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Research article

Suitability of nitrogen rich compounds for gun propellant formulations

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ABSTRACT

This paper reports the suitability of a novel nitrogen rich compound, guanidinium-5-aminotetrazolate for RDX-based high-energy gun propellant formulations in respect of flame temperature as well as the burning rate characteristics. It has been found that the partial replacement of RDX with guanidinium-5-amino tetrazolate at the rate of five parts decreases the flame temperature of the propellant by about 120 K without adversely affecting the burning rate characteristics, i.e. linear rate of burning co-efficient and pressure exponent.

1. Introduction

NC–RDX-based compositions impart high force constant to gun propellant formulations but adversely boost the flame temperature beyond the safety limit of the gun material [1]. Higher flame temperature not only increase the gun erosion but also responsible for the increase of burning rate characteristics, i.e. linear burning rate co-efficient, β_1 and pressure exponent, α [2]. Burning rate characteristics of the propellant can be defined as: $r = \beta P^{\alpha}$, where r = rate of burning, β = burning rate co-efficient, P = chamber pressure, α = pressure exponent, β_1 = linear burning rate co-efficient at $\alpha = 1.0$ Therefore the trend is on to partially replace RDX with the nitrogen rich compounds (NRC) [3]. NRCs derive their energy from the combination of higher heats of formation and generation of large volume of gases mainly nitrogen. The propellant combustion gases rich in nitrogen act to re-nitride bore surfaces during firing and inhibit erosive surface reactions [4]. Moreover the lowered hydrogen concentration in the combustion gas of some of the propellants may also reduce hydrogen-assisted cracking of the bore surface [5]. In view of these versatile characteristics, NRCs have received major attention of gun propellant community. Literature survey reveals that azides, tetrazoles, triazines and triaminoguanidine salts are the possible categories of NRCs for the NC-based propellant formulations in order to achieve low flame temperature and minimal barrel erosion [6–8].

However, the latest experimental studies indicate that the incorporation of triaminoguanidine salts (TAGN and TAGAZ) into propellant matrix reduces the flame temperature but the propellant undergoes fast burning. As a result, they exhibit higher values for the burning rate characteristics [9,10]. A higher value of β_1 necessitates increase in web size of the propellant grain. Increase in web size in turn poses problems in manufacture, loadability and brittle fracture of the grain particularly at sub-zero temperature. Similarly, a large magnitude of α leads to exponential rise in burning rate and pressure, which affect the safety of the gun.

Hence, the choice of nitrogen rich compound needs to be done meticulously to ensure that their incorporation does not adversely affect the burning rate characteristics, i.e. β_1 and α. Damse et al. [11] investigated the decomposition mechanism for the nitrogen rich compounds under five different categories and explored the possibility of guanidinium-5-aminotetrazolate (GA) as a suitable candidate for gun propellant formulations in order to reduce the burning rate characteristics. In view of this, systematic studies have been carried out on the propellant compositions containing guanidinium-5-aminotetrazolate as the nitrogen rich compound in this paper. Experimental results in respect of ballistic parameter, sensitivity, thermal stability, and mechanical properties have been obtained and compared with that of the vis-à-vis compositions containing TAGN and TAGAZ so as to establish the suitability of NRC for the gun propellant formulations.

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2. Experimental

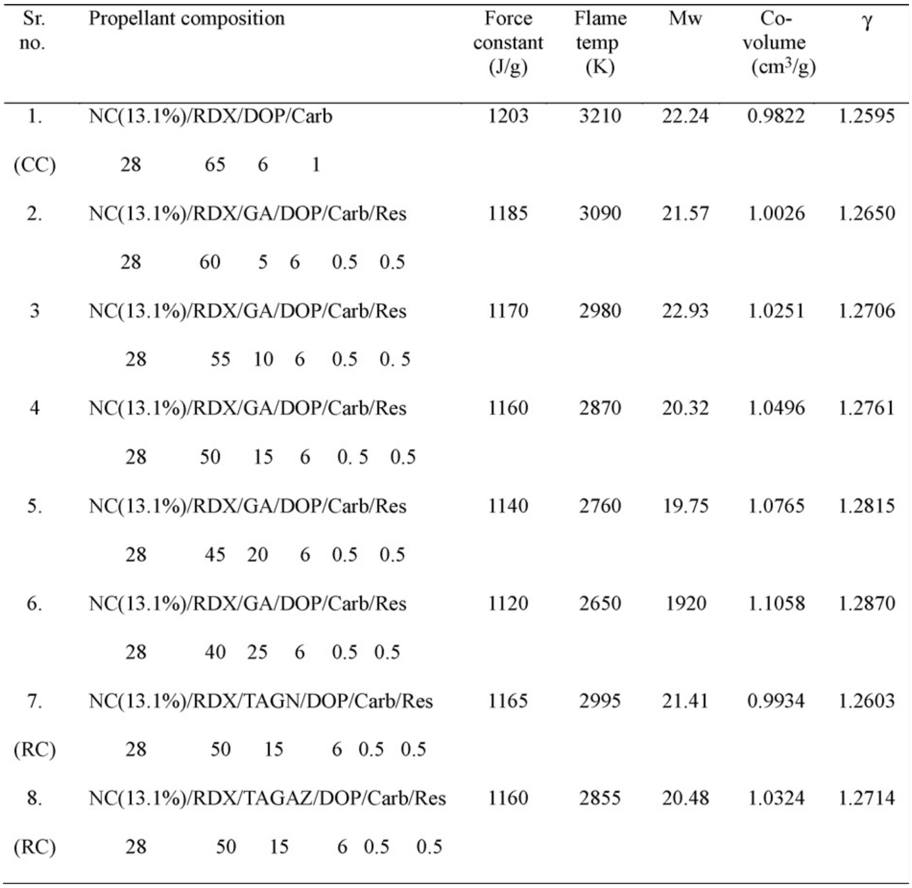
2.1. Materials

Materials like nitrocellulose (NC) of 13.1 N% and RDX of average particle size (5 μm) have been procured whereas the materials like DOP, carbamite, resorcinol and solvents were purchased from the commercial source. However, TAGN, TAGAZ and GA were synthesized in the laboratory on the lines of the reported procedures [12–14] and characterized by using the modern instrumental techniques, viz. FTIR, NMR and elemental analysis The purity of the compounds have been determined on the basis of HPLC technique and found more than 98%.

2.2. Propellant formulation and processing

A propellant composition containing 28% NC (13.1 N%), 65% RDX, 6% DOP and 1% carbamite was referred as the control composition for the present study and five different compositions were formulated with the partial replacement of RDX with GA. Two more compositions have also been formulated with 15 parts replacement of RDX with TAGN and TAGAZ respectively in order to compare the performance of GA-based propellant. It is to be noted that an additional stabilizer, resorcinol has been introduced into GA-, TAGN- and TAGAZ-based propellants (Table 1). Theoretical thermo-chemical parameters of the compositions were computed using 'THERM' programmer [15]. The compositions were prepared on the laboratory scale (1 kg batch) using the standard solvent method [16]. The 30% ethyl acetate was used for the GA-, TAGN- and TAGAZ-based compositions whereas, 30% acetone/alcohol of 70:30 ratio has been used for the preparation of the control composition. The propellants were made in to multitubular shape having seven-hole geometry and subjected to evaluation tests for the determination of various performance parameters.

Table 1
Theoretically calculated thermo-chemical parameters of the propellant compositions.



Sr. no.	Propellant composition	Force constant (J/g)	Flame temp (K)	Mw	Co-volume (cm^3/g)	γ
1. (CC)	NC(13.1%)/RDX/DOP/Carb 28 65 6 1	1203	3210	22.24	0.9822	1.2595
2.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 60 5 6 0.5 0.5	1185	3090	21.57	1.0026	1.2650
3	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 55 10 6 0.5 0. 5	1170	2980	22.93	1.0251	1.2706
4	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 50 15 6 0. 5 0.5	1160	2870	20.32	1.0496	1.2761
5.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 45 20 6 0.5 0.5	1140	2760	19.75	1.0765	1.2815
6.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 40 25 6 0.5 0.5	1120	2650	1920	1.1058	1.2870
7. (RC)	NC(13.1%)/RDX/TAGN/DOP/Carb/Res 28 50 15 6 0.5 0.5	1165	2995	21.41	0.9934	1.2603
8. (RC)	NC(13.1%)/RDX/TAGAZ/DOP/Carb/Res 28 50 15 6 0.5 0.5	1160	2855	20.48	1.0324	1.2714

CC: control composition; RC: reference composition; Carb: carbamite; Res: resorcinol.

2.3. Performance evaluation

2.3.1. Ballistic evaluation

The compositions were fired in a 700 cm^3 closed vessel (CV) at 0.20 loading density for the evaluation of the ballistic parameters such as force constant, flame temperature and he burning rate characteristics [17].

2.3.2. Measurement of sensitivity

Impact sensitivity was measured by fall hammer method using 2 kg drop weight and 20 mg of the sample. The height refers to 50% probability of explosion of the compositions [18]. Friction sensitivity was measured by Julius peter apparatus using 10 mg sample. The values refer to the minimum weight under which the sample of the composition did not ignite [19].

2.3.3. Thermal stability

The compositions were subjected to Abel heat test at 160 °F temperature. Time required for getting the brown ring to starch iodide paper was recorded. The compositions were subjected to methyl violet test at 120 °C temperature. Time required for changing the colour of methyl violet paper was recorded. The compositions were subjected to Bergman and Junk (B&J) test, at 120 °C temperature for 5 h. The total gaseous volume of nitrogen oxides evolved was measured titrimetrically [20]. The specification limit for the acceptance

Table 2
CV results of the propellants.

Sr. no.	Propellant composition	Force constant (J/g) Theo	Force constant (J/g) Exptl	Flame temp (K)	Linear burning rate coefficient β_1 (cm/S/MPa)	Pressure exponent α
1. (CC)	NC(13.1%)/RDX/DOP/Carb 28 65 6 1	1203	1200	3210	0.14	0.84
2.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 60 5 6 0.5 0.5	1185	1182	3090	0.14	0.85
3	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 55 10 6 0.5 0. 5	1170	1168	2980	0.14	0.85
4	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 50 15 6 0. 5 0.5	1160	1157	2870	0.15	0.90
5.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 45 20 6 0.5 0.5	1140	1137	2760	0.13	0.80
6.	NC(13.1%)/RDX/GA/DOP/Carb/Res 28 40 25 6 0.5 0.5	1120	1118	2650	0.13	0.80
7. (RC)	NC(13.1%)/RDX/TAGN/DOP/Carb/Res 28 50 15 6 0.5 0.5	1165	1163	2995	0.30	1.40
8. (RC)	NC(13.1%)/RDX/TAGAZ/DOP/Carb/Res 28 50 15 6 0.5 0.5	1160	1157	2855	0.30	1.40

Loading density: 2.0 g/cm^3, volume = 700 cm^3. Estimated limits: β_1 = not more than 0.15 cm/s/MPa, α = not more than 1.0. Maximum chamber pressure = 280 MPa.

criterion of the propellant on the basis of thermal stability tests, viz. Abel heat test is not less than 10 min; methyl violet test is not less than 40 min till there is no brown fumes appeared and for B&J test is not less than 0.5 cm^3/5 g.

2.3.4. Mechanical properties

For determination of the mechanical properties so-called 'minisamples' in dumbbell shape was punched out of the propellant strips and dried up to 1% volatile matter level. Tensile strength, percentage elongation and flexural properties were determined in the Instron Universal Machine (Model 1185). For the determination of % compression multitubular grains having $L/D = 1.0$ was made and subjected to Instron machine [21]. The specification limit for the % compression is not less than 10.00 and tensile strength is not less than 100 kg f/cm^2.

3. Results and discussion

Theoretical data in respect of thermo-chemical parameters of the propellant compositions based on GA, TAGN and TAGAZ are presented in Table 1. It is reported that the incorporation of TAGN, TAGAZ and GA into propellant matrix renders a system strongly autocatalytic perhaps due to formation of alkaline medium in the system as a result of evolution of ammonia gas. This renders poor thermal stability to the propellant. To overcome this problem a supplementary stabilizer, resorcinol has also been incorporated into propellant matrix along with the carbamite in 0.5:0.5 parts [22]. However, 1.0 part of carbamite has been used for the control composition containing single oxidizer, RDX. Theoretical calculations indicate that the successive replacement of RDX with guanidinium-5-amino tetrazolate (GA) at the rate of five parts leads to decrease the flame temperature (T_f) of the propellant in the range 110–120 K with decrease in force constant to the order of 15–20 J/g (Table 1). It is further seen that the replacement of RDX with GA to the extent of 15 parts decrease the flame temperature (T_f) of the propellant by about 340 K with decrease in force constant by about 43 J/g, whereas the same replacement of RDX with TAGN leads to decrease T_f by about 125 K with decease in force constant by about 38 J/g and that with TAGAZ decreases T_f by about 355 K with decrease in force constant by about 43 J/g (Table 1). The results of the ballistic evaluation from CV test for the propellant compositions are presented in Table 2. It was found that experimentally determined values of force constant are in good agreement with the theoretically calculated values. The highest potential of TAGAZ and GA to reduce the flame temperature of the propellant at only marginal decrease in force constant is attributed to their higher nitrogen content (TAGAZ = 85 N%, GA = 78 N%), positive heat of formation (ΔH_f TAGAZ = +414 kJ/mol and GA = 85.9 kJ/mol), low molecular weight (Mw) of the combustion gases, TAGAZ = 17 and GA = 16.8 and higher specific heat of gases (γ) TAGAZ = 1.2770 and (γ)GA = 1.2750 as compared to that of TAGN and RDX. However, the values of linear rate of burning co-efficient (β_1) and pressure exponent (α) for the propellants containing TAGN and TAGAZ found to increase towards the higher level as compared to the propellants based on GA (Table 2). Higher burn rate characteristics exhibited by the propellants containing triaminoguanidine salts (TAGN and TAGAZ) are attributed to the homolytic fission of N–NH$_2$ bonds available within the molecular structure of TAGN and TAGAZ which could produce highly reactive and unstable (NH$_2$) radicals. The energy (104.3 kJ/mol) released by the dissociation of NH$_2$ radicals acts as a source of heat for the decomposition process followed by the triaminoguanidinium salts that ultimately contributes to enhance the burning rate characteristics [23]. It is a known fact that decomposition of an explosive material depends upon the generation of free radicals that forms a nuclease of chain process and hence materials that help in the generation of free radicals or removal of barrier in their

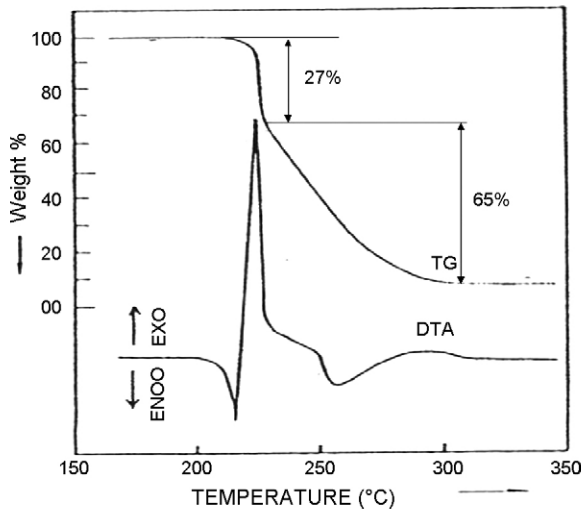


Fig. 1. Thermal analysis of triaminoguanidine nitrate.

generation would lower the activation energy [24].

In contrast, the propellants containing GA have lower values of burning rate characteristics (β_1 and α) and thus they exhibit the suitability for gun propellant formulations (Table 2). The lower values of burning rate characteristics obtained with the GA-based propellants are attributed to the favorable decomposition mechanism followed by GA as investigated on the basis of thermal analysis. Results obtained on the basis of TG, DTA, TG–FTIR, DSC and Py-GC–MS experiments indicate that GA undergoes decomposition with the initiation of ring opening of the heterocyclic tetrazole structure with the evolution of hydrogen azide. This is further followed by the formation of thermally stable cyclic azines like melamine species in the gaseous phase [25]. It is well reported that the melamine and its higher homologues retard the heat and mass transfer rates at the surface of the propellant and thus act as burning rate modifier [26]. Hence, the propellants containing GA exhibit lower burning rate characteristics. These findings have been further supported by the thermo-chemical analysis carried out by Kubota et al. [23]. It has been brought out from the TG–DTA profiles that the triaminoguanidinium salts like TAGN containing the facile N–NH_2 bonds undergo rapid exothermic decomposition whereas the compounds like GN and GA lacking the facile N–NH_2 bonds undergo slow exothermic decomposition (Figs. 1–3). Damse et al. investigated the fact that the nitrogen rich compounds undergoing rapid exothermic decomposition (as shown in the TG–DTA profile of TAGN) exhibit higher burning rate characteristics whereas the compounds undergoing slow exothermic decomposition (as shown in the TG–DTA profile of GN and GA) exhibit lower burning rate characteristics [11].

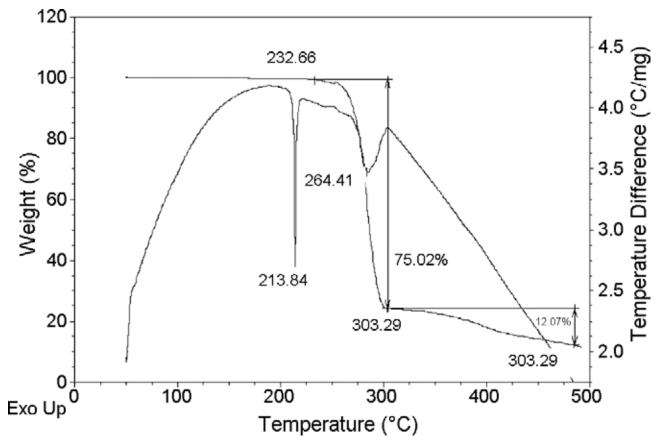


Fig. 2. Thermal analysis of guanidine nitrate.

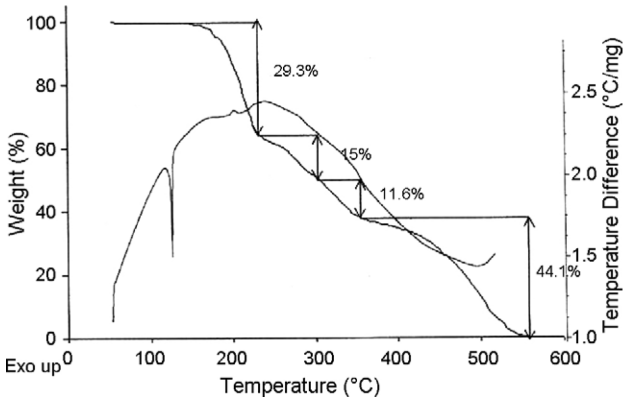


Fig. 3. Thermal analysis of guanidinium-5-aminotetrazolate.

Results obtained on the impact sensitivity test in terms of $H_{50\%\text{expl}}$ and friction sensitivity test as the dead load indicate that the GA-based propellants are less sensitive than the TAGN-based propellants and comparable to the TAGAZ-based propellants. This is quite consistent with the order of oxygen balance of the nitrogen rich compound constituting the propellant formulation (OB_{100}, GA = 84.0, TAGN = 33.3 and TAGAZ = 87.0). However, the data of sensitivity obtained for the compositions under the present investigation indicate that the compositions are safe ($H_{50\%\text{expl}}$ = 45–50 cm and friction = 26–30 kg) for the gun propellant applications.

Results of thermal stability tests like Abel heat test, methyl violet test and B&J test indicate that the GA-based propellants are thermally stable (Abel heat test = 13 min, methyl violet test = 80 min without evolution of the brown fumes, B&J test = 0.80 cm^3/5 g) and the level of thermal stability is quite comparable to that of the TAGN- and TAGAZ-based propellants (Abel heat test = 12–13 min, methyl violet test = 60–80 min without evolution of the brown fumes, B&J test = 0.60–0.80 cm^3/5 g). However, the thermal stability for all the propellants have been improved with the incorporation of an additional stabilizer, resorcinol. This is due to the fact that resorcinol can offer an activated aromatic ring for substitution reactions with oxides of nitrogen to take place at ortho and para position, due to strong electron donating mesomeric effect of OH group [22].

Experimental data obtained on mechanical properties in respect of tensile strength (125 kg f/cm^2), percentage elongation (1.5%), breaking displacement (1.4), compressive strength (310 kg f/cm^2) and percentage compression (13.00) indicate that the GA-based propellants have reasonably good mechanical strength and is quite comparable to that of the TAGN- and TAGAZ-based propellants. This is attributed to the structural integrity of the propellant matrix improved due to addition of the nitrogen rich compounds, viz.; TAGN, TAGAZ and GA. As the nitrogen rich compounds contain more number of amine (–NH_2) hydrogen atoms, they can form a network of intermolecular hydrogen bondings with the oxygen atoms of nitro groups available in the molecular structure of RDX. Thus, the propellants containing TAGN, TAGAZ and GA have better mechanical properties than the propellant containing only RDX as the energetic oxidizer. Moreover, the nitrogen rich compounds have higher re-enforcements effect than RDX.

4. Conclusions

Guanidinium-5-aminotetrazolate (GA) has been found to be a suitable candidate amongst the energetic nitrogen rich compounds studied in this paper. It reduces the flame temperature of the propellant significantly without adversely affecting the burning rate characteristics. In contrast the other nitrogen rich compounds like triaminoguanidine nitrate and triaminoguanidine azide though reduce the flame temperature of the propellant, they increase the burning rate characteristics beyond the desired level of the gun propellant. Moreover, the incorporation of GA maintains the level of sensitivity, thermal stability and mechanical properties within the acceptable range of gun propellant.

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