



Method of Producing Uniformly Shaped and Sized Particles of 2,4,6-Triazido-1,3,5-triazine by Emulsion Crystallization

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Abstract: Generally, 2,4,6-triazido-1,3,5-triazine or cyanuric triazide (CTA) is obtained from the synthetic process as long, sharp edged crystals or fine/agglomerated particles. These are very sensitive and not suitable for detonator filling, leading to poor performance. We report herein a method for the preparation of uniformly shaped and sized particles of CTA with a free-flowing crystalline nature suitable for detonator applications. The uniformly shaped free-flowing CTA crystals are obtained by emulsion crystallization using a non-solvent at elevated temperature. The free-flowing CTA particles prepared were characterized using spectroscopy, SEM, and particle size analysis techniques. The results show that the CTA crystals obtained by emulsion crystallization are smooth surfaced, nearly spherical grains with a free-flowing nature. Furthermore, the results show that CTA crystals have a higher bulk density (BD) compared with normal CTA crystals prepared by crash precipitation. The thermal behaviour of the CTA crystals obtained by emulsification crystallization was investigated by conducting experiments such as DSC and using an explosion temperature tester.

Keywords: cyanuric triazide, emulsion crystallization, spherical free-flowing crystals, green primary explosive

1 Introduction

Primary explosives are sensitive compounds used in small quantities to generate a detonation wave to initiate a less sensitive secondary booster or main charge

explosive. During the past eight decades, the most prominent primary explosives which have found application in military devices are mercury fulminate (MF), lead azide (LA), silver azide (SA), lead styphnate (LS) and tetrazene (Figure 1) [1-4]. Unfortunately, all of the existing primaries suffer from the presence of toxic metals, excessive sensitivity, low storage life, and environmental hazards. One of the modern and principal trends in the development of energetic materials is the search for the so-called green, environmentally benign primary explosives. This has led to intensified R and D work in the ordnance community to develop lead-free initiating compounds, which can overcome the limitations of the conventional initiators [5-7]. A number of materials based on organic/inorganic compounds have been proposed and even realized in applications [8-10].

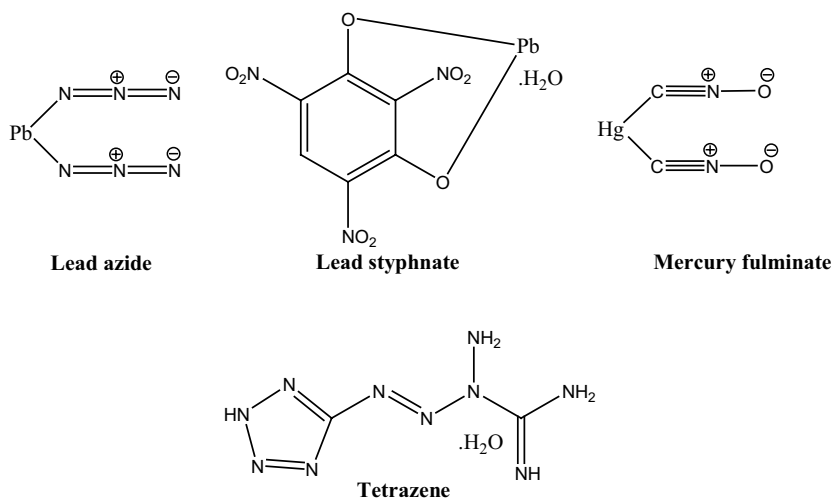


Figure 1. Molecular structures of conventional primary explosives.

The high nitrogen containing 2,4,6-triazido-1,3,5-triazine (cyanuric triazide, CTA) is a known energetic material with high impact and friction sensitivity and energy performance comparable to lead azide. CTA was first synthesized by Ott *et al.* [11] and its structural characterization was reported by researchers [12, 13]. It is a heavy metal-free, polyazide containing only carbon and nitrogen atoms (C_3N_{12}). CTA was preliminarily investigated as a primary explosive at ARDEC, but was discarded due to its high sensitivity [14]. In recent times, CTA is being reinvestigated and tested for explosive performance in initiating devices at ARDEC in order to realize its practical use [15].

However, although CTA is envisaged as an efficient initiating explosive, it is not employed in practice owing to its high sensitivity due to its unusual crystalline

nature. The crystal morphology and particle size of energetic materials plays a vital role in the sensitivity aspects of high energy materials (HEMs). Normally, the synthesised CTA form long, sharp edged rods, with sensitive crystals, which limits its practical application. The conventional crystallization methods, using different organic solvents, have failed to control the particle size and morphology. We have previously reported that preparation and characterization of fine particles ($\sim 5 \mu\text{m}$) of CTA by the crash precipitation method, in the anticipation that fine particles of CTA would be less sensitive than long, rod shaped crystals [16]. Moreover, the use of long, sharp edged crystals or fine/agglomerated particles in detonator filling, results in higher sensitivity to mechanical stimuli and less solid loading. It also leads to poor explosive performance characteristics. In view of this, there is a need for high bulk density, uniformly shaped, free-flowing CTA crystals, to fill small tubular detonators and meet the required performance. In continuation of our R and D on the development of green primary explosives [17], we report herein, for the first time, a process for the preparation of nearly spherically shaped, free-flowing CTA crystals, with improved bulk density (BD), using an emulsion crystallization technique, together with the characterization of the product.

2 Experimental

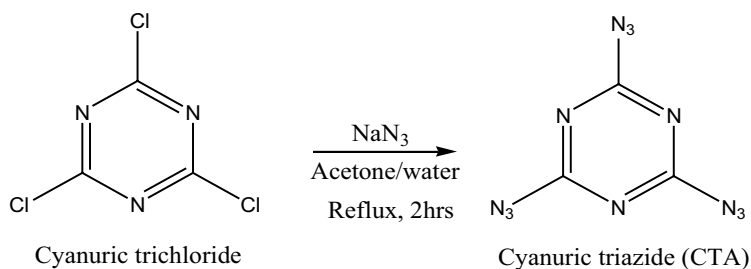
2.1 Materials and methods

All of the reagents and solvents used in the present study were of analytical reagent grade. FT-IR spectra were recorded on a Nicolet FTIR-5700 FTIR spectrophotometer, in a KBr matrix. Raman spectra were recorded using a Renishaw in Via Raman microspectrometer. The spectra were collected in the range $100\text{-}3500 \text{ cm}^{-1}$. The sample was excited with a Renishaw HPNIR laser (785 nm). ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument and ultraviolet spectra were recorded on a Thermo Scientific EVOLUTION 201 UV-Visible spectrophotometer. Thermal stability was studied on a DSC-7 Perkin Elmer instrument. Measurements were performed at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in closed aluminum sample pans under nitrogen (flow rate $50 \text{ mL}/\text{min}$) with an empty identical aluminum sample pan as a reference. Thermogravimetric Analysis (TGA) studies were carried out on a SDTA-851e Mettler Toledo instrument operating at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere with 1 mg samples. Scanning electron microscopic (SEM) analysis was carried out using an AUANTA 200 ESEM-FEI instrument. High performance liquid chromatography (HPLC) was undertaken on an Ultimate-3000 Dionex HPLC

system, operating temperature 25 °C, using a reverse phase C-18 column (4 mm × 250 mm) in the isocratic mode. Particle size analysis was carried out using a BECKMAN COULTER LS 13 320 Laser Diffraction Particle Size analyzer. The bulk density (BD) of the samples was measured by tapping a graduated cylinder containing a known mass of CTA crystals. The cylinder was repeatedly dropped from a specified height, at a constant drop rate, until the apparent volume of the sample in the vessel became almost constant. The impact sensitivity was determined by the Fall Hammer method using a 2.0 kg weight, and friction sensitivity was determined on a Julius Peter's BAM tester at 27 °C and 52% RH.

2.2 Synthesis of CTA

The CTA used for the emulsion crystallization was synthesized according to a literature reference, as shown in the Scheme 1 [16].



Scheme 1. Synthesis of CTA.

2.3 Emulsion crystallization of CTA

The emulsion crystallization technique involves melting a solid at slightly above its melting point in an inert liquid medium which serves as the continuous phase [18]. With vigorous stirring, the molten solid forms small and minute particles, which, upon cooling, crystallise into hard spherical particles. Depending on the amount of mechanical energy supplied, the resulting particles will vary in size. In the present case the process involved melting the CTA (mp: 93 °C) in water maintained above the melting point of CTA (~95 °C). The water was in a flat-bottomed glass vessel, placed on a magnetic stirrer hotplate. The temperature of the water was controlled by a thermocouple immersed in the water. The stirring of the water and molten CTA was achieved with a rectangular flat magnetic pellet. The CTA melted in the water and the stirring of the water aided in the formation of molten CTA grains. After the complete formation of the molten grains, the whole assembly was slowly cooled to ambient temperature, whereby

the molten CTA crystallized to hard spherical grains which were later removed from the water by filtration and dried under vacuum.

3 Results and Discussion

3.1 Spectral analysis

The CTA crystals obtained by emulsion crystallization were subjected to spectral characterization to confirm the structure and as well as the purity. The results of FT-IR and HPLC (purity >99%) were found to be in satisfactory agreement with literature values [17]. The Raman spectrum ($\Delta\nu$) of CTA (Figure 2) showed a weak peak at 2144 cm^{-1} for the asymmetric stretching vibration of the azide group (N_3), a strong peak at 1337 cm^{-1} for the symmetric stretching vibration of the azide group and other peaks for $\text{C}=\text{N}$, $\text{C}-\text{N}$ and $\text{N}=\text{N}$, observed at 173, 238, 331, 471, 562, 709, 983, 1153, 1195, 1426, 1534 cm^{-1} . The ^{13}C NMR spectrum (Figure 3) exhibited a single resonance at 170.98 ppm for the aromatic carbons (3C) in the symmetrical triazine ring, and the UV spectrum of CTA (Figure 4) exhibited a high intensity band at 236 nm, corresponding to the aromatic azide group. Other physicochemical properties of CTA prepared by this method were analysed and the results were found to be in good agreement with literature data.

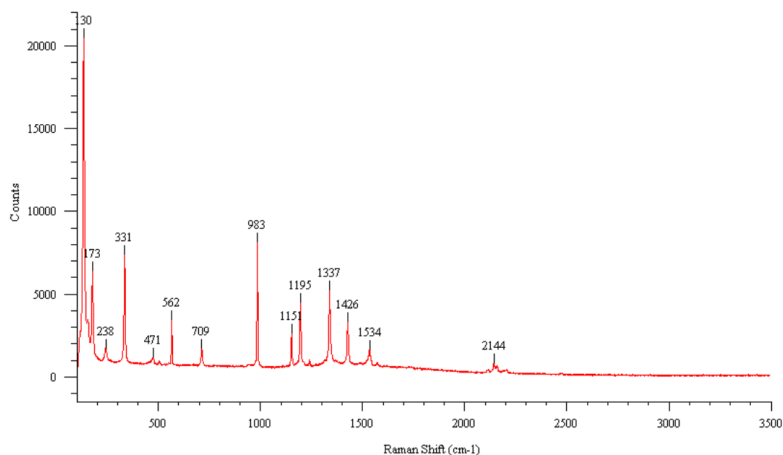


Figure 2. Raman spectrum of CTA.

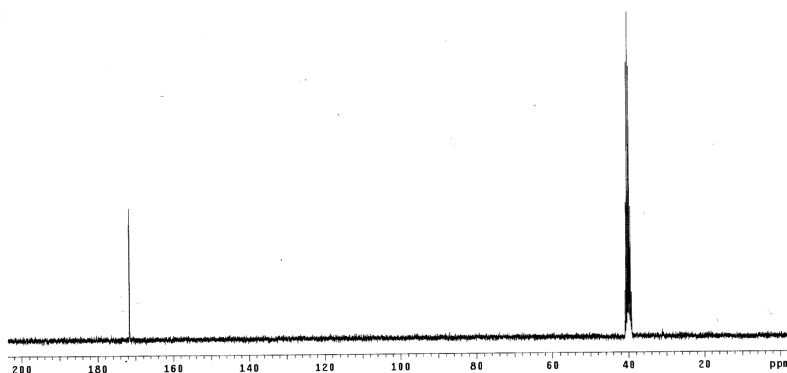


Figure 3. ^{13}C NMR spectrum of CTA (solvent: DMSO-d_6).

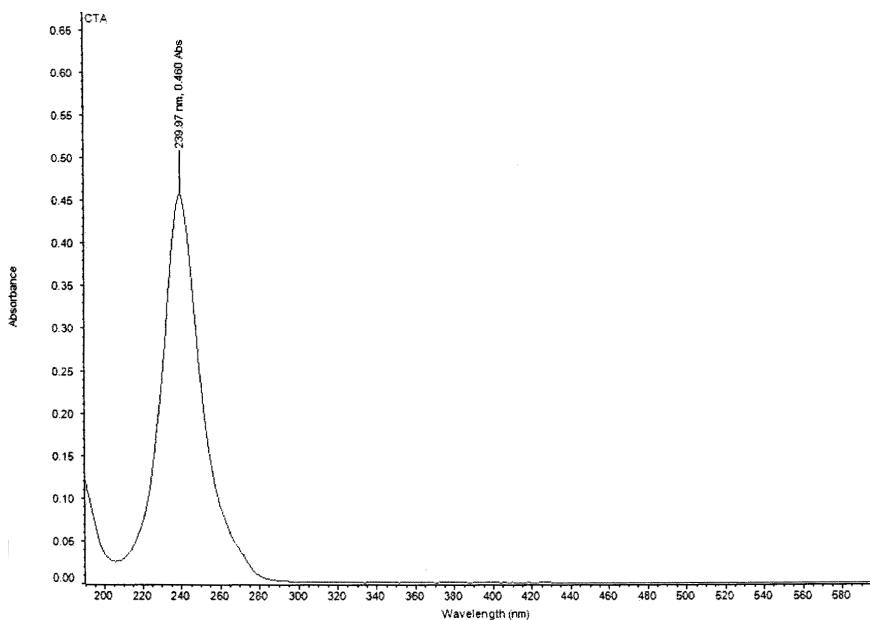


Figure 4. UV spectrum of CTA (solvent: methanol).

3.2 Particle shape and size of CTA

The scanning electron microscope (SEM) images of CTA crystals obtained by emulsion crystallization are shown in Figure 5, along with those of CTA crystals obtained by crash precipitation (Figure 6a) and also normal crystallized CTA (Figure 6b) for comparison.

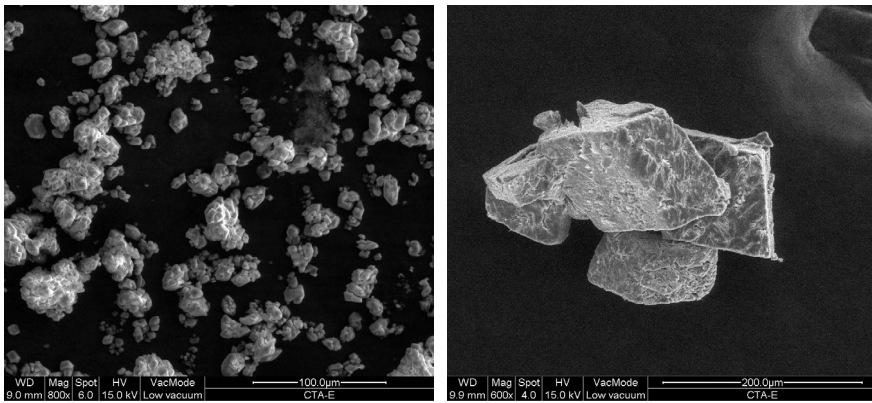


Figure 5. SEM images of CTA crystals from emulsion crystallization.

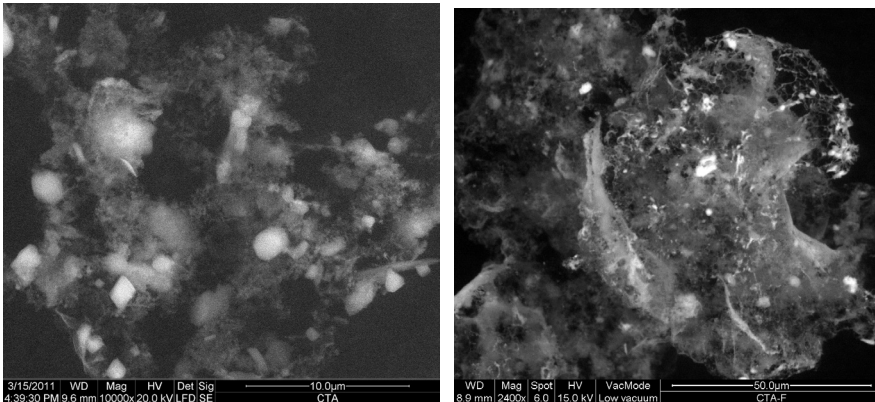



Figure 6a. SEM images of CTA crystals from crash precipitation 

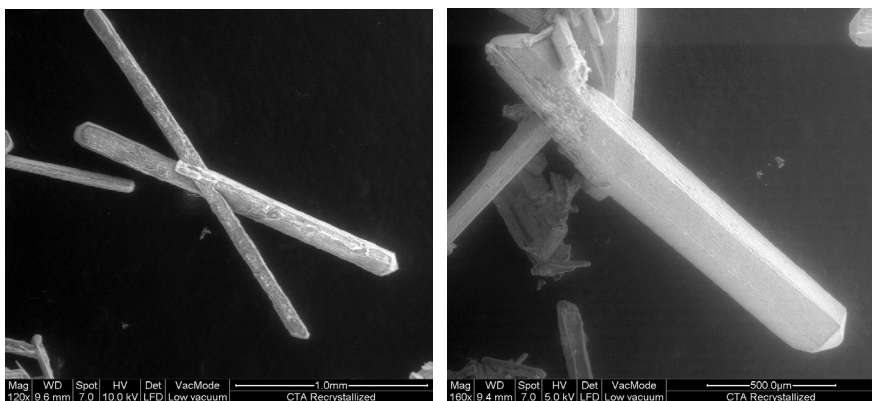


Figure 6b. SEM images of CTA crystals from normal crystallization.

The SEM images of emulsion crystallized CTA crystals are shown in Figure 5. It can be seen that the CTA crystals are free flowing, cubic/diamond shaped with smooth surfaces. Similarly, particle size analysis of emulsion crystallized CTA (Figure 7) shows a narrow range of particle sizes (20-200 μm ; mean particle size 80.2 μm), compared to CTA crystals from precipitation crystallization. By contrast, SEM images of CTA crystals obtained by precipitation show fine agglomerated crystals (Figure 6a) with a wide range of particle sizes (10-1000 μm) (Figure 8). The emulsion crystallized CTA had a bulk density of 0.920 g/cm^3 , which is again higher than that of CTA crystals from precipitation crystallization (0.780 g/cm^3).

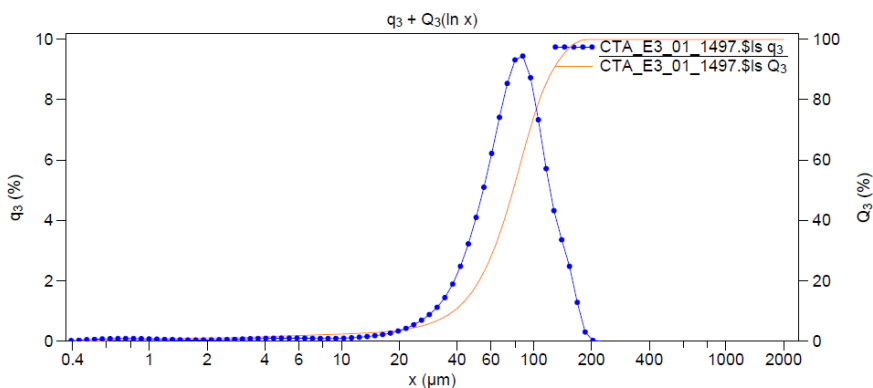


Figure 7. Particle size distribution of CTA crystals from emulsion crystallization.

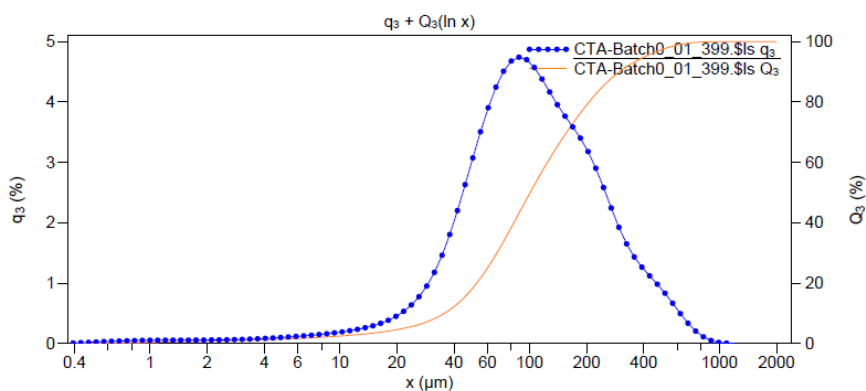


Figure 8. Particle size distribution of CTA crystals from crash precipitation.

3.3 Thermal analysis

The DSC results of emulsion crystallized CTA exhibited an endothermic peak with maximum at 94.0 °C with $\Delta H = 146.6$ J/g, followed by a broad exothermic peak at 219.0 °C (T_{\max}) with $\Delta H = -2553$ J/g, indicating a higher thermal stability than CTA obtained by simple precipitation crystallization (< 190 °C). The activation energy for the exothermic decomposition of emulsion crystallized CTA, at four different heating rates (5, 10, 15 and 20 °C/min; Figure 9), was calculated using the ASTM standard method [19] (based on a Kissinger correlation) and found to be 152 kJ/mol (Table 1 and Figure 10).

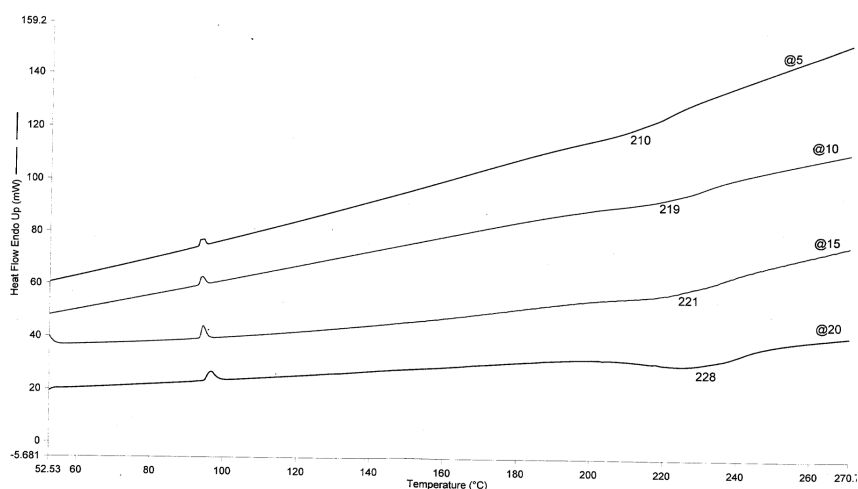


Figure 9. DSC traces at different heating rates of CTA crystals from emulsion crystallization.

Table 1. DSC data at various heating rates for emulsion crystallized CTA (Kissinger method)

Heating rate, β [°C]	Peak T_{\max} [°C]	Peak T_{\max} [K]	T_{\max}^2	$\frac{1}{T_{\max}}$	$\frac{\beta}{T_{\max}^2}$	$-\ln\left(\frac{\beta}{T_{\max}^2}\right)$	Slope
5	210	483.15	233434	0.00206975	2.14193E-05	10.7512164	18224.7153
10	219	492.15	242212	0.00203190	4.12862E-05	10.0949820	
15	221	494.15	244184	0.00202368	6.14290E-05	9.69762803	
20	228	501.15	251151	0.00199541	7.96333E-05	9.43807864	

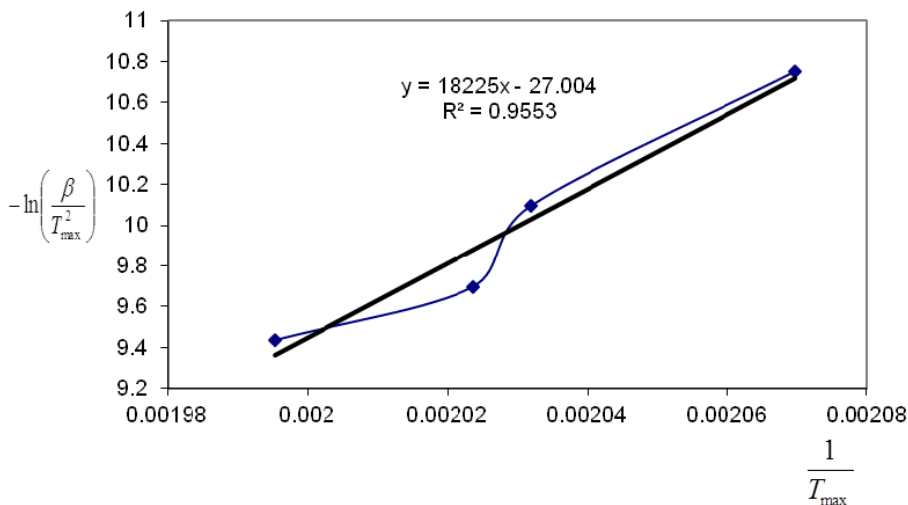


Figure 10. Plot for emulsion crystallized CTA.

3.4 Explosion temperature

The measurement of the explosion temperature gives an idea of the thermal stability of a test sample. The explosion temperature of CTA crystals was tested using an *OZM* Automatic Explosion Temperature Tester AET-402 in which less than 10 mg of the sample were heated at 5 °C/min. Repetitive tests indicated that CTA's decomposition starts at 173.9 °C (onset) and shows a very sharp explosion peak maximum at 205 °C (*Note*: the test sample detonated violently, damaging the sample tubes, thus the quantity of the sample was limited during these tests). Similarly, flame sensitivity is a typical feature for all classes of energetic materials. A few mg of CTA sample on a nickel spatula were heated directly in a flame; detonation without deflagration was observed. This is indicative of the efficiency of CTA to initiate less sensitive secondary explosives by the detonation shockwave.

3.5 Sensitivity to impact, friction and ESD

The impact sensitivity of CTA obtained from emulsion crystallization was determined by the Fall Hammer method using a 2.0 kg weight and tetryl (CE) used as the standard ($h_{50\%}$, 54 cm). The measured impact and friction sensitivity of CTA was 28 cm and < 50 g (low explosion) respectively. The results are indicative of the improvement in the insensitiveness of these CTA crystals compared to CTA crystals obtained from the standard re-crystallization method, which are very sensitive to impact and friction (impact: < 10 cm; friction: < 10 g). The spark

sensitivity of emulsion crystallized CTA crystals was measured to be 2.5 mJ at 35 °C and 55% RH, which is again an improvement in spark insensitivity compared to the reported value (1.2 mJ). As seen in Table 2, the sensitivity characteristics of CTA is very similar to that of lead azide and reveals its potential to replace toxic lead azide in detonating devices.

Table 2. Sensitivity of CTA and Lead Azide (LA) for comparison

S. No.	Properties	Cyanuric triazide (CTA)	Lead azide (LA)
1	Impact (2 kg), $h_{50\%}$, [cm]	18-25	24
2	Friction, [g]	< 50	10
3	ESD, [mJ]	2.5	4.7
5	Open flame test	Detonation without DDT	-

4 Conclusions

The present work has demonstrated a method for making spherically shaped, free-flowing particles of CTA, having improved bulk density, by an emulsion crystallization technique, together with the characterization of some spectral and thermal properties. The CTA crystals were almost spherical in shape and the particle size distribution, as measured, was in the range 20-200 μm , with a mean particle size 80.2 μm . Furthermore, the CTA crystals obtained from emulsion crystallization exhibited smooth surfaces, were free-flowing crystals and had improved bulk density (0.920 g/cm^3), which are more suitable for filling detonators with higher solid loading, as compared to CTA from the precipitation method. Interestingly, the decomposition temperature (DSC) of CTA obtained from emulsion crystallization is 219.0 °C, which is higher than that of the normal, precipitated CTA crystals (< 190 °C). Additionally, emulsion crystallized CTA exhibits better insensitivity characteristics than normal CTA crystals. The optimized process for making free-flowing CTA is being scaled up to 50 g per batch, with similar yield and purity.

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