

Gilson da Silva\*  
National Industrial Property Institute  
Rio de Janeiro – Brazil  
gilsondasilva@uol.com.br

Elizabeth da Costa Mattos  
Institute of Aeronautics and Space  
São José dos Campos – Brazil  
elizabethecm@iae.cta.br

\*author for correspondence

# Synthesis of 2,4,6-triamino-1,3,5-trinitrobenzene

**Abstract:** The 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) is perhaps the most thermostable and insensitive explosive known. Its low sensibility to shock makes it suitable for military and civil applications. TATB application is done either alone or in combination with another high energetic material. This study aimed at reporting the review about many processes to produce TATB and the problems associated with them, as well as suggest techniques like Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC), which can be useful in the characterization of this energetic compound.

**Keywords:** TATB, Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry, Plastic-bonded explosive.

## LIST OF SYMBOLS

TATB	2,4,6-triamino-1,3,5-trinitrobenzene
HE	high explosive
PBX	plastic-bonded explosive
HMX	octogen
RDX	hexogen
TCB	1,3,5-trichlorobenzene
TCTNB	1,3,5-trichloro-2,4,6-trinitrobenzene
DCA	3,5-dichloroanisole
NMP	N-methylpyrrolidinone
VNS	vicarious nucleophilic substitution
DMSO	dimethyl-sulfoxide
ATA	4-amino-1,2,4-triazole
DATB	diamino-trinitrobenzene
DAP	diaminopicric acid
FT-IR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
HNS	2,2', 4,4', 6,6'-hexanitrostilbene
PETN	pentaerythritol tetranitrate

## INTRODUCTION

Insensitive explosives have been receiving a great deal of attention in connection with low vulnerability. The high energy content and low sensitivity are intrinsically connected to the size, shape and defects of the crystals, as well as the molecule's structure and compatibility with the binder.

The 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) is an explosive with a high melting point and thermal stability, it has been applied in situations where insensitivity to

impact hazards is important. Other potential applications include the use of TATB as the booster or main charge explosives for down-hole oil perforation at elevated temperature surroundings (Lee, 1996).

TATB is a high explosive (HE) that can be combined with plastic binder to produce a plastic-bonded explosive (PBX) composition, which is heat-resistant and highly insensitive. It is insoluble in organic solvents and has a melting point above 400°C. TATB was firstly prepared in 1888 by Jackson and Wing, in agreement with Akhavan (2004), from tribromotrinitrobenzene. It has also been prepared on a laboratory scale from 2,4,6-trinitrotoluene through selective reduction of the 4-nitro group, nitration to pentanitroaniline, and, then, ammonolysis.

Among the various insensitive HEs, TATB is an attractive insensitive explosive as it satisfies the safety requirements at high temperatures, and it is resistant to accidental initiation and explosion (Boddu et al., 2010). This is perhaps the most thermoresistant insensitive explosive, and it can be used in modern warheads in the military and in deep oil well explorations. Table 1 shows its properties.

Table 1: Properties of TATB (Meyer, 2007)

Characteristics	
Color	Yellow-brown
Form	Crystalline solid
Molecular weight/g.mol <sup>-1</sup>	258.1
Melting temperature/°C	350
Decomposition temperature/°C	350
Thermal ignition temperature/°C	384
Crystal density at 20°C/g.cm <sup>-3</sup>	1.93
Energy of formation/kJ.kg <sup>-1</sup>	-425
Enthalpy of formation/kJ.kg <sup>-1</sup>	-597.9
Oxygen balance	-55.80%
Nitrogen content	32.60%

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The presence of impurity and by-product of synthesis process can bring serious compatibility problems when using TATB in certain types of ordinance, as well as in the use of other HE like octogen (HMX) and hexogen (RDX). Therefore, the production process must be carefully studied and its influence, evaluated.

## SYNTHESIS

TATB can be manufactured by the nitration of 1,3,5-trichlorobenzene (TCB) to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and the amination of TCTNB to TATB. The major impurity brought in this process is ammonium chloride, which is a by-product, and smaller amounts of tetrachlorodinitrobenzene partial amination. The presence of these amounts of ammonium chloride can produce serious compatibility problems in the use of TATB.

Benziger (1977) found that TCTNB is highly resistant to hydrolysis and the presence of a sufficient amount of water during the amination of TCTNB to TATB results in a TATB product, which is essentially free of ammonium chloride. Then, Benziger (1977) developed a process comprising the nitration of TCB to TCTNB followed by amination to TATB, where, in the amination step, sufficient water can be added to the solvent for the TCTNB to render the ammonium chloride to a semi-deliquescent condition. The process is conducted in toluene as a solvent, in the ratio of about ten parts toluene to one part TCTNB by weight, and in the presence of about 2.5% by weight of water in the toluene.

The process described by Benziger (1977) is conducted in a Pfaudler reactor, which is capable of operating over a range of 20 to 150°C, with 0.69 MPa pressure; agitation is provided by an anchor-type blade at speeds from 20 to 200 rpm. A glass-lined, concentric tube reflux condenser, integral with the Pfaudler reactor is also used.

The reactor is charged with 56.7 kg of oleum, 7.2 kg of sodium nitrate is then added at slow rate, with full agitation with the jacket cooling kept in 60 to 70°C. After finishing the  $\text{NaNO}_3$  addition, the contents of the reactor are brought to a temperature of 100°C. The reactor is charged with 2.5 kg of TCB, and the jacket temperature increased quickly to 145-155°C and kept for four hours. The contents of the reactor are cooled to 40°C and discharged in a recipient with 113 kg of crushed ice. Full agitation is provided in this step with a vacuum pump to remove the nitrous fumes. The TCTNB precipitates in the form of heavy white crystals that are pumped through the plate and frame press. The cake is washed with a lot of water until the wash water

gets pH 6-7, it is also dried in open trays in a forced-draft oven at 60°C, for 16 hours.

The amination step is conducted with 2.7 kg of TCTNB dissolved in 27 kg of toluene, where 6.8 kg of water (2.5%) is added. After being clarified by filtration using Celite filter, the reactor system is sealed, and heating is continued until the contents are at 145°C. The jacket steam is turned off at this time and ammonia gas is added to the gas phase in the reactor, through an opening on the top of the kettle, in the ratio of 0.36 kg/h. When the  $\text{NH}_3$  overpressure reaches about 34 kPa, the reactor system is purged of residual air by venting through the reflux condenser. The system is then resealed and the reaction gone about three hours with moderate agitation, temperature at 150°C and the pressure remained at 240 to 270 kPa. The termination of the amination reaction is marked by a sharp rise in the system pressure to about 413 kPa. The  $\text{NH}_3$  flow is stopped, the system is cooled to about 60°C and vented, water is added with good agitation. The TATB can be recovered by filtration using the plate and frame press, equipped with cotton cloths backed with filter paper. The cake is washed three times with water and dried in open trays in a forced-draft oven at 100°C for 16 hours.

The water addition can reduce the chlorine to 0.20%, instead of the 0.60% of Cl found in the product without the water addition. When water is present, the only change in process conditions is a moderate increase in system pressure.

Benziger (1984) taught a method of making fine-grained TATB, where the energetic material shows increased sensitivity over TATB produced by previously known method, and it does not require grinding of the TATB as a final step. The method comprises the amination of TCTNB while dissolved in an emulsion of organic solvent, preferably toluene, in water. The emulsion includes a protective colloid, and is prepared with the water volume being greater than the toluene volume, so the water is the continuous phase and the toluene is the dispersed one of the emulsion. Amination is preferably conducted by introducing gaseous ammonia into the emulsion. The particle size of the product TATB is effectively controlled by the size of the toluene droplets in the emulsion.

Ammonium oleate can be used as an emulsifying agent, and the emulsion is prepared *in situ* by the reaction between oleic acid and gaseous ammonia. The TCTNB, which will be aminated, is insoluble in water and, soluble in toluene. Then, in an emulsion consisting on toluene droplets dispersed in water, TCTNB added to the emulsion will reside in the toluene droplets and the size of the TCTNB-containing toluene droplets determines the maximum size of the TATB particles, which are

formed upon the TCTNB amination. The method is preferably conducted using an emulsion, containing from approximately 50 to 75% by volume water, with the remainder preferably consisting on toluene.

Ott and Benziger (1991) proposed the preparation of TATB from 3,5-dichloroanisole, in which the nitration of 3,5-dichloroanisole (DCA) under relatively mild conditions gave 3,5-dichloro-2,4,6-trinitroanisole in high yield, and purity followed by the ammonolysis of this latter compound to give the TATB. Another route is to first chlorinate this intermediate to give 1,3,5-trichloro-2,4,6-trinitrobenzene, which can be ammonolyzed to produce TATB.

The conditions necessary to effect the introduction of the third nitro group into the trichloro compound starting material, 1,3,5-trichlorobenzene, to produce 1,3,5-trichloro-4,6-trinitrobenzene, are quite severe. An excess of 90 to 95% nitric acid (4.35:2 ratio mol) and 25 to 30% oleum (20 mol) are used at a reaction temperature of 150°C, with vigorous stirring for 2.5 hours. After quenching the mixture with water, the product was isolated in 91% yield, 89% purity. The conversion was 0.80 mole of 1,3,5-trichloro-4,6-trinitrobenzene per mole of 1,3,5-trichlorobenzene. The ammonolysis step can be conducted without removing the by-products.

The nitration of 3,5-dichloroanisole has the activating effect of the methoxyl group on electrophilic aromatic substitution. Then, the process shows excellent yield at lower temperature (100°C), without the need of nitric acid excess or the use of oleum and the complete conversion of the starting material were obtained when the excess of nitric acid was merely 5% over the stoichiometric amount in 125°C of temperature for two hours.

The displacement of the chlorine and methoxy groups of 3,5-dichloro-2,4,6-trinitroanisole by ammonia occurred to give TATB. Ammonolysis of the reactions using limited amounts of ammonia give a mixture of TATB and starting materials 1,3,5-trichloro-4,6-trinitrobenzene or 3,5-dichloro-2,4,6-trinitroanisole, with only very small quantities of mono- and diamino compounds. However, from reactions in which mixtures of 1,3,5-trichloro-4,6-trinitrobenzene and 3,5-dichloro-2,4,6-trinitroanisole were treated with limited quantities of ammonia, it was found that 3,5-dichloro-2,4,6-trinitroanisole reacted several times faster than 1,3,5-trichloro-4,6-trinitrobenzene. Ammonolysis at low temperature results in TATB precipitating as extremely small crystals. Nevertheless, this reaction does not occur at low temperatures, since ammonium chloride is insoluble in toluene, and when better solvents for the chloride, such as dimethylformamide or dimethyl

sulfoxide, are employed, or added to the toluene, the yield of TATB is substantially reduced, even at low temperatures. Figure 1 shows the reactions sequence.

Lee and Kennedy (2002) described a method for producing fine-grained TATB powders with improved detonation-spreading performance and, hence, increased shock sensitivity when compared with that for ultrafine TATB. The method consists on a single-step amination of trichloro-trinitrobenzene using ammonium hydroxide solution in a sealed vessel, where a solution of trichloro-trinitrobenzene in a solvent is ultrasonically mixing and a solution of ammonium hydroxide in a cooled, sealed vessel such that an emulsion of triaminotrinitrobenzene is formed; and separating the triamino-trinitrobenzene from the emulsion.

During the step of ultrasonically mixing the solutions, the temperature is maintained between 1 and 15°C. A solution of TCTNB in toluene is added to an ammonium hydroxide solution in an air-sealed sonication reactor, having a sonicator horn powered by a 20 kHz (275-330W), with the horn disposed below the liquid level, between 10 and 40 minutes. The TATB was collected by filtration, washed sequentially with water, toluene and acetone, and dried in an oven. The material produced has approximately 6 µm median particle diameter, and increased shock sensitivity.

A method to convert surplus nitroarene explosives (picric acid, ammonium picrate) into TATB is proposed by Mitchell et al. (2005). This method consists on three steps where the picric acid or ammonium picrate is converted into picramide; the latter is converted into TATB; and the last step is the purification of TATB.

Picramide is formed by suspending picric acid or ammonium picrate with an ammonium salt in a dipolar aprotic solvent, and then heating the suspension under low pressure. The mole equivalents of ammonium salt to picric acid ranges from 2 to 30 and the mole equivalents of ammonium salt to ammonium picrate ranges from 1 to 30. The suspension is typically heated between 2 to 22 hours to temperatures in the range of 175 to 185°C, under 138 to 552 kPa of pressure.

The reaction of picric acid or ammonium picrate with an ammonium salt in dipolar aprotic solvents, such as sulfolane or N-methylpyrrolidinone (NMP), for several hours at 175-185°C, followed by a water wash, produces picramide, which is free of cyanuric acid and ammonium salts. Ammonium hydroxide (28% NH<sub>3</sub> in H<sub>2</sub>O) is unsatisfactory for use like a NH<sub>3</sub> reagent, as picric acid/ammonium picrate is decomposed to black solids when exposed to the ammonium hydroxide. A

good conversion of ammonium picrate or picric acid to picramide (87-94%) can be obtained when the ammonium salt is diammonium hydrogen phosphate  $[(\text{NH}_4)_2\text{HPO}_4]$  or ammonium carbamate  $(\text{NH}_4\text{CO}_2\text{NH}_2)$ , and the substrate concentrations are between 1.1 to 2.5 M. The picramide obtained in these syntheses can be used, without purification, to produce TATB.

The conversion of picramide to TATB using vicarious nucleophilic substitution (VNS) chemistry depends on the particular reagent employed, where the partial or full replacement of DMSO (dimethyl-sulfoxide) with less expensive solvents can be done. The VNS synthesis involves heating a VNS reagent with picramide in the selected solvent/solvent mixture and heating to reflux temperatures, while concomitantly distilling off the solvent.

Hydroxylamine in combination with a strong base, an aprotic dipolar solvent (DMSO) and an elevated temperature (65-95°C), reacts with picramide to yield TATB in 50 to 74% yield with about 97% purity. The concentration of picramide is typically 0.1 to 0.25 M, which gives rise to highly viscous reaction suspensions.

DMSO is an effective solvent in the vicarious nucleophilic substitution synthesis of TATB. The substitution of DMSO by methanol or toluene as methanol-toluene mixtures predictably provides TATB in lower yield and contaminated with DATB from the incomplete amination of picramide. Reaction of picramide with 4-amino-1,2,4-triazole (ATA) in methanol (60°C) in the presence of sodium methoxide provides primarily DATB and little or no TATB.

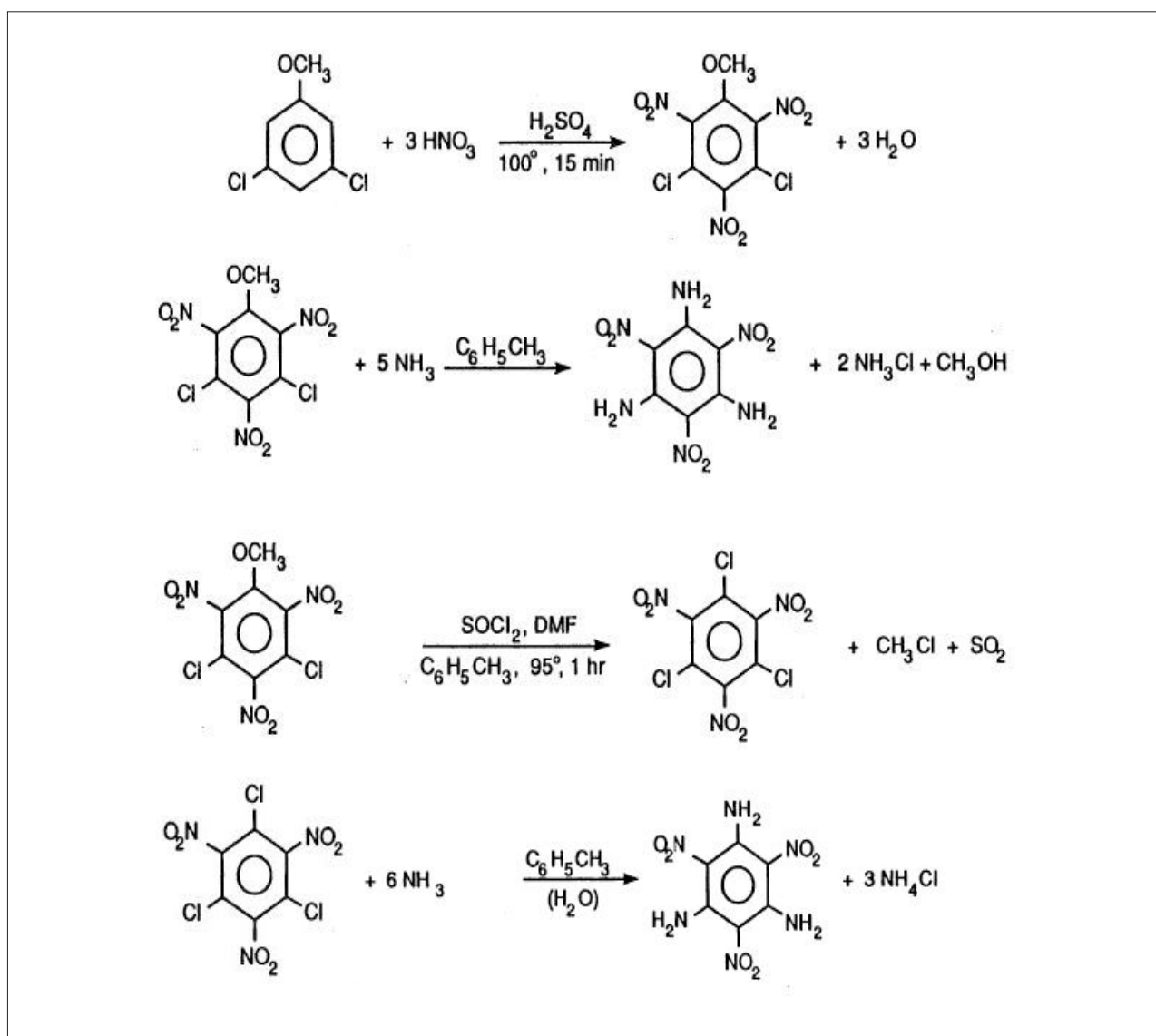


Figure 1: Reactions sequence of Ott and Benziger process.



The low solubility of TATB in most solvents is the problem of purification process. Impure TATB contains from 1 to 15% of impurities that can be eliminated by converting impure TATB preparations to relatively soluble derivatives, which, after purification, are converted to purified TATB by ammonolysis (from 90 to 130°C for 0.5 to 4 hours). Figure 2 shows the reactions sequence of the method proposed by Mitchell et al. (2005).

In another publication, Mitchell et al. (2006) taught a method to convert surplus nitroarene explosives, such as picric acid and ammonium picrate in trinitrophenol and TATB. The process is conducted directly by amination of picric acid by vicarious nucleophilic substitution of hydrogen yield diaminopicric acid. Treatment of diaminopicric acid with sodium hydroxide in water or water DMSO mixtures produces, upon neutralization with acid, trinitrophenol and its subsequent conversion into TATB.

The picric acid, ATA and sodium methoxide react in a mixture of methanol, toluene and DMSO to produce diaminopicric acid (DAP) in 68% yield. But, the replacement of ATA

with 1,1,1-trimethylhydrazinium chloride, a more active vicarious nucleophilic substitution reagent, affords DAP in 91% yield. DAP is heated in aqueous base (e.g., alkyl hydroxide) and acidified to yield trinitrophenol (TNP) in 84% yield. TNP can be used to produce TATB by means of Wolff-Limbach or Bellamy syntheses. Although, DAP can be directly converted to TATB by its reaction with diammonium hydrogen phosphate.

Picric acid (1.20 mmol) and 1,1,1-trimethylhydrazinium halide (6.00 mmol) are dissolved in a mixture of DMSO (3.6 mL) and toluene (4.8 mL) and a 25% by weight of sodium methoxide solution in methanol (3.00 mL, 13.1 mmol) is added. The suspension formed is stirred and heated from room temperature to 95°C over one hour, after that, being cooled to 4°C, treated with glacial acetic acid (14 mL) and warmed to room temperature with stirring. The precipitated material is collected and washed with acetic acid and water giving, after vacuum drying (80°C), 0.176 g of diaminopicric acid.

Diaminopicric acid (0.748 mmol) and diammonium hydrogen phosphate (7.50 mmol) are suspended in dry sulfolane (3 mL), and they are stirred. The suspension

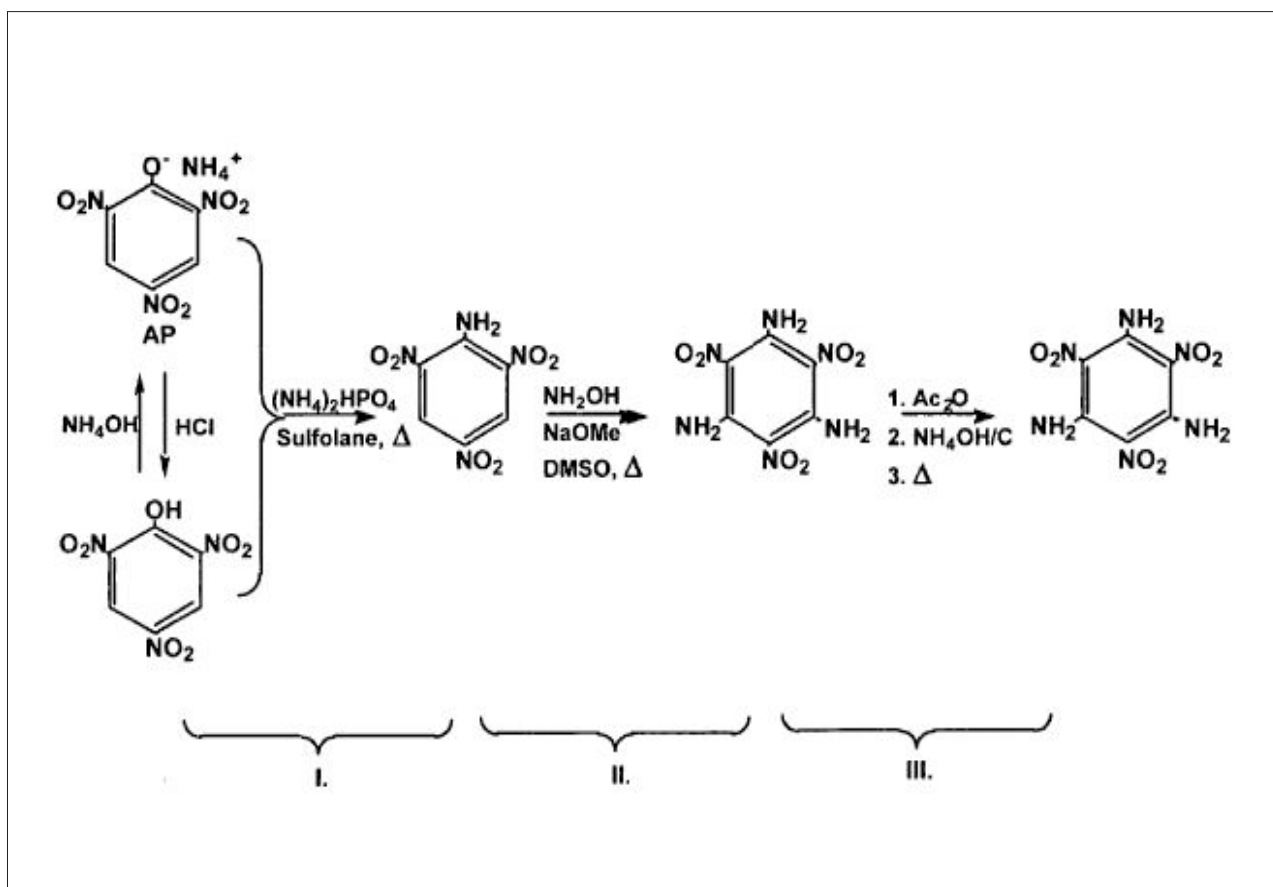


Figure 2: The three-step conversion of picric acid or ammonium picrate to TATB.

is heated with stirring from room temperature at 177°C over two hours and kept in this condition for six hours. The reaction system is cooled to 4°C and the resulting suspension is mixed with water (40 mL). The precipitated product is collected, washed with water and dried to yield TATB in the form of a brown solid (80%). The process is represented in Fig. 3.

## CHARACTERIZATION

The molecular structure of TATB crystal is triclinic. Strong hydrogen bonding is indicated by the lack of a distinct melting point and the almost total insolubility of TATB in common solvents. The only suitable solvent seems to be concentrated sulfuric acid ( $H_2SO_4$ ). The inorganic impurity  $NH_4Cl$  is trapped within the TATB crystal as discrete crystals (Dobratz, 1995).

This structure is similar to that of graphite, which indicates anisotropy for all directionally dependent properties. This effect is particularly obvious in thermal expansion and thermal cycling (Dobratz, 1995).

In agreement with Schmidt, Mitchell and Pagoria (1998) study, chemicals analysis such as nuclear

magnetic resonance (NMR) or chromatography are not practicable to TATB, due its low solubility in most solvents. Then, Fourier Transform Infrared Spectroscopy (FT-IR) can be applied to the quantification of this HE. The amine N-H stretching modes in TATB produce two characteristic absorptions at approximately 3225 and 3325  $cm^{-1}$ , while those for DATB occur at 3360 and 3390  $cm^{-1}$ , using Nujol mull preparations for the samples. Schmidt, Mitchell and Pagoria reported yet the detection of DATB in TATB at concentrations of 1% or greater by means of FT-IR.

The Differential Scanning Calorimetry (DSC) thermogram of the TATB presents an exothermic peak between 360 and 390°C with the maximum peak in 385°C, related by Boddu et al. (2010) as the thermal decomposition of the material, showing its excellent thermal stability in respect to the others HE (for example: 285°C to HMX, 241°C to RDX and 318°C to HNS).

An efficient characterization routine can be the application of the elementary analysis, FT-IR and thermal analysis (DSC and TG), by means of the results comparison with a standard material, as shown by Silva

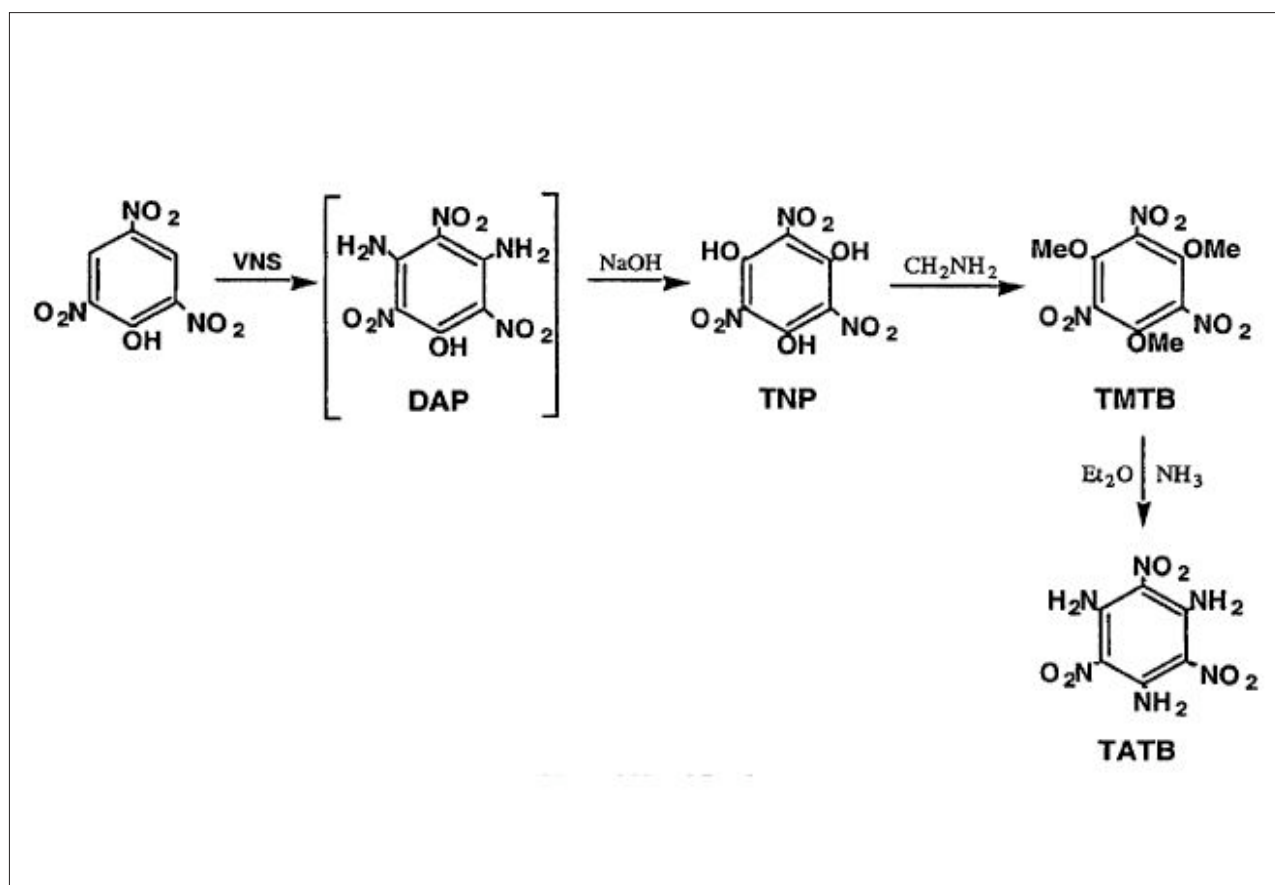


Figure 3: The production process of TATB by conversion of surplus nitroarene (Mitchel et al., 2006)

(2006) and Mattos (2004) used for characterization of HNS and HMX, respectively.

## PERFORMANCE

Benziger (1976) taught a highly insensitive and heat-resistant PBX containing 90% by weight of TATB and 10% by weight of a fully saturated copolymer of chlorotrifluoroethylene and vinylidene fluoride, using a slurry process. In agreement with his study, the Kel-F 800® or Kel-F827® are the preferred binder, because they are chemical resistant, they have thermal stability, high density, elastomeric properties, and solubility characteristics enabling the use of the slurry process in preparing molding powder.

A slurry of TATB in water is prepared by mixing powdered TATB in water. A Kel-F 800 lacquer is prepared by dissolving of Kel-F 800 in butyl acetate. The TATB/water slurry is heated to 75°C, with agitation, and the Kel-F 800 lacquer heated to 40°C is added. The resultant dispersion is heated with a steam sparger to distill the solvent as the butyl acetate/water azeotrope. The sparger is used to reduce the supposed heating surface, because during the formation of the molding powder granules, the mixture adheres strongly to heated surfaces. The degree of the dispersion agitations also effects particle size. Then, the agitation is preferentially reduced during the solvent removal step.

The dispersion is then cooled to 40°C and filtered. Finally, the resultant powder is dried at 100°C in a forced draft oven. This produces a material with 90% by weight of TATB and 10% by weight of Kel-F 800, having a bulk density of approximately 0.9 g/cm<sup>3</sup>. A density of 1.920 g/cm<sup>3</sup>, 98.7% of the theoretical maximum density, can be obtained by pressing larger pieces at 120°C and 137.9 MPa psi.

A high performance explosive composition was taught by Hildebert and Pierre (1992), this composition can be prepared by mixing 40 to 60% by weight of TATB, 35 to 58% by weight of a second explosive (chosen among HMX, RDX, PETN and HNS) and 2 to 5% by weight of a thermoplastic binder chosen in the poly-ether phenolic group, whose vitreous transition temperature is between 70 and 120°C and the dilatation coefficient is equal or higher than  $6.10^5/^{\circ}\text{C}$ . In agreement with them, the composition shows sensibility in the same level than the second explosive, but the security is almost the same of the TATB. The binder improves the tensile strength and mechanical properties of the composition.

The binder should be soluble in an organic solvent immiscible in water. A lacquer is produced by the polymer

addition in the organic solvent. The two explosives are dispersed in water and, after that, the lacquer is introduced in the explosive suspension. The organic solvent is eliminated by means of the increment in the system temperature (evaporation). A filter should be used to separate solid particles of the explosive to the liquid portion. These solid particles are dried and the warhead is produced by means of the melting and compression of them in a cast (120 to 140°C and 180 to 220 MPa).

## FINAL CONSIDERATIONS

The analysis of the synthesis processes studied shows several possibilities for the starting material in the TATB's synthesis. Obviously, the choice of the reagents must be made considering not only the cost, but also the activating effect of each radical in the aromatic ring, which reduces the complexity of the synthesis mechanism and increases, typically, the reaction rate.

Particularly, the synthesis of TATB in an emulsified system may be advantageous, since, due its low solubility, the recrystallization process (commonly performed in HE) can be complex and inefficient, hence the advantage of obtaining the reduced size of TATB particle. As noted, the energy performance of TATB is suitable for its use in warheads, even when its use is done in association with other HE. The literature also provides information for the appropriate characterization of the material.

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