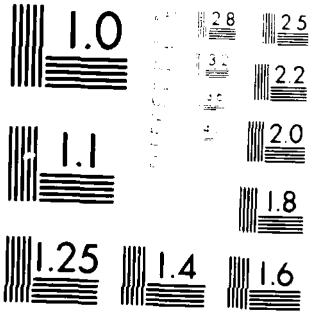
AD-A122 974 2-PICRYL-5-NITROTETRAZOLE: SYNTHESIS AND EXPLOSIVE 1/1
PROPERTIES(U) MATERIALS RESEARCH LABS ASCOT VALE
(AUSTRALIA) R J SPEAR ET AL. JUL 82 MRL-R-859
UNCLASSIFIED F/G 19/1 NL

END
DATE
FILMED
2-83
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

MRL-R-859 AR-003-042

12

DEPARTMENT OF DEFENCE SUPPORT

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-859

2-PICRYL-5-NITROTETRAZOLE : SYNTHESIS AND EXPLOSIVE PROPERTIES

Robert J. Spear and Paul P. Elischer

Approved for Public Release

JULY, 1982

DEPARTMENT OF DEFENCE SUPPORT

MATERIALS RESEARCH LABORATORIES

REPORT

MRL-R-859

2-PICRYL-5-NITROTETRAZOLE : SYNTHESIS AND EXPLOSIVE PROPERTIES

Robert J. Spear and Paul P. Elischer

ABSTRACT

2-Picryl-5-nitrotetrazole (PNT) has been synthesised by reaction of anhydrous sodium 5-nitrotetrazole with picryl chloride and obtained in suitable physical form by crystallisation from acetone-hexane. Impact, thermal and electrostatic sensitivity are all typical of a primary explosive. PNT ignites from match-head or hot wire to a powerful explosion but does not detonate unless initiated by a strong shock such as from detonating lead azide. RDX can be detonated by 100 mg of PNT but heavy confinement is required. PNT shows excellent promise as a replacement for tetrazene as an energetic sensitizer in stab (and percussion) sensitive mixtures.

Approved for Public Release

POSTAL ADDRESS: Chief Superintendent, Materials Research Laboratories
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

DOCUMENT CONTROL DATA SHEET

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-R-859	AR-003-042	UNCLASSIFIED

TITLE

2-PICRYL-5-NITROTETRAZOLE : SYNTHESIS AND EXPLOSIVE PROPERTIES

AUTHOR(S)	CORPORATE AUTHOR
SPEAR, R.J. and ELISCHER, P.P.	Materials Research Laboratories P.O. Box 50, Ascot Vale, Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
July , 1982	DST 78/115	DSTO

CLASSIFICATION/LIMITATION REVIEW DATE	CLASSIFICATION/RELEASE AUTHORITY
	Superintendent, MRL Physical Chemistry Division

SECONDARY DISTRIBUTION

Approved for Public Release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Tetrazoles
Sensitivity
Nitrotetrazoles
2-Picryl-5-Nitrotetrazole
PNT
Synthesis
Explosive properties

COSATI GROUPS 1901 0703

ABSTRACT

2-Picryl-5-nitrotetrazole (PNT) has been synthesised by reaction of anhydrous sodium 5-nitrotetrazole with picryl chloride and obtained in suitable physical form by crystallisation from acetone-hexane. Impact, thermal and electrostatic sensitivity are all typical of a primary explosive. PNT ignites from match-head or hot wire to a powerful explosion but does not detonate unless initiated by a strong shock such as from detonating lead azide. RDX can be detonated by 100 mg of PNT but heavy confinement is required. PNT shows excellent promise as a replacement for tetrazene as an energetic sensitizer in stab (and percussion) sensitive mixtures.

CONTENTS

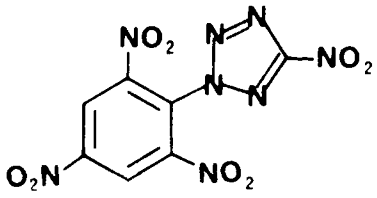
2-PICRYL-5-NITROTETRAZOLE : SYNTHESIS AND EXPLOSIVE PROPERTIES

1. INTRODUCTION

Primary explosive fillings in service stores are largely based on three materials: lead azide, tetrazene and lead styphnate. Lead azide and lead styphnate form the main explosive constituent in stab sensitive and percussion sensitive mixtures such as NOL 130, with tetrazene as the energetic sensitizer. Lead azide is the main primary explosive constituent in detonators while lead styphnate is commonly used in primers and in electrically initiated compositions. The increasing demands for these stores to have extended shelf life, to be able to function under a diverse range of climatic conditions and to be less prone to accidental initiation by external stimuli cannot be adequately fulfilled given the technical shortcomings of these materials. There is consequently a considerable need to develop new compounds to replace these materials in primary explosive compositions. Specifically, new energetic materials are sought with comparable (or better) initiating properties but of enhanced thermal and hydrolytic stability and/or reduced susceptibility to electrostatic initiation.

Our approach at MRL has been to systematically screen selected materials for potential as intiating explosives. The compounds selected fall into two broad categories: those already reported in the literature but whose explosive properties have not been studied in detail, and new compounds structurally related to materials which have been shown to have some properties of primary explosive. These materials are synthesised, subjected to routine sensitivity testing, then explosive properties are assessed.

One class of compounds which has shown the desired characteristics for providing new candidate primary explosives is the tetrazoles. Tetrazene, as well as the very promising mercuric [1-4] and silver [1,2] salts of 5-nitrotetrazole, are included in this class. We have previously reported detailed studies of 1- and 2-methyl-5-nitrotetrazole [5,6] and have now extended these studies to 2-picryl-5-nitrotetrazole (PNT). PNT has been reported only once, in a conference paper [2], where it was described as being "very explosive and sensitive to friction" and of "doubtful hydrolytic stability". In this report we describe the synthesis of PNT and determination of its explosive properties. In contrast to ref [2] we have found PNT to be a very promising primary explosive material

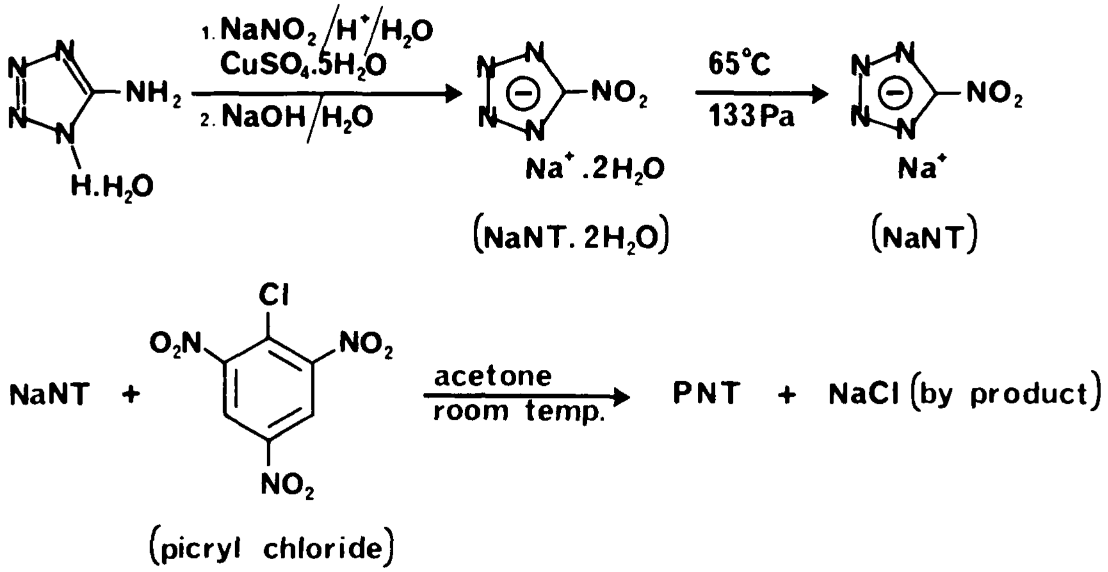


PNT

2. SYNTHESIS

The preparation of PNT has previously been reported via "reaction of sodium nitrotetrazole with picryl chloride" [2]. Sodium 5-nitrotetrazole can be readily prepared by diazotization of tetrazole-5-amine monohydrate in the presence of cupric ion and excess nitrite followed by reaction of the intermediate copper salt with aqueous sodium hydroxide [4]. The product from this reaction is the dihydrate (NaNT.$2H_2O$) which can be dehydrated to the very sensitive anhydrate (NaNT).

In our hands, reaction of NaNT.$2H_2O$ with dry picryl chloride in dry acetone gave good yields of PNT but there was always contamination by a second product which could not be removed by recrystallisation. This second product could readily be detected microscopically as long yellowish needles, in marked contrast to the almost colourless prismatic clusters of PNT. In addition, PNT melted with thermal decomposition (copious evolution of gas) at 165.5-168°C while these long needles melted without decomposition at 135-145°C. Picric acid occurs as irregular prisms which melt sharply at 121.5-122.5°C, hence this second product is not picric acid, but is probably a co-crystal or complex of picric acid, formed by hydrolysis of picryl chloride or PNT, and PNT. However, the wide melting range suggests that it is not a uniform compound and its composition was not further investigated. Dehydration of NaNT.$2H_2O$ by addition of chemical drying agents such as anhydrous sodium or magnesium sulfate to the acetone solutions of NaNT.$2H_2O$ prior to reaction with picryl chloride was not successful - the second product still formed. The problem was successfully overcome by dehydration of NaNT.$2H_2O$ to NaNT at 65°C under vacuum then dissolution in dry acetone followed by addition of dry picryl chloride. This procedure is detailed below as Scheme 1.



Scheme 1. Stepwise preparation of PNT.

PNT was isolated directly from the reaction mixture by filtration of the by-product sodium chloride, reducing the volume of the acetone filtrate then addition of hexane. PNT was isolated in three crops, overall yield 66.0%, as small clusters of almost colourless prisms. Although the recovery in each recrystallisation is not particularly high, it was easily the best of a number of solvent systems which were investigated. Increase in the hexane-acetone ratio led to separation into two immiscible layers upon cooling and lower recovery of product. The product was analytically pure (C, H, N microanalysis). It exhibited only a single peak at δ9.58 ppm in the proton nmr spectrum, indicating that it was also isomerically pure. However, we can only tentatively assign PNT as the 2-picryl isomer. Tetrazolate anions with electronegative substituents at C5 overwhelmingly undergo alkylation and acylation at N2 in preference to N1 [7]. In the absence of a second isomer, which could not be detected even in the crude reaction mixture, picrylation is assumed by analogy to have occurred at N2.

Three experimental batches of PNT (Batches A, B, C) were prepared for testing. Batch A (6.2 g) was prepared from the products of a number of small scale preparations by recrystallisation from acetone-hexane. Batch C (12.1 g) was identical with Batch A and was prepared directly from a large scale preparation of PNT. Batch B was obtained by crystallisation of the Batch A filtrate, which had been contaminated by condensed water, from ethyl acetate-hexane. Batch B consisted of yellowish clumps of tiny crystals contaminated by needles of the hydrolysis product referred to above. The appearance of hydrolysis products which were not present in the crude reaction mixture or Batch A certainly cast doubts upon the hydrolytic stability of PNT. However, a sample of Batch A has been stored in a loosely stoppered container under normal atomspheric conditions for over 2 years and shows no deterioration measurable by hot stage microscopy or DSC. a more complete investigation of the hydrolytic (and thermal) stability of PNT is currently being undertaken.

3. SENSITIVITY TO INITIATION BY EXTERNAL STIMULI

PNT was subjected to the standard sensitivity tests for primary explosives: ball and disc then Rotter impact (impact sensitivity), electric spark test (sensitivity to electrostatic initiation) and temperature of ignition (T of I, thermal sensitivity). The results for these tests are detailed in Table 1. Sensitivity to friction could not be assessed due to unavailability of appropriate test equipment.

The sensitivity of PNT to mechanical stimuli is typical of a primary explosive. The value for the figure of insensitiveness (F of I) of 13 indicates that PNT is very sensitive to mechanical impact; it is comparable with lead styphnate (12) and lower than lead azide (20) [8]*. The inability to initiate in the ball and disc test, where susceptibility to pinching action rather than direct impact is tested, suggests from our experience that PNT is a relatively soft material.

Sensitivity to electrostatic initiation is also typical of a primary explosive. PNT ignites consistently at spark energies of 0.045 J, comparable with lead styphnate under these test conditions. However the ignition threshold of lead styphnate using the more sensitive approaching needle test is 8 µJ [9]. A more accurate description of the electrostatic sensitivity of PNT must await availability of equipment for the approaching needle test.

PNT ignites to a violent explosion above 150°C (T of I test, Table 1). Variations in the T of I values for Batches A-C are small and probably result from variations in particle size distributions. The DSC trace consists of a single sharp exotherm (Table 1) and samples larger than 0.35 mg build up to a runaway explosive reaction. Explosion of samples during T of I testing is not unexpected since the sample sizes (50 mg) are quite sufficient to build up to a self propagating explosive reaction. However explosion of

---

* The F of I values for lead styphnate and lead azide were obtained relative to lead 2,4-dinitroresorcinate = 11 [8]. Our testing method gives values relative to RDX = 80, hence the values quoted in [8] may not be directly comparable to our result for PNT.

such small samples under DSC conditions is much less common and is a strong indication that PNT readily propagates from ignition to explosion.

In summary, PNT functions as a primary explosive in the sensitivity tests employed here and should accordingly be handled with extreme caution. The previous report that PNT was "very sensitive to friction" [2] (although no data was given) will be checked upon availability of suitable instrumentation.

4. EXPLOSIVE PROPERTIES

4.1 *Initiating Properties*

The initiating properties of PNT were assessed using a series of experimental detonators. The results are listed in Table 2, entries 1-15.

The ability of PNT to initiate under normal firing conditions was assessed as detailed in entries 1-4. The results show that PNT initiates readily either from match-head igniter (entries 1,2) or hot wire resulting from capacitor discharge of 0.08 J (entry 3). Although a powerful explosion was observed in all cases, evidenced by fragmentation of the detonator tubes, no denting or cratering of the brass witness block was observed. The fact that the witness blocks were not marked (dented) is indicative of an explosion rather than a detonation. The possibility that the length of the PNT column in entry 1 was insufficient to ensure build-up to detonation was not substantiated by the result for the larger column (entry 2). Increase of confinement by pressing into a mild steel detonator tube again resulted in a powerful explosion but not detonation (entry 4).

Two experimental detonators were prepared with an initial increment of lead azide RD1343 then an increment of PNT (entries 5,6). The aim here was to determine whether PNT could be induced to detonate, the powerful shock from detonating lead azide providing the initiation means. Firing of both detonators resulted in cratering of the witness block while a detonator filled with lead azide then methyl cellulose (entry 7), chosen to provide an inert filling of comparable density to PNT, did not dent the wintess block upon firing. The markings on the witness block in entries 5 and 6 were comparable with a single increment lead azide detonator but substantially less than a lead azide - RDX detonator [6]. Clearly PNT will detonate but the power output upon detonation is considerably lower than RDX.

A series of detonators were then prepared in perspex tubes with an increment of PNT followed by an increment of the shock sensitive secondary explosives RDX or tetryl. The aim here was to assess whether the power produced by explosion of PNT was sufficient to induce secondary explosives to detonation. The results are detailed in Table 2, entries 8-14. In all cases a powerful explosion resulted with denting but not cratering of the witness block. The dents were substantially less than for a comparable lead azide-RDX detonator [6] while a detonator with a secondary filling of inert lead monoxide produced no dent in the witness block (entry 10). Increase of the PNT increment up to 400 mg still did not result in detonation of the secondary although an enhanced explosion does result (entries 12-14). Confinement of the PNT-RDX charge in a mild steel tube (entry 15) resulted in a detonation with destruction of the tube and a distinct deep indentation of the witness block, comparable with a similar lead azide-RDX charge. The ability of PNT to detonate sensitive secondaries is clearly very dependent upon confinement. Lack of sufficient confinement cannot be overcome or compensated for by increasing the quantity of PNT up to 400 mg, cf. only 100 mg which was used in the more confined charge.

A number of experimental detonators were fired with Batch B PNT as filling and in general performed similarly to comparable detonators containing the purer Batches A or C. However, in one case a detonator containing 400 mg of Batch B and 100 mg of RDX only deflagrated - a loud "whooshing" sound (and no explosion) was heard, the tube was not fragmented, and the contents were consumed leaving a black residue (cf. entries 12, 13, Table 2). Since Batch B contains small quantities of hydrolysis products, this result suggests that such impurities could markedly effect explosive properties of PNT although any firmer conclusions must await more detailed studies.

4.2 Stab Sensitization Properties

The ability of PNT to function as an energetic sensitizer in stab sensitive compositions was assessed using admixtures of Batch A with lead azide RD 1343. Experimental detonators were prepared by pressing an increment of lead monoxide (250-300 mg) then the experimental composition (35-52 mg) into mild steel tubes at 600 MPa. The lead monoxide functions as an inert back filling and ensures that initiation results directly from the needle penetrating the explosive increment, and not by processes such as cracking or friction between the explosive and a hard backing surface. The experimental detonators differed from conventional stab detonators in that they were not fitted with a closing disc nor were they spotted with varnish.

Stab initiation energies were determined by the use of a free falling needle of a similar design to strikers used in fuzes. Each experiment was assessed as fire or no fire by sound (very loud!) and close visual inspection of the detonator tube. no partial ignitions which failed to propagate were detected even under microscopic examination. At least 25 detonators were tested for each composition. The data were analysed using the Bruceton method [10] and the results represent the 50% fire level. The stab initiation energies are listed in Table 3 together with results for comparable lead azide RD 1343 - tetrazene admixtures.

The results in Table 3 demonstrate the potential of PNT as a sensitizing agent. Pure lead azide RD 1343 is relatively insensitive to stab initiation and requires initiation energies of about 1000 mJ. Addition of PNT dramatically lowers the energy required for initiation, the minimum being 8.6

mJ for 2% PNT. Increase in the percentage content of PNT from 2% increases the stab initiation energies, and this is consistent with PNT being a relatively soft material (like tetrazene) which desensitizes the hard lead azide particles to friction from impact of the needle. Results for the tetrazene - lead azide admixtures show a similar trend. The minimum initiation energy, 3.5 mJ, corresponding to 2-10% tetrazene, is significantly lower than for PNT and most probably reflects the relative ignition temperatures: tetrazene, 136°C, PNT 156°C (Batch A). Sensitization of other hard primary explosives by PNT will be assessed in the near future, particularly silver azide, with which tetrazene is incompatible [2], and mercuric 5-nitrotetrazole.

The stab initiation energy for pure PNT compacted at 600 MPa is 75.2 mJ. Compacted pure tetrazene is even less impact sensitive and will not initiate at impact energies of 280 mJ. Since an initiation energy of 75.2 mJ is far too high for practical use, a series of detonators were prepared by pressing PNT at a range of pressing loads in the anticipation that the initiation energies could be substantially lowered. Experimentally determined initiation energies are listed in Table 4. The results do not differ within experimental error and indicate that the initiation energy for pressed PNT is independent of pressing load over the ranges studied here. There is no evidence that PNT has a tendency to dead press.

5. CONCLUSION

The synthesis of 2-picryl-5-nitrotetrazole (PNT) from readily available starting materials in good overall yield has been demonstrated. The high sensitivity to impact (F of I 13), low ignition temperature (T of I 155°C) with ignition leading to a violet explosion, and ignition by electrostatic discharge at energies as low as 0.045 J are all typical of a primary explosive and clearly demonstrate the need to handle PNT with caution. PNT readily ignites from match-head or hot wire to a powerful explosion but will not detonate under any of the conditions of confinement studied here. RDX can be detonated in a normal detonator geometry using 100 mg of PNT but heavy confinement is required. Compacted admixtures of PNT with lead azide display high sensitivity to stab initiation (initiation energies as low as 8.6 mJ) while compacts of pure PNT require stab initiation energies of 65-75 mJ, a value far too high for practical use. PNT thus demonstrates good potential as an initiating explosive and particularly as an energetic sensitizer for stab and percussion sensitive compositions. Although there is no apparent deterioration of PNT stored under normal atomspheric conditions for over 2 years, hydrolytic stability in solution appears to be suspect. A detailed study of the hydrolytic and thermal stability of PNT has commenced and the results will be reported in a future publication.

6. EXPERIMENTAL

General

All chemicals used in the syntheses described below were available commercially or from previous studies. Infrared spectra were recorded on a Unicam SP 1000 spectrophotometer and proton magnetic resonance spectra were recorded at 60 MHz on a Varian HA 60 IL spectrometer with tetramethylsilane as internal reference. Microanalysis was performed by Amdel, Australian Microanalytical Service, Melbourne.

Sodium 5-nitrotetrazolate dihydrate

Sodium 5-nitrotetrazolate dihydrate was prepared from tetrazole-5-amine monohydrate according to the method of Gilligan and Kamlet [4]. The crude product was purified by dissolution in the minimum of boiling acetone followed by filtration and precipitation by addition of an equal volume of hexane. After cooling and filtration, the pure product was obtained as irregular chunky white crystals.

2-Picryl-5-nitrotetrazole (PNT)

Sodium 5-nitrotetrazolate anhydrate, prepared by dehydration of the dihydrate ([illegible] g) at 65°C and 133 Pa for 24 h, was added to dry acetone (30 ml), the flask stoppered, then swirled for several minutes till dissolution was complete. Dry picryl chloride (5.[illegible] g) was added in one portion, the flask was restoppered and then allowed to stand for 48 h. The mixture was filtered under suction, the solid product (sodium chloride) washed with a small volume of acetone, and the filtrate concentrated to 15 ml. Hexane (27 ml) was added to the hot solution. Crystallisation commenced upon cooling and was completed by standing overnight. The product was collected by suction filtration, washed with chilled 1:1 acetone-hexane ([illegible] ml) and sucked dry to give PNT (3.2 g) as clumps of very small almost [illegible] crystals. The filtrate was evaporated to dryness under [illegible], [illegible] acetone-hexane ([illegible] ml) was added and the resulting solid was filtered off. Treatment with hot acetone, hot filtration then addition of hexane gave a second crop of PNT (0.85 g) identical with the first crop. A further 0.3 g could be obtained by repeating the recrystallisation on the mother liquors. The first two crops melted with vigorous thermal decomposition at 165-169°C while the third crop underwent this process at 155-162°C. Total yield of PNT = 4.35 g, 66.0%. Found: C, 25.8%; H, 0.7; N, 34.0. $C_7H_2N_8O_8$ requires C, 25.8; H, 0.6; N, 34.3. Ir (KBr disc): 3030, 1600, 1550, 1530, 1348, 1320, 1313, 1290, 1073, 979, 971, 895, 814 cm^{-1}. Nmr ($CDCl_3$): δ 9.58, s.

Preparation of Experimental Batches of PNT

The first experimental batch of PNT, referred to as Batch A in the text, was obtained by recrystallisation of the combined products from a number of small scale preparations. Thus PNT (13.9 g) was dissolved in hot acetone (85 ml), hot filtered and the filtrate reduced to 60 ml. Addition of hexane (60 ml) followed by standing overnight gave PNT (6.2 g) as almost colourless crystals which could be seen by microscopy to be clumps of tiny prismatic crystals.

A second batch, referred to as Batch B in the text, was obtained from the filtrate from the Batch A preparation. The filtrate was allowed to evaporate and it was noticed that water had condensed into the crude crystal mass. Purification was by dissolution in hot ethyl acetate (45 ml), removal of water by pipette and then hot filtration followed by addition of hexane (55 ml). After standing overnight, the product was filtered off (5.8 g) and consisted of small yellowish clumps of crystals which could be seen by microscopy to be small clusteres of prisms contaminated by a few yellow needles of the hydrolysis product (see Section 2).

A third batch, referred to as Batch C in the text, was obtained by performing the standard preparation on a larger scale. Batches A and C were identical with each other and with the first two crops described above in the standard preparation.

Lead azide was type RD 1343 and was obtained as a single batch (Batch 7) from MFF St. Marys, NSW.

Lead styphnate was type RD 1303 obtained from MFF St. Marys, NSW.

RDX was an experimental batch of type RD 1347 prepared at MRL.

Tetryl was stock held at MRL, originally obtained from US sources.

Sensitivity Tests

The instruments used for Ball and Disc, Rotter Impact, the Electric Spark Test and Temperature of Ignition (T of I) measurements were constructed in this establishment to test specifications.

Sensitivity to impact was initially assessed by the Ball and Disc test but no ignitions were observed at the maximum drop height (30 cm). Rotter Impact was conducted on samples of 27 mg using a 2 kg weight falling from heights of 30-55 cm over 5 cm intervals. The figure of insensitivity (F of I) was calculated by comaprison with a sample of RDX (F of I = 80) determined using a 5 kg drop weight.

Sensitivity to electrostatic initiation was assessed by the electric spark test and violent explosions occurred at all testing energies : 4.5, 0.45, 0.045 J.

Thermal behaviour was initially studied at a heating rate of 10°C/min using a Leitz Ortholux microscope with an attached Mettler FP-2 hot stage, and subsequently by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2B. Experimental conditions were vented aluminium pans under a flowing nitrogen atmosphere (15 ml/min), heating rate 10°C/min. Ignition temperatures were determined on an instrument built to specifications for the ERDE T of I test. Samples of 50 mg were heated at 5°C/min and measurements were performed in triplicate.

Investigation of Explosive Properties

Experimental detonators were fired remotely using an 18 V, 0.08 J capacitor discharge firing box which discharged either through a match-head igniter or a platinum bridgewire. The performance of each experimental detonator was assessed by use of a brass witness block, with particular importance being placed upon whether a detonation occurred. The dent imparted to a witness block by a detonation has a distinctly cratered appearance with splaying at the edges. The absence of a dent or the presence of a slight indentation which slopes gradually in from the edges indicates that an explosion has occurred but build-up to detonation has not been achieved. Although largely a qualitative test, depth of dent studies have been used to determine detonator performance and a number of experimental variables which affect the depth have been identified [11].

a. *Initiation using Match-head Igniter*

Experimental detonators were prepared by pressing weighed amounts of explosive into flat bottom aluminium ICI detonator tubes, 5.57 mm i.d., approximate wall thickness 0.3 mm, using an Eltor press at a pressure of 90.7 MPa. A type E ICI match-head was then crimped into the detonator tube.

b. *Initiations using Hot-wire*

Experimental detonators were prepared from detonator tubes constructed either of perspex of mild steel to which had been fitted a bridgewire device using Eastman 910 adhesive. The bridgewire device was constructed of bakelite with copper terminals across which had been spot welded a 0.038 mm diameter platinum wire. The entire assembly is shown diagrammatically in Figure 1 and a more detailed description can be found in ref. [6]. Explosive charges were prepared by pressing weighed amounts of explosive directly into the detonator tubes using an Eltor press. Where two increments were used, the initiating charge was pressed in first then the secondary charge was added and pressed on top. The pressing pressures were 166 MPa for the 4.12 mm i.d. tubes and 90.7 MPa for the 5.57 mm i.d. tubes.

Determination of Stab Sensitivity

a. *Preparation of Sensitized Mixtures*

The PNT was cautiously crushed between filter paper using a wooden spatula and then sieved remotely through a 300 micron sieve to break up aggregates and ensure reasonable homogeneity of particle sizes. No problems were encountered during this procedure. Explosive compositions were prepared by adding PNT to lead azide RD 1343 in the appropriate ratios to achieve a batch size of 1-1.5 g, eg. lead azide RD 1343 (1.00 g), PNT (0.20 g) for the 16.6% composition. Mixing was achieved by fold mixing on a sheet of paper and appeared to be very good with no tendency to separate upon standing.

Preparation of Experimental Detonators

Experimental detonators were prepared in mild steel tubes, 6 mm o.d., 3.2 mm i.d., length 6 mm, prepared from commercially available tubing. A back filling of lead monoxide was first pressed into the tube in two increments using a remotely controlled Pongrass press at a pressure of 600 MPa. The overall column length of lead monoxide was 4 mm, requiring a mass of 250-300 mg; variations resulted from small variation in diameter of the tubes. The experimental composition was then added on top and the unit repressed. In the case of the sensitized mixtures of lead azide and PNT, the mixture was also pressed on at 600 MPa. Detonators using pure PNT were prepared by pressing the PNT onto the lead monoxide at a number of pressures ranging from 650 MPa to 320 MPa. In all cases sufficient composition or PNT was added to result in an explosive compact which was visually flat and almost flush with the top of the detonator tube. The masses ranged from ~ 20 mg of pure PNT at the lower pressing loads to ~ 52 mg of lead azide containing 1-5% PNT. In one instance a detonator containing 35 mg of the 40% PNT - RD 1343 composition exploded in the mould during pressing. Damage to both mould and drift was not appreciable.

Determination of Stab Initiation Energies

The experimental set up, consisting of a drop tower test rig fitted with a quick release mechanism, has previously been described in detail [12]. Three strikers were used: 14.5 g for most determinations, 55.2 g where initiation energies in excess of 55 mJ were required, and 135 g for pure lead azide RD 1343. The striker body was refitted with a new neddle after every test whether or not a fire occurred. The needle was silver steel hardened to 650 HV with a 0.08-0.20 mm flat on the tip. In each experiment the striker was released from a pre-set height to impact on the experimental detonator supported in an aluminium holder held in a mild steel base. Each testing was assessed as fire or no fire by sound (very loud for a positive fire) and visual inspection of the detonator tubes. A fire resulted in splaying and cracking of the tube and ejection of much of the lead monoxide. A no fire resulted only in an obvious indentation into the compacted explosive. The detonators were not retested after a no fire and were destroyed chemically.

Preliminary determinations were conducted at a number of heights to obtain an approximate 50% fire level. The needle height was then varied using regular intervals of approximately 10% of this fire level. A minimum of 25 detonators were tested for each experimental composition. Results were analysed by the Bruceton method [10] and represent the 50% fire level. Standard deviations have not been included; the Bruceton method of analysis is designed to give an overall estimate of the population from a limited number of samples. Statistical interpretation of the results derived from sample sizes used here give a reliable estimate of 50% functioning levels but not for standard deviations.

7. ACKNOWLEDGEMENTS

The technical assistance of Mr A.M. Pitt is gratefully acknowledged. We would also like to thank Mr J.R. Bentley and Mr R. Bird for helpful discussions. Mr R.J. Swinton is thanked for his careful attention in performance of the sensitivity tests.

8. REFERENCES

1. Jenkins, J.M. and White, J.R. (1970). ERDE TN 21.

2. Bates, L.R. and Jenkins. J.M. (1975). "Search for New Detonants," Proc. Int. Conf. on Primary Explosives, ERDE, Waltham Abbey, UK.

3. Scott, C.L. (1975). "Mercuric 5-Nitrotetrazole as a Lead Azide Replacement", Proc. Int. Conf. on Primary Explosives, ERDE, Waltham Abbey, UK.

4. Gilligan, W.H. and Kamlet, M.J. (1976). NSWC/WOL/TR 76-146. Microfiche AD-A036 086.

5. Spear, R.J. (1980). MRL-R-780.

6. Spear, R.J., Elischer, P.P. and Bird, R. (1980). MRL-R-771.

7. Butler, R.N. (1969). Leicester Chem. Rev., 10, 12; Butler, R.N. (1977). Adv. Heterocyclic Chem., 21, 323.

8. Mortlock, H.N. and Wilby, J. (1966). Explosivestoffe, 3, 49.

9. Jenkins, J.M. (1975). "Improvements in Delay and Priming Compositions", Institut für Chemie der Treib- und Explosivestoffe, I.C.T., 6th. Annual Conf., June 11-13.

10. Culling, H.P. (1953). NAVORD Report 2101, US Naval Ordnance Laboratory, Whiteoak, Maryland.

11. Savitt, J. (1979). "The Steel Dent Test and Santa Cruz Facility HNS I End Tips", Proc. 10th. Symp. on Explosives and Pyrotechnics, San Francisco, Calif., USA, and earlier references cited therein.

12. Bentley, J.R. and Elischer, P.P. (1981). MRL-R-776.

TABLE 1 MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY DATA FOR 2-PICRYL-5-NITROTETRAZOLE[a]

TEST	OBSERVATION/RESULT
Mechanical Sensitivity	
Ball and Disc	No fires at 30 cm (max. height)
Rotter Impact	F of I 13 (RDX = 80); 100% fires at 55 cm 0% fires at 30 cm 50% fires at 42.1 cm (calc.) Mean gas volume 21 ml
Electrostatic Sensitivity	
Electric Spark Test	Fires at 4.5, 0.45 and 0.045 J
Thermal Sensitivity	
T of I	Batch A: 155, 156, 158°C) Batch B: 150, 151, 152°C) all samples Batch C: 151, 152, 153°C) explode violently
Hot Stage Microscopy	Batches A and C: No change till 159°C when crystals begin to shatter. Continues randomly till 165.5°C when evolution of gas and liquefaction commences. Liquefaction complete by 168°C with copious gas evolution which continues to ~ 200°C. Batch B: Clumps of crystals with some needles. Needles soften and melt 135-145°C (hydrolysis product), clusters begin to shatter 158°C, 163-5°C observe melting with vigorous evolution of gas.
DSC	Onset of exotherm ~ 156°C, peak maximum 166°C. Samples larger than 0.35 mg exploded at 162.5-163.5°C.

---

[a] Data refers to Batch A unless specified.

TABLE 2 DATA FROM EXPERIMENTAL FIRINGS OF DETONATORS FILLED WITH 2-PICRYL-5-NITROTETRAZOLE (PNT)

Entry	Explosive Filling		Detonator Tube	Result/Observation [a]
	Primary Increment (mg)	Secondary Increment (mg)		
1 [b]	PNT Batch A (125)	-	aluminium [c,d]	Tube fragmented, witness block not marked.
2 [b]	PNT Batch B (500)	-	aluminium [c,d]	Tube fragmented, witness block not marked.
3	PNT Batch A (50)	-	perspex [e]	Perspex holder fragmented, witness block not marked.
4	PNT Batch A (225)	-	steel [e]	Tube flared but not cracked and only a slight dent in witness block.
5	Lead Azide (50)	PNT Batch A (200)	perspex [e]	Witness block dented and spotted by cratering.
6	Lead Azide (50)	PNT Batch C (175)	perspex [e]	Witness block dented and cratered.
7	Lead Azide (50)	Methyl cellulose (175)	perspex [e]	No indentation or cratering on witness block.
8	PNT Batch A (100)	RDX (100)	perspex [e]	Slight indentation in witness block.
9	PNT Batch A (100)	Tetryl (100)	perspex [e]	Slight indentation in witness block.
10	PNT Batch A (100)	Lead Monoxide (150)	perspex [e]	Witness block not marked.
11	PNT Batch A (200)	Tetryl (100)	perspex [d]	Slight dent in witness block.
12	PNT Batch A (400)	RDX (100)	perspex [d]	Definite dent in witness block.
13	PNT Batch C (400)	RDX (100)	perspex [d]	Tube fragmented, witness block dented, but no cratering.
14	PNT Batch C (400)	Tetryl (100)	perspex [d]	Very slight indentation on witness block.
15	PNT Batch A (100)	RDX (100)	steel [e]	Tube destroyed, massive indentation of witness block comparable with lead azide-RDX detonator.

[a] all witness blocks were brass

[b] entries 1 and 2 were fired by match-head igniter, all other entries by hot wire ignition.

[c] ICI No. 8 detonator tube

[d] 5.57 mm i.d., pressing pressure 90.7 MPa

[e] 4.12 mm i.d., pressing pressure 166 MPa

TABLE 3 STAB INITIATION FOR ADMIXTURES OF PNT AND TETRAZENE WITH LEAD AZIDE RD 1343[a]

PARTS PNT OR TETRAZENE : LEAD AZIDE	% PNT OR TETRAZENE	STAB INITIATION ENERGIES (mJ)	
		PNT	TETRAZENE
100 : 0	100	75.2	>280
1 : 1	50	-	7.9
40 : 60	40	24.3 [b]	-
30 : 100	23.1	-	4.7
20 : 100	16.7	23.4	-
10 : 100	9.1	11.1	3.3
5 : 100	4.8	9.4	3.5
2 : 100	2.0	8.6	3.6
1 : 100	1.0	13.6	6.1
0.5 : 100	0.5	14.6 [b]	-
0 : 100	0	~ 1000	~ 1000

[a] Pressing load 600 MPa for all detonators

[b] Batch C. All other entries refer to Batch A

TABLE 4 STAB INITIATION ENERGIES FOR EXPERIMENTAL DETONATORS OF PNT PRESSED AT VARIOUS PRESSING LOADS

Pressing Load (MPa)	Stab Initiation Energy (mJ)
320	71.8 [a], 74.9 [b]
400	70.0 [a]
450	71.7 [a]
560	75.2 [b]
650	65.8 [a]

[a] Batch A PNT

[b] Batch C PNT

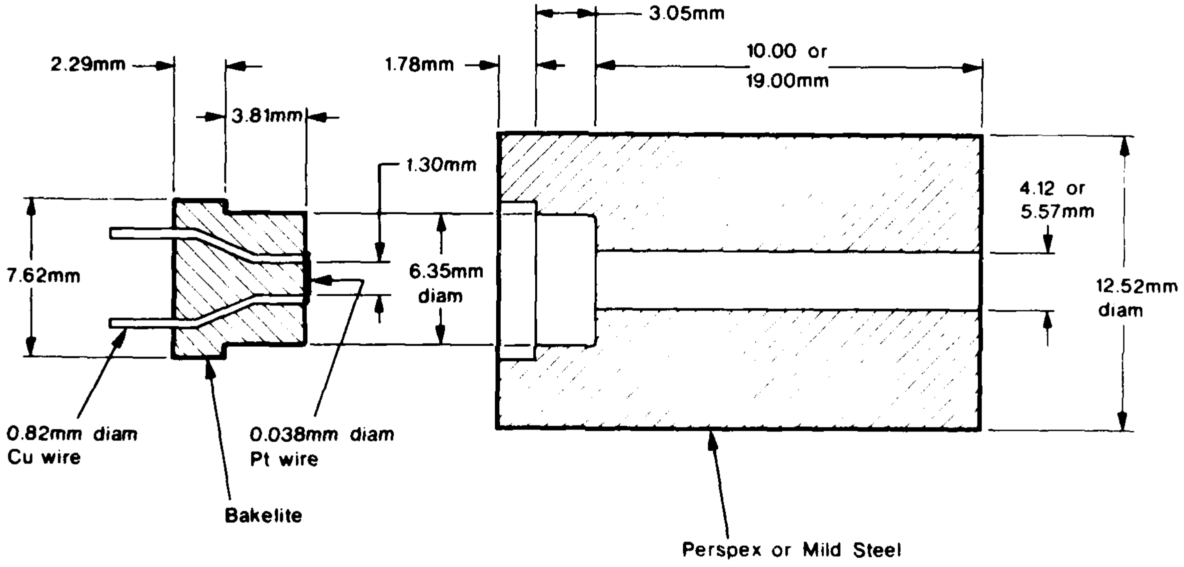


FIG. 1. Schematic diagram of detonator tube and bridgewire device assembly used in experimental detonators.

DISTRIBUTION LIST

MATERIALS RESEARCH LABORATORIES

Chief Superintendent	
Superintendent, Physical Chemistry Division	
Dr B.W. Thorpe	
Mr R. Bird	
Mr R. Spear	
Mr P.P. Elischer	
Mr J.R. Bentley	
Dr J. Eadie	
Library	(2 Copies)

DEPARTMENT OF DEFENCE AND DEFENCE SUPPORT

Chief Defence Scientist/Deputy Chief Defence Scientist/ Controller, Projects and Analytical Studies Superintendent, Science and Technology Programme	1 Copy
Army Scientific Adviser	
Air Force Scientific Adviser	
Navy Scientific Adviser	
Librarian, (Through Officer-in-Charge), Materials Testing Laboratories, ALEXANDRIA, N.S.W.	
Senior Librarian, Aeronautical Research Laboratories	
Senior Librarian, Defence Research Centre Salisbury, S.A.	
Librarian, R.A.N. Research Laboratory	
Officer-in-Charge, Document Exchange Centre	(17 Copies)
Technical Reports Centre, Defence Central Library	
Central Office, Directorate of Quality Assurance - Air Force	
Deputy Director Scientific and Technical Intelligence, Joint Intelligence Organisation.	
Librarian, Bridges Library	
Librarian, EDE	
Defence Scientific & Technical Representative, Australia High Commission, London.	(Summary Sheets only)
Counsellor Defence Science (Attention: Dr J. Stals)	(Summary Sheets only)
Head of Staff, British Defence Research & Supply Staff (Aust.)	
Controller, Munitions Supply Division	

OTHER FEDERAL AND STATE DEPARTMENTS AND INSTRUMENTALITIES

NASA Canberra Office, Woden, A.C.T.
The Chief Librarian, Central Library, C.S.I.R.O.
Library, Australian Atomic Energy Commission Research Establishment
Secretary, Department of Science, Woden, ACT
Librarian, State Library of NSW, Sydney NSW

MISCELLANEOUS - OVERSEAS

Library - Exchange Desk, National Bureau of Standards, U.S.A.
UK/USA/CAN/NZ ABCA Armies Standardisation Representative (4 Copies)
The Director, Defence Scientific Information & Documentation Centre, India
Military, Naval and Air Adviser, High Commission of India, Canberra
Director, Defence Research Centre, Kuala Lumpur, Malaysia
Exchange Section, British Library, U.K.
Periodicals Recording Section, Science Reference Library, British Library, U.K.
Library, Chemical Abstracts Service
INSPEC: Acquisition Section, Institution of Electrical Engineers, U.K.
Engineering Societies Library, U.S.A.
Director, Propellants, Explosives & Rocket Motor Establishment, U.K.
Director, Royal Armament Research & Development Establishment, U.K.

LMED

-83