MLM--3629

DE90 008176

TATB Purification and Particle Size Modification: An Evaluation of Processing Options

David W. Firsich, Raymond Thorpe, and Lloyd A. Cox

Issued: March 15, 1990

MOUND

operated by

EG&G MOUND APPLIED TECHNOLOGIES

P.O. Box 3000, Miamisburg, Ohio 45343-3000

for the

U. S. DEPARTMENT OF ENERGY

Contract No. DE-AC04-88DP43495

DISCLAIMER

Contents

Abstract

Triaminotrinitrobenzene (TATB) is an insensitive high explosive with desirable safety characteristics. Mound is currently interested in developing a high purity, high surface area form of this compound to increase its potential applications. This paper describes recent development efforts. After setting purification and surface area goals, a number of processing procedures were tested to determine their practicality and effectiveness. The purification procedures included sulfuric acid recrystallization, dimethylsulfoxide/NaOH recrystallization, Soxhlet extraction, thermal gradient sublimation, and high-temperature recrystallization. Techniques identified for increasing surface area included crash precipitation of TATB and processing TATB in a fluid energy mill.

An evaluation of the data suggested that a two- or three-step process will be necessary to produce the desired results. A sulfuric acid recrystallization used in conjunction with a high-temperature recrystallization is recommended to achieve the necessary purity. This should be followed by a crash precipitation or milling step to meet surface area requirements.

Introduction

The compound 1,3,5-triaminotrinitrobenzene (TATB) is an ordnance material referred to as an insensitive high explosive (IHE) because of its high resistance to initiation. Although stimuli are available to detonate this material, it remains inert for purposes of handling and storage. Its superior safety characteristics have not gone unnoticed by the weapons community, which is interested in incorporating it into a variety of components. However, TATB is currently used only as a main charge; i.e., a pressed block that is ignited by a smaller detonator containing a different explosive compound.

TATB uses could be extended to detonators if TATB powder could be made to meet certain purity and surface area specifications; however, at the present time such a "detonator-grade" TATB does not exist. Purification and surface area modification have proved to be difficult problems and are still under investigation. This report presents a review of the objectives, available techniques, and current status in the effort to develop detonator-grade TATB. The topics of purification and surface area modification are discussed separately, followed by concluding remarks about future development plans.

Purification

Purification Objectives

Detonator-grade TATB is intended for use within a small, sealed, metallic detonator housing. Its particle size must remain constant over a 20-year service life to maintain firing reliability. TATB purity

requirements are a consequence of these conditions. These requirements include a low chloride, acid, and base content (to minimize the potential for inducing metallic corrosion) and a low residual solvent content (to prevent a solvent-assisted change in surface area). It is also desirable to limit the amount of ionic species in general to avoid providing charge carriers which could promote corrosion.

A quantitative guide to acceptable impurity levels can be obtained by examining an existing detonator material, pentaerythritol tetranitrate (PETN). Detonator-grade PETN typically contains about 35 ppm chloride (up to a maximum of 200 ppm), 80 ppm sulfate (up to a maximum of 160 ppm), and 200 ppm nitrate (up to a maximum of 400 ppm). These numbers serve as a guide and do not necessarily represent the exact purity required for detonator-grade TATB.

The TATB processed at Mound is manufactured at Pantex, Amarillo, Texas. As received, this material contains approximately 4000 ppm chloride and 300 ppm sulfate. Over 99% of the chloride must be removed to reach the PETN guideline of 35 ppm. This challenge is complicated by the fact that the chloride is present in more than one form. Most of the chloride exists as ammonium chloride occluded in TATB crystals, while the remainder is in the form of partially chlorinated TATB derivatives. The latter are expected to have chemical and physical properties similar to TATB, making their separation difficult.

TATB Solubility

TATB has been tested for solubility in a large number of solvents, and the results have invariably been disappointing. One of the best solvents found to date is dimethylsulfoxide (DMSO), which becomes saturated at about 0.10 g/L at room temperature [1].

There are sound chemical reasons for the insolubility of TATB; the principal one is the unwillingness of TATB molecules to separate from each other in the solid state. The TATB molecule is a six-membered carbon ring with alternating amino and nitro group substituents (Figure 1). X-ray crystallography has shown that the solid is made up of TATB molecules arranged in layers, similar to graphite [2]. The molecular arrangement is such that an amino group on one molecule can hydrogen bond with a nitro group on an adjacent molecule in the same layer (Figure 2). Because of the symmetry of the TATB molecule, every amino and nitro group can engage in this type of interaction, thereby generating a tremendous hydrogen bonding contribution to the lattice energy of TATB. Solid TATB is thus in an energetically favored state compared to individual TATB molecules stabilized by solvation, which explains the low solubility observed. The high lattice energy of TATB also contributes to its low volatility and high melting point.

A second chemical rationale for the low solubility of TATB is its ability to hydrogen bond in an intramolecular fashion. Figure 1 shows that a TATB amino group can hydrogen bond with a nitro group on the same molecule. This ties up electron

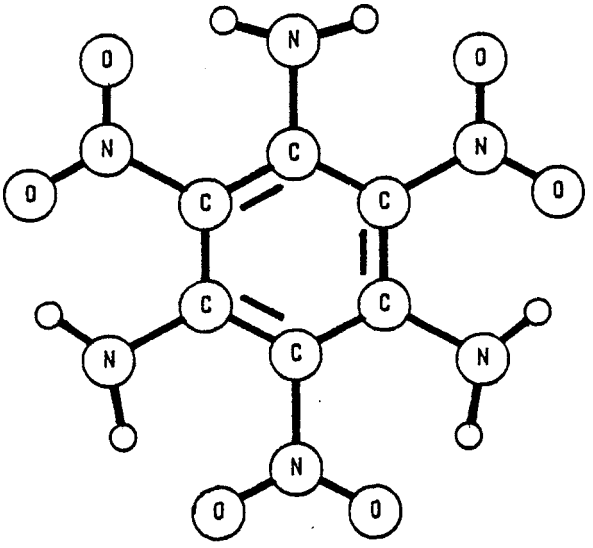

Figure 1 – Structure of a TATB molecule.

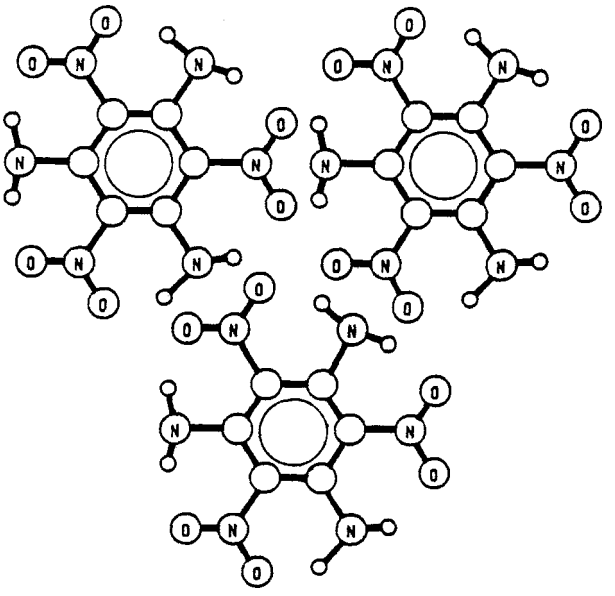

Figure 2 – Intramolecular hydrogen bonding with a TATB layer.

clouds that otherwise could interact with solvent molecules. The net result is loss of potential solvent stabilization. It is not surprising that only the most polar solvents solubilize TATB to any degree.

Most common purification methods require the compound to possess substantial solubility to be effective. These techniques (such as liquid chromatography, saturation recrystallization, and solvent/nonsolvent recrystallization) cannot be applied to TATB in the traditional way. Discussed below are a number of alternative purification processes that have been tested, their advantages, and their disadvantages. Each was applied to the starting material cited above. A summary of the results is shown in Table 1.

TATB Purification Techniques

The Cady Method – Sulfuric Acid Recrystallization

The Cady method, devised by Howard Cady of Los Alamos National Laboratory (LANL), calls for dissolving TATB in sulfuric acid, followed by precipitation with water. The term "dissolve" is not strictly accurate here; when placed in sulfuric acid, TATB reacts to form a protonated derivative that is soluble in sulfuric acid [3]. The addition of water removes the added proton, and TATB precipitates from solution.

The process has a number of attractive features. Fairly large amounts of TATB (about 10 wt %) will "dissolve" in sulfuric acid; thus, practical quantities are readily

Table 1 - PURIFICATION METHODS

Processing Methods	Chloride Content (ppm)	Sulfate Content (ppm)	Advantages	Disadvantages
Starting Material	4000	300		
Cady	200-600 [a]	4500	Produces powder with a high surface area. Large quantities readily processed.	High sulfate content. Concern over residual acid in powder.
McGuire	300-2600 [a]	3500	Produces powder with a high surface area.	Chloride reduction uncertain. Concern over residual base in powder.
Vacuum Soxhlet Extraction [b]	350	1250	Produces powder with a lower sulfate content than Cady and McGuire methods. No acids or bases used in this process.	Slow. Produces small quantities and powder with a low surface area.
Thermal Gradient Sublimation	500	----	Removes chlorinated derivatives. No potential sulfate contamination.	Slow. Produces small quantities.
High-Temperature Recrystallization [b]	200	1900	Uses no acids or bases.	Produces powder with a low surface area.

[a] Range of observed results.

[b] Dimethylsulfoxide solvent.

processed. The sulfuric acid converts much of the chloride impurity into HCl, which can then be removed by maintaining a vacuum over the solution. Finally, the crash precipitation that occurs when water is added produces a powder with a fine particle size (surface area typically 25 m^2/g).

These advantages are tempered by some drawbacks. Although the chloride content is reduced from 4000 to 200–600 ppm, the sulfate content rises from 300 to approximately 4500 ppm. In addition, there remains a lingering concern that residual acid is present in the powder.

The McGuire Method - DMSO/NaOH Precipitation

The McGuire method is credited to Lester Rigdon, Gordon Moody, and Ray McGuire of Lawrence Livermore National Laboratory (LLNL). TATB is "dissolved" in a mixture of DMSO, NaOH, and water. An acidic water solution is then added to precipitate TATB. As in the Cady method, "dissolved" TATB is thought to exist as a derivative in the DMSO/NaOH solution; the addition of acidic water returns it to its original chemical (and insoluble) state.

The McGuire method produces powder with a high surface area comparable to that of the Cady method. The amount of chloride reduction it achieves is presently unclear. One experiment resulted in a reduction from 4000 to 300 ppm, whereas another (with the same starting material) yielded 2600 ppm. In both cases the product sulfate level rose to 3500 ppm. The source of the sulfate is thought to be residual DMSO, which is converted to sulfate in the predigestion step of the sulfate analysis procedure.

DMSO/NaOH precipitation has most of the advantages and disadvantages of the Cady method. The "solubility" of TATB obtained using this method (2 wt %) is not as great as that obtained using the Cady method, but it is certainly sufficient for a viable process. A powder with a high surface area is produced and chloride content is reduced, although the amount of reduction remains unresolved. The process disadvantages include the apparent presence of residual DMSO in the product and the possible presence of residual base.

Vacuum Soxhlet Extraction

Vacuum Soxhlet extraction is a continuous extraction of TATB using DMSO solvent. The traditional Soxhlet extraction technique is employed with two variations. Because of the tendency of DMSO to degrade when held near its boiling point, the process is conducted under a vacuum sufficient to suppress the DMSO boiling point from 189°C to 80°C. In addition, the extractor was modified so that the vapors from the boiling solvent heat the extraction thimble (Figure 3). This improves the extraction efficiency, since TATB is more soluble in warm solvent. The extraction solution eventually becomes saturated, and TATB begins to precipitate.

Vacuum Soxhlet extraction produces faceted crystals of TATB with particle sizes ranging from 5–40 μm (Figure 4). The relatively large particle size and smooth

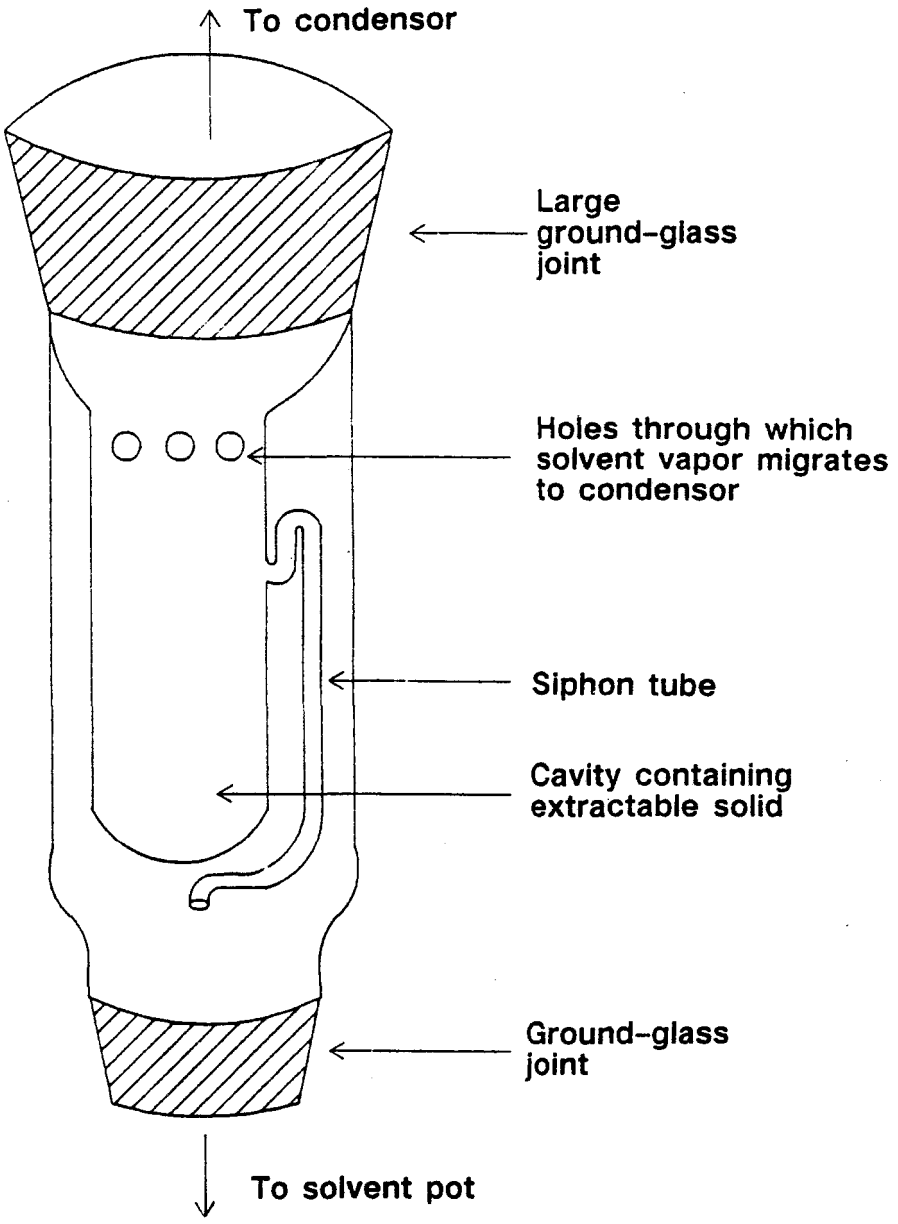

Figure 3 – Modified Soxhlet extractor.

particle surfaces each contribute to the undesirably low surface area (about 0.2 m^2/g). The chloride content is reduced to 350 ppm, but the sulfate rises to 1250 ppm. Residual DMSO solvent is thought to be the source of the increased sulfate, as previously noted for the McGuire method.

The benefits of the process include chloride reduction and a final sulfate content lower than that obtained by the Cady and McGuire methods. However, the method is slow; only 1 g of product is generated from a 3-week extraction using 1 L of DMSO. Although multiple extractors could be put into place to overcome this

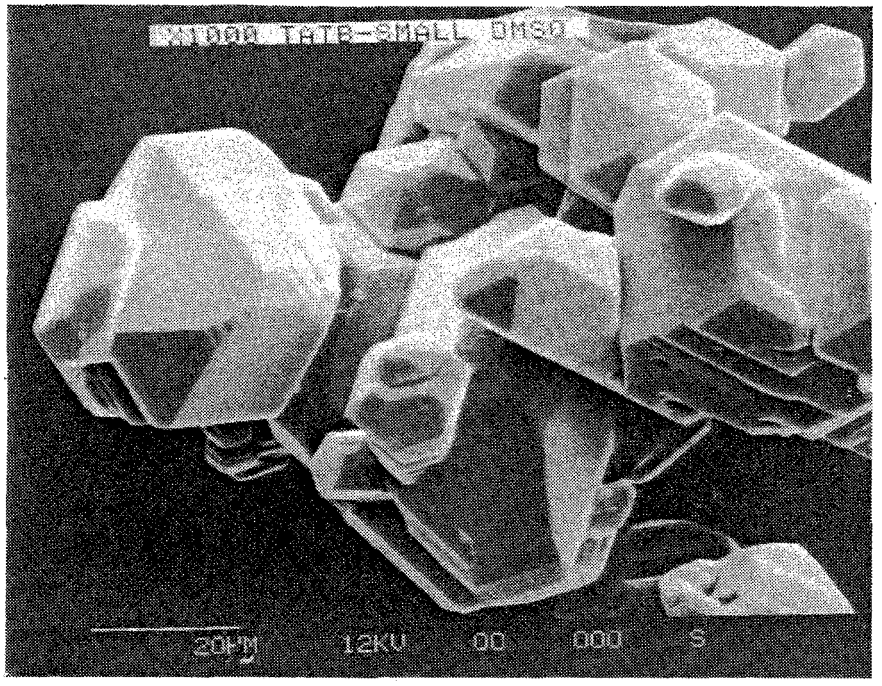

Figure 4 – SEM image of TATB crystals from Soxhlet extraction.

deficiency, this would require considerable effort and would be highly complex. Another drawback of the method is that it produces powder with a low surface area.

Thermal Gradient Sublimation of TATB

TATB can be induced to sublime under the proper vacuum and temperature conditions. If placed in the warmest zone of a thermal gradient, it will sublime down the gradient onto a cooler surface. Chlorinated derivatives of TATB may be sublimed under similar conditions, but because they are more volatile than TATB [4], these derivatives condense onto a different temperature zone. Thermal gradient sublimation thus separates TATB from closely related chlorinated derivatives.

The thermal gradient sublimation of TATB has been attempted only on a laboratory scale using a commercially available sublimator (Figure 5). Insufficient quantities were generated for a complete analysis, but the chloride content was measured at 500 ppm. It was presumed that sulfate was also reduced because sublimation introduces no new sulfur-containing species. Particle size, or surface area, was not measured.

This technique (also known as zone refining) could be an attractive process for TATB purification, except for one consideration. Even with an applied vacuum of 10^{-4} torr, it is necessary to heat TATB to over 170°C for sublimation to occur at a useful rate. Scaling up the method would involve heating substantial quantities of powdered TATB at high temperatures for extended periods (perhaps one week). This is undesirable from a safety point of view. This problem might be circumvented by employing an ultra-high

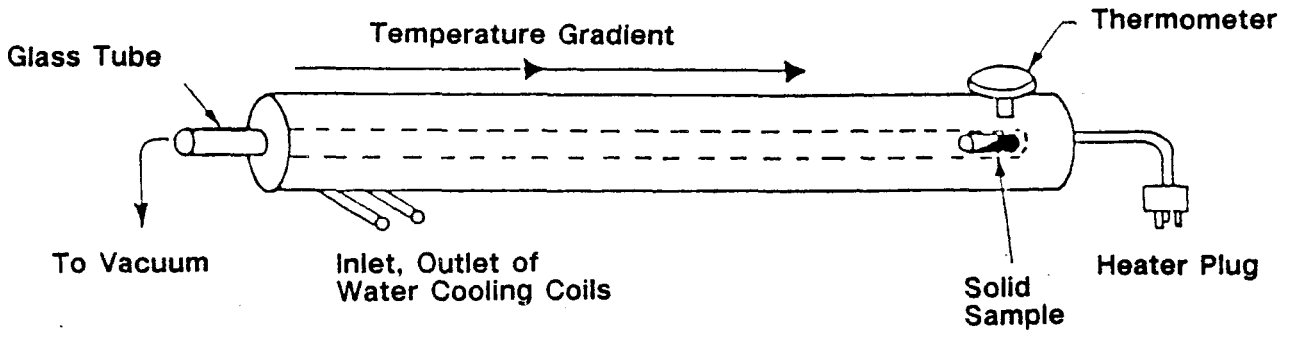

Figure 5 – Thermal gradient sublimator.

vacuum system (10^{-8} torr) which could effect TATB sublimation at lower (and safer) temperatures. However, to achieve the desired separation, the ultra-low pressure would have to be held steady throughout the processing period. An evacuated zone with a large length-to-diameter ratio would also be needed to account for the increased mean free path operating at low pressures. The cost and maintenance of a high-vacuum system are other considerations impacting the feasibility of thermal gradient sublimation.

Perhaps the most useful result to come from the sublimation experiment was confirmation that chlorinated derivatives of TATB are more volatile than TATB. This suggests that they are also more soluble than TATB, based on lattice energy arguments discussed earlier. If this is the case, the prospects for purifying TATB by recrystallization are enhanced.

High-Temperature Recrystallization

The high-temperature recrystallization approach was developed by Don Ott of LANL, who determined that the solubility of TATB improves dramatically at elevated temperatures [5]. For example, TATB solubility in DMSO rises from 0.10 g/L at room temperature to 5 g/L at 145°C. Ott's procedure involves placing an excess of TATB in a high-boiling solvent and bringing the mixture to a relatively high temperature until all the solid dissolves. The hot solution is then cooled slowly, without stirring, while TATB precipitates.

In the case of DMSO, Ott observed a significant solubility increase above 125°C, which he attributed to the thermally assisted breakdown of the intermolecular hydrogen bonding in solid TATB. The key to purification is to start above 125°C and slowly cool the solution, allowing TATB crystals to grow with the exclusion of other molecules. One added benefit of the elevated temperature is that the ammonium chloride impurity in TATB apparently sublimes up onto the cool neck of the recrystallization vessel during the precipitation period.

One high-temperature DMSO recrystallization has been performed to date; the resulting product contained 200 ppm

chloride and 1900 ppm sulfate. The increased sulfate content was again attributed to occluded DMSO. Surface area was not measured, but it is expected to be as low as or lower than that obtained by Soxhlet extraction using DMSO.

High-temperature recrystallization is attractive because it employs no acids or bases that can end up in the product. Although DMSO solvent is incorporated into the product, an alternative solvent might not show this behavior. To minimize the likelihood of incorporation, a solvent with a large or irregular shape could be used. Many unexplored possibilities for this purification method remain.

The inherent disadvantages of high-temperature recrystallization are easy to list. Material with a high surface area is not produced, and the amount of TATB that can be processed (0.5 wt %) is low. Finally, the present level of DMSO incorporation is unacceptable; new high-temperature solvents that are not incorporated need to be discovered.

Supercritical Chromatography

Supercritical chromatography was briefly considered as a potential purification method. The premise was that TATB might have substantial solubility in supercritical carbon dioxide, ammonia, nitrous oxide, or isopropyl alcohol. If this were the case, purification with supercritical chromatography (a technology in its infancy) might be possible.

Contacts with vendors of supercritical equipment generated only one company that will consider testing the solubility of TATB under supercritical conditions: furthermore, all supercritical chromatography chemists contacted doubted that TATB would show any improved solubility in supercritical media. Finally, it was learned that some supercritical solvents (ammonia, e.g.) cannot be used for chromatography at this time because the proper chromatographic column material and hardware have yet to be developed.

In spite of the negative comments of the experts who were contacted, there is no substitute for an actual experiment. The solubility of TATB in liquid CO_2 and N_2O and in supercritical CO_2 and NO_2 will be tested. If any solubility is observed, supercritical chromatography as a purification technique will have to be reexamined.

Surface Area Modification

Surface Area Objectives

The insensitivity that makes TATB desirable from a safety standpoint can become a problem if the powder does not fire when needed. Detonator-grade TATB is expected to initiate when impacted with a high velocity slapper disc. Experiments by Will Hemsing at LANL have shown that only TATB powder with a high surface area (small particle size) will be initiated by such a stimulus.

Powder with a high surface area is produced by both the Cady and McGuire TATB processing methods. Each includes a crash precipitation step that results in TATB with a surface area of approximately 25 m^2/g. These powders have shown satisfactory slapper initiation characteristics, whereas others with 14-m^2/g

surface areas have not. The Mound goal for surface area must therefore be close to (or above) 25 m^2/g.

Surface Area Modification Techniques

Crash Precipitation

Crash precipitation is a rapid precipitation from solution caused by a quick and turbulent change of conditions, such as rapid addition of a nonsolvent. The Cady and McGuire methods precipitate TATB from concentrated room temperature solutions by the addition of water and dilute acid, respectively. Another crash precipitation approach might be to quickly freeze a hot solution of TATB/solvent, then remove the solvent by freeze-drying. A third potential technique could involve precipitating TATB from a hot organic solvent by rapidly adding a cold nonsolvent. "Crashing" TATB from solution does not allow time for large crystals to grow; thus, a high surface area is produced. However, solvent can become occluded during the precipitation as the TATB molecules rush to aggregate.

Fluid Energy Mill

The fluid energy mill grinds powders by colliding streams of suspended particles into one another. This treatment will soon be applied to TATB, with the intent of grinding TATB down to a submicron size that will have a high surface area.

The mill at Mound will be available within a few months. Its past application to another explosive powder, cyclotetramethylenetetranitramine (HMX), indicated that there is a limit to how fine a powder can be ground. With HMX, the smallest particles achieved were on the order of 1 μm; a similar result for TATB would represent an unacceptably low surface area. Another concern with milling is potential contamination of TATB by residues or small particulates in the mill.

Other Methods

An attempt was made to cleave TATB crystals by the action of an ultrasonic horn. A 250-W ultrasonic horn was immersed in a suspension of TATB in a variety of solvents. After 1 hr of sonication, the solvent was removed and the TATB powder was analyzed by scanning electron microscopy (SEM). The faceted, crystalline TATB which was used as starting material had not been cleaved; only the particle edges were rounded off. Extended periods of sonication yielded the same disappointing result.

Reducing particle size by thermally shocking powdered TATB was also attempted. TATB powder was heated to 150°C and then quickly added to liquid nitrogen (-196°C). The recovered powder was examined by SEM, which showed that no crystalline cleavage had occurred.

Conclusions And Recommendations

At this time there is no single-step process that will produce the purity and surface area needed to qualify TATB as detonator grade. Based on present knowledge, a two- or three-step process seems to be required. The discovery of a highly effective solvent for TATB could change this

situation, but, after years of unsuccessful searching, this seems unlikely.

Investigation of the three-step approach described below is recommended. First, TATB should be processed using the Cady method. This procedure is relatively simple to execute, it reduces chloride substantially, and it allows large amounts of TATB to be processed in one batch. Second, for greater purification, a high-temperature recrystallization using an organic solvent should be performed. This procedure will remove any acid residue and should provide enhanced purity through the crystal growth step. Occluded solvent in the product may be a problem, but this can be minimized by slowing the rate of crystal growth or by choosing a high-temperature solvent with incompatible molecular dimensions. Finally, a third step is needed to produce the desired surface area. Milling should be attempted until a solvent-based crashing technique that gives maximum surface area with minimum solvent inclusion is found. The search for such a technique will continue.

This three-step approach will be pursued at Mound. The Cady method needs no further development. Raymond Thorpe of Mound has considerable experience and expertise with this process. However, high-temperature recrystallization is a new process at Mound and will require some development. DMSO will be used as the solvent, and methods to control the slow growth of TATB crystals will be devised. In addition, new high-temperature solvents to test TATB solubility and inclusion properties will be selected. The discovery of a suitable solvent would present new options for crash precipitation and/or high-temperature recrystallization.

References

1. Gibbs, T. R., and A. Popolato (ed.), *LASL Explosive Property Data*, University of California Press (1980).

2. Choi, C. S., and J. E. Abel, *Acta Cryst., B28*, 193-201 (1972).

3. Harris, B. W., *Carbon-13 NMR Analyses of TATB and Related Compounds in Sulfuric Acid*, LA-8629-MS, Los Alamos National Laboratory (1981).

4. Firsich, D. W., J. *Hazard. Mat., 9*, 133-137 (1984).

5. Ott, D. G., and T. M. Benzinger, *J. Energetic Mat., 5*, 343-353 (1987).