

# Tetraamminecopper(II) Nitrate and Its Effects on Ammonium Nitrate

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**Abstract:** Tetraamminecopper(II) nitrate (TACN) is a complex copper salt which is easily formed when ammonium nitrate (AN) comes into contact with copper. It is considered to be an unwanted contaminant of AN because of its sensitivity to mechanical stimuli and significant explosive properties. The formation of TACN by the reaction of copper with molten ammonium nitrate was demonstrated by powder diffraction. Friction and impact sensitivity testing was performed and field experiments were then conducted to reveal the detonation parameters of TACN and its initiation capability towards ammonium nitrate. The dependence of the detonation velocity on charge diameter was revealed and the ideal detonation velocity of  $3500 \text{ m s}^{-1}$  at  $0.87 \text{ g}\cdot\text{cm}^{-3}$  was measured. AN with the addition of 16 wt.% of TACN was found to detonate when initiated with a small booster charge. Moreover, TACN was able to initiate detonation in fertilizer grade ammonium nitrate under massive steel confinement. TACN should be therefore considered as a possible contributory initiation source in some large scale accidents. In this article, some properties of TACN are revealed which could be useful for the investigation of accidents.

**Keywords:** ammonium nitrate, complex salt, copper, detonation, initiation

## 1 Introduction

It is well known that the reaction of ammonium nitrate (AN) with copper can lead to the formation of the complex salt tetraamminecopper(II) nitrate (TACN) [1]. The presence of TACN as an impurity in AN is undesirable because of its higher sensitivity to mechanical and thermal stimuli. Originally, the reaction was investigated by ammunition designers as the Amatol (ammonium nitrate + trinitrotoluene) explosive was melted in copper kettles and cast into warheads [2]. It was shown that the formation of TACN under these conditions is unlikely. However, the same source also states that TACN is formed easily when copper is subjected to the action of ammonia, air and moisture at 100 °C.

Ammonium nitrate is mostly prepared on a large scale for agricultural use as a fertilizer, but it is also an ingredient in explosives. Fertilizer grade ammonium nitrate (FGAN) and related fertilizers have been involved in a number of catastrophic accidents during the past hundred years. Some recent examples of large fires with subsequent explosions occurred in France (2003), Iran (2004) and Romania (2004) [3]. In 2014, 53 tons of FGAN loaded on a truck detonated shortly after a traffic accident near Charleville, Australia. Although it is believed that burning fuel spilled from the diesel tanks and possibly sensitized the ammonium nitrate, the actual process of initiation of the detonation is still not fully understood. TACN has been suggested as playing a role in some of these accidental ammonium nitrate explosions.

The available literature provides little information on TACN. The impact and friction sensitivity measurements given by [2, 4-5] show that the impact sensitivity is on the level of secondary explosives. Burning rates and some estimated thermal properties of various TAC salts are provided in [6]. Crystallographic data for TACN are shown in [7]. The relative

brisance of TACN measured by the Sand Test is 41% that of TNT according to [4]. The detonation velocity determined by the d’Autriche method is  $2800 \text{ m}\cdot\text{s}^{-1}$  (unconfined) and  $3500 \text{ m}\cdot\text{s}^{-1}$  (steel tube) according to [5]. Unfortunately, the sample density and dimensions were not specified. In this article, the sensitivity characteristics and detonation parameters of TACN are reported and its ability to initiate ammonium nitrate is examined.

## 2 Experimental

**Caution:** Tetraamminecopper(II) salts have significant explosive properties and should be handled with care.

### 2.1 Materials

The tetraamminecopper(II) nitrate (TACN) was prepared according to [8]. Powdered fertilizer grade ammonium nitrate (FGAN) produced by Synthesia a.s. was used, and contained 99.6 wt.% ammonium nitrate, 0.19 wt.% hydrophobizing agent and less than 0.1 wt.% moisture. The other chemicals used were of analytical purity. The FGAN/TACN and FGAN/Cu mixtures, with a molar ratio of 1/1, were prepared by mixing the dry powdered components. Electrolytic copper was used. For the detonation experiments, Semtex 1A, commercial plastic bonded explosive based on pentaerythritol tetranitrate (83.5%) and inert polymer binder with a density of  $1.42 \text{ g}\cdot\text{cm}^{-3}$ , was used for the booster charges. The FGAN/TACN mixtures for the detonation experiments contained 4, 8 and 16 wt.% of TACN.

### 2.2 Analyses and sensitivity measurements

The density of TACN was determined using an AccuPyc 1340 (Micromeritics) helium pycnometer. The thermal analyses were performed using a DTA-551Ex differential thermal analyzer (OZM Research) and tester, an AET-400 (OZM Research) automatic explosion

temperature. The samples were placed in glass micro-test tubes (open system with static air atmosphere) and heated at  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The AET-400 was chosen because it allowed samples large enough for XRD analyses (250 mg) to be used, which could be heated up to a desired temperature and then cooled quickly by removing the test tube from the instrument.

The diffraction pattern of TACN title compound was collected at room temperature using an X'Pert<sup>3</sup> Powder  $\theta$ - $\theta$  powder diffractometer with para-focusing Bragg-Brentano geometry and Cu  $K\alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ , generator setting: 40 kV, 30 mA). An ultrafast PIXcel detector was employed to collect XRD data over the angular range from  $5^{\circ}$  to  $80^{\circ}$   $2\theta$  in increments of  $0.026^{\circ}$   $2\theta$  and a counting time of 56.865 s/increment. The HIGHSCORE PLUS V 3.0e software package (PANalytical, Almelo, Netherlands) was used to smooth the data, to fit the background, and to eliminate the  $K\alpha_2$  component, and the tops of the smoothed peaks were used to determine the peak positions and intensities of the diffraction peaks. The  $d$ -values were calculated using Cu  $K\alpha_1$  radiation ( $\lambda = 1.5406\text{ \AA}$ ). A search-match procedure using  $d$ ,  $I$  values was performed in the database PDF4+ [9] to obtain the phases present in the sample. Semi-quantitative analysis was used to calculate the estimated mass fractions of the identified phases. The semi-quantitative analysis in HighScore Plus software works on the basis of the RIR (Reference Intensity Ratio) values (often called  $I/I_c$  values). It determines the estimated mass fractions of the identified phases. This method is known as the normalized RIR method [10]. The normalization used in this method assumes that the sum of all identified phases is 100%. This means that there are no unidentified crystalline phases, or any amorphous phase present in the sample. Only under these conditions can a meaningful semi-quantitative result be obtained.

The impact sensitivity was measured using a Kast fall hammer produced by Reichel and Partner, with a 2 kg hammer. Both the guide ring (BFH-SR) and cylinders (BFH-SC) were produced by OZM Research. Samples were placed between the two cylinders centered by the

guide ring and impacted by the 2 kg falling hammer. At least fifteen trials were conducted at each energy level. The sample volume was 40 mm<sup>3</sup>.

The sensitivity to friction was determined using an FKSM-08 BAM device supplied by OZM Research. BFST-Pt-100S type ceramic test plates and BFST-Pn-200 pestles were used, all produced by OZM Research. At least fifteen trials were conducted at each energy level. The sample volume was 10 mm<sup>3</sup>.

### **2.3 Characterization of the explosive properties**

The detonation velocities of TACN and its mixtures with FGAN were measured discontinuously using plastic fiber optic (POF) probes (Figure 1a). The POF probes were used for switching the electronic chronometer on and off. The operating frequency of the counter was 50 MHz, which corresponds to a resolution below 4 m·s<sup>-1</sup>. The explosives were tapped into polypropylene (FGAN/TACN) or aluminum (TACN) tubes with 2 mm walls. The probes were introduced into the explosive charges through holes drilled in the casing. The first probe was positioned at a distance of at least three charge diameters from the detonator. A booster charge of 10 g and 50 g of Semtex 1A plastic bonded explosive was used for TACN and FGAN/TACN shots, respectively. The probe tips were covered with aluminum tape to shield light preceding the reaction front and thus ensuring activation only by the passing shockwave [11].

Experiments with the initiation of FGAN by TACN were conducted in massive steel tubes with an internal diameter of 12 mm and a wall thickness of 14 mm, giving a metal/explosive mass ratio of 55. The tubes were made from axially drilled round bars with a length of 90 mm and for most of the experiments, three were stacked together. The charge density of FGAN was  $0.85 \pm 0.05$  g·cm<sup>-3</sup>. The initiation was conducted from above and an aluminum witness plate with dimensions of 50×50×8 mm was placed below the charge.

Hard steel or soft foamed polystyrene (PS) backing block was placed under the witness plate (Figure 1b).

The detonation velocity of TACN in the steel tube was determined using the continuous fiber optic probe method described in [12]. The probe was prepared by perpendicular drilling of 9 holes with a diameter of 0.25 mm into the POF cable with 1 mm core diameter and 2.2 mm outer diameter. The probe was inserted parallel with the charge axis and connected to the optoelectronic receiver and digital oscilloscope (Figure 1c).

**Figure 1.** Schematic cross-sections of the detonation experiments: a) detonation velocity measurement; b) detonation capability of AN by TACN; c) detonation velocity of TACN under strong confinement.

### 2.3 Calculation of the detonation parameters

The detonation parameters for TACN were calculated using the Explo5 V6.03 thermochemical code (OZM Research). Modified semi-empirical Becker-Kistiakowsky-Wilson (BKW) and fluid Exp-6 equations of state were used and compared. The BKWN-M ( $\alpha = 0.5$ ;  $\beta = 0.154$ ;  $\kappa = 9.37$ ;  $\theta = 3650$ ;  $\varepsilon = 1.54$ ) parameter set was used [13, 14].

## 3 Results and Discussion

### 3.1 Formation of TACN by the reaction of AN and Cu

It has been stated in [2] that TACN can be formed by the prolonged contact of copper with ammonium nitrate, air and moisture. On the other hand, copper was not considered problematic when inserted into a kettle with molten ammonium nitrate by [3]. In our experiments, the formation of TACN by the reaction of powdered copper with molten

ammonium nitrate was studied by differential thermal analysis of FGAN/Cu mixtures (20 mg samples in open cells, Figure 2). The FGAN/TACN mixture started to melt at 140-145 °C, the FGAN/Cu mixture at 145-150 °C. Both mixtures decomposed violently above 270 °C. It is assumed that ammonium nitrate reacts with copper in the presence of trace amounts of moisture forming low-melting complex compounds which lower the melting point of the mixture below that of ammonium nitrate. The formation of the copper complexes is exothermic and corresponds to the broad exothermic peak after the melting of the FGAN/Cu mixture.

**Figure 2.** DTA thermographs of TACN, FGAN, FGAN/Cu and FGAN/TACN. The molar ratio of the mixtures was 1/1.

Slightly larger quantities of the FGAN/Cu mixture (250 mg) were heated in a heating block of the AET to obtain sufficient quantities of the melted material for XRD analysis. The explosion temperature of the mixture in this case was 188 °C. The results of X-ray diffraction of the mixture sampled at 185 °C are shown in Figure 3; the composition of the sample is summarized in Table 1.

**Figure 3.** X-ray powder diffraction pattern of FGAN/Cu heated to 185 °C, using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The calculated peak positions of the reference patterns present are shown by coloured vertical bars.

**Table 1.** Composition of the FGAN/Cu mixture (molar ratio 1/1) at 185 °C

Component	Content [wt.%]
Cu	20
Cu <sub>2</sub> O	20
NH <sub>4</sub> NO <sub>3</sub>	30
Cu(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	15
Cu(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	5
Cu <sub>2</sub> (NO <sub>3</sub> )(OH) <sub>3</sub>	5
Cu(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> )OH	5

When the mixture melts, some fast reactions occur between the components and the composition of the mixture changes significantly. The copper is partially oxidized forming cuprous oxide and several copper amine complexes. Hazardous properties can be expected primarily from the copper tetraammine nitrate, copper diammine nitrate and probably copper diammine nitrite hydroxide. All of these compounds contain both a fuel and an oxidizing group within the single molecule, which indicates that such molecules may be considered as belonging to the hazardous materials group. Increasing the FGAN/Cu ratio in the mixture will probably lead to an increase of the TACN content in the reaction products. We focused our study on research into the hazardous aspects of TACN.

### **3.2 Sensitivity of TACN to impact and friction**

Using a series of tests at various energy (impact height) levels, the probability of initiation was determined by Probit analysis [15]. The most frequent result at high impact energies was an explosion of the whole sample accompanied by a loud bang. At low energies, partial explosion (a part of the sample was recovered) or just a colour change in the sample usually occurred. In addition, at least one complete explosion was also registered at the lowest energy level experiments. Any sign of decomposition was recorded as a positive result. The results show relatively high scatter, but it can still be concluded that the sensitivity of TACN to impact is slightly lower than that of RDX, which is well-known as a sensitive military explosive (Figure 4).

**Figure 4.** Initiation probability of TACN by impact at various energy levels.

The typical reaction of TACN to friction is just a change in colour from blue to brown. Audible explosions of samples during friction sensitivity testing were not observed. The results were again evaluated using Probit analysis (Figure 5).



**Figure 5.** Initiation probability of TACN by friction at various force levels.

### 3.3 Critical diameter and velocity of detonation of TACN

TACN charges with different diameters were detonated in order to determine the critical diameter at which stable detonation occurs. TACN charge densities were determined from their mass and volume. The tubes, with internal diameters of 31, 16, 8, 6 and 4 mm, were filled with TACN and initiated by 10 g of Semtex 1A. Detonation occurred in all cases and the critical diameter of TACN in Al tubes is thus lower than 4 mm. For comparison, the critical diameter for RDX at  $1.2 \text{ g}\cdot\text{cm}^{-3}$  confined in a plastic tube is about 3 mm [16].

**Figure 6.** Determination of the theoretical maximum detonation velocity of tapped TACN.

The detonation velocity was measured during these experiments using two independent devices. The measured difference between the two results was less than  $12 \text{ m}\cdot\text{s}^{-1}$ . The detonation velocity was then plotted against the inverse charge diameter, which allowed the maximum detonation velocity at a given density to be obtained (Figure 6). The extrapolated maximum detonation velocity was  $3498 \text{ m}\cdot\text{s}^{-1}$  at  $0.87 \pm 0.04 \text{ g}\cdot\text{cm}^{-3}$ , which agrees well with the value presented in [5] ( $3500 \text{ m}\cdot\text{s}^{-1}$ ). The ideal detonation velocity obtained by thermochemical calculations using the Exp-6 equation of state in Explo5 (Table 2) is in excellent agreement with the experimental data.

**Table 2.** Results of Explo5 calculations for TACN at a density of  $0.87 \text{ g}\cdot\text{cm}^{-3}$ 

Equation of state for products	Detonation velocity ( $\text{m}\cdot\text{s}^{-1}$ )	Detonation pressure (GPa)	Adiabatic gamma	Reaction products (mol%) <sup>1</sup>				
				H <sub>2</sub> O	N <sub>2</sub>	Cu(l)	Cu <sub>2</sub> O(l)	H <sub>2</sub>
Modified BKW	3684	3.22	2.67	59.8	30.0	9.6	0.2	0.2
Exp-6	3470	2.80	2.74	59.8	30.1	9.1	0.5	0.5

<sup>1</sup> The remainder up to 100% consists of trace amounts of NH<sub>3</sub>, NO and OH.

The reaction products predicted by the code were mainly water, nitrogen, copper and a small amount of copper(I) oxide and hydrogen. The detonation pressure of TACN predicted by the calculations was 2.80-3.38 GPa. The critical initiation pressure of molten ammonium nitrate depends largely on its density. Above 230 °C, the density of the material decreases due to auto-aeration from the thermal decomposition products. At 245 °C (density  $1.25 \text{ g}\cdot\text{cm}^{-3}$ ), the critical initiation pressure falls to 2.4 GPa and reaches its minimum reported value of 0.65 GPa at 260 °C (density  $0.8 \text{ g}\cdot\text{cm}^{-3}$ ) [17]. When the molten material is mixed with hollow glass microspheres at 190 °C, the critical initiation pressure is 0.8 GPa (density  $0.95 \text{ g}\cdot\text{cm}^{-3}$ ) [17]. Therefore, the calculated results suggest that a TACN detonation might enable molten AN to undergo a shock to detonation transition when its density falls below ca  $1.25 \text{ g}\cdot\text{cm}^{-3}$ .

An attempt was also made to measure the detonation velocity in a mixture of FGAN with TACN, which could help to evaluate the possible sensitizing effect of TACN. However, detonation only proceeded in FGAN with 16 wt.% of TACN. With 8 wt.% TACN, detonation ceased within 4-5 charge diameters as evidenced by the fact that the second velocity probe

was not activated and some debris of the mixture was found. With 4 wt.% TACN, even the first velocity probe was not activated. From that it can be concluded that the sensitizing effect of TACN on FGAN towards initiation by a shockwave is relatively weak. The detonation velocity measurements are summarized in Table 3.

**Table 3.** Detonation velocity measurements

No.	Sample	Casing material	Casing wall thickness [mm]	Internal charge diameter [mm]	Charge density [ $\text{g}\cdot\text{cm}^{-3}$ ]	Detonation velocity [ $\text{m}\cdot\text{s}^{-1}$ ]
1	TACN	Al	2	31	0.86	3080
2	TACN	Al	2	16	0.83	2710
3	TACN	Al	2	8	0.87	2060
4	TACN	Al	2	6	0.88	1920
5	TACN	Al	2	4	0.92	1530
6	FGAN + TACN 4%	PP <sup>1</sup>	2	36	0.94	-
7	FGAN + TACN 8%	PP	2	36	0.92	-
8	FGAN + TACN 16%	PP	2	36	0.91	1480
9	TACN	Steel	14	12	0.86	3506

<sup>1</sup>Polypropylene

### 3.4 Initiation of FGAN by TACN

Testing of the initiation ability of TACN towards FGAN was challenging. Unconfined charges of FGAN are difficult to detonate even by large boosters and require diameters of about 300 mm for granular material [18]. Even when using steel tube confinement, the requisite charge dimensions are relatively large. However, massive steel confinement and particle size reduction can lead to a dramatic reduction in the charge diameter required, to the level of a few millimeters, as shown by [19].

The effect of thick walled charges of FGAN on the witness plate was significant with both steel and polystyrene bases. There was no difference on the witness plate between initiation performed with Semtex 1A (Figure 7a, b) or with TACN (Figure 7c, d). The witness plate damage was more pronounced with increasing tube length, *i.e.* charge length, which suggests that detonation was complete and that there was no attenuation. The mass of TACN used was less than 10 grams. For comparison, the effect of a non-reactive shock wave on the witness plate was examined in the same arrangement by an experiment with the tube filled with inert material (sucrose) instead of FGAN. The resulting small dent is shown in Figure 7e. It may be concluded that TACN is able to initiate detonation in very heavily confined FGAN.

**Figure 7.** Witness plates from FGAN initiation experiments with polystyrene (a, c) and steel (b, d) base plates. The initiation was performed with plastic bonded explosive (a, b) and TACN (c, d). Inert material (sucrose) was used instead of FGAN in the case of (e).

The detonation velocity of TACN was measured in one of the experiments (No. 9 in Table 3). It showed a gradual increase during the first 30 mm of the detonation run and then reached its steady value of  $3506 \text{ m}\cdot\text{s}^{-1}$ , which is in perfect agreement with the extrapolated detonation velocity in charges with aluminum confinement. The detonation velocity was inferred from the slope of the regression line in Figure 8. The physical and explosive parameters of TACN are summarized in Table 4.

**Figure 8.** Detonation front tracking in steel confined TACN shows that the detonation velocity reached its steady value after 30 mm.

**Table 4.** Summary of physical and explosive properties of TACN

Compound	TACN
Molecular formula	H <sub>12</sub> N <sub>6</sub> O <sub>6</sub> Cu
Molar mass (g·mol <sup>-1</sup> )	255.67
Enthalpy of formation (kJ·mol <sup>-1</sup> )	-828 [6]
Enthalpy of combustion (kJ·mol <sup>-1</sup> )	-644 [6]
Density, pycnometric (g·cm <sup>-3</sup> )	1.91 (1.93 [20])
Melting point (°C)	215
(DTA, 20 mg, 5 °C·min <sup>-1</sup> )	
Onset of exothermic decomposition (°C)	271
(DTA, 20 mg, 5 °C·min <sup>-1</sup> )	
Friction force leading to 50% of positive results (N)	214
Impact energy leading to 50% of positive results (J)	11.4
Detonation velocity at 0.87 g·cm <sup>-3</sup> (m·s <sup>-1</sup> )	3500
Critical diameter of detonation under 2 mm aluminum confinement (mm)	<4

## 4 Conclusions

It has been shown that tetraamminecopper(II) nitrate (TACN) can be formed when ammonium nitrate comes into contact with copper at elevated temperatures. Once formed and deposited, TACN is a source of risk because of its sensitivity to impact, friction and heat. In this respect, TACN resembles the military explosive RDX. Although the detonation parameters of TACN are inferior to those of RDX, it has been proved that even low density

TACN is able to initiate detonation in fertilizer grade ammonium nitrate under massive steel confinement. The detonation velocity calculated by Explo5 using the Exp-6 equation of state agreed with experiment. The calculated detonation pressure and data from the literature for the shock sensitivity of molten ammonium nitrate suggest that TACN might be able to initiate detonation even in molten ammonium nitrate when its density drops below  $1.25 \text{ g}\cdot\text{cm}^{-3}$ . TACN should be considered as a possible contributory source of initiation in cases of accidental ammonium nitrate explosions, especially when confined.

### Acknowledgments

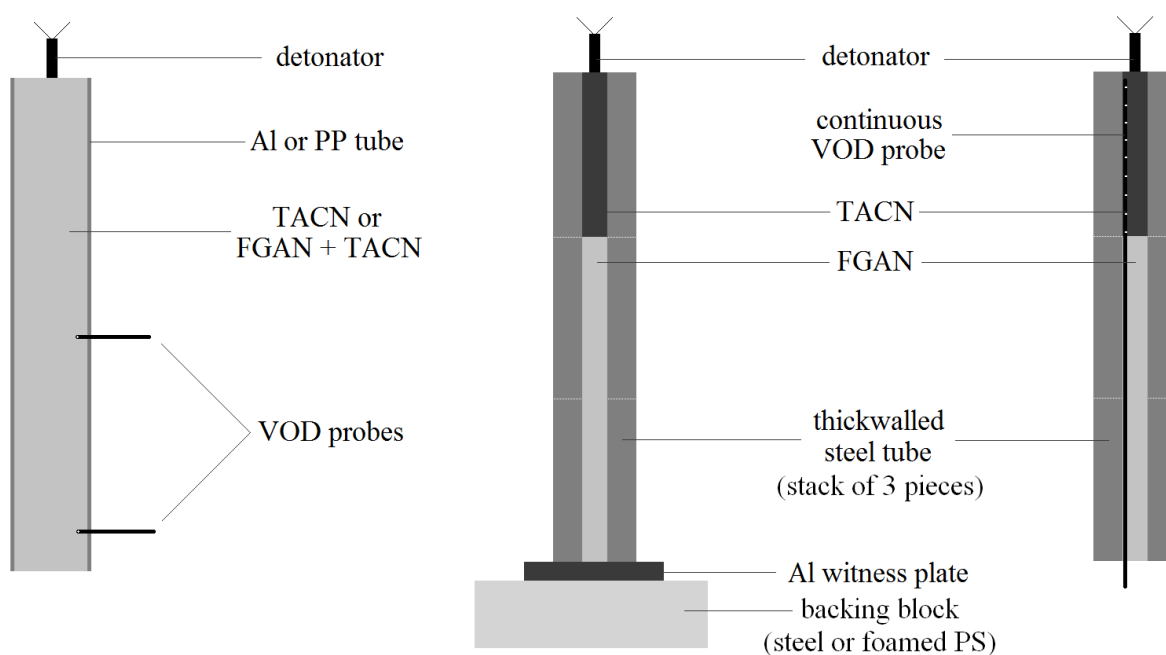
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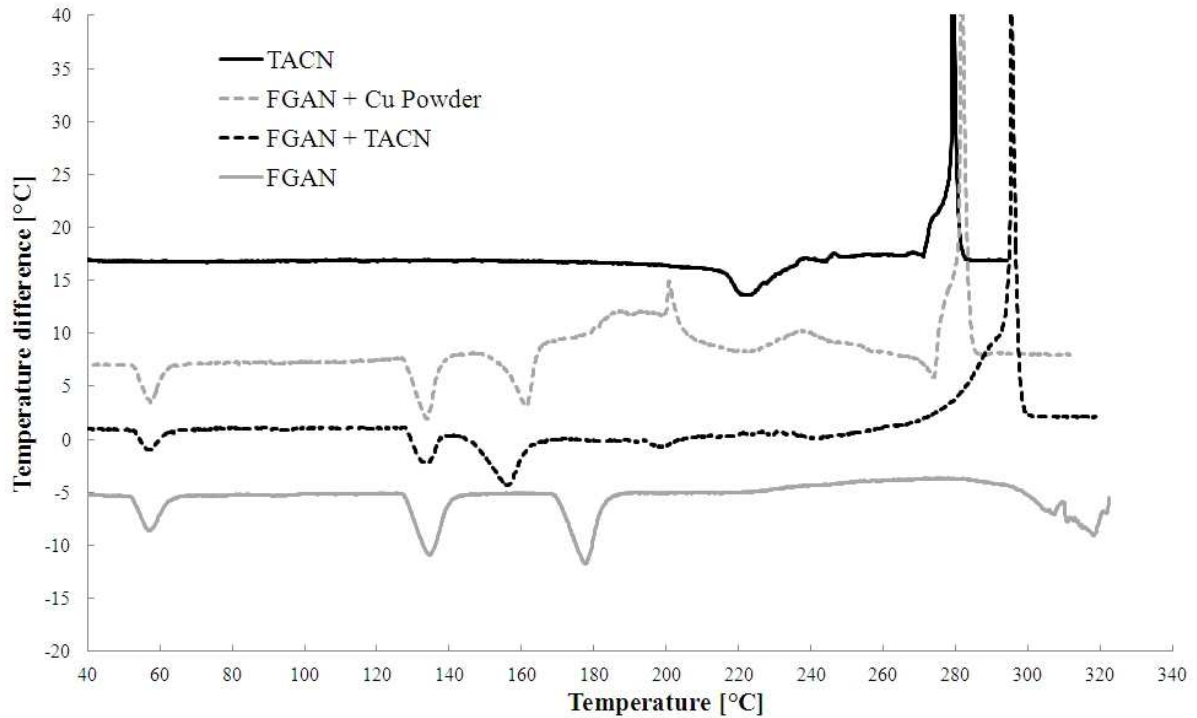
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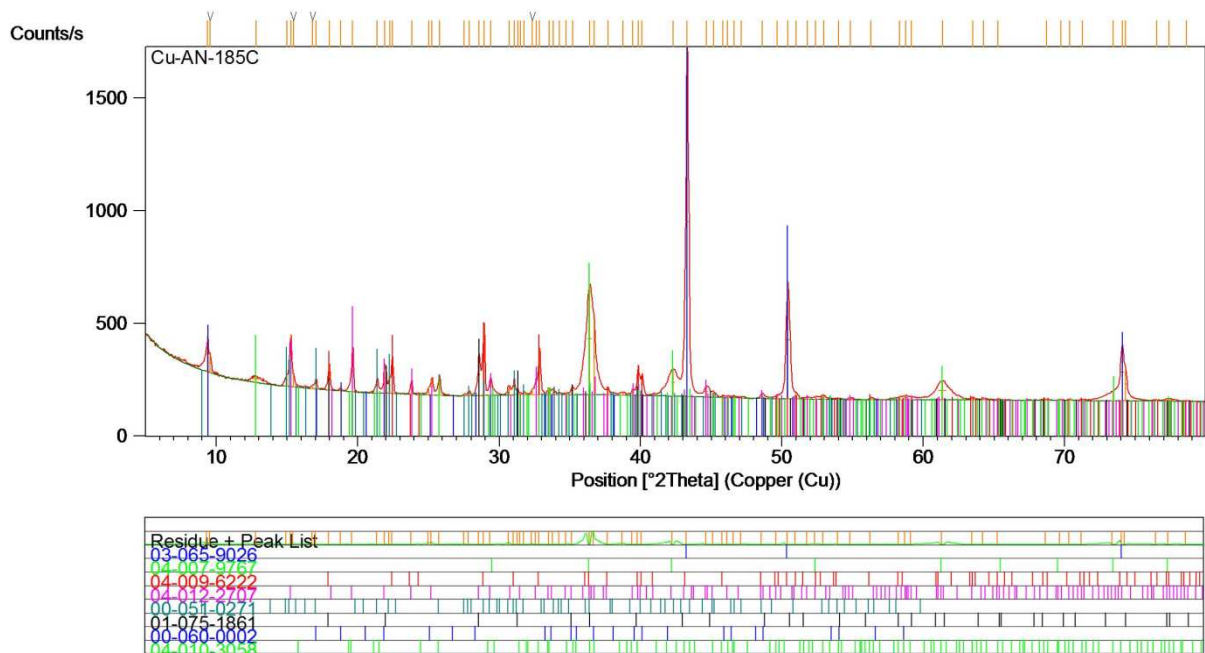




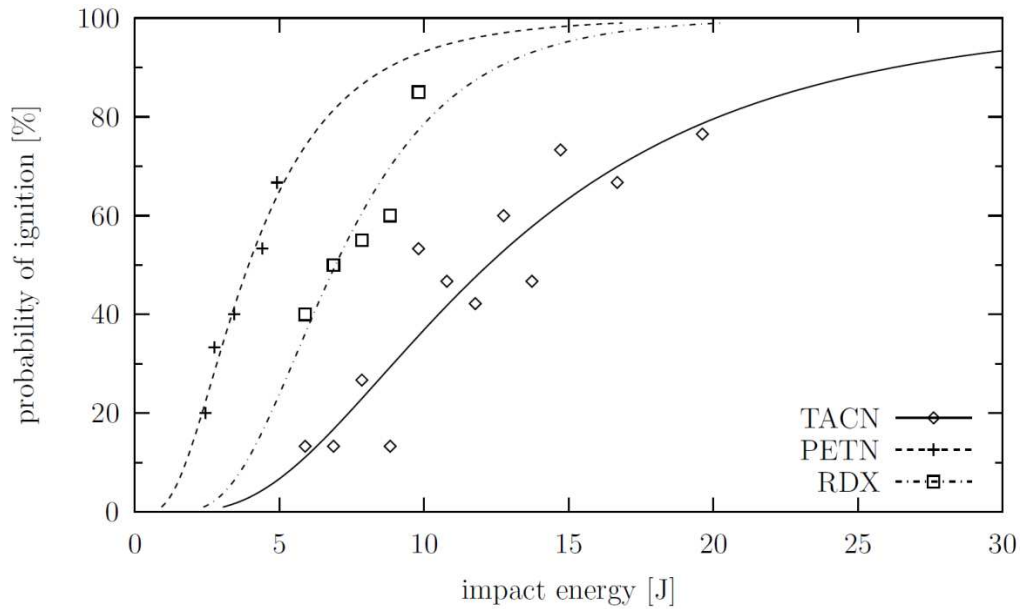
**Figure 1.** Schematic cross-sections of the detonation experiments: a) detonation velocity measurement; b) detonation capability of AN by TACN; c) detonation velocity of TACN under strong confinement.



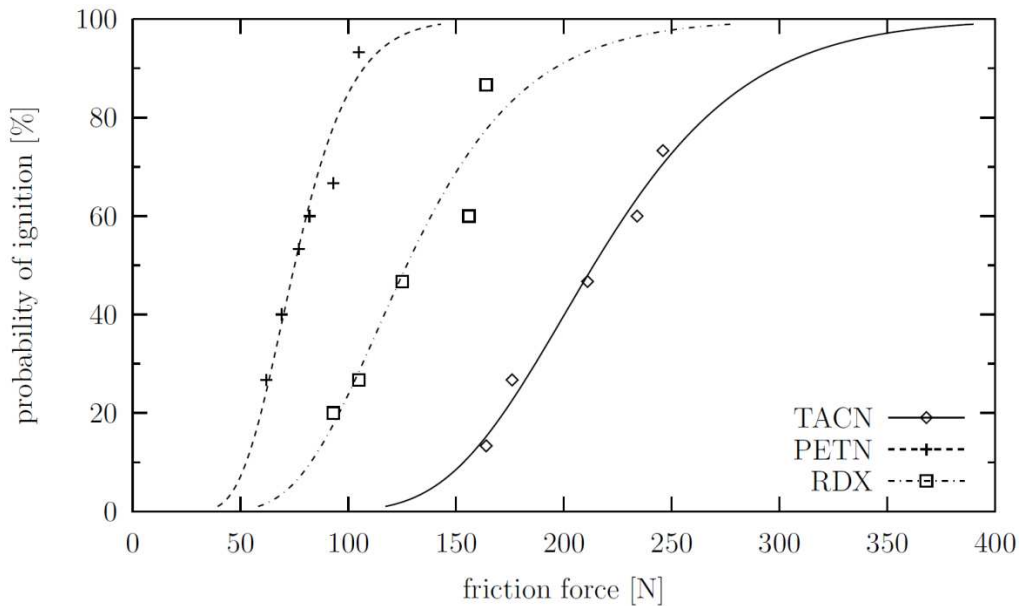
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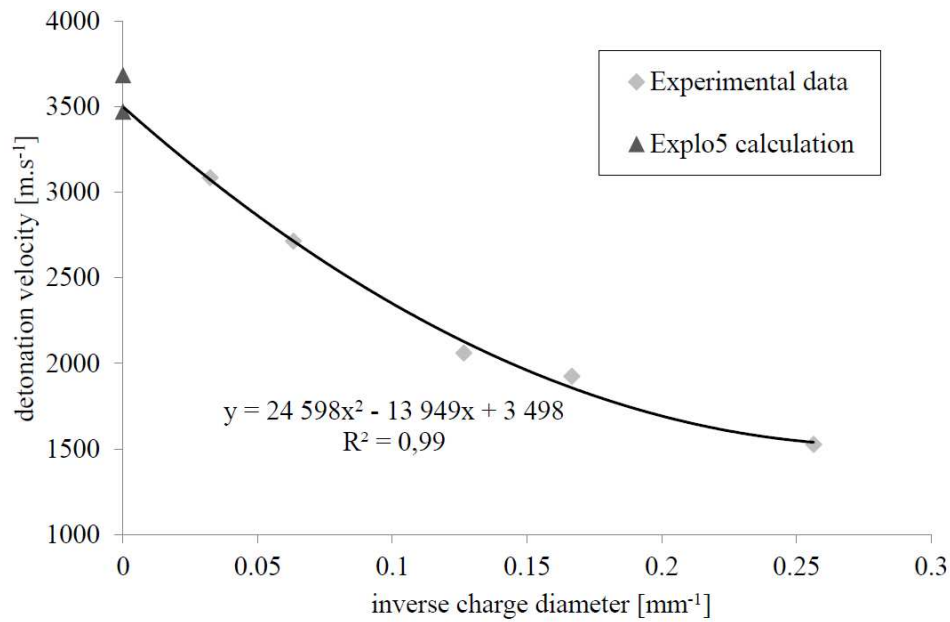
**Figure 3.** X-ray powder diffraction pattern of FGAN/Cu heated to 185 °C, using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The calculated peak positions of the reference patterns present are shown by coloured vertical bars.



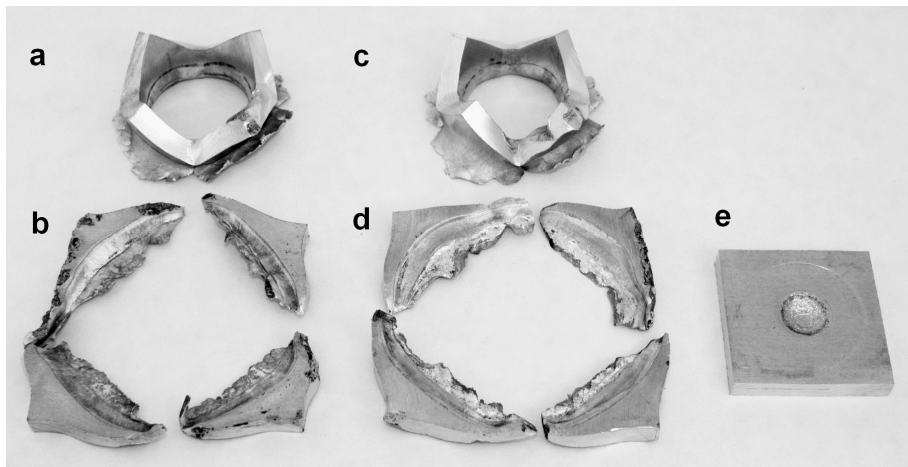
**Figure 4.** Initiation probability of TACN by impact at various energy levels.



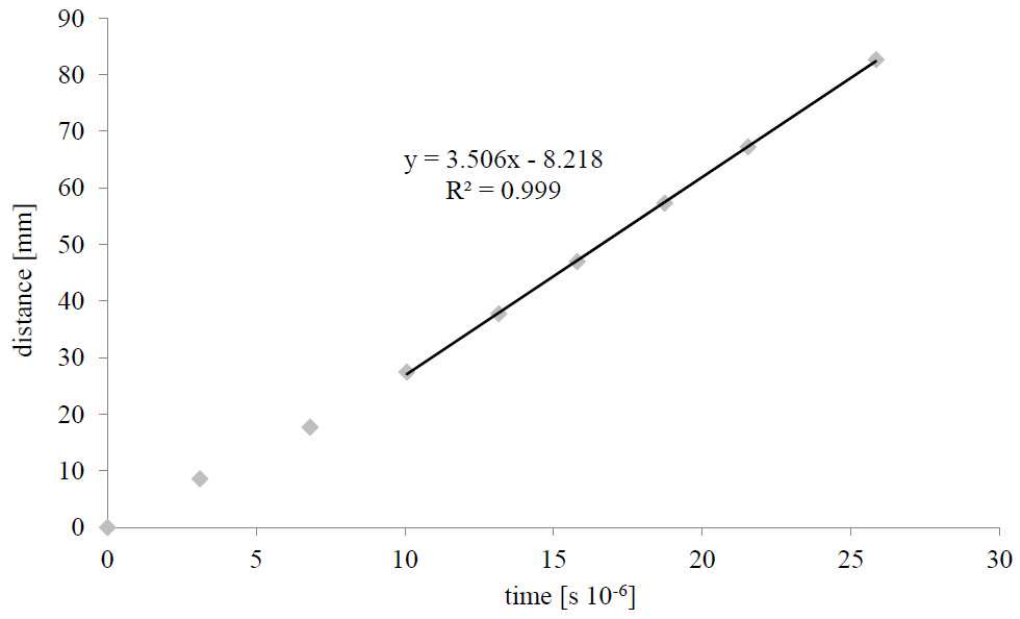
**Figure 5.** Initiation probability of TACN by friction at various force levels.



**Figure 6.** Determination of the theoretical maximum detonation velocity of TACN at a density of  $0.87 \text{ g cm}^{-3}$



**Figure 7.** Witness plates from FGAN initiation experiments with polystyrene (a, c) and steel (b, d) backing blocks. The initiation was performed with plastic bonded explosive (a, b) and TACN (c, d). Inert material (sucrose) was used instead of FGAN in the case of (e).



**Figure 8.** Detonation front tracking in steel confined TACN showing that the detonation velocity reached its steady value after 30 mm.