

Method for preparation of fine TATB (2–5 μm) and its evaluation in plastic bonded explosive (PBX) formulations

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Abstract

There is a need of fine 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (2–5 μm) for various high explosive formulations to achieve desired mechanical strength, ease in processing and finally, provide better performance of end product. The reprecipitation method for TATB has been developed using concentrated sulfuric acid as a solvent. The reprecipitation parameters of TATB were optimized to achieve required fine TATB of particle size \sim 2–5 μm . The characteristic properties of fine TATB thus obtained have been confirmed by FTIR, DSC and TG-FTIR. The spectroscopic and thermal data obtained for fine TATB were compared with standard coarse TATB and found chemically unchanged during particle size reduction. In the present study, the preparation of fine TATB was also attempted using ultrasonication method. The fine (2–5 μm) TATB has been introduced to study in the bimodal high explosive formulations. High explosive formulations based on coarse (55 μm) and fine TATB (\sim 2–5 μm) with 10% polyurethane were studied. It was observed that properties like bulk density (1.70 g/cm^3), mechanical strength/compressed strength (115.9 mg/cm^2), %elongation (6.36) were improved for fine TATB in comparison with coarse TATB (\sim 55 μm) alone in high explosive formulations. © 2006 Elsevier B.V. All rights reserved.

Keywords: Fine TATB; Preparation; Characterization; PBX formulation

1. Introduction

The most important insensitive high explosives (IHEs) for use in modern nuclear warheads is 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), because its resistance to heat and physical shock is greater than that of any other known material of comparable energy [1]. The Department of Defence, U.S., is also studying the possible use of TATB as nuclear stockpile and an insensitive booster material, because even with its safety characteristics, a given amount of that explosive has more power than an equivalent volume of 2,4,6-trinitrotoluene (TNT). The high stability of TATB favors its use in military and civil applications where insensitive type explosives are required [2]. In addition to its application as HE, TATB is used to produce the important intermediate benzenehexamine. Benzenehexamine has been used in the preparation of ferromagnetic organic salts and in the synthesis of new heterocyclic molecules [3].

In addition to its military uses, TATB has been proposed for use as a reagent in the manufacture of components for liquid crystal computer displays [4]. There is also interest in employing the explosive in the civilian sector for deep oil well explorations, where heat insensitive explosives are required. Other potential applications include the use of TATB as the booster or main charge explosive for down-hole oil perforation at elevated temperature surrounding. However, one major problem with the utility of TATB is the resistance to initiation as required.

TATB was prepared by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) in toluene with anhydrous ammonia gas in a pressurized reactor [5]. TATB thus produced has particle size of 50 μm or larger and is suitable for most application. However, fine-grained TATB is desirable for ease of initiation. However, there is a need of fine particle TATB (<10 μm) for several high explosive formulations under development at HEMRL to achieve the ease in processing and desired mechanical strength and performance of the end product. Plastic bonded explosive (PBX) 9502 has been formulated as a insensitive high explosive comprised of 95% TATB and 5 wt% Kel-F800TM binder. Several studies on PBX 9502 have shown significant differences between

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the mechanical properties and postulated that the differences were related to various aspects of TATB particles size and distribution [6]. Coarse TATB based formulation generally provides brittle PBX, which can sustain damage in normal handling and succumb to extreme temperature suing or thermal stocks, while too soft a PBX may be susceptible to creep and lack dimensional stability or strength to achieve safe and stable PBXs. HEMRL is presently studying the bimodal (containing fine and coarse particle size TATB) charge explosives based on TATB.

Ultrasound [7] is sound of a frequency that is beyond human hearing, i.e., above 16 kHz. Applying ultrasound to crystallizing systems offers a significant potential for modifying and improving both the processes and products. Although ultrasonic has been used for years in research and diagnostics, its use in chemical processes has undergone development in the recent years. This is because high-intensity systems have become available that can deliver power ultrasound on industrially relevant scales. The use of ultrasound in promoting chemical reactions has been widely investigated and been developed recently as an intensification technology, driven by requirements for environmentally clean processing crystallization intuitively appears to be an obvious area in which ultrasonic irradiation could be beneficial. When ultrasound is applied to liquids of either a homogeneous or heterogeneous system, acoustic cavitations results. That is, the formation, expansion and implosive collapse of micro bubbles generated during the high frequency oscillation of liquid molecules. The work was therefore under taken to develop the technique for the reduction of particle size of TATB from 55 to 2–5 μm range using reprecipitation as well as sonocrystallization methods. The paper discusses the details of process for the preparation of fine TATB, its characterization and thermolysis. The fine TATB based PBX formulations are also discussed.

2. Structure and solubility of TATB

The structure of TATB (Fig. 1) contains unusual features. X-ray diffraction pattern of crystalline TATB reveals that C–C bond orders are approximately 1.2 and the amine C–N and N–O bond orders are nearly 1.5. The molecule is nearly planer and has extensive system of hydrogen bonds [8] and intermolecular

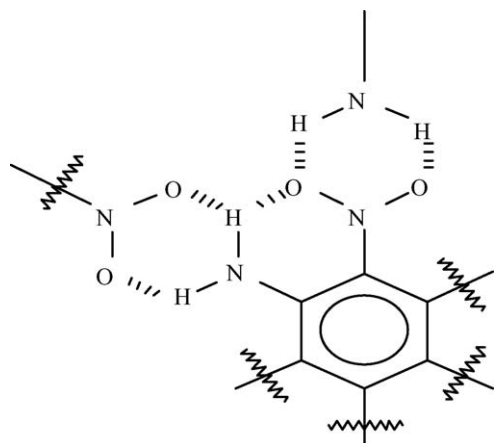


Fig. 1. Hydrogen bonding of TATB.

Table 1
Solubility of TATB in various solvents

S. no.	Solvents	Solubility (ppm, at room temperature)
1	Methanesulfonic acid	820
2	Hexamethylphosphortriamide	150
3	Ethanesulfonic acid	120
4	DMSO	70
5	Hexafluoroacetone sesquihydrate	68
6	<i>N</i> -Methyl-2-pyrrolidone	58
7	<i>N,N</i> -Dimethylacetamide	33
8	DMF	27
9	Tetramethylurea	26
10	Dimethyl methylphosphonate	22
11	<i>N,N</i> -Dimethyl propionamide	16
12	Conc. HNO_3	14
13	3-Methylsulfolane	13
14	Pyridine	12
15	Trimethylphosphate	11
16	Acetone, dimethylcarbam oxychloride	3
17	Acetonitrile, acetic anhydride, trifluoroacetic acid, acetic acid	1

interactions as shown in Fig. 1 contributing to its exceptional thermal stability and low solubility except in concentrated sulfuric acid.

Solubility of TATB in “super acids” such as chlorosulfonic acid, fluorosulfonic acid and trifluoromethane sulfuric acid was measured more than 20% (w/v) whereas aniline, dimethylformamide, phenylhydrazine, ethylenediamine and gammabutyrolactone was measured about $\sim 0.1\%$ (w/v). Estimated solubility of TATB in various solvents are summarized in Table 1. TATB is known to be insoluble in benzene, chloroform, ethanol and glacial acetic acid [9].

The current work discusses the details of process for the preparation of fine TATB by chemical and ultrasound method, its characterization and thermal analysis. The fine TATB based PBX formulations are also discussed.

3. Experimental

3.1. Materials and methods

AR grade sulfuric acid was used in this process. The IR spectra (FTIR-1600 spectrophotometer) were recorded on a Perkin-Elmer using KBr matrix. The DSC studies was carried out on a Perkin-Elmer DSC-7 instrument operating at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen (40 ml/min) atmosphere and the mass of the sample used was less than 1 mg. The thermal properties of TATB were studied by simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) and the mass of the sample used was 0.5 mg under N_2 atmosphere (100 ml/min) (Mettler Toledo Star System). The sensitivity to impact of TATB was determined by using a 2 kg drop weight (fall hammer method). The results are reported in terms of height for 50% probability of explosion of the sample was determined. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding, CE), as reference. The friction sensitivity of

the compound was determined using a Julius Peter's apparatus [10].

3.2. Preparation of fine particle TATB using concentrated H_2SO_4

During the study on reduction of coarse TATB having 55 μm particle size, the initial experiments were carried out for a batch size of 10 g and the reaction parameters/conditions were established. Subsequently the process of reduction of particle size has been scaled up to 150 g/batch sizes. The details of the experiments are described below.

To a 500 ml glass beaker, placed on stand well equipped with mechanical stirrer, 40 ml of concentrated sulfuric acid ($d = 1.9 \text{ g/cm}^3$) was transferred. The 10 g of coarse TATB (55 μm particles) was added slowly over a period of 10 min with stirring at room temperature. After addition of TATB, the stirring was continuous till the TATB gets completely dissolved. The clear solution thus obtained was filtered through glass wool; the brownish clear solution was obtained. The brownish acid solution was then added drop by drop to 500 ml ice-cold water with constant stirring. Very fine light yellow colored precipitate of TATB was obtained. After the addition of acid solution completed, the stirring was continued for 1 h. The TATB with dilute acid mixture was then filtered through fine glass sieve. The fine TATB thus obtained was washed with plenty of warm water ($\sim 50^\circ\text{C}$) till filtrate gets neutralised to pH 7 followed by acetone and dried under vacuum at $\sim 95^\circ\text{C}$ for 5 h. The fine particle TATB powder thus obtained was subjected to particle size analyzer, structural and thermal analysis. The same procedure was optimized to scale up for 150 g batch size by dissolving 150 g of coarse TATB in 550 ml of concentrated sulfuric acid at room temperature.

3.3. Preparation of fine particle TATB using ultrasound

Experiments were performed in stainless steel low power ultrasonic bath (Dakshin Ltd., India), the internal dimensions of bath of 0.15 m \times 0.15 m \times 0.15 m. The bath has three transducers located at the bottom, arranged in a triangular fashion. The bath was driven at 20 kHz frequency with power rating of 120 W.

Two grams of TATB was suspended in 50 ml of dimethylsulfoxide (DMSO) and was subjected to ultrasound bath and the sample was sonicated for further 15 min. TATB was filtered, dried and weighed. Five samples (suspended TATB in DMSO) were prepared by keeping the flasks at different locations in the bath to study the effect of pressure-intensity on particle size, all five samples gives same result and there is no effect, on changing the locations.

3.4. Formulation of plastic bonded explosive (PBX) with bimodal TATB (80:20)

3.4.1. Formulation of polyurethane lacquer

Calculated quantity ($\sim 109 \text{ g}$) of granular polyurethane dissolved insufficient quantity ($\sim 250 \text{ ml}$) of methylethylketone

(MEK) solvent in steam double jacketed vessel at $\sim 65\text{--}70^\circ\text{C}$ till to get clear solution.

3.4.2. Process for PBX formulation

A calculated quantity of coarse and fine (9:1 ratio = 90%) particle TATB is added into the water jacketed vessel to one-third of its capacity. This mass is then stirred at a speed of 200–300 rpm. Circulate the steam in double jacketed vessel to rise the content temperature to $65\text{--}70^\circ\text{C}$ temperature. After attaining the set temperature, the prepared polyurethane (10%) lacquer is added drop wise through separating funnel over a span of 15 min. Raise the inside vessel temperature to $\sim 90^\circ\text{C}$ by maintaining the steam circulation. Continue the digestion keeping under the same condition for 25–30 min further. Cut off the steam and start the circulation of cold water with stirring till the ambient temperature is achieved. Filter the content under the suction and wash with water. The product thus obtained is spread over the trays for air drying. Weigh the desired quantity of above product and transfer to a specified mould and press under 1.5 tonnes/cm² pressure with dwell time of 10–12 s.

4. Results and discussion

TATB dissolved in sulfuric acid and it is quickly solvated and protonated as shown in Fig. 2. The degree of protonation and solvation is proportional to the concentration of the sulfuric acid and thus, TATB is precipitated by diluting the solution with water.

For the characterizations of fine particles, the results from FTIR, DSC, DTA and TGA experiments were quite useful. The same methods were also used to characterize coarse TATB particles in order to find out if any chemical changes are occurring during the size reduction process. The scanning electron microscope (SEM) of coarse TATB ($\sim 55 \mu\text{m}$) was also taken for comparison study. This established chemical method of reduction of TATB particle size could be easily scaled up from 150 g batch level to pilot plant scale under normal safety nerves. The

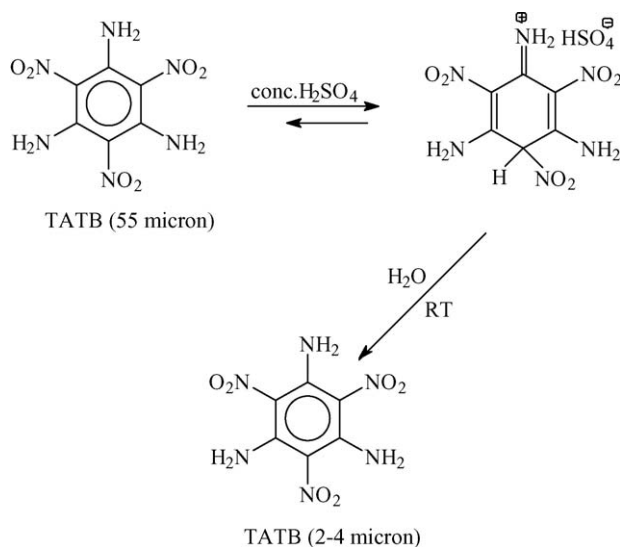


Fig. 2. Protonation of TATB in H_2SO_4 .

Table 2
Characteristic properties of fine particle TATB & coarse TATB

S. no.	Property	Observation	
		Experimental for fine TATB	Reported for coarse TATB
1	Average particle size (μm) by fisher sub sieve sizer	2	22
2	Distribution of particle size (μm) by Malvern	5	55
3	Impact sensitivity ($h_{50\%}$, cm)	124	170
4	Friction insensitiveness (kg)	36	36
5	DTA exotherm (onset, 0°C)	250	255
6	FT-IR (cm^{-1})	3220	3313–3324
		1610	1608–1614
		1568	1568–1574
		1226	1222–1224
7	DSC		
	Peak temperature (T_{max}) ($^\circ\text{C}$) ΔH , (J/g)	385 –457.71	384.70 –458.66
8	TGA (%weight loss, at onset temp.)	82.3% (253 $^\circ\text{C}$)	81.6% (258 $^\circ\text{C}$)

reaction conditions and solvent quantity for reduction of coarse TATB have been optimized for smaller batch size (~ 10 g) and finally, scaled up to 150 g/batch size.

Using ultrasound to generate nuclei in a relatively reproducible way offers a well-defined starting point for the crystallization process, and allows the focus to be on controlling the crystal growth for the remainder of the residence time in the crystallizer. This approach has been used successfully to manipulate crystal size distribution and, hence, to modify solid/liquid separation behavior, washing and product purity, product bulk density, and power flow characteristics. However, there are some limitations of these method which includes low scale process (5–10 g level) and expensive ultrasound equipment.

4.1. Sensitivity test

The fine particle TATB powder is lemon color in appearance and can be pressed to a density of 1.82 g/cm^3 . Samples of fine particle TATB were submitted for small scale sensitivity test. Results from these tests are tabulated in Table 1 in comparison with coarse TATB. Fine TATB has more sensitivity than coarse TATB because, fine TATB has more surface area so that sensitivity directly proportional to surface area.

4.2. Particle size and thermal analysis

Particle size distribution of fine particle TATB 2–5 μm was determined by Malvern particle size analyzer using water as dispersing media and the average particle size 2–5 μm was

Table 3
Characteristic properties bimodal (coarse/fine, 9:1 ratio) PBX formulations

S. no.	Properties	Fine TATB PBX formulation	Coarse TATB PBX formulation
1	Bulk density (g/cm^3)	1.70	1.58
2	Mechanical strength/compression strength (kg/cm^2)	116.9	95–100
3	%Elongation	6.36	5.4
4	Decomposition temperature (DSC, T_{max} , $^\circ\text{C}$)	380	375

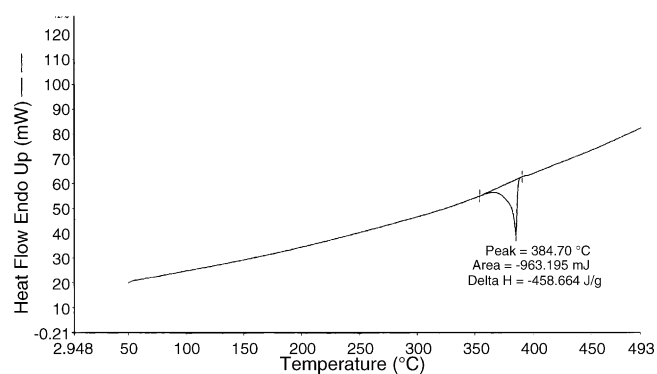


Fig. 3. DSC profile of fine TATB.

determined by Fisher sub-sieve sizer. The thermal analysis data are give in the Table 2. The DSC results (Fig. 3) of fine TATB shows that exothermic decomposing at the temperature range of 360–390 $^\circ\text{C}$ ($T_{\text{max}} = 385^\circ\text{C}$) with heat output $\Delta H = -457.71$ mJ. The TGA results (Fig. 4) of fine TATB reveal that 82.3% weight loss accure in the temperature range from 250 to 353 $^\circ\text{C}$.

4.3. Bimodal (coarse and fine TATB; 9:1 ratio) PBX formulations

The fine ($\sim 5\ \mu\text{m}$) TATB has been introduced to study in the bimodal high explosive formulations. High explosive formulations based on coarse (55 μm) and mixture (bimodal) consist of coarse and fine (9:1 ratio = 90%) particle TATB with 10% polyurethane were studied. The obtained results are summa-

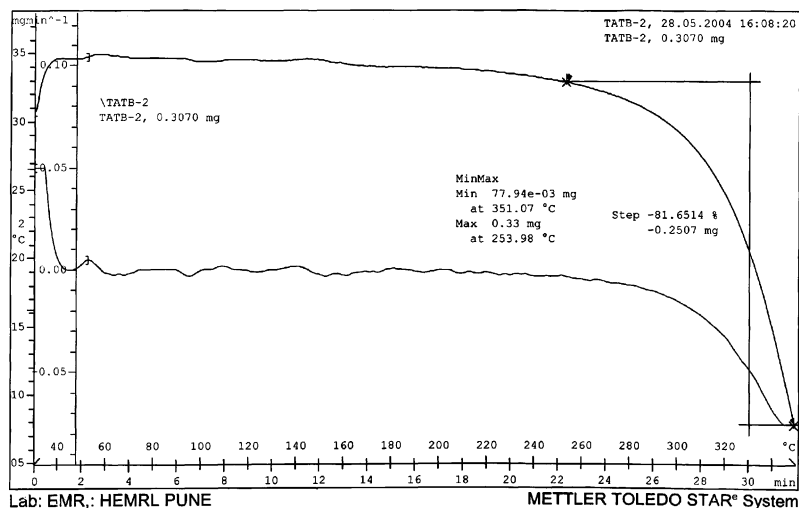


Fig. 4. TGA profile of fine TATB.

rized in Table 3. It was observed that properties like bulk density, mechanical strength/compressed strength and %elongation were improved in comparison to coarse TATB (55 μm) alone in PBX formulations.

5. Conclusion

A simple and efficient laboratory method for reduction of coarse TATB from 55 to 5 μm at 150 g batch level is successfully established and can be further scaled up to pilot plant scale with available infrastructure. No any chemical change occurs in the process of making fine particles of TATB from the coarse one as described in this report.

High explosive formulations based on coarse (55 μm) and fine TATB ($\sim 2\text{--}5\ \mu\text{m}$) with 10% polyurethane were studied. Bimodal formulation of TATB has been selected and studied for explosive/thermal properties. The formulation based on fine TATB showed thermal decomposition at temperature 380 °C. It was observed that properties like bulk density, mechanical strength/compressed strength and %elongation were improved in comparison to coarse TATB ($\sim 55\ \mu\text{m}$) alone in high explosive formulations.

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