



## **Thermal Analysis and Sensitivity Studies on Guanylurea Dinitramide (GUDN or FOX-12) Based Melt Cast Explosive Formulations**

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**Abstract:** Guanylurea dinitramide (GUDN or FOX-12) is a stable salt of dinitramidic acid with good thermal stability, and is a good candidate for insensitive formulations. Thermal analysis reveals the compatibility of GUDN with benchmark explosives such as RDX and TNT in melt cast explosive formulations. The paper describes a thermal and sensitivity study of GUDN with RDX and TNT. In the present study GUDN was evaluated as a possible replacement for RDX/TNT based aluminized and non aluminized melt cast explosive formulations. The thermal properties of the composition were investigated as well as its sensitivity to impact and friction. Its thermal decomposition behavior was compared to a control composition based on RDX and TNT. The thermal and sensitivity results proved the worth of these compositions for melt cast explosive applications.

**Keywords:** guanylurea dinitramide, FOX-12, insensitive explosive, sensitivity, thermal analysis

### **1 Introduction**

In the last twenty years military explosives and energetic materials in general have changed significantly. This has been due to several factors which include new operational requirements such as Insensitive Munitions (IM) [1], but also the availability of new materials and new assessment and modelling techniques. The common explosives like 2,4,6-trinitro toluene (TNT) [2], 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are most widely used in the explosive formulations [2]. So, there is a need to develop new ingredients and formulations, which are insensitive to

common stimuli [3] while still retaining the desired performance characteristics. The major requirement is the reduction of the hazards to personnel equipment and structures due to accidental initiation of a weapon due to stimuli such as rough handling, fragment impact and thermal cook-off. GUDN has attracted considerable interest because it is expected that its sensitivity could be as low as that of TATB, while its performance has been found comparable with that of RDX and HMX [4]. TNT based melt cast high explosive compositions have immense importance as energetic fillers for warheads and projectiles due to their extensive applications in high explosives formulations.

GUDN is a colorless crystalline solid and stable salt of dinitramidic acid. It has good thermal stability, low water solubility and is also non-hygroscopic [5]. GUDN is an energetic material with low vulnerable to impact and friction stimuli and hence is a good candidate for insensitive munitions [6]. Its thermal stability is comparable to RDX and superior to that of ammonium dinitramide (ADN). GUDN may also find applications in LOVA propellants [7] and melt cast and PBX high explosive formulations [8]. Any energetic material, before its direct use in propellant formulations, needs to be tested for its stability, sensitivity and compatibility with additives that help with the processing of the energetic ingredients [9, 10]. Besides the advantage of low sensitivity, GUDN burns at an extremely low temperature, which is important in automatic guns where barrel erosion is often a problem [11]. Thermal and compatibility studies of GUDN based compositions are one of the interesting areas in the field of insensitive munition systems. Such studies support the belief that GUDN is a prime candidate as an energetic filler in insensitive munitions. Hence, the compatibility of the GUDN with other explosives is of prime importance.

In the present work, thermal and sensitivity studies of GUDN in combination with TNT and RDX were performed in order to determine the worth of GUDN in melt cast explosive formulations. The thermal behavior and the kinetics of RDX/TNT, GUDN/TNT, and GUDN/TNT/Al mixtures were studied using differential scanning calorimetry (DSC) and thermogravimetry (TG). The thermal and sensitivity results obtained for GUDN based compositions showed GUDN to be a promising candidate for use in melt cast formulations.

## 2 Materials and Methods

### 2.1 Materials

The chemicals used were of analytical reagent grade. Guanylurea sulfate was synthesized from dicyandiamide by treatment with aqueous  $\text{H}_2\text{SO}_4$ . The GUDN

was synthesized at HEMRL, Pune, India. It was prepared by nitration of the ammonium salt of sulphamic acid using concentrated  $\text{HNO}_3/\text{H}_2\text{SO}_4$  at  $-20\text{ }^\circ\text{C}$  to  $-50\text{ }^\circ\text{C}$  with a further treatment of an aqueous suspension of guanylurea sulfate. The other materials such as TNT, RDX and Al powder were used from the in-house resources. The GUDN-based, aluminized and the non-aluminized melt cast formulations (namely GUDN/TNT/Al and GUDN/TNT) as well as RDX-based aluminized and non-aluminized melt cast formulations (RDX/TNT/Al and RDX/TNT) that were studied are summarized in Table 1.

**Table 1.** Formulations of GUDN and RDX based explosives studied

Formulation	RDX [%]	GUDN [%]	TNT [%]	Al [%]
GUDN/TNT	–	40	60	–
RDX/TNT	30	–	70	–
GUDN/TNT/Al	–	25	60	15
RDX/TNT/Al	25	–	60	15

## 2.2 Processing of the explosive formulations

The compositions were processed by a standard, melt-cast technique involving the addition of RDX or GUDN to molten TNT, with continuous stirring in a steam jacketed anchor blade mixer. This was followed by the addition of aluminum powder to the melt (in the aluminized formulations GTA and RTA). The mixtures were stirred for about 10-15 min and then transferred to a mould. After cooling to ambient conditions, the charge was extracted and machined to the required dimensions. 10 g of each mixture of the above melt cast compositions were prepared.

## 2.3 Thermal analysis

A TG/DSC (Mettler Toledo, DSC1) apparatus was used to investigate the thermal properties of the samples. For the pure components (GUDN, RDX, TNT, and Al), the DSC measurements were performed at a single heating rate of 10 K/min.

A weighed sample (0.1-0.3 mg) was placed in an aluminum pan which was then hermetically sealed and placed in the sample holder of the Perkin-Elmer DSC-7 instrument. An empty sealed aluminum pan was used as a reference. DSC measurements of the compositions were performed at four different heating rates, namely 5 K/min, 10 K/min, 15 K/min and 20 K/min. The DSC data were recorded as mW versus temperature/time from  $50\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$ . An inert atmosphere was maintained by using a nitrogen gas purge at a rate of 40 mL/min throughout the experiment.

The Kissinger model [12] was applied for the determination of the activation energy with an assumption of first-order reaction.

### 2.3 Determination of sensitivity parameters

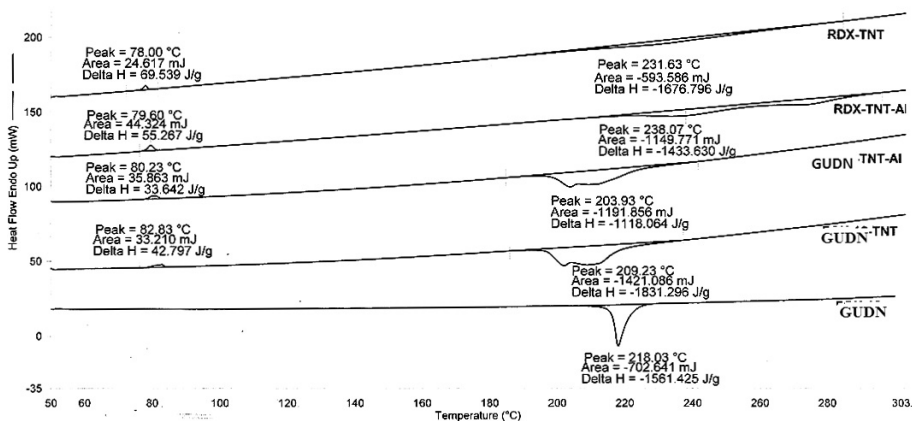
Standard methods were used for the determination of the friction and impact sensitivity. The sensitivities of the explosive compositions to impact stimuli were determined using the fall hammer method (2 kg drop mass) using the Brucceton staircase approach and the results are given in terms of the statistically obtained 50% probability of explosion ( $h_{50}$ ). The friction sensitivity was determined by using a BAM friction apparatus.

## 3 Results and Discussion

### 3.1 Thermal decomposition characteristics

The DSC curve for pure GUDN showed a sharp exothermic peak at 218.0 °C (Figure 1). The stepwise formulation was carried out to study the effect of GUDN and RDX on melt cast explosive compositions. The DSC curve of GUDN/TNT showed melting of TNT at 82.8 °C. Similarly, the DSC curve of RDX/TNT, GUDN/TNT/Al and RDX/TNT/Al had an endotherm in the temperature range of 78 °C to 80 °C corresponding to the melting of TNT. In the DSC trace for GUDN/TNT, GUDN decomposed exothermically at 209.2 °C. A shift in the decomposition temperature of GUDN was observed as the composition of the formulation was changed. However, in the case of GUDN/TNT/Al, it was observed that the TNT melted at 80.2 °C whereas GUDN decomposed at 203.9 °C. However, the observed enthalpy of decomposition decreased from 1831.3 J/g to 1118.1 J/g (Table 2). In the DSC curve for RDX/TNT, an endothermic peak occurred at 78 °C representing the melting of TNT and an exothermic peak was seen at 231.6 °C indicating the decomposition of RDX. However, in the case of RDX/TNT/Al, it was observed that in the composition containing 25% RDX, 60% TNT, and 15% aluminum, the TNT melted at 79.6 °C and the RDX decomposed at 238.1 °C. Aluminum also affected the decomposition behavior of RDX so that it showed a two-stage decomposition pattern. This two-stage decomposition could be due to the decomposition of RDX and TNT in the presence of aluminum. It was observed that in a normal DSC pan, TNT did not exhibit a decomposition peak. In our earlier observations of TNT, decomposition was observed at 295 °C in a high pressure sealing cup.

Sample ID: GUDN (TNT+AI) (25-60-15) @10 (270314)  
 Sample Weigh: .....



1) Heat from 50.00°C to 500.00°C at 10.00°C/min

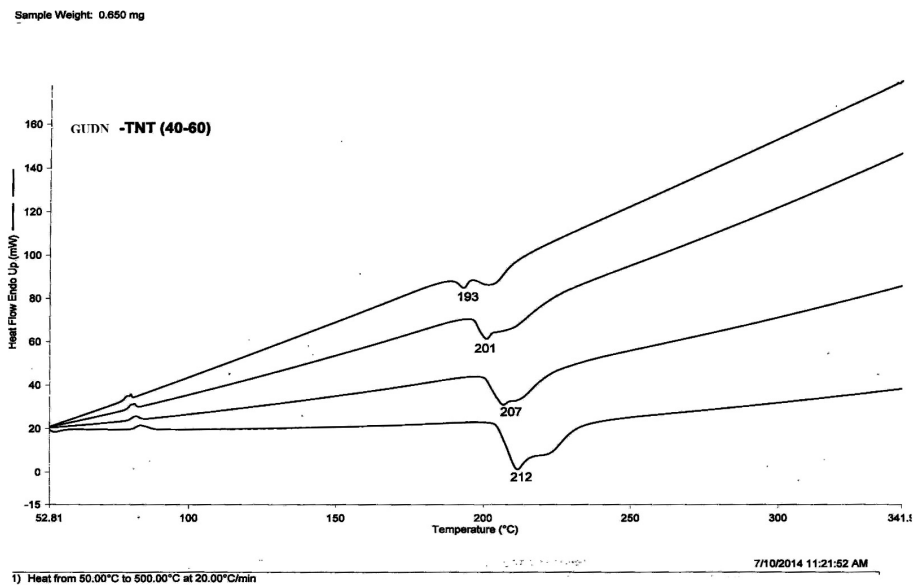
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**Figure 1.** DSC Curves for RDX/TNT, RDX/TNT/AI, GUDN/TNT/AI, GUDN/TNT and GUDN at a heating rate of 5 K/min

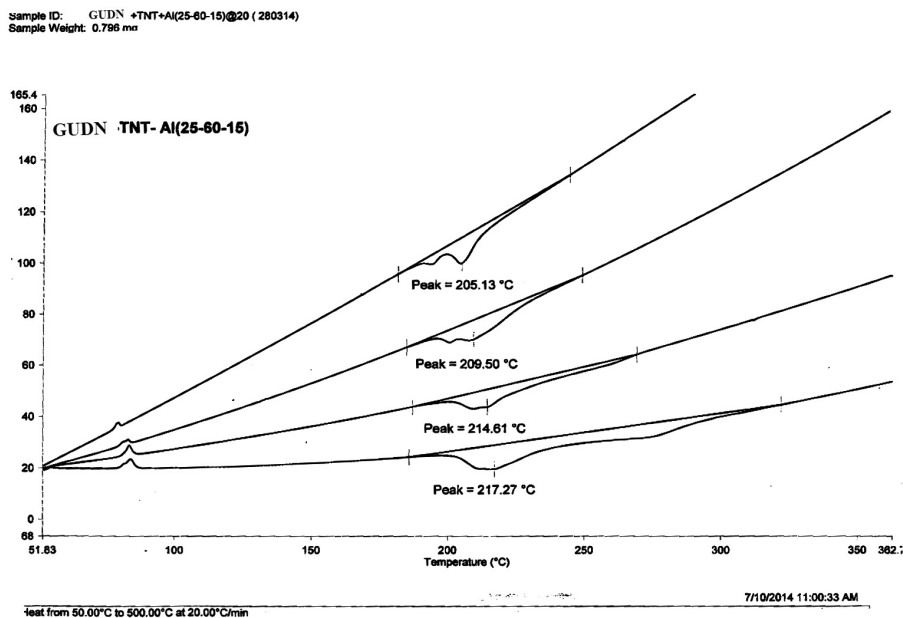
**Table 2.** Decomposition temperatures and thermal effects of GUDN and RDX based compositions

Sample	Sample mass [mg]	Heating rate [K/min]	Temp. range [°C]	Peak Endo		Peak Exo	
				Temp [°C]	$\Delta H$ [J/g]	Temp [°C]	$\Delta H$ [J/g]
GUDN	0.496	5	50-350			218.0	1561.4
RDX	0.292	10	50-300	203.3	144.0	238.0	1988.2
GUDN/TNT	0.496	5	50-350	82.8	42.8	209.2	1831.3
RDX/TNT	0.744	5	50-350	78.0	69.5	231.6	1676.8
GUDN/TNT/AI	0.954	5	50-500	80.2	33.6	203.9	1118.1
RDX/TNT/AI	1.160	5	50-500	79.6	55.3	238.1	1433.6

To examine the thermal behavior of GUDN based compositions, DSC experiments were carried out at four different heating rates: 5 K/min, 10 K/min, 15 K/min and 20 K/min (Figures 2 and 3). The decomposition kinetics of RDX, GUDN and their compositions were studied by the thermal analysis method (Table 3). Exothermic peaks at 230.6 °C, 231.6 °C, 241.7 °C and 249.2 °C were observed in RDX/TNT compositions.



**Figure 2.** DSC curves of a GUDN/TNT composition at heating rates of 5 K/min, 10 K/min, 15 K/min and 20 K/min



**Figure 3.** DSC Curves of a GUDN/TNT/Al composition at heating rates of 5 K/min, 10 K/min, 15 K/min and 20 K/min

Moreover, in the case of RDX/TNT/Al, decomposition was observed at 231.2 °C, 238.2 °C, 244.5 °C and 246.3 °C. The activation energy of RDX/TNT computed from the DSC results was found to be 29.8 kcal/mole whereas that obtained for RDX/TNT/Al was 43.7 kcal/mole. It may be inferred from the exothermic peak temperatures of the GUDN/TNT and GUDN/TNT/Al that the decomposition temperature of TNT shifts from 295 °C to 260 °C. On the other hand, the decomposition temperatures of RDX/TNT and RDX/TNT/Al were at about 231 °C which is closer to the decomposition temperature of RDX (238 °C). This observation clearly indicates the greater thermal stability of GUDN based melt cast compositions as compared to RDX based compositions.

**Table 3.** Decomposition kinetics of RDX/TNT, RDX/TNT/Al, GUDN/TNT and GUDN/TNT/Al at different scanning rates

Heating Rate [K/min]	RDX/TNT [°C]	RDX/TNT/Al [°C]	GUDN/TNT [°C]	GUDN/TNT/Al [°C]
5	230.6	231.3	277.6	228.2
10	231.6	238.2	283.4	240.2
15	241.7	244.5	300.2	245.7
20	249.2	246.3	309.9	264.6
$E_a$ [kcal/mol]	29.8	43.7	22.1	18.0

### 3.2 Sensitivity characteristics

The results of the characteristics determined for these formulations as compared to the standard explosive TNT are given in Table 4. The GUDN-based aluminized and non-aluminized formulations were found to be more impact insensitive than the corresponding RDX-based formulations.

**Table 4.** Sensitivity characteristics of the formulations

Formulation	Sensitivity	
	Impact $h_{50}$ [m]	Friction [kg]
GUDN/TNT	0.84	36
RDX/TNT	> 0.70	30
GUDN/TNT/Al	0.78	36
RDX/TNT/Al	> 0.70	36
TNT	1.30	32

## 4 Conclusions

A thermal decomposition study revealed the good thermal stability of GUDN/TNT formulations compared to RDX/TNT. Mixtures of GUDN and TNT decompose at a specific temperature. Initial thermal studies allow us to recommend GUDN as a low vulnerability, more energetic and compatible composition than RDX-based formulations.

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