Influence of Guanylurea Dinitramide (GUDN) on the Thermal Behaviour, Sensitivity and Ballistic Properties of the B-KNO₃-PEC Ignition System

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Abstract: Boron and potassium nitrate are the key components for the ignition system of the igniter composition for rocket propellants. Boron-potassium nitrate-ethyl cellulose (B:KNO₃:PEC) in proportions of 30:70:10 is a well established igniter composition. The composition delivers a maximum pressure in the range 4.0-4.6 MPa in closed vessel firing at a loading density of 0.01 g/cm³. For the effective ignition of a large booster stage propellant (length more than 4 m), an enhancement in the maximum pressure, without affecting safety, is a prime requirement. The use of guanylurea dinitramide (GUDN) in an igniter composition has not been reported in the literature. Hence, the present study on the effect of GUDN on the combustion behaviour and sensitivity of the B/KNO₃ composition (30/70) has been carried out. Several compositions containing different weight percents of GUDN were prepared. Their thermal behaviour was determined by thermal analysis DSC-TGA. Their sensitivities to external stimuli such as impact, friction and spark were evaluated. The results of closed vessel firings indicated that GUDN-based igniter compositions produced higher peak pressures (up to 4.5 MPa to 5.8 MPa), with invariably lower burning times, compared to the control composition. The REAL computer programme indicated an increase in the flame temperature of the composition from 2238 K to 2425 K on addition of GUDN. All of the compositions were insensitive towards friction up to 36 kg, and towards spark up to 5 J energy.

Keywords: ballistics, guanylurea dinitramide, igniter, sensitivity, thermal analysis

1   Introduction

In most ignition systems, the solid propellant ignition is dominated by a thermal induction interval during which the temperature of the propellant surface is raised by external heating to the temperature at which the chemical reaction rates become significant. Propellant exothermic reactions rapidly become the dominant heat source and ignition of the propellant is achieved. The propulsive force of a solid rocket motor is derived from the controlled combustion of the solid propellant fuel at high temperature and pressure [1]. The function of the igniter is to initiate this combustion reaction in a restricted and predictable mode and at a specific rate. The performance of an igniter has a significant effect on the overall performance of the propulsion system. Specifically, the mass and the energy fluxes from the igniter and the fraction of condensed particles in the igniter; the combustion products influence the amount and the rate of heat transfer to the solid propellant surface during the ignition transition period. Therefore, the selection of the igniter composition depends on the combustion behaviour and physicochemical characteristics of the propellant. Other characteristics to be considered are flame temperature, safety, sensitivity towards impact, friction and spark, shelf life, cost effectiveness and availability of raw materials [2]. Most modern high performance rockets use a boron-potassium nitrate pyrotechnic composition for the ignition of the solid rocket propellant. The low molecular weight, high heat output, ready ignitibility with KNO_3, liberating a large amount of heat, and persistence in burning, make the boron-potassium nitrate based pyrotechnic composition a very efficient igniter composition [3]. The decomposition of potassium nitrate is an endothermic reaction and can be activated by the addition of high explosives which decompose exothermically [4].

Guanylurea dinitramide (GUDN) is a white crystalline solid and is a stable salt of dinitramidic acid, with good thermal stability, low water solubility and is non-hygroscopic [5]. GUDN is an energetic material with low vulnerability to impact and friction and is a good candidate for insensitive munitions [5]. Its thermal stability is comparable to RDX and superior to that of ammonium dinitramide (ADN). GUDN can find application in LOVA propellants [6], melt cast and PBX high explosive formulations [7-9]. Besides the advantages of its low sensitivity, GUDN burns at an extremely low temperature, which is important in automatic guns where barrel erosion is often a problem.

In view of this we have carried out studies on the effect of GUDN on the ignition of B/KNO$_3$/PEC (plasticized ethyl cellulose) compositions, using 5 and 10 parts of GUDN in order to observe the effect on pressure output, ignition delay and rise time. Three compositions were prepared, B/KNO$_3$/PEC (30/70/10), B/

KNO$_3$/PEC/GUDN (30/70/10/5) and B/KNO$_3$/PEC/GUDN (30/70/10/10) in granular form (passing 25 BSS and retaining on 52 BSS). The compositions were evaluated for various performance parameters such as heat output, impact sensitivity, friction sensitivity and spark sensitivity. Closed vessel tests indicated that the GUDN based igniter compositions produced higher peak pressures with invariably shorter burning time at up to 4.5 MPa to 5.8 MPa. The addition of GUDN resulted in higher heat output and a slight increase in sensitivity towards impact. The thermal-analysis results showed a change in the decomposition temperature of B/KNO$_3$/PEC from 499 °C to 515 °C on addition of GUDN. The REAL computer programme indicated that the addition of GUDN increased the flame temperature of the composition from 2238 K to 2425 K.

2   Experimental

Amorphous boron (purity >95% and particle size <1 µm) Ecka U.K., and KNO$_3$ (grade I having purity >99% and particle size 63-90 µm) were used. Guanylurea sulfate was synthesized from dicyandiamide by treatment with aqueous H$_2$SO$_4$. GUDN was synthesized by nitration of the ammonium salt of sulphamic acid with conc. HNO$_3$/H$_2$SO$_4$ at −40 °C to −50 °C, and further treatment with an aqueous suspension of guanylurea sulfate. The synthesized GUDN [10] was thoroughly characterized using UV, FTIR and DSC, and had purity of 98-99%. The igniter compositions were fired in a 100 cm^3 closed vessel with a loading density of 0.01 g/cm^3 to determine the ballistic parameters, such as the maximum pressure (P$_{max}$) and the ignition delay (ID) time. To determine the ballistic properties, the pellets were assembled in an Al (0.5 mm) canister of torridial shape. The igniter was loaded in a vented vessel motor of volume 5.5 L with a throat diameter of 8.5 mm, and was initiated by a single pyrocartridge (PC100). A fall hammer apparatus was employed to measure the impact sensitivity (2 kg drop weight) and the friction sensitivity was measured on a Julius Peters apparatus (20 mg sample).

2.1 Preparation of igniter composition

The igniter composition selected for the study comprised 30 parts by weight of a metal fuel − boron (grade I) having particle size <1 µm, 70 parts by weight of inorganic oxidizer − potassium nitrate (KNO$_3$ grade I) having particle size 63-90 µm and 10 parts by weight of plasticized ethyl cellulose as an inorganic fuel-binder. The composition was prepared by mixing accurately weighed boron/potassium nitrate (30/70) by passing through a 600 µm sieve three times for uniform mixing. The composition was then mixed with the required amount of

GUDN to prepare the three compositions in which the GUDN percentage was varied from 5 parts to 10 parts. This dry mixture was then mixed with the binder solution in a planetary mixer to obtain a homogeneous dough. This dough was then granulated by passing through a 600 μm sieve and retaining on 300 μm sieve to obtain granules of size 300-600 μm. The compositions were analyzed for their thermal, ballistic and sensitivity behaviour.

2.2 Thermal analysis

Thermal analysis of the igniter compositions was carried out using DSC-TGA (Perkin Elmer Ltd.) at a heating rate of 10 °C/min. The thermal analysis results are listed in Table 1. The DSC data for the $B/KNO_3/PEC$ composition exhibited two endothermic peaks at 139 °C and 337 °C, which are due to the crystalline transition of KNO_3 from orthorhombic to trigonal, and the phase transition of KNO_3, respectively. There was an exothermic peak at 499 °C, which is attributed to the oxidation of B to B_2O_3 and BO *etc*. The addition of GUDN shifted this exothermic peak to 515 °C and 552 °C with 10 and 20 parts of GUDN, respectively. This indicates that GUDN influences the oxidation reaction of boron. The results are listed in Table 1. The DSC curves of the standard composition and the GUDN-based igniter compositions are displayed in Figures 1-3.

Table 1. Thermal analysis of the igniter compositions

| Composition	Decomposition stages	Weight loss [%]	Temperature range [°C]	Endo peak [°C]	Exo peak [°C]
ME-445 B:KNO₃:PEC 30:70:10	I	3.17	83.43-223.85	139.58	
	II	10.11	233.85-372.30	337.88	499.41
	III	20.61	372.30-542.03		
ME-498 Expt No-1 B:KNO₃:PEC; GUDN (10%)	I	2.22	75.44-161.30	137.84	
	II	6.16	161.30-215.22	198.07	
	III	14.25	215.22-375.63	334.39	515.13
	IV	19.11	375.63-596.61		
ME-499 B:KNO₃:PEC; GUDN (20%)	I	1.60	77.09-175.22	137.28	
	II	6.55	175.22-233.79	203.55	
	III	15.23	233.79-414.83	332.64	552.40
	IV	14.74	414.83-562.41		
	V	3.58	562.41-690.96		
ME-500 B:KNO₃:PEC; GUDN (30%)	I	1.31	99.15-182.06	135.35	
	II	11.03	182.04-225.42	204.68	
	III	20.10	225.42-380.60	331.38	--
	IV	49.40	380.60-732.04		

The DSC-TGA behaviour of the standard composition (ME-445) is shown in Figure 4. The TGA curve of the B/KNO$_3$/PEC showed endothermic peaks at 139.58 °C and 337.88 °C. It also showed an exothermic peak at 499.91 °C. The total weight loss was 33% weight up to 550 °C. This may correspond to decomposition of the binder content in the composition. The weight loss from 400 °C to 515 °C was 19.11%, which may be due to evolution of gaseous products during the oxidation-reduction reaction of the fuel and oxidizer in the composition. The DSC-TGA behaviour of the composition containing 10% GUDN (Figure 1) showed a three stage decomposition at 137.84 °C, 198.07 °C and 334.39 °C. It also showed an exothermic peak at 515.13 °C. The total weight loss was 44.72% up to 600 °C. In the case of 20% GUDN in the igniter composition, the DSC-TGA curve (Figure 2) showed endothermic peaks at 137.28 °C, 203.55 °C, and 332.64 °C. The exothermic peak was observed at 552.40 °C with a total weight loss of 41.67% up to 700 °C. The DSC-TGA of the composition containing 30% GUDN (Figure 3) showed a three stage decomposition at 135.35 °C, 204.68 °C, and 331.38 °C. The total weight loss was 81.83% up to 800 °C.
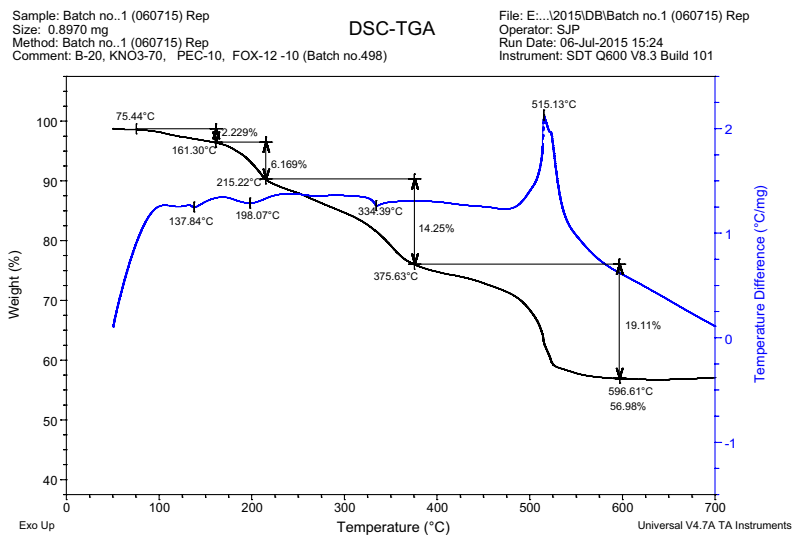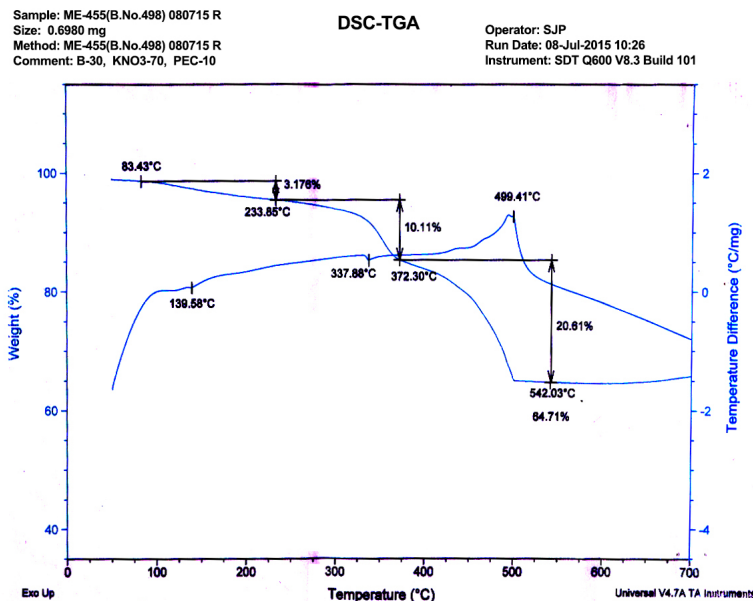

Figure 1.   DSC-TGA curves of igniter composition (GUDN 10%)
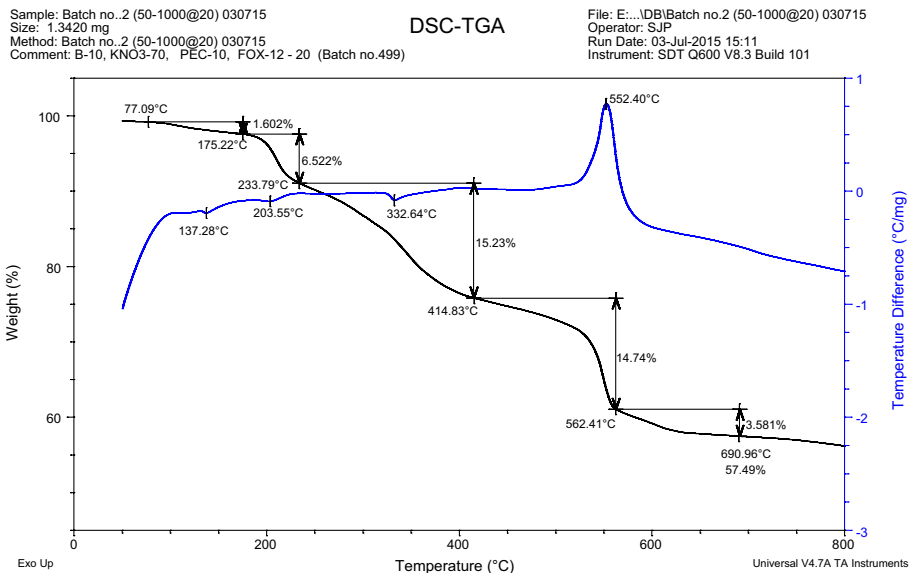
Figure 2.   DSC-TGA curves of igniter composition (GUDN 20%)
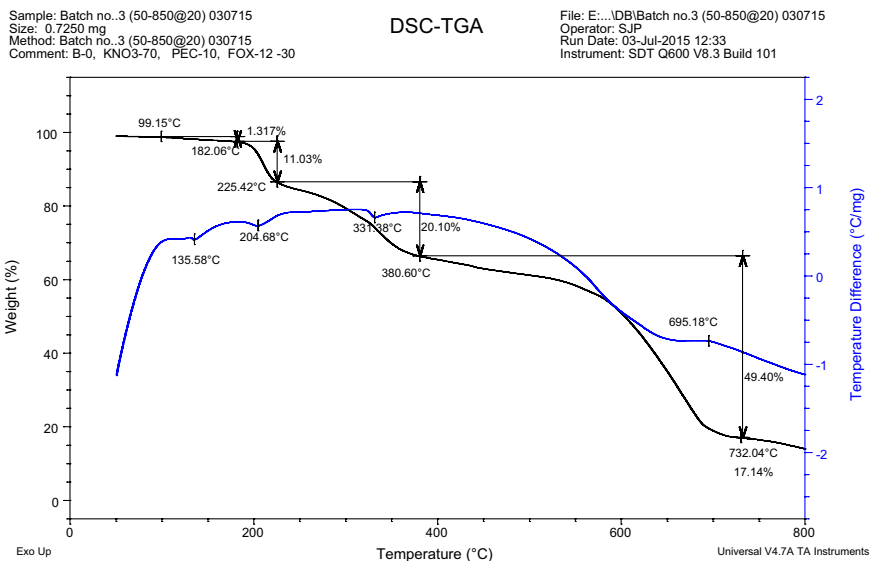
Figure 3.   DSC-TGA curves of igniter composition (GUDN 30%)

Figure 4.   DSC-TGA curves of the standard igniter composition (ME-445)

The DSC-TGA curves of GUDN-based compositions revealed that as the amount of GUDN was increased from 0 to 20 parts, the percent weight loss increased from 33.89% to 41.67%. Meanwhile the composition without boron but with 30 parts GUDN showed an enhanced weight loss of up to 81.84%. From the TGA curves it was observed that as the percent of GUDN was increased from 0% to 20%, the exothermic peak shifted from 499 °C to 552 °C. In the case of 30 parts of GUDN without boron no extra exothermic peaks were observed.

2.3 Sensitivity tests

The impact sensitivities (height of 50% explosion) were measured using a Fall Hammer apparatus by the Bruceton Staircase method (2 kg drop weight) and sensitivities to friction were measured by a Julius Peters friction sensitivity apparatus (20 mg sample). The sensitivities to spark were determined by placing a 10 mg sample between two electrodes at a separation of 2.0-2.5 mm and the spark energy was varied from 15 mJ to 5 J.

Table 2.   Friction and impact sensitivity of the igniter compositions

Sr. No.	Composition	Sensitivity results		
		Impact test		Friction sensitivity [kg]
		H_{50} m	F of I (Figure of insensitiveness)	
1	ME-445 B:KNO$_3$:PEC (30:70:10)	0.52	66	36
2	ME-498 B:KNO$_3$:GUDN:PEC (30:70:10:10)	0.52	66	36
3	ME-499 B:KNO$_3$:GUDN:PEC (30:70:20:10)	0.55	70	36
4	ME-500 B:KNO$_3$:GUDN:PEC (30:70:30:10)	insensitive up to 1.7	100	36

The results of the impact, friction and spark sensitivity tests on the compositions are listed in Tables 2 and 3. They were found to be unchanged by the addition of GUDN. All of the compositions were highly insensitive towards friction and the compositions having 20% and 30% GUDN were less impact sensitive than the control composition (ME-445).

Table 3.   Results of spark sensitivity

Sr. No.	Composition	Capacitance [µF]	Voltage [kV]	Energy at spark gap [J] ±15% tolerance	Ignited/ not ignited	Temp. [°C]	RH [%]
1	B:KNO$_3$:PEC 30:70:10	0.03	8	0.960	not ignited	30	56
2	B:GUDN: KNO$_3$:PEC 30:10:70:10	0.1	9	4.05	not ignited	30	56
3	B:GUDN: KNO$_3$:PEC 10:20:70:10	0.1	10	5.0	not ignited	30	56
4	B:GUDN: KNO$_3$:PEC 0:30:70:10	0.1	10	5.0	not ignited	30	56

2.4 Theoretical calculations for the analysis of the igniter compositions

The thermodynamic parameters of $B:KNO_3:PEC:GUDN$ based igniter compositions at equilibrium were calculated at constant volume using REAL programme.

**Table 4.** Theoretical calculations for the analysis of the igniter compositions

Composition	Flame temp. [K]	Pressure [MPa]	Entropy [kJ/kg]	Cp [kJ/kg]
B:GUDN:KNO$_3$:PEC 30:10:70:10	2347.44	0.1000	7.9037	1.7133
B:GUDN:KNO$_3$:PEC 10:20:70:10	2381.21	0.1000	8.2665	1.7954
B:GUDN:KNO$_3$:PEC 0:30:70:10	2425.73	0.1000	8.6227	1.8780

For this $B:KNO_3:PEC$ (30:70:10) was used as the base composition and boron was partially substituted by GUDN (10, 20 and 30 parts). It was observed that the addition of GUDN enhances the flame temperature of the B/KNO_3 composition from 2238 K to 2425 K due to the formation of species like N_2. As the amount of GUDN was increased from 0 to 10 parts in the formulation, the concentrations of KBO_2, B_2O_3, B_2O_2, BO and N_2 species also increased considerably, which leads to the enhancement of the flame temperature of the igniter compositions. The GUDN significantly influenced the combustion behaviour of the $B:KNO_3$ compositions.

Table 5. Concentrations of chemical species at equilibrium (mol/kg)

Composition	B$_2$O$_3$	KBO$_2$	BO	HBO	N$_2$
B:KNO$_3$:PEC (30:70:10)	0.068	4.340	0.122	0.738	0.052
B:GUDN:KNO$_3$:PEC (30:10:70:10)	0.0781	2.3195	0.2721	0.9934	0.1922
B:GUDN:KNO$_3$:PEC (10:20:70:10)	0.0724	1.5765	0.3382	1.155	0.3207
B:GUDN:KNO$_3$:PEC (0:30:70:10)	0.0630	0.9966	0.4312	1.3019	0.5989

2.5 Closed vessel tests (ballistic properties)
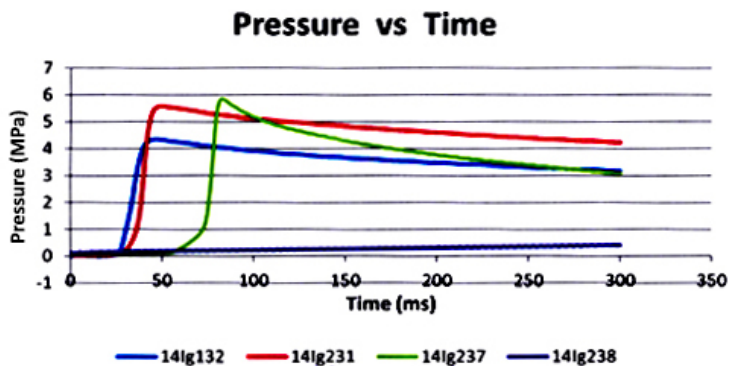
Figure 5.   Comparison of CV-results of GUDN-based igniter compositions with the standard composition. (14lg 132 − standard ME-445 igniter composition, 14lg 231 − composition with 10% GUDN, 14lg 237 − composition with 20 % GUDN, and 14lg 238 − composition with 30% GUDN).

Table 6.   Results of the CV-firings of GUDN-based igniter compositions

Sr. No.	Composition	P_{max} [MPa]	Ignition delay [ms]	Time to P_{max} [ms]
1	B:GUDN:KNO$_3$:PEC (30:10:70:10)	5.37	32.40	23.40
2	B:GUDN:KNO$_3$:PEC (10:20:70:10)	5.84	201.00	75.00
3	B:GUDN:KNO$_3$:PEC (0:30:70:10)	Not getting fired	--	--

Figure 5 shows the graph of the CV-results with respect to pressure and delay time. A Parr Adiabatic Bomb calorimeter (100 cm^3 capacity) was used to determine the Cal-Val (Figure 4) of the igniter composition in air, and ballistic performance evaluations such as pressure maximum (P_{max}) and rise time/BTPm. The results showed that maximum P_{max} values 5.5 MPa were achieved for GUDN. The rise time (BTPm) decreased with addition of GUDN. The calorimetric value showed an increasing trend on addition of GUDN. A higher P_{max} value and lower rise time (BTP$_m$) were observed for GUDN-based igniter compositions (Table 6).

3   Conclusions

The effect of GUDN on the ignition of a B/KNO$_3$/PEC composition was studied to check for changes in the pressure output, ignition delay and rise time. For this study three compositions, B:KNO$_3$:PEC (30:70:10), B:KNO$_3$:PEC:GUDN (30:70:10:5) and B:KNO$_3$:PEC:GUDN (30:70:10:10) in granular form were prepared. The closed vessel tests indicated that the GUDN-based igniter compositions produced higher peak pressures with invariably lower burning times, up to 4.5 MPa to 5.8 MPa. It was observed that addition of GUDN increased the P$_{max}$ value and decreased the rise time (BTPm). However addition of GUDN decreased the heat output and slightly increased the sensitivity towards impact. The thermal analysis results showed a lowering of the decomposition temperature of B/KNO$_3$/PEC on addition of GUDN. The REAL computer programme indicated an increase in the flame temperature of the composition from 2238 K to 2425 K on addition of GUDN. The CV firing data showed higher P$_{max}$ values and lower rise times (BTP$_m$) for GUDN-based compositions. The addition of GUDN also lowers the decomposition temperature of the B/KNO$_3$ igniter system without altering the friction and impact sensitivities.

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