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**ATB—Strong Basic Reactions
Provide Soluble Derivatives
in Simple Qualitative High Explosive Spot Test**

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TATB—Strong Basic Reactions Provide Soluble Derivatives for Simple Qualitative High Explosive Spot Test

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TATB -- STRONG BASIC REACTIONS PROVIDE SOLUBLE DERIVATIVES FOR SIMPLE QUALITATIVE HIGH EXPLOSIVE SPOT TEST

by

Betty W. Harris

Abstract

Reactions of TATB in aqueous, strongly basic solutions gave metal salts of 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB) also called trinitrophloroglucinol. Thus, we prepared potassium, sodium, and barium salts. The mono- and diammonium salts were prepared by treating THTNB with ammonia and ammonium hydroxide, respectively. Some explosive properties of the salts were evaluated. From the physical characteristics of the salts in various solvents, a spot test was developed for known high explosives (HE) containing TATB.

I. INTRODUCTION

High explosives (HE) may become scattered among fragmented materials during field testing of weapons. It would obviously be desirable to identify the HE promptly so it can be removed before it burns or detonates. 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), in particular, is difficult to distinguish from colored inert materials. It is insoluble in most solvents and does not respond to known identification tests. This is attributed to the fact that it is a symmetrical, strongly hydrogen-bonded compound (Fig. 1). We have developed a test for TATB based upon its reaction with strong bases. However, the products from these reactions are energetic compounds.

II. EXPERIMENTAL

A. Reaction of TATB with Strong Bases, NaOH, KOH, Ba(OH)₂

Six and one-half grams (0.025M) of TATB were dissolved in 100 ml of 3M M(OH)_x, where M = Na, K, Ba; X = 1, 2. The solution was heated on a hot plate at 83-85°C for 2.5 h, then cooled at room temperature overnight. During

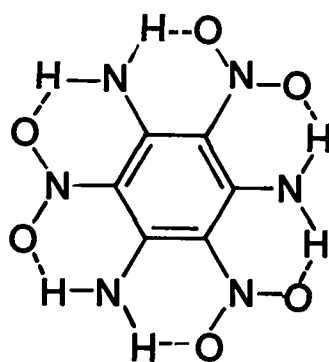


Figure 1. Structure of TATB showing the hydrogen bonding between the hydrogen of the amine group and the oxygen of the nitro group.

cooling large orange crystals precipitated, which were filtered through a medium-pore sintered-glass crucible and air dried. A 75:25 per cent mixture of water:ethanol was used to recrystallize the salts. The ratio of the solvent mixture was changed to 25:75 water:ethanol in some recrystallization processes. Samples of the respective salts were taken for elemental and DTA analyses. Then the remainder of the sample was oven-dried at 130°C for several hours.

Additional tests were run on the salts. Nuclear Magnetic Resonance (NMR) spectra were run for identification. Spark-gap, hammer, and impact-sensitivity tests were also performed.

B. Reaction of Ammonium Hydroxide with THTNB

Several batches of the sodium salt of trinitrophenol were combined and treated with 6N H_2SO_4 . A quantitative yield of 1,3,5-trihydroxy-2,4,6-trinitrobenzene, THTNB, was obtained.

One hundred milliliters of concentrated ammonium hydroxide were used to dissolve 1.4882 g (0.006 M) THTNB. The solution was heated just below boiling temperature for 30 min. The water was removed on a Rota-Vac and orange crystals precipitated. The product was recrystallized from water. Elemental and DTA analyses were obtained. The compound was identified as the diammonium salt of 1,3,5-trinitrophenol.

Also, an attempt was made to prepare the diammonium salt compound by bubbling NH_3 through an aqueous solution of THTNB. The mono-ammonium salt was the final product.

C. Spot Test for Explosive Compositions

Milligram quantities of selected explosives were placed on Whatman No. 2, 9-mm filter paper. A few drops of the test solution (ethylenediamine, diethylamine, or BW_H reagent) were added. Characteristic colors were observed for positive reactions.

III. RESULTS AND DISCUSSION

The salts of trihydroxytrinitrobenzene (THTNB), isolated as hydrates, were orange-yellow compounds that became yellow upon heating. Recrystallization from ethanol also gave a yellow precipitate. Sufficiently concentrated base solution, 3-5 M, gave tri-metal, sodium and potassium salts as the major products (Reactions 3 and 4). More dilute aqueous solution of base gave predominately the mono- and di-sodium or potassium salts. Our infrared analysis

gave positive evidence that the amine group was still present in the mono- and di-metal salts. Elemental analyses were in agreement with those calculated.

A DTA endotherm at 140°C was accredited to the removal of water of crystallization (Table I). The endotherm shifted to higher temperatures (150–165°C) when ethanol was used as a recrystallization solvent. We did not determine whether this was caused by an entrapped solvent or by the production of THTNB as an impurity (Reaction 5). Exotherms are also listed in Table I.

Elemental analyses and other data suggest that barium hydroxide reacts with TATB to form the diphenoxy barium salt, such as the one shown in Reaction 1, Structure 1. Again, the amine groups are detected by infrared spectroscopy. The half salt was prepared by heating the product from Reaction 1 in hot water (Reaction 2).

Concentrated ammonium hydroxide was effective in preparing the diammonium salt from THTNB, but we were not successful in forcing the reaction to go to the triammonium derivative (Reaction 6). When ammonia gas was bubbled through the aqueous THTNB solution, only the mono-ammonium salt was produced (Reaction 7). We attempted to confirm the presence of the two ammonium ions in the partially reacted molecules by ^{13}NMR , but were unsuccessful (Table II); the exchange of the ammonium ions and the negative oxygen was too rapid.

Determination of the explosive properties of these salts showed that the potassium and sodium salts are insensitive in the hydrated form; however, the dry salts are sensitive to spark and impact (Tables III and IV). The hydrated salts have an impact sensitivity comparable to that of granular TNT, whereas, that of the dried salt more closely parallels the sensitivity of Composition A-3. Some recrystallized forms of the barium salts detonated during elemental analyses.

Finally, the colors produced when TATB reacted with a strong base to form the metal-organic salts are essential to the spot test. Table V gives an indication of the color exhibited by each compound. Radical anion, free radicals, and charge-transfer and Meisenheimer complexes have been suggested as species that might produce the color. However, we believe that Reactions 8 and 9, giving the resonance-stabilizing anion, are more plausible. The characteristic orange color of the TATB anion produced from the reaction of TATB

with BW_H reagent is distinctive among the explosives (Table V). The BW_H solution is stable, easy to use, and chemically safe. BW_H reagent is a mixture of dimethylsulfoxide (DMSO), strong base (NaOH, KOH, or $BA(OH)_2$) and water. The composition can vary.

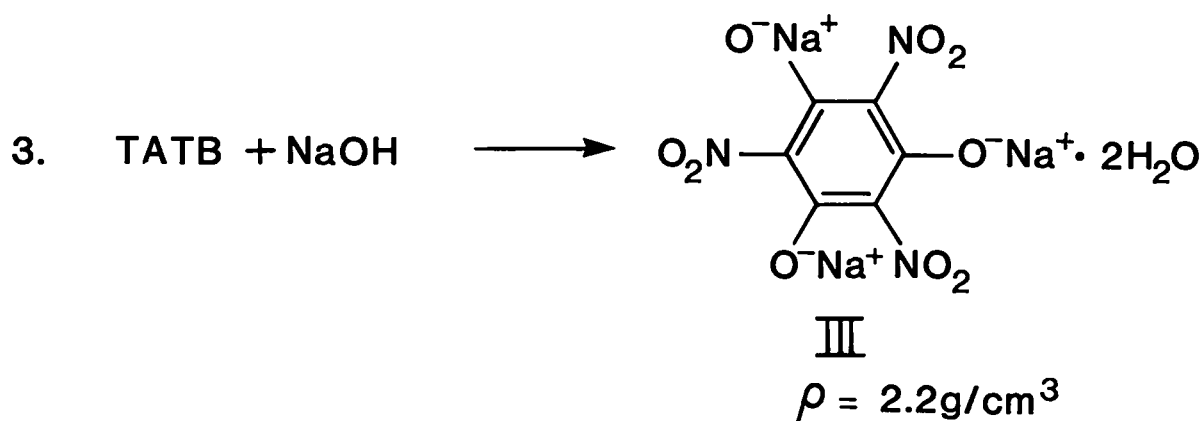
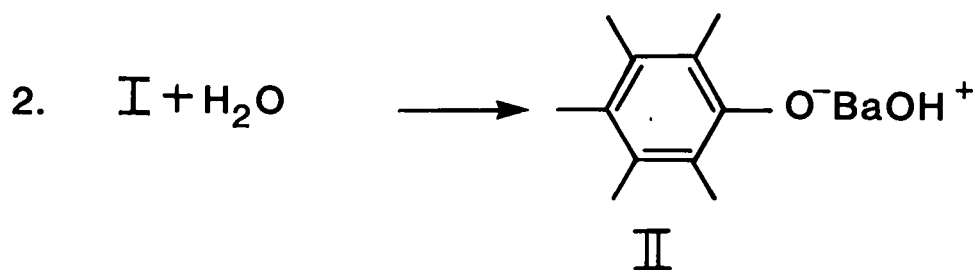
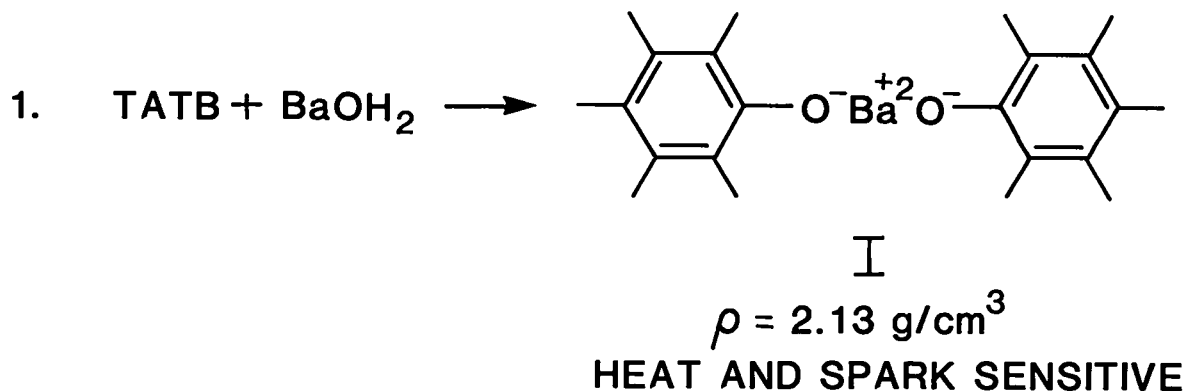
IV. CONCLUSION

Solutions of ethylenediamine/DMSO and diethylamine/DMSO give slightly positive results with TATB. This is consistent with observations from other polynitrocompounds.^{1,2,3} However, more TATB should be solubilized for a distinctive positive test. This can be achieved with BW_H reagent that utilizes a strongly basic solvent. It has been known for sometime that polynitrocompounds react with strong bases to give colored solutions.^{4,5,6} This has proven to be an excellent test for TATB.

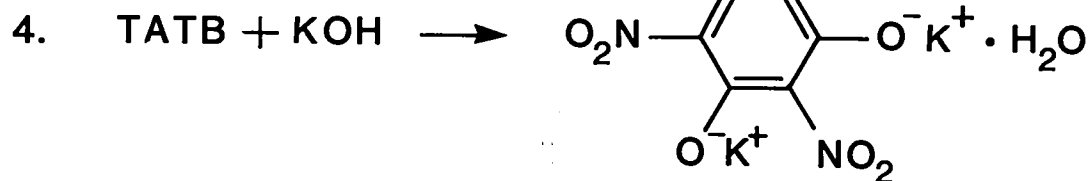
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REACTIONS OF TATB AND THTNB WITH BASIC SOLUTIONS



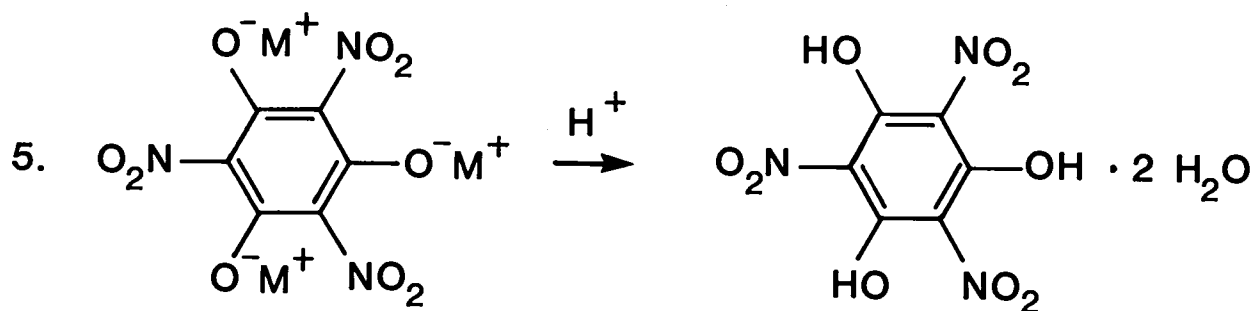
IMPACT SENSITIVITY 166cm
 IMPACT SENSITIVITY (DRIED) 75.9 cm
 SPARK SENSITIVE WHEN DRY



IV

$$\rho = 2.61 \text{ g/cm}^3$$

IMPACT SENSITIVITY, 148 cm
 IMPACT SENSITIVITY (DRIED) 85.1 cm
 SPARK SENSITIVE

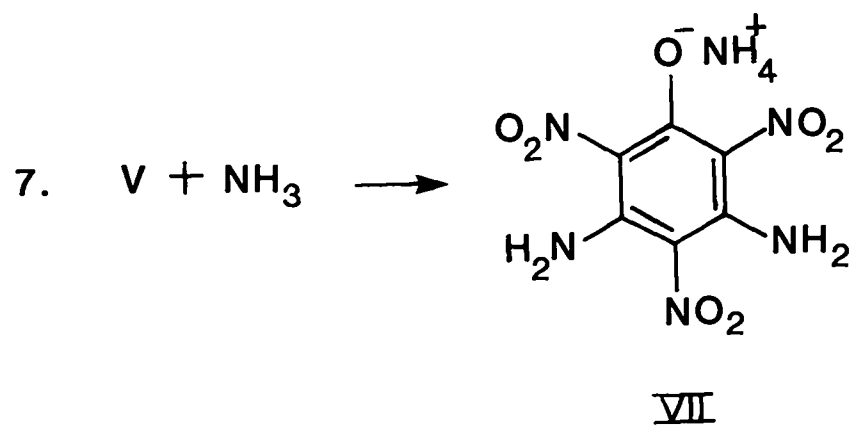
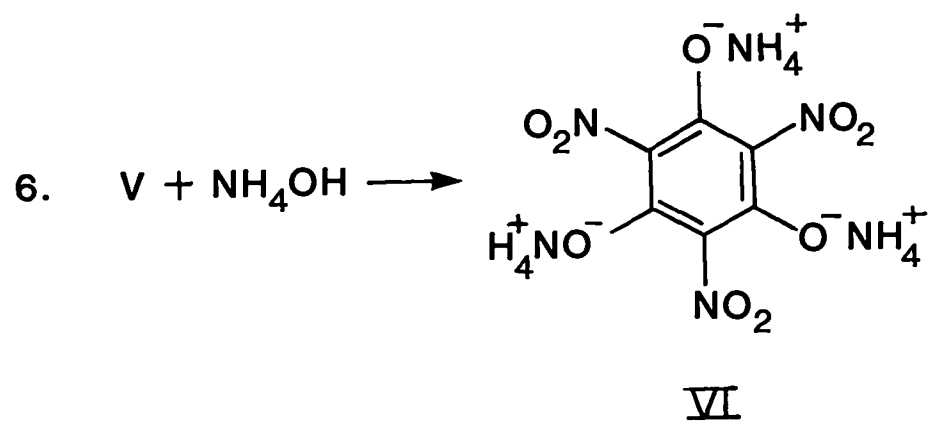


$\text{M} = \text{K}, \text{Na}$

V

$$\rho = 1.91 \text{ g/cm}^3$$

IMPACT SENSITIVITY (DRY) 39.2 cm
 SPARK SENSITIVITY 0.83 J



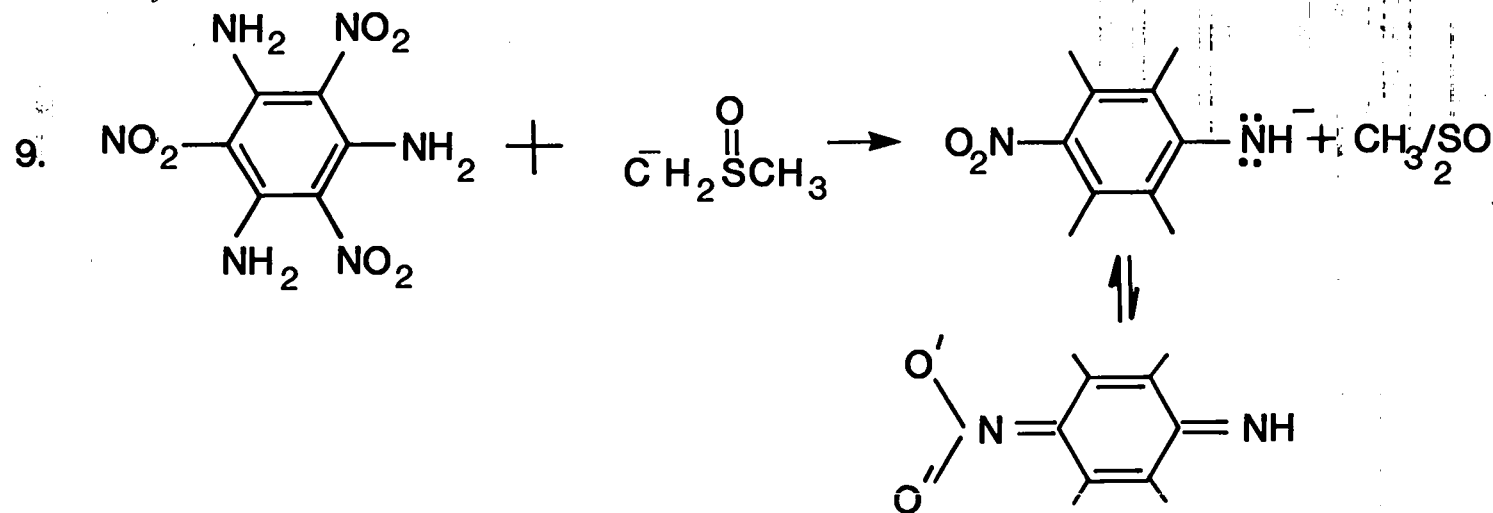
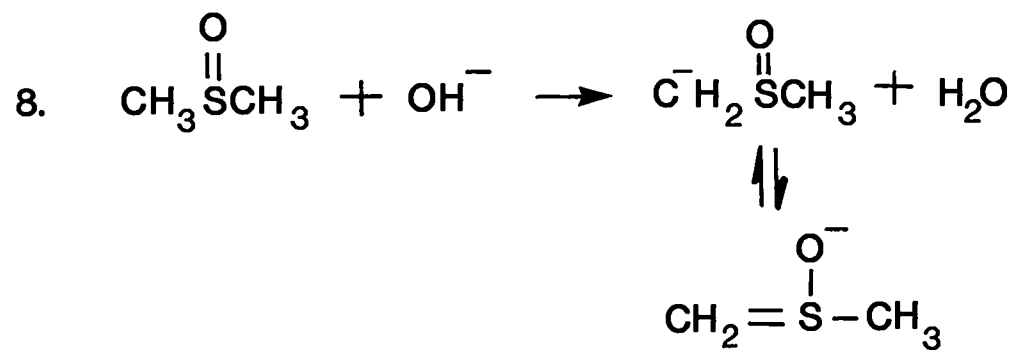


TABLE I

DTA ANALYSES OF PRODUCTS ISOLATED FROM THE REACTION OF TATB WITH STRONG BASE, NaOH, KOH, Ba(OH)₂.
ALSO, THE AMMONIUM SALTS FROM THE REACTION OF CONCENTRATED NH₄OH WITH THTNB. HEATING RATE 20°C/MIN.

<u>Compound</u>	<u>Molecular Formula</u>	<u>Hydration^a</u>	<u>Endotherm (°C)</u>	<u>Exotherm(s) (°C)</u>
THTNB	C ₆ H ₃ N ₃ O ₉	2H ₂ O	155, 168	178
Na ₃ ⁺ (THTNB ⁻³)	C ₆ H ₄ N ₃ O ₁₁ Na ₃	2H ₂ O	140	245, 295, 345
Na ₂ ⁺ (THTNB ⁻²) ^b	C ₆ H ₆ N ₄ O ₁₀ Na ₂	2H ₂ O	140	225
K ₂ ⁺ (THTNB ⁻²) ^b	C ₆ H ₆ N ₄ O ₁₀ K ₂	2H ₂ O	150	265
K ₃ ⁺ (THTNB ⁻³)	C ₆ H ₂ N ₃ O ₁₁ K ₃	1H ₂ O	140	275
(NH ₄ ⁺)(THTNB ⁻¹) ^a	C ₆ H ₈ N ₅ O ₇	Dried	—	232
(NH ₄ ⁺) ₂ (THTNB ⁻²) ^c	C ₆ H ₁₀ N ₈ O ₈	Dried	—	257
Ba ⁺⁺ (THTNB ⁻¹) ₂	C ₁₂ H ₈ N ₁₀ O ₁₄ Ba	—	—	295, 355 (Doublet)

^aRecrystallization from 25:75 water:ethanol causes the endotherm to be shifted to higher temperatures (150–165°C range).

^bAminodihydroxytrinitrobenzene (ADHTNB) is the correct anion.

^cDiaminohydroxytrinitrobenzene (DADHTNB) is the correct anion.

TABLE II

 ^{13}C -NMR OF THTNB AND ITS SALTS IN D_2O

Compounds	Chemical Shifts (ppm) ^a	
THTNB	145.88	114.97
$\text{K}_3^{+1}(\text{THTNB}^{-3})$	150.70	118.67
$\text{Na}_3^{+1}(\text{THTNB}^{-3})$	149.30	117.60
$(\text{NH}_4^+)_2(\text{THTNB}^{-2})$ ^b	152.60	116.62

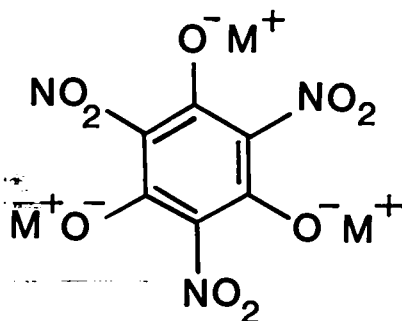
^aTypical structure of salts is^bThe presence of only two peaks suggests a rapid exchange of ammonium ions among groups.

TABLE III
SPARK GAP SENSITIVITY OF PRODUCTS
ISOLATED FROM THE REACTION OF TATB WITH STRONG BASE

Compound ^a	Mean Energy (J) ^b		σ (J)	
	3-mil Foil	10-mil Foil	3-mil Foil	10-mil Foil
1. Ba ⁺² (THTNB ⁻²)	0.36	0.87	0.03	0.025
2. K ₂ ⁺² (THTNB ⁻²)	1.94	2.08	0.22	0.04
3. Na ₂ ⁺² (THNB ⁻²)	0.40	2.76	0.008	0.36
4. Na ₂ ⁺² (THTNB ⁻²)	2.83	3.26	0.062	0.098
5. K ₂ ⁺³ (THTNB ⁻²)	3.39	7.7	0.09	0.676
6. K ₃ ⁺³ (THTNB ⁻³)	0.19	0.17	0.01	0.1
7. Na ₃ ⁺³ (THTNB ⁻³)	0.50	0.53	0.01	0.014

^aCompounds 4 and 5 were dried in the oven at 130°C for 2 days. Compounds 1, 2, 3, 6, and 7 were dried in the oven at 130°C for 4 days.

^bRef:

	<u>E₅₀</u>	
PETN	0.40 J,	Steel electrode, 10-mil foil
RDX	0.87 J,	Steel electrode, 10-mil foil
TNT	4.00 J,	Steel electrode, 10-mil foil

TABLE IV
IMPACT SENSITIVITY OF PRODUCTS ISOLATED FROM
REACTION OF TATB WITH STRONG BASE

Compound ^a	Sensitivity ^b		
	50% Height (Log Units)	(cm)	σ (Log Units)
Type 12			
$\text{Na}_2^{+2}(\text{THTNB}^{-2})$ (from H_2O) dried in oven 20	2.2201	0.017 166	0.048 (10 shots)
$\text{Na}_2^{+2}(\text{THTNB}^{-2})$ (from H_2O) dried in oven 40	1.8801	75.9	0.048 (10 shots)
$\text{K}_3^{+3}(\text{THTNB}^{-3})$ (from H_2O) dried in oven 40	1.9301	85.1	0.083 (10 shots)
$\text{K}_3^{+3}(\text{THTNB}^{-3})$ (from H_2O) (Hydrated)	2.1701	148	0.017 (10 shots)
$\text{Ba}^{++}(\text{THTNB}^{-1})_2$ Some impurities	1 GO at 320 cm (10 shots)		
$\text{Na}_3^{+3}(\text{THTNB}^{-3})$	1 GO at 320 cm		
Type 12B			
$\text{Ba}^{++}(\text{THTNB})_2$	2.2801	191	0.035 (10 shots)
$\text{Na}_3^{+3}(\text{THTNB}^{-3})$	1 GO at 320 cm		
$\text{Na}_3^{+3}(\text{THTNB}^{-3})$	2.0736	119	0.170

^aThe mono- and di-metal salts have aminohydroxytrinitrobenzene anion rather than THTNB as shown.

^bRef: RDX Type 12: $H_{50} = 22$ cm; Type 12B: $H_{50} = 41$ cm
PETN Type 12: $H_{50} = 12$ cm; Type 12B: $H_{50} = 37$ cm

TABLE V

RESULTS OF SPOT TEST OF POLYNITROCOMPOUND USED IN
HE COMPOSITION WITH DIETHYLAMINE, ETHYLENEDIAMINE, AND BW_H REAGENT^a

<u>Compound</u>	<u>Ethylenediamine</u>		<u>Diethylamine</u>	<u>BW_H Reagent</u>
Solvent	H ₂ O	DMSO	DMSO	DMSO
Kel-F	NR	NR	NR	NR
HMX	NR	NR	NR	NR
PETN	NR	NR	NR	NR
Tetryl	Red	Red	Red	Red
RDX	NR	NR	NR	NR
TNT	Wine	Wine	Wine	Purple
TATB	Yellow- Orange	Yellow- Orange	Yellow	Bright Orange

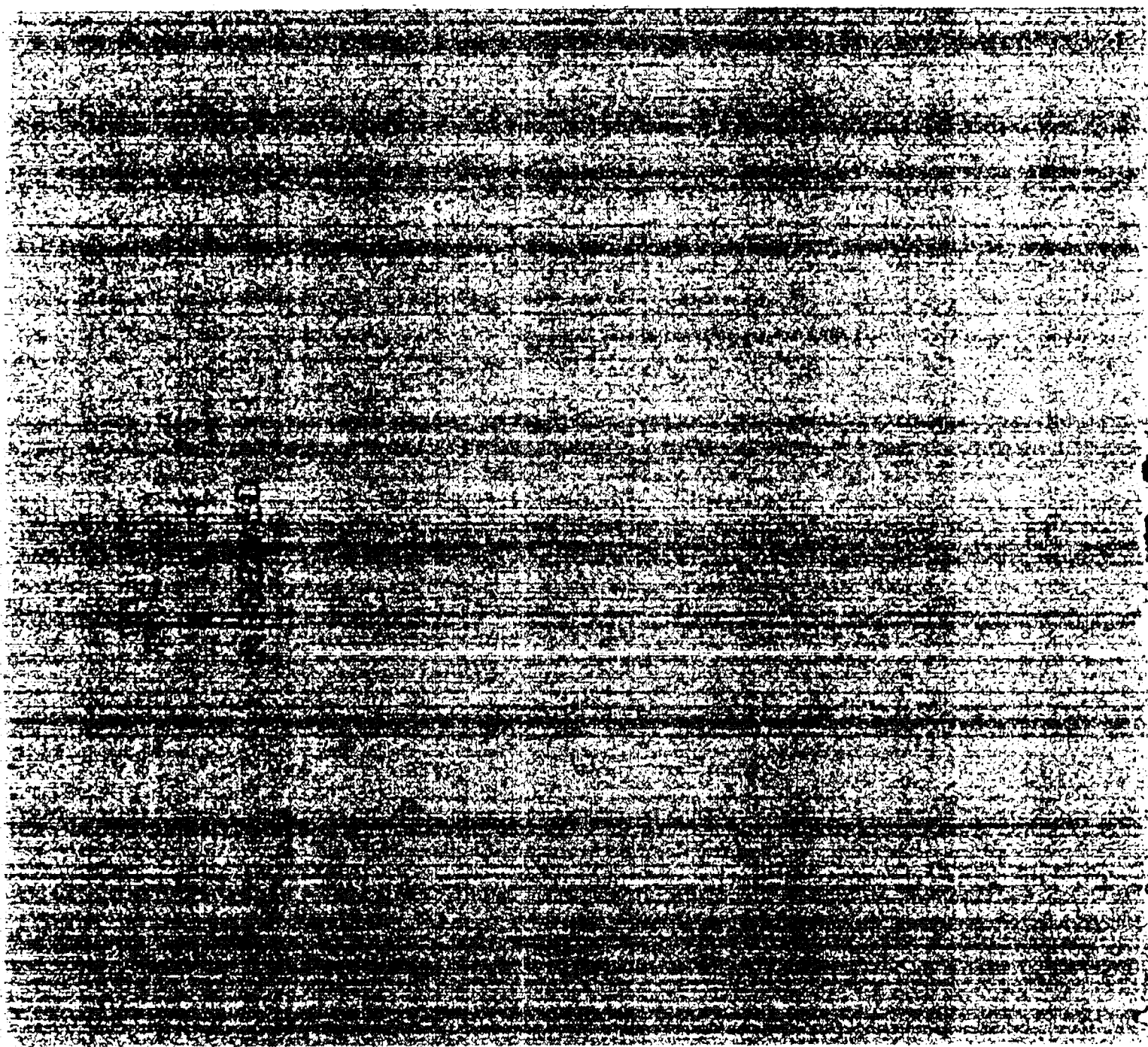
^aAlso tested with BW_H reagent were Cyclotol and Composition B, which gave a purple color. PBX 9404, PBX 9010, and PBX 9011 gave negative test results.

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