combustion gases per unit mass of a propellant to realise higher percentage of H_2 , H_2O , NH_3 , CH_4 and N_2 rather than CO and CO_2 in the combustion products¹⁻⁴. Most of these propellants contain either cyclic or linear nitramines, such as cyclotrimethylene trinitramine (RDX), cyclo-tetramethylene tetranitramine (HMX), triaminoguanidine nitrate (TAGN), nitroamino guanidine (NAGu), and triaminoguanidine ethylene-dinitramine (TAGEDN) as energetic oxidisers (Fig. 1). Attempts have also been made to replace the less energetic plasticiser di-octyl phthalate (DOP) by an energetic plasticiser, such as glycidyl azide polymer (GAP) to achieve a further increment in the impetus⁵.

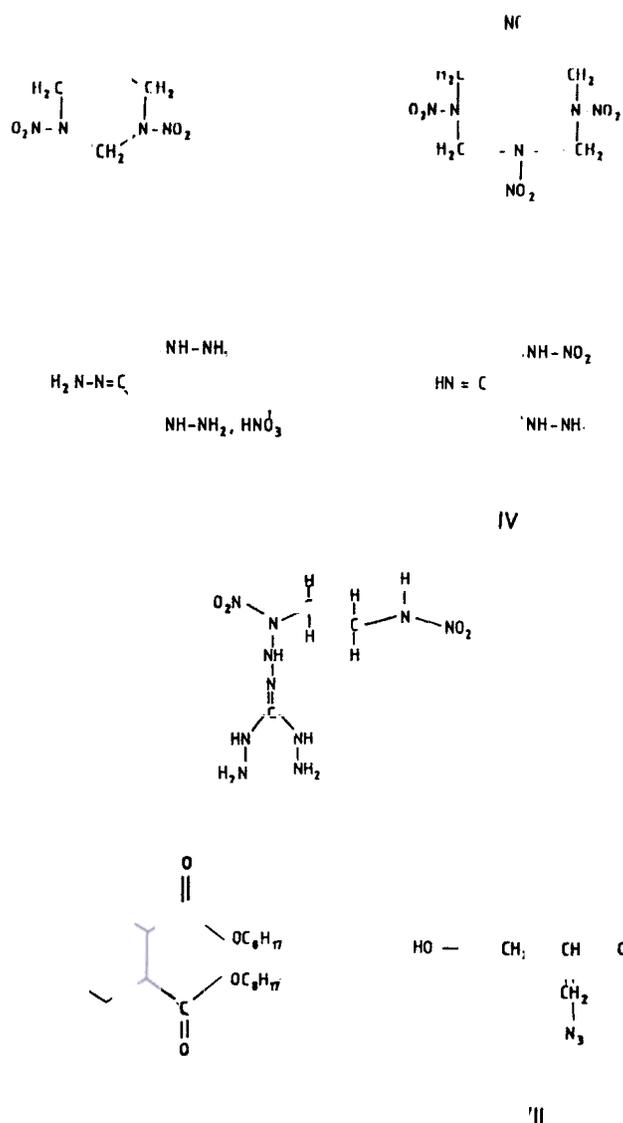


Figure Chemical structures of RDX, HMX, TAGN, NAGU, TAGEDN, DOP and GAP as I, II, III, IV, V, VI, and VII, respectively.

The main disadvantage of RDX-NC matrix-based gun propellants was the higher level of adiabatic T_f which leads to gun barrel erosion⁶. Therefore, families of gun propellant formulations containing nitroguanidium salts mixed with secondary high explosives, such as RDX or HMX were proposed to provide mean molecular weight of combustion gases 20–30 per cent lower and moderate isochoric T_f , yielding comparable or higher impetus than the propellant containing single oxidiser, i.e. RDX. In the present study, TAGN has been selected as a co-oxidiser along with RDX to

reduce T_f and GAP as an energetic plasticiser to enhance the impetus. TAGN is a unique energetic material which produces relatively high concentration of hydrogen. The low molecular weight of combustion products increases the impetus when TAGN is used in gun propellant⁷. The major combustion products of TAGN are N_2 , H_2 and H_2O . The low T_f (2250 K) and higher nitrogen content (58 per cent) in the molecules of TAGN make the propellant cool burning with high impetus. GAP is an energetic and self-sustaining combustible polymer, which acts as an energetic plasticiser, mainly due to its higher heat of formation ($\Delta H_f = +117$ K cal/mole), higher density (1.3 g cm^{-3}) and low molecular weight combustion products (Mw) than DOP.

This paper presents the results of a systematic study conducted on TAGN-based propellants to obtain higher energy at relatively lower T_f suitable for tank gun ammunitions.

2. EXPERIMENTAL PROCEDURE

TAGN was prepared by hydrazinolysis of guanidine nitrate with hydrazine hydrate⁸ (80 per cent). One mole of guanidine nitrate required three moles of hydrazine hydrate for complete reaction. The reaction was conducted at 368 K in a three-necked flask provided with an efficient stirrer. Ammonia liberated during the reaction was allowed to escape. After the reaction was complete, the contents of the flask were cooled to get crude TAGN which was washed free from ammonia and then recrystallised twice in water to achieve the pure product. The purity of TAGN was confirmed by m.p. (489 K) and IR spectral analysis. Pure TAGN was ground and sieved through 60 BSS sieve. Particle size was determined by Fischer sub-sieve sizer and found to be around 18 μm . Yield was 70 per cent.

GAP was synthesised by the following method:

200 ml of 1,1,1-trichloroethane (TCE), 100 g each of sodium azide and ethylene glycol were taken in a three-necked flask fitted with a reflux condenser and a nitrogen inlet tube. The mixture was stirred and the temperature of the reaction flask was brought to 343 K. Epichlorohydrine (ECH)

100 g was added dropwise through an addition funnel at a rate to ensure that no excessive exothermic reaction associated with the opening of the epoxide ring resulted. (To control the exothermicity of ECH, it can be diluted with TCE). After the complete addition of ECH, the temperature was raised to 353-358 K. The reaction was maintained at this temperature for 15-20 hr and finally cooled to ambient temperature. The reaction mixture was extracted with dichloromethane, washed thoroughly with water to remove salts and ethylene glycol and then dried over sodium sulphate. Solvent was removed using roto-evaporator to yield the azide polymer in 85 per cent. This process has been scaled up to 5 kg/batch. The quantitative conversion of ECH to GAP was confirmed by the disappearance of bands in the IR spectra corresponding to $C-Cl$ (740 cm^{-1} - 660 cm^{-1}) and the appearance of a sharp signal at 2150 cm^{-1} which is assigned to $C-N_3$. Elemental analysis of low molecular weight GAP was in close agreement with the theoretical values. Molecular weight determined by VPO method was of the order of about 390, corresponding to degree of polymerisation (n) of 4.

Three different compositions based on nitrocellulose (NC) of 13.1 nitrogen content, GAP of number average molecular weight 390, RDX of average particle size $5\text{ }\mu\text{m}$, TAGN of particle size $18\text{ }\mu\text{m}$ and stabilisers were formulated along with the control composition containing a single oxidiser, i.e. RDX. Theoretical performance of the compositions was computed using THERM program⁹. Propellant compositions were made on a laboratory scale (1 kg batch) by solvent process¹⁰. In the first step, fine RDX was dehydrated by ethyl alcohol and coated with the required quantity of GAP on dry weight basis. Exact percentage of GAP and the uniformity of its coating to RDX was confirmed by gravimetric experiments using toluene saturated with RDX as the solvent for extraction of GAP.

The residue was dried in an oven at 383 K to make it free from toluene so as to get constant weight. All the samples were subjected to impact

and friction sensitivity tests to find out the safety-related information. Propellant compositions based on TAGN were prepared by using 30 per cent ethyl acetate. The control composition containing single oxidiser, i.e. RDX was processed using 30 per cent mixture of acetone and alcohol in 70:30 ratio. The ingredients were kneaded in an incorporator for 6 hr to achieve a homogeneous propellant dough. The dough was subsequently extruded in a multi-tubular configuration at 50 bar by hydraulic press. The propellant grains were dried in an oven at 318-323 K till the volatile matter was reduced to 1 per cent. The dried propellant samples were tested for physical measurements like web size and density, and finally subjected to evaluation tests.

3. ME HODOLOGY

3. Ballistic Evaluation

The compositions were fired in a 700 ml closed vessel (CV) at 0.15 g/ml density of loading for evaluation of ballistic parameters.

3.2 Measurement of Sensitivity

Impact sensitivity was measured by fall-hammer method using 2 kg drop weight and 20 mg sample. The height used refers to 50 per cent probability of explosion of the compositions. Friction sensitivity was measured by Julius Peter's apparatus using 10 mg sample. The values obtained refer to the minimum weight under which the sample of the composition did not ignite.

3.3 Thermal Characteristics

The deflagration temperature was obtained on 5 mg sample by gradually raising the temperature at the rate of 278 K/min in the Julius Peter's furnace. The temperature at which the sample ignited was recorded. The decomposition temperature was recorded using a differential thermal analyser (DTA). DTA curves were recorded in an inert atmosphere using 10 mg sample in platinum crucibles at heating rate of 283 K/min (Table 4). Calorimetric values of the compositions were

determined by Julius adiabatic calorimeter of 300 ml at 1 atm using 1g of the sample.

3.4 Thermal Stability

3.4.1 Abel Heat Test

The compositions were subjected to Abel heat (AH) test at 338.5 K. Time required for getting brown ring on the exposed starch iodide paper was recorded using a stop watch.

3.4.2 Methyl Violet Test

The compositions were subjected to methyl violet (MV) test at 393 K. Time required for changing the colour of methyl violet paper to salmon pink was recorded using a stop watch.

3.4.3 Bergman & Junk Test

The compositions were subjected to Bergman and Junk (B & J) test at 393 K for 5 hr. The total gaseous volume of nitrogen oxide evolved was measured titrimetrically.

3.5 Mechanical Properties

For determining mechanical properties, samples in dumbell shape were punched out of the propellant strips and dried up to the remanant volatile matter of 1 per cent. Tensile strength, percentage elongation and flexural properties were determined using an Instron universal materials testing machine (model-1185). For determination of percentage compression, the multi-tubular grains having $L/D = 1$ were made and tested using Instron machine.

Table 1. Chemical formulations and theoretically calculated ballistic performance of TAGN-based propellants

| Sr. No | Composition | | | | | | Impetus (J/g) | Flame Temp. (K) |
|--------|-------------|-----|-----|-----|-----|------|---------------|-----------------|
| | NC | GAP | Car | Res | RDX | TAGN | | |
| cc | 24 | 5 | .0 | | 70 | 0 | 1300 | 3600 |
| 2 | 24 | 5 | 0.7 | 0.3 | 50 | 20 | 1242 | 3216 |
| 3 | 24 | 5 | 0.7 | 0.3 | 45 | 25 | 1224 | 3136 |
| 4 | 24 | 5 | 0.7 | 0.3 | 40 | 30 | 1210 | 3060 |

*CC - Control composition, Car - Carbamate, Res - Resorcinol

4. RESULTS & DISCUSSION

Theoretical performance of the propellant compositions indicates that the successive replacement of RDX with TAGN into propellant composition at the rate of 7 per cent leads to decrease in T_f by 80 K with decrease in impetus by 15 J/g (Table 1). The results of ballistic evaluation from CV tests for each of the propellant compositions are presented in Table 2. It was observed that the experimentally determined values of impetus were in good agreement with the theoretically calculated values. The values of linear burning rate coefficient (β_1) and pressure exponent (α) determined by CV tests were found to increase successively. The marginal decrease in impetus is attributed to the significant decrease in the heat of explosion (calorimetric value) of TAGN (992 cal/g) as compared to that of RDX (1510 cal/g) resulted due to lower oxygen balance of TAGN (-33 per cent than that of RDX (-21.6 per cent). The lower T_f realised by TAGN-based propellants is attributed to the higher nitrogen content (58 per cent) of TAGN as compared to that of RDX (37 per cent). The gases evolved from the decomposition of TAGN are less

Table 2. Data on closed vessel tests

| NC | Composition | | | RDX | TAGN | P_{max} (MP _a) | Impetus (J/g) | Pressure exponent (α) | β_1 (cm/s/MP _a) |
|----|-------------|-----|-----|-----|------|------------------------------|---------------|--------------------------------|-----------------------------------|
| | GAP | Car | Res | | | | | | |
| 24 | 5 | 1.0 | — | 70 | | 225 | 1301 | 1.00 | 0.16 |
| 24 | 5 | 0.7 | 0.3 | 50 | | 214 | 1242 | 1.10 | 0.21 |
| 24 | 5 | 0.7 | 0.3 | 45 | | 211 | 1226 | 1.12 | 0.29 |
| 24 | 5 | 0.7 | 0.3 | 40 | | 207 | 1204 | 1.15 | 0.36 |

Closed vessel volume = 700 ml, loading density = 0.15 g/cc, web size of propellant = 1.5 mm, propellant density = 1.6 g/cc

erosive than those from the decomposition of RDX because of its low temperature of explosion. The T_f of TAGN is reported to be 2055 K as against 3255 K of RDX.

A higher burn rate is attributed to an homolytic fission of $>N-N<$ bonds in TAGN, producing highly unstable and reactive amino (NH_2) radicals. The energy released by the dissociation of NH_2 radicals is the source of heat produced at an early stage of the TAGN decomposition process and the same contributes towards the enhancement of burning rate characteristics. In contrast, RDX undergoes thermal decomposition *via* heterolytic fission of $>N-N<$ bonds producing ionic species rather than highly reactive and unstable free radicals. Secondly, the melt layer phenomenon that occurs during combustion of RDX is also reported to be responsible for the lower burning rate of the propellant¹¹. The burning rate of TAGN, is almost double than that of RDX, even though the energy contained in the unit mass of TAGN is less than that of RDX and, therefore, the increasing trend of β_1 and α was observed in the propellant compositions in which RDX was successively replaced by TAGN, from composition Nos. 1-4.

Results of sensitivity to impact and friction (Table 3) indicate that the level of sensitivity of the compositions is within the limits of safety and comparable to the control composition containing only RDX as an oxidiser. This may be attributed to an identical order of oxygen balance of the compositions¹².

Data on deflagration temperature indicates that the gradual decomposition of NC extended from

Table 3. Data on sensitivity

| Composition | | | | | | | Impact sensitivity H_{50} (cm) | Friction sensitivity (kg) | F of |
|-------------|-----|-----|-----|-----|------|----|--|------------------------------|------|
| NC | GAP | Car | Res | RDX | TAGN | | | | |
| 24 | 5 | 1.0 | - | 70 | 0 | 35 | 21 | 30 | |
| 24 | 5 | 0.7 | 0.3 | 50 | 20 | 37 | 22 | 32 | |
| 24 | 5 | 0.7 | 0.3 | 45 | 25 | 37 | 22 | 32 | |
| 24 | 5 | 0.7 | 0.3 | 40 | 30 | 37 | 22 | 32 | |

Percentage relative humidity = 55-60

433 K to the ignition temperature of the propellant. The decreasing trend of the ignition temperature indicates that the early decomposition of TAGN is responsible for the lower ignition temperature of the propellant. Decomposition temperatures of the compositions were found to be below 473 K and

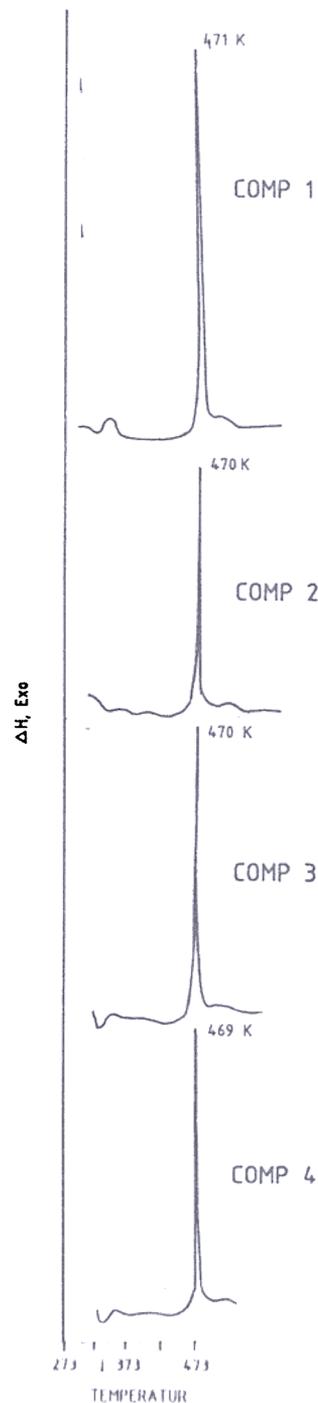


Figure 2. DTA curves

comparable to those of the RDX-based compositions (Table 4). An exothermic decomposition of GAP corresponds to cleavage of azide group structure ($-CH_2-N=N_2$ to $-C=N, N_2$ and H_2) with the release of heat energy¹³ to the order of 171 K cal/mole. The heat released in the condensed zone results in early decomposition of TAGN and RDX. Further, the decreasing trend of the decomposition temperatures is attributed to the presence of $>N-N<$ bonds in TAGN molecule. A single sharp exotherm indicates the uniformity and single mass decomposition (Fig. 2). Calorimetric values of the compositions were found to be in the decreasing order from composition 1 to 4. This may be attributed to the decreasing exothermicity of the reaction contributing for the successive heat output. (Table 4).

Results of thermal stability by AH test, MV test and B & J test indicate that the propellants are thermally stable (Table 5).

Data on mechanical properties of the compositions (Table 6) indicates that the tensile strength, percentage elongation, flexural properties and percentage compression were found to be reasonably good and nearly identical to the control composition containing only RDX as an oxidiser. This may be attributed to an identical level of polymeric and plasticiser content. |

CONCLUSION

Partial replacement of RDX by TAGN at the rate of 7 per cent into NC-based high energy gun propellants exhibit decrease in the T_f by 80 K, with marginal decrease in impetus (15 J/g). However, it increases the pressure index (α) and linear burning rate coefficient (β_1) by 0.02 units and 0.06 cm/s/MPa, respectively in the compositions containing 40-50 per cent RDX and 20-30 per cent TAGN. |

Table 4. Data on thermal characteristics tests

| NC | GAP | Composition | | | | Ignition Temp. (K) | Decomposition Temp.(K) | Calorimetric value (cal/g) |
|----|-----|-------------|-----|-----|------|--------------------|------------------------|----------------------------|
| | | Car | Res | RDX | TAGN | | | |
| 24 | 5 | | | | | 472 | 471 | 1180 |
| 24 | 5 | | 0.3 | 50 | 20 | 471 | 470 | 1070 |
| 24 | 5 | | 0.3 | 45 | 25 | 471 | 470 | 1040 |
| 24 | 5 | | 0.3 | 40 | 30 | 471 | 469 | 905 |

Table 5. Data on thermal stability

| NC | GAP | Composition | | | | AH test at 338.5 K (min) | MV test at 393 K (min) | B & J test at 393 K (ml/5g) |
|----|-----|-------------|-----|-----|------|--------------------------|---|-----------------------------|
| | | Car | Res | RDX | TAGN | | | |
| 24 | 5 | 1.0 | - | 70 | 0 | 11 | > 180 (no brown fumes or explosion in 5 hr heating) | 0.25 |
| 24 | 5 | 0.7 | 0.3 | 50 | 20 | 14 | 75 | 0.60 |
| 24 | 5 | 0.7 | 0.3 | 45 | 25 | 14 | 80 | 0.60 |
| 24 | 5 | 0.7 | 0.3 | 40 | 30 | 14 | 80 | 0.60 |

Table 6. Data on mechanical properties

| NC | GAP | Composition | | | | Tensile strength (kgf/cm ²) | Percentage elongation | Flexural test (mm) | Percentage compressibility |
|----|-----|-------------|-----|-----|------|---|-----------------------|--------------------|----------------------------|
| | | Car | Res | RDX | TAGN | | | | |
| 24 | 5 | 1.0 | - | 70 | 0 | 120 | 1.4 | 112 | 13.0 |
| 24 | 5 | 0.7 | 0.3 | 50 | 20 | 111 | 1.3 | 1.1 | 12.8 |
| 24 | 5 | 0.7 | 0.3 | 45 | 25 | 105 | 1.3 | 1.0 | 12.7 |

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