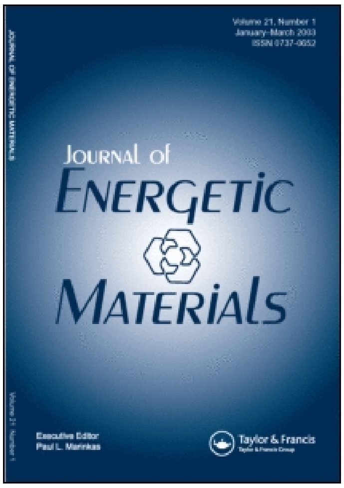

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Synthesis and characterization of sonochemically-aminated 1,3,5-triamino-2,4,6-trinitrobenzene

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SYNTHESIS AND CHARACTERIZATION OF SONOCHEMICALLY-AMINATED 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE

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ABSTRACT

A novel method has been achieved for the preparation of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) from TCTNB in toluene by amination with ammonium hydroxide solution under the influence of ultrasonic irradiation. Samples of this sonochemically-aminated TATB (FP-TATB) were studied for its powder characteristics. It was found that the arithmetic median diameter (vol%) and BET surface area of FP-TATB are 15 micrometers and 1.2 m^2/g, respectively. To evaluate shock initiation, samples of FP-TATB were pressed to high density (1.8g/cc) and subjected to initiation spot-size testing, and the results were compared with those from micronized TATB (UF-TATB), an IHE booster material. Data from this test indicated that the FP-TATB is slightly more sensitive to shock initiation than the UF-TATB as measured by the dent depth of the witness plate.

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INTRODUCTION

The compound 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is an explosive with a high melting point and thermal stability that has been applied in situations where insensitivity to impact hazards is important. In the past, production grade 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.(1) TATB thus produced is suitable for most applications requiring a particle size ranging from 30 to 60 micrometers. However, for applications requiring higher sensitivity to shock initiation, fine-grained TATB is desirable. TATB with an arithmetic median of 6 micrometers, produced by Lawrence Livermore National Laboratory (LLNL) and Pantex, has been qualified as an insensitive high explosive (IHE) according to U.S. Department of Energy (DOE) standards.(2) Unfortunately, the processes involved in the production of such TATB (UF-TATB) are complicated and time-consuming.(3)

Ultrasound is a sound with frequencies beyond human hearing, i.e. above 20 kHz. When ultrasound is applied to liquids of either a homogeneous or heterogeneous reaction system, acoustic cavitation results. Rate enhancement of chemical reactions accompanied by higher production yield has been demonstrated under the influence of ultrasonic irradiation (ultrasonication).(4)

Recently, the synthesis of nanostructured catalysts with selective hydrogenation reactivity by ultrasonication was reported by Suslick and his coworkers.(5) Ultrasound is also widely used in promoting dispersion of one liquid phase into another through emulsification.

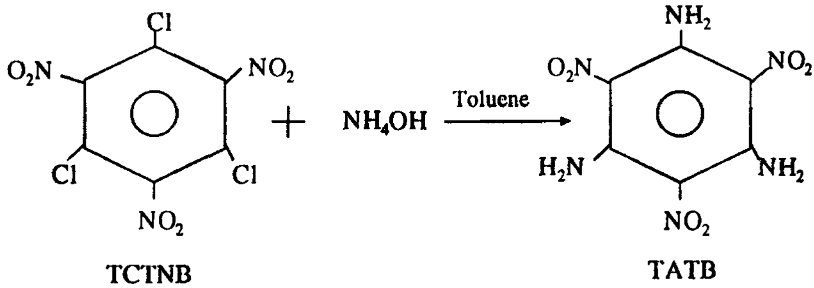
In an attempt to develop a simple method to synthesize TATB that will have particle size and shock initiation sensitivity comparable to UF-TATB, we have studied the synthesis of TATB by ultrasonication. In this article, the synthesis of sonochemically-aminated TATB (FP-TATB) will be described. Results from the powder characterization of both UF-TATB (91190-135m-003) and FP-TATB (KYL-I-58s) powders will be reported. Results from initiation spot-size testing of the two TATBs will also be presented.

EXPERIMENTAL

Preparation of FP-TATB (KYL-I-58s)

An ultrasonic liquid processor (Misonix XL2020) equipped with a 0.5-inch probe, operating at 20 kHz with a variable amplitude power-supply output was used for the preparation of FP-TATB. The power output was set at 60% of maximum 550 watts. A solution of TCTNB in toluene was added to an ammonium hydroxide solution in a 300 ml beaker (Pyrex No. 1040). The amination reaction began by immersing the sonicator horn into the two-phase mixture and turning the power on.

(To avoid potential ammonia gas escaping to the air, the beaker was covered with a piece of aluminum foil before the reaction started.) After a 40 minute sonication time, the resulting emulsion was left overnight at ambient temperature. The resultant FP-TATB, produced by Reaction 1, was collected by filtration, followed by washing the solids sequentially with hot water, toluene, and acetone. The resulting lemon-colored solids were then dried at 98°C in a vacuum oven overnight.



(1)

Particle Sizing

All particle sizing was done on a Horiba LA-900 Laser Scattering Particle Size Distribution Analyzer. This instrument uses the principles of the Mie scattering theory for measuring the size and distribution of particles suspended in a liquid medium. Two light sources, a 632.8 nm He-Ne laser and a blue and red monochromed tungsten lamp, are used in the instrument. After the light beam has been scattered by the particles in the measuring cell, it passes through the condenser lens and is focused on the 18 unit detector. The intensity and angle of scattered light are converted into electrical signals, which are then used to calculate the size distribution of the particles.(6) The instrument is capable of measurements from 0.04 to 1000 μm.

A small amount (~15mg) of the TATB powder was suspended in deionized water for particle sizing. Deionized water was also used as the dispersion fluid (~200ml) in the particle sizer. A peristaltic pump was used to circulate the sample and dispersion medium through the measuring cell. The sample was added drop-wise to the measuring cell until the percent transmission was in the desired range as indicated by the manufacturer. Duplicate samples of both FP- and UF-TATB powders were analyzed three times each.

Various methods of sample dispersion were examined. Samples were dispersed through the use of the instrument's internal pumping system and ultrasonic bath (USB), the use of a 40 Watt ultrasonic probe (USP), and the addition of the dilute non-ionic surfactant Triton®X-100 (TX, manufactured by Rohm & Haas Company).

Surface Area Measurements

The surface area measurements were performed on a Quantachrome

Autosorb-1. This instrument operates by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressure by the static volumetric method. The data is obtained by admitting or removing a known quantity of adsorbate gas into or out of a sample cell containing the solid sample maintained at a constant temperature below the critical temperature of the adsorbate. As adsorption or desorption occurs the pressure in the sample cell changes until equilibrium is established. The quantity of gas adsorbed or desorbed at the equilibrium pressure is the difference between the amount of gas admitted or removed and the amount required to fill the void space around the adsorbent. The volume-pressure data is then reduced by the Autosorb-1 into BET (Brunauer-Emmett-Teller) surface area.(7) Nitrogen was used as the adsorbate gas. Five pressure data points, restricted to the linear region of the isotherm with a P/P_0 range of 0.05 to 0.35, were used. Samples of TATB were vacuum outgassed for 24 hours at room temperature before the analysis.

Initiation Spot-Size Testing

The spot-size test involves initiation of a pressed TATB pellet (1.80g/cm^3) by the impact of an explosively driven steel flyer plate.(8) The flyer plate diameter was varied to determine the initiation spot-size sensitivity of the TATB acceptor. The donor explosive was a 1.6 g/cm^3 density PETN pellet, 6.35 mm in diameter and 3-mm thick, which was initiated by an electrical slapper. The TATB sample pellet was in contact with an aluminum witness plate, and the depth of the dent on the plate was measured as an indication of the output of the test material. Testing was done at room temperature, approximately 22°C. Samples of both FP-TATB and UF-TATB powders were tested at flyer diameters of 3.0 mm and 4.0 mm.

RESULTS AND DISCUSSION

Synthesis of FP-TATB

Lemon-colored TATB was obtained by the amination of TCTNB in toluene with ammonium hydroxide solution under the influence of ultrasonic waves. This method of preparing TATB by ultrasonication is unique and economic. The amination reagent used is an ammonium hydroxide solution (NH_4OH), instead of ammonia gas, thus eliminating the tedious monitoring of gas pressure during amination. This method is more economical since the process is less complicated and time-consuming than previously documented methods, and the hazardous solvent toluene used in the process is regenerated from the waste stream by distillation and can be employed for further amination reactions.

Particle Size Distribution

The samples suspended in deionized water alone, with no additional method of powder disbursement, were difficult to keep in suspension. The high surface tension of the water resulted in a "skin" of powder that tended to adhere to glassware and instrument parts. Powder suspended in deionized water alone tended to re-agglomerate readily, making it difficult to obtain representative particle size distribution data. As a result, both the water alone samples of UF-TATB and FP-TATB resulted in a larger median particle size and wider particle size distribution (see Figure 1) than the same powder when some additional method of powder dispersion was employed. Figures 2 and 3 compare the particle size distribution for UF-TATB and FP-TATB samples suspended in deionized water alone with the samples suspended in deionized water plus the use of an additional powder dispersion method.

According to the results obtained in these experiments, for these two powders, the use of deionized water alone was not sufficient to ensure adequate suspension of the powder. An additional dispersion method, such as sonication and/or the use of a surfactant, resulted in a more uniform suspension of the powder. However, the exact method of powder dispersion had very little effect on the median particle size or particle size distribution, as shown in Figures 4 and 5. The arithmetic median, displayed in vol %, of FP-TATB was found to be~15 µm, while the median of UF-TATB was found to be ~5µm. Tables 1 and 2 summarize the particle size results. The addition of a small amount of dilute Triton X-100 greatly aided sample dispersion. Although the use of the ultrasonic bath or probe alone were acceptable methods of sample dispersion, as shown in Figures 3 and 4, the addition of the surfactant made cleaning of the instrument between sample runs much easier.

TABLE 1: UF-TATB Particle Size Results (based on volume)

Preparation	Mean (μm)	Median (μm)
DI water	18.84	8.83
DI water, USB	5.70	5.06
DI water, USP	5.70	5.12
DI water, Triton® X-100	6.35	5.65
DI water, Triton® X-100, USB	5.67	5.01
DI water, Triton® X-100, USP	5.65	4.95

TABLE 2: FP-TATB Particle Size Results (based on volume)

Preparation	Mean (μm)	Median (μm)
DI water	42.04	27.16
DI water, USB	15.95	12.68
DI water, USP	13.77	12.41
DI water, Triton® X-100	16.04	14.70
DI water, Triton® X-100, USB	15.56	13.39
DI water, Triton® X-100, USP	14.91	12.97

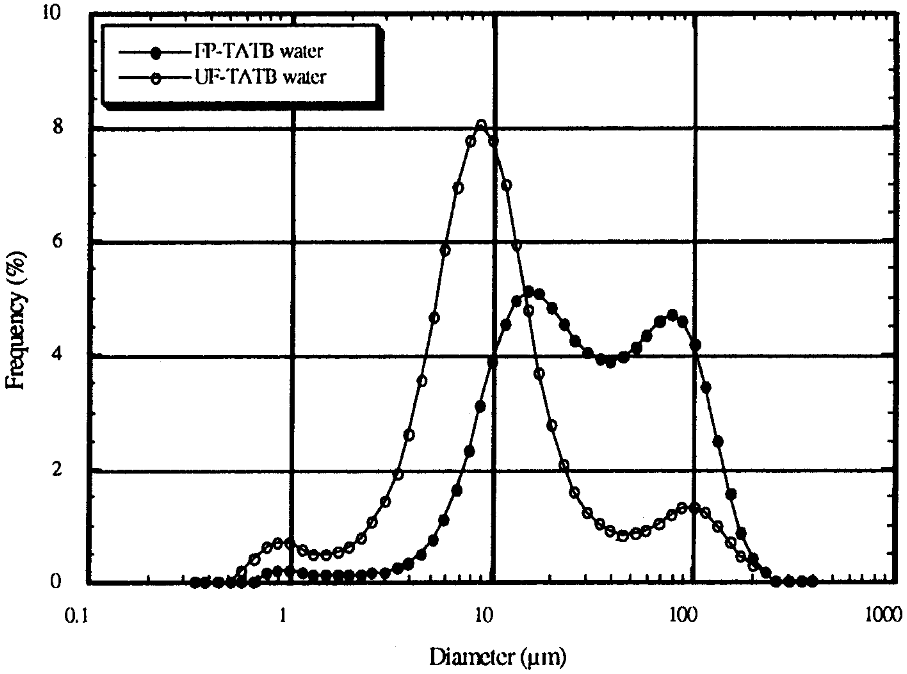


FIGURE 1

UF-TATB and FP-TATB, suspended in deionized water, particle size distribution

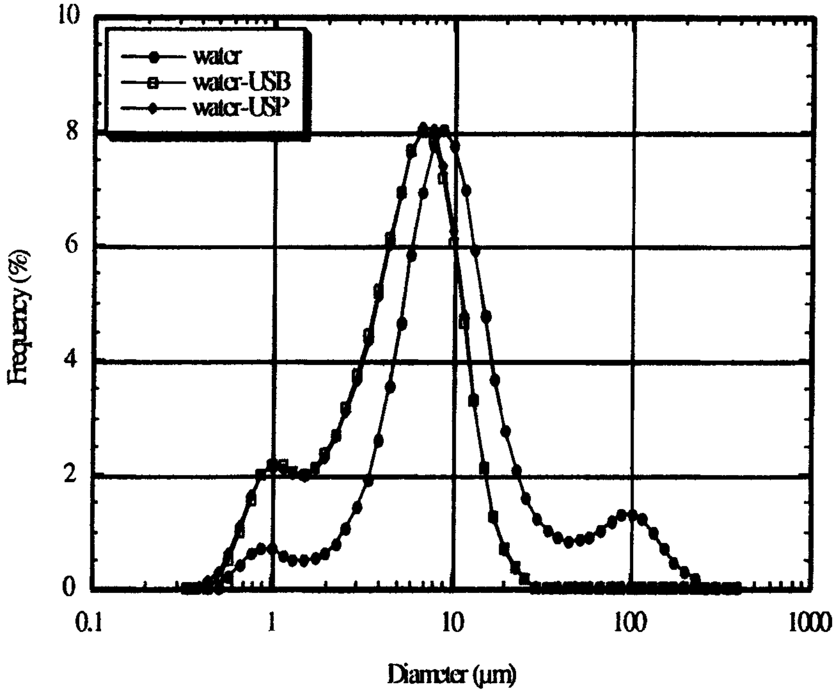


FIGURE 2

Comparison of the particle size distribution of UF-TATB samples suspended in deionized water with samples suspended in deionized water plus the use of an additional powder dispersion method.

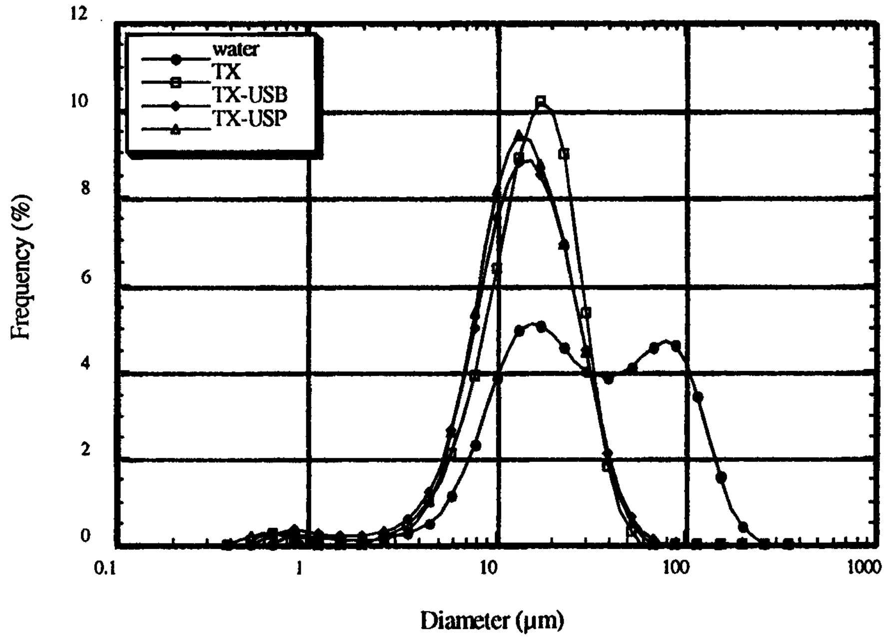


FIGURE 3

Comparison of the particle size distribution of FP-TATB samples suspended in deionized water with samples suspended in deionized water plus the use of an additional powder dispersion method.

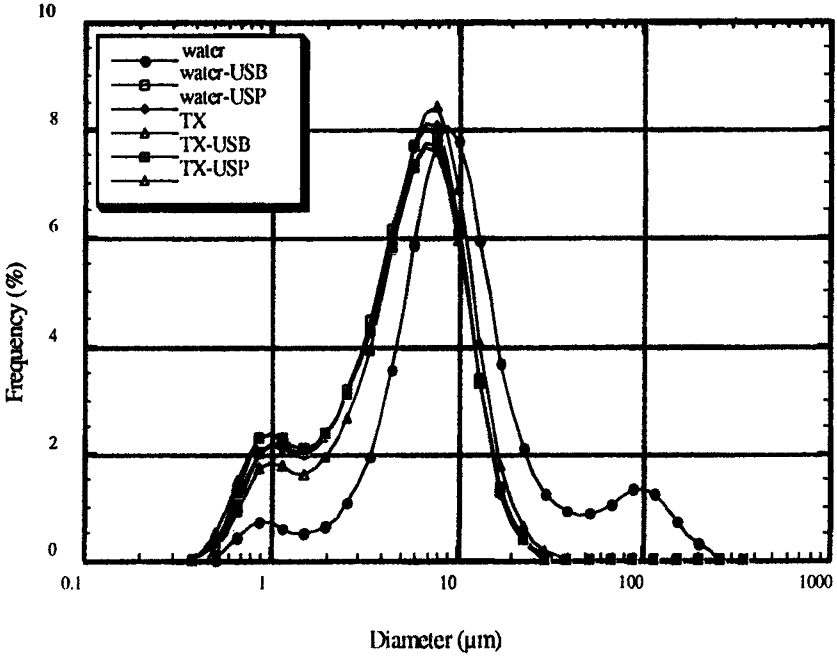


FIGURE 4

Comparison of powder dispersion methods for UF-TATB.

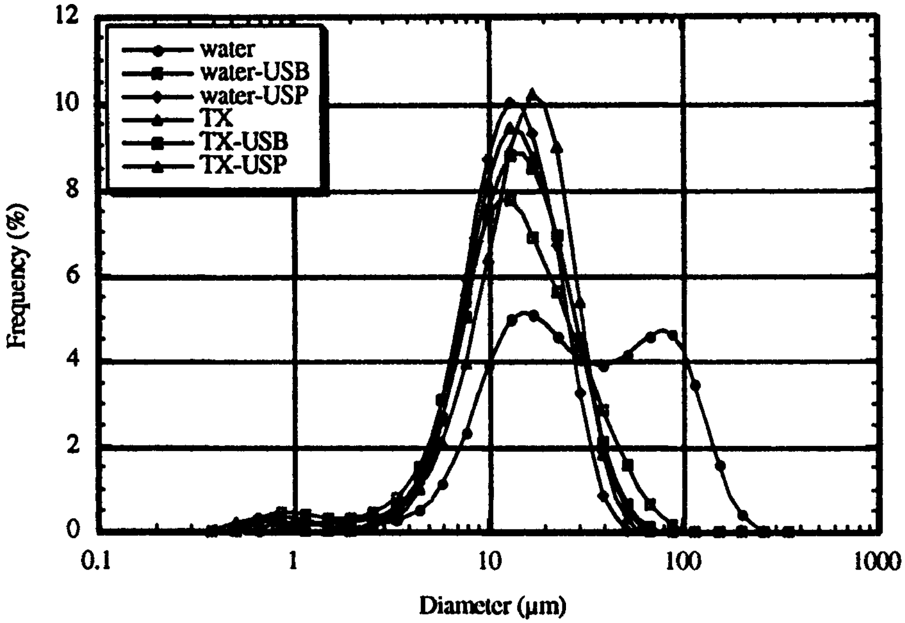


FIGURE 5

Comparison of powder dispersion methods for FP-TATB.

BET Surface Areas

Nitrogen was used as the adsorbate gas for the measurement of surface areas of both FP- and UF-TATB samples. The samples were vacuum outgassed for 24 hours at room temperature. It was found that FP-TATB has a surface area of 1.2 m^2/gm while the surface area of UF-TATB is 2.5 m^2/gm.

Initiation Spot-Size Testing

Initiation spot-size testing was used as a screening tool to reveal the difference in shock sensitivity of different explosive materials. Results of the tests conducted on both FP-TATB (KYL-I-58s) and UF-TATB (91190-135m-003) samples at flyer diameters 3.0 and 4.0 mm are presented in Table 3. The data reported is an average of four tests for each TATB sample. It can be seen that FP-TATB produced slightly deeper dents than the UF-TATB, suggesting a slightly higher initiation sensitivity at both flyer diameters. Naturally, the responses at flyer diameter 4.0 mm from both samples are stronger than those at diameter 3.0 mm.

TABLE 3: Initiation Spot-Size Test Data on TATB Samples

Flyer Diameter (mm)	Dent Depth (mm)	
	FP-TATB (KYL-I-58s)	**UF-TATB (91190-135m-003)**
3.0	0.926 ± 0.074	0.816 ± 0.095
4.0	1.634 ± 0.080	1.571 ± 0.104

CONCLUSIONS

We have demonstrated that fine-particle TATB can be made by a simple, one-step amination from TCTNB and ammonium hydroxide solution under the influence of ultrasonic irradiation (ultrasonication). This sonochemically-aminated TATB (FP-TATB) has particle size and surface area comparable to UF-TATB, an IHE booster material. Results from powder characterization studies on both TATBs illustrated that the arithmetic median particle diameters of FP-TATB is 15 micrometers while that of UF-TATB is 5 micrometers. The BET surface areas of both FP-TATB and UF-TATB powders were found to be 1.2 m^2/g and 2.5 m^2/g, respectively. Results from initiation spot-size testing indicated that FP-TATB is slightly more sensitive to shock initiation than UF-TATB, as measured by the dent depth of the witness plate. Hence, this simpler process can be considered to produce shock sensitive TATB for booster applications, in lieu of the more extended process used to produce UF-TATB.

ACKNOWLEDGMENTS

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