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MELBOURNE, VICTORIA

REPORT

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1-METHYL-5-NITROTETRAZOLE AND 2-METHYL-5-NITROTETRAZOLE

PART 2

ASSESSMENT OF THEIR POTENTIAL AS INITIATING EXPLOSIVES: MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY, AND EXPLOSIVE PROPERTIES

Robert J. Spear, Paul P. Elischer and Roy Bird

Approved for Public Release

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ABSTRACT

1-Methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2) have been assessed as initiating explosives. Although isomers, they exhibit markedly different thermal and explosive properties. 2 is an energetic material with properties both of primary and secondary explosives. It exhibits sensitivity to mechanical and electrostatic shock comparable with primary explosives but does not ignite to explosion when unconfined. When confined, it burns to a powerful explosion but this explosion does not proceed to detonation nor will it detonate even sensitive secondary explosives. 2 will detonate when initiated by lead azide. In contrast, 1 possesses similar mechanical sensitivity to 2 but is difficult to initiate by hot wire and then only undergoes an explosion with low power output. Both 1 and 2 enhance the stab sensitivity of lead azide, but neither to an appreciable extent. 2 exhibits similar initiating properties but much lower sensitivity to electrostatic discharge than lead styphnate and has the potential to replace this material in some applications. In additon, 2 is a castable purely organic compound which readily initiates from a hot wire to produce a substantial gas output, and could thus find specific practical applications. No practical use of 1 can be envisaged at this stage.

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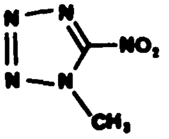
PART 2

ASSESSMENT OF THEIR POTENTIAL AS INITIATING EXPLOSIVES: MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY, AND EXPLOSIVE PROPERTIES

1. INTRODUCTION

Research and development of primary (initiating) explosives over the last fifty years has been concerned mainly with overcoming the technical shortcomings of the few traditional materials. This has become increasingly important with the requirement for many modern munitions to have an extended life and to operate under increasingly severe conditions. A search is thus being undertaken for new energetic materials with comparable performance but greater thermal and hydrolytic stability than tetrazene and lead azide and which are less susceptible to ignition by electrostatic discharge than lead styphnate and lead azide. The class of compounds which has so far yielded the most promising candidates for replacement of these three traditional materials is the tetrazoles, particularly mercuric 5-nitrotetrazole (1-3) and related metal salts. We have, as part of our current research effort, been investigating the isomeric tetrazoles 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2), the synthesis, characterisation and detection of which we reported previously (4). Both 1 and 2 have a number



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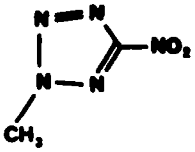

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of interesting and potentially favourable properties; they are low melting solids (1, m.p. 40-1°C, 2, m.p. 85-6°C (4)), thus are castable and could belong to the very limited class of primary explosives which melt below their ignition temperature, and, being purely organic (i.e., containing no metal atoms) could have minimum compatibility problems.

The work described in this report is directed primarily towards the assessment of 1 and 2 as initiating explosives. Partial investigations of explosive properties of 1 and 2 have previously been reported in three publications (3,5,6). Von Herz (5), in a very early study of tetrazole metal salts, reported the preparation of a "methyl ester" by reaction of silver 5-nitrotetrazole with iodomethane, and claimed it to be a powerful detonant although with an unfavourable melting point of 85°C (the melting point identifies it as 2). More recently, Bates and Jenkins (3), as part of an extensive study of explosive properties of tetrazole derivatives, reported limited explosive and sensitivity data for 2. The initiation of 1 and 2 using a hot wire has also been reported by Tarver et al. (6), who used cast charges of 1 and 2 to study deflagration to detonation of primary explosives. The picture of the explosive behaviour of 2 which emerges from these studies is incomplete and at times conflicting while data for 1 are so limited that no firm conclusions can be made with respect to its potential as an initiating explosive.

The broad areas over which the behaviour of 1 and 2 have been investigated are sensitivity to mechanical, electrostatic and thermal shock, and explosive properties, particularly the ability to detonate or to initiate secondary explosives to detonation. The results described in this report lead to a clear picture of the potential of 1 and 2 as initiating explosives. Although 1 and 2 differ only in their molecular arrangement, there are marked differences particularly with respect to explosive properties. An attempt has been made to rationalise these differences between 1 and 2, and give further insight into the effect of differing molecular structure on explosive properties.

2. MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY

All explosives are subjected to a range of tests to assess their safe handling characteristics. Since both 1 and 2 were being assessed as potential primary explosives, they were subjected to the standard tests for primary explosives : ball and disc then Rotter impact (F of I) (impact sensitivity), electrostatic spark test (sensitivity to electrostatic discharge) and temperature of ignition (heat sensitivity). The ERDE emery paper friction test (friction sensitivity) was unfortunately not available, hence no results were obtained for 1 and those for 2 are from previously published data (3). Results for these tests, plus some qualitative test data, are listed in Table 1.

The F of I values for 1 and 2* (Table 1) are considerably lower than sensitive secondary explosives such as tetryl and PETN (7) and indicate impact sensitivities only slightly less than commonly used primary explosives, e.g., lead azide, which has an F of I of 20 (7). A feature of the Rotter impact results is the relatively high standard deviations (SD) for the recrystallised samples, and large gas volumes from initiations (Table 1). The large SD values possibly reflect inhomogeneity of crystal sizes within individual samples. 1 tends to recrystallise as large needles of varying sizes (Figure 1(a)). Attempts to produce smaller, more homogeneous crystals by rapid crystallisation were unsuccessful due to the low melting point. Samples of 1 were accordingly crushed between sheets of filter paper prior to testing (no problems were encountered during this procedure) but a range of crystal sizes was still obvious from visual inspection (Figure 1(b)). In contrast, 2 recrystallises as small platelets which tend to aggregate (Figure 1(c)); sublimed samples are obtained as larger irregular sized plates (Figure 1(d)). The lower F of I value for sublimed 2 relative to recrystallised 2 most likely results from the higher purity achieved by sublimation, which is also reflected in a slightly enhanced melting point (4). Alternatively, the larger sublimed crystals could be more brittle and propagate more readily. The friction test data (Table 1), although only available for 2, again demonstrate high mechanical sensitivity.

The electrostatic spark sensitivity data (Table 1) are extremely interesting. While 1 is insensitive at the discharge energies used (testing was carried out at 4.5, 0.45 and 0.045 J), 2 is much more sensitive, in parallel with the results of Tarver et al. for hot wire initiation (6). The spark sensitivity of 2 is comparable with a sensitive secondary such as PETN, but is three orders of magnitude less sensitive than most primary explosives. Lead styphnate, for example, gives consistent ignitions at 0.045 J using this test but the initiation threshold using a more sensitive electrostatic test is ca. 0.045 mJ.

When 1 or 2 was subjected to the Temperature of Ignition test, both merely volatilised or decomposed to gaseous products under the experimental conditions. This behaviour is apparent when studied by hot stage microscopy. In the case of 1, the crystals melt (40-41°C) to form a pool of liquid which remains unchanged till about 160°C where bubbling is observed to commence. The bubbling becomes very vigorous around 210°C and continues till 250°C (heating rate 10°C/min), the temperature at which observation was stopped. 2 behaves similarly, melting (85-6°C) to form a pool of liquid which begins to volatilise with some bubbling at about 150°C. The subsequent processes are much faster than for 1 and appear to be completed by 210°C. Tetrazole derivatives typically undergo smooth thermal decompositions (8).

Two qualitative experiments were conducted to further assess the ignitability of 1 and 2 (Table 1). When samples of either are dropped onto a hot plate at 300°C, they do not ignite but bubble furiously with slight

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* The F of I value for 2 of 9 quoted previously (3) is apparently incorrect. No fires were observed in the ball and disc test (3) which is consistent with the data reported here but not with such a low F of I value.

evolution of smoke, nor will 1 or 2 burn to explosion if ignited on filter paper but both burn smoothly with a smoky flame.

The thermal behaviour of 1 and 2 was subjected to more quantitative investigation using differential scanning calorimetry (DSC). Typical DSC curves are shown in Figures 2(a) and (b) respectively. Both exhibit sharp melting endotherms followed, at higher temperatures, by a complex series of exotherms and endotherms. Note that 2 decomposes thermally at a lower temperature than 1, as was observed in the hot stage microscopy experiments. The thermal decomposition of a considerable number of tetrazoles have been studied both via kinetics and product distributions (8) and, in a number of cases, competing single or multistep reaction pathways are indicated. The number of exotherms in the DSC curves for both 1 and 2 suggest a similarly complicated reaction scheme, but elucidation must await further investigation.

Under the experimental conditions employed in this study, primary explosives normally ignite and either react very rapidly to yield a sharp exotherm or detonate. The smooth thermal decomposition of 1 and 2, considered together with the results from the qualitative ignition experiments described above, is more typical of secondary explosives. For example, the DSC curve for the primary explosive tetrazene (Figure 2(c)) (9) shows an intense sharp exotherm indicating a definite temperature of ignition at 416K, whereas the DSC curves for 1 and 2 indicate that thermal decomposition occurs before a definite temperature of ignition is reached. The thermal behaviour of 1 and 2 suggest that neither will be a candidate as a replacement for tetrazene, which is normally used as a sensitising agent in stab sensitive compositions where a low temperature of ignition is required (10).

3. EXPLOSIVE PROPERTIES

The few reports of explosive properties of 1 and 2 are limited in scope and, particularly for 2, at times conflicting. The earliest report of 2, by von Herz (5), described it as a powerful detonant. Bates and Jenkins (3), in contrast, summarised the explosive properties of 2 as "it did not detonate RDX and has no stab sensitising properties". No details were given of the experiments which led to these conclusions. Tarver et al. (6), in their study of hot-wire initiation of 1 and 2, noted for 2 that "detonation definitely occurred and that the aluminium charge holders were damaged to roughly the same extent as an equivalent mass of lead azide", while for 1 "explosion" of some charges was noted.

The explosive properties of 1 and 2 were accordingly investigated along several lines. Firstly, what stimulae are needed to initiate 1 and 2 and do they detonate? Secondly, will either detonate secondary explosives? Clearly, an answer to these questions should resolve the conflicting conclusions from previous reports (3,5,6). It was also decided to investigate whether either 1 or 2 possessed any stab sensitising ability as displayed by the related tetrazene (10). Details of all experimental procedures are fully described in Section 5.

3.1 Initiation by Match-Head Igniter

125 mg charges of 1, 2 and lead azide were pressed into aluminium detonator tubes and fired from a match-head igniter. All three explosives were initiated under these conditions and the results and observations are summarised in Table 2. The charge of 1, although initiation was accompanied by much noise, failed to split the detonator case. Doubling the mass (to 250 mg) only caused the tube to split. By comparison, the charge of 2 exploded violently with much noise and fragmented the detonator tube into several pieces. A witness block was not, however, dented, a result which can be contrasted with the lead azide detonator which fragmented the tube into many pieces and gave a crater on a witness block typical of a detonating primary explosive. Pressing a large (1.0 g) charge of 2 into a mild steel detonator tube and firing produced substantial fragmentation of the tube but a brass witness block was not dented. It is clear from these experiments that 1 only undergoes an explosion with low power output while 2 produces a powerful explosion with high gas pressure but does not detonate under these conditions.

3.2 Initiation by Hot Wire (Capacitor Discharge)

Charges of 1 and 2 were pressed into 4.12 mm i.d. perspex detonator tubes (Figure 3(a)) and initiated by capacitor discharge (18 V, 0.08 J) across a 0.038 mm diameter platinum wire. Full experimental details are given in Section 5 and the results are summarised in Table 3, entries 1-16.

The most apparent observation is that 1 will not initiate under these conditions but only undergoes thermal decomposition in the vicinity of the wire, leaving most of the charge undisturbed (Entries 1,2). As a result of this, and the low power indicated from the match-head initiated firings, experiments were not carried out to determine whether 1 would initiate secondary explosives.

In contrast, 2 initiated readily from the hot wire with much resultant noise and shattering of the tube (Entries 3,4). However, a witness block remained undented hence a build up to detonation had not occurred. Further charges were pressed with a secondary increment to investigate whether 2 would initiate other explosives (Entries 5-14). Lead azide (Entry 5) was induced to detonate, giving the characteristic indentation and cratering of the witness block. The secondary explosive RDX (Entries 6-10) was not detonated, although initiating increments of 2 up to 400 mg were used, neither was tetryl (Entries 11,12). The more sensitive PETN was initiated to the extent of slight indentation of the witness block, as did RDX on one occasion, but the effect was much less than would be expected from a detonating secondary explosive and no cratering was observed. Clearly, at this level of confinement, 2 does not detonate even sensitive secondary explosives. Interestingly, firing of charges pressed with a second increment of the inert filling lead monoxide (Entries 15,16) gave, in two out of three firings, indentation of the witness block similar to the PETN experiments. Since lead monoxide is inert, the only function it could be providing would be additional confinement for the charge of 2. A series of experiments were thus carried out whereby charges of 2 with secondary increments were confined under increasingly restrictive conditions. The results of these experiments are detailed in Table 4, Entries 1-7.

The initial experiment, that of confining the 2/RDX charge in a perspex tube plugged tightly with a brass plug (Entry 1) was unsuccessful as the RDX obviously failed to detonate. A further series of experiments were conducted using steel detonator tubes (Figure 3(b)). At this level of confinement, with a witness block adhered to the open tube end, 2 initiated lead azide (Entry 2), cratering the witness block and cracking the steel tube. However, an analogous charge of 2 and RDX (Entry 3) lead to indentation but not cratering of the witness block and left the steel tube unchanged except for ejection of the bridgewire device, markedly in contrast with a lead azide/RDX charge (Entry 4) which gave deep cratering of the witness block and splitting of the steel tube. A charge of 2 with PETN (Entry 5) resulted in substantial indentation of the witness block but no cratering, and expansion but not cracking of the detonator tube, the total damage being much less than from the lead azide/RDX charge. Photographs of witness blocks and detonator tubes from these experiments are shown in Figures 3(c)-(f).

A further increased confinement was tested by pressing 2 and RDX into a brass tube which was then confined in a brass block and fitted with a glass to metal seal bridgewire device (Entry 6). Initiation of the charge led to ejection of the brass tube which was enlarged in diameter and severely flared (Figure 3(g)), but the brass block was undamaged and unreacted RDX could clearly be seen still inside. Repetition of the experiment using only the brass tube with a witness block (Entry 7) resulted in splitting of the tube into two (Figure 3(h)) but no indentation of the witness block.

The results of these experiments indicate that 2 will initiate to explosion but will not, under any confinement conditions investigated here, detonate RDX or PETN; explosion of the latter is indicated. Lead styphnate and tetrazene exhibit similar properties as initiating explosives. In an effort to further understand the explosive properties of 1 and 2, charges of varying length and comparable density were pressed and cast into 4.12 mm i.d. perspex tubes and function times for capacitor discharge initiation were measured. The function time is the time interval between closing the firing circuit and shorting of an ionisation probe situated at the top of the charge. Full details of the firing and ionisation probe circuits are given in Section 5. Measurements of function times for pressed and cast charges of 1 and 2 are given in Tables 5 and 6 respectively.

The results for the pressed charges (Table 5) are extremely informative. The 25 mg and 50 mg charges of 1, lengths 1.20 and 2.56 mm respectively, and the 25 mg, 1.27 mm charge of 2 failed to short the ionisation probe or fragment the detonator tube and thus did not explode. Tarver et al. (6) had previously concluded, from a larger series of tests, that 1 mm charges of 2 definitely failed to 'detonate' while 2 mm charges usually 'detonated', suggesting a critical length for 'DDT' of about 2 mm. Although our experiments show that 2 does not detonate, we would conclude that 2 (and 1) exhibit definite deflagration regimes and, in the case of 2, build-up to explosion cannot occur for charge lengths less than about 1.5 mm. A second observation from Table 5 is the erratic and at times long function times for both 1 and 2. This can be contrasted with other primary explosives fired under these experimental conditions (11) which give extremely reproducible function times (which vary with charge length); e.g., lead azide, 7.5-10.0 µs, lead styphnate, 38-52 µs, diazodinitrophenol, 29-40 µs. Tetrazene, however, gives rather erratic function times (11). In all firings of 1 and 2, the bridgewire burnt out in 16-18 µs as evidenced from a voltage time monitor, hence the long functioning times most probably result from burning regimes which have extremely variable times for transition to explosion. Measurement of function times on cast charges (Table 6) gave similar results to the pressed charges for 2 but for 1 were much less sensitive to initiation and all failed to explode. Tarver et al. (6) report having fired at least 35 charges of 2 of varying lengths but that only 15 gave 'good outputs', probably reflecting the erratic function times observed here.

One of the most important properties of an initiating explosive is that it have a very short, consistent, function time for any given set of conditions. The erratic functioning times for 1 and 2, coupled with their inability to initiate secondary explosives, indicate a relative insensitivity and reflect their poor performance as primary explosives.

3.3 Initiation by Exploding Bridgewires and Primary Explosives

Since all the previous experiments had indicated that 2 and 1 could not be induced to detonate from a hot wire, a short investigation using more vigorous initiating conditions was undertaken.

A series of experimental detonators using either lead styphnate or lead azide as an initiator with a second increment of 2 or 1 were pressed. The results of these firings are summarised in Table 4, Entries 8-12. Lead styphnate (Entry 8) did not induce 2 to detonate since the witness block was only moderately dented, in contrast to the lead styphnate/lead azide detonator (Entry 9) which gave cratering of the witness block characteristic of detonation. Use of lead azide (100 mg) as the initiating charge (Entries 10,11) with 2 pressed into a 4.12 mm i.d. perspex tube gave evidence of detonation by some cratering of the witness block, but a second detonator prepared from a larger charge of 2 (550 mg) pressed into a 5.57 mm i.d. perspex tube definitely detonated as shown by cratering of the witness block, which can be seen in Figure 3(i). In contrast, a detonator prepared from lead azide and 1 (Entry 12) failed to dent the witness block.

Pressing of 1 and 2 into 5.57 mm i.d. perspex tubes and initiating by exploding the platinum wire on a high voltage firing circuit (3000 V, 4.5 J, full details are given in Section 5) gave a powerful explosion of 2, as evidenced from denting of an aluminium witness block, but no cratering was observed. An analogous detonator pressed with PETN gave a large crater of the witness block. Only one detonator filled with 1 was prepared and under these conditions it failed to fire; the force from the exploding wire plus thermal decomposition of 1 in the vicinity of the wire sheared the perspex tube off at the top of the bridgewire device, but the sample of 1 remaining in the top half of the tube was undisturbed.

3.4 Stab Sensitising Ability

Practically all percussion primer mixes and stab sensitive compositions used in munitions incorporate the tetrazole, tetrazene, as a stab sensitising agent. It was of interest to test whether 1 or 2 posessed any stab sensitising capacilities, although a substantial effect seemed unlikely from the DSC and ignition experiments discussed previously. Bates and Jenkins (3) had previously stated that 2 possessed no stab sensitising properties, although no experimental details were given.

Lead azide was chosen as the material for assessment of 1 and 2. Experimental detonators were prepared from lead azide and lead azide mixed with 10% of 1 or 2 (see Section 5 for full details) and results are given in Table 7. Lead azide is not particularly stab sensitive and under the experimental conditions employed here a value of about 980 mJ was obtained.* Both 1 and 2 do sensitise lead azide, but only by factors of 2 and 4 giving initiation energies of 490 and 245 mJ respectively. This can be compared to a 10% w/w composition of lead azide and tetrazene which consistently initiates at energies as low as 3 mJ (10), thus there is little likelihood of any practical application of either 1 or 2 as a stab sensitiser. Stab sensitivity has been shown to be directly related to temperature of ignition (10) and the poor sensitising ability of 1 and 2 is probably due to their difficulty in achieving ignition. Alternatively, it may be due to the fact that they melt before ignition, particularly in the case of 2.

4. CONCLUSION

1 and 2, although isomeric and differing only in the relative position of two functional groups about a tetrazole ring, exhibit markedly different explosive properties. 2 is by far the more interesting. It is an energetic material possessing properties of both primary and secondary explosives. It exhibits a high sensitivity to mechanical impact, at least as high as many commonly used primary compositions, and a high sensitivity to electrical initiation. It will not, however, explode when ignited if unconfined, nor ignite merely by heating, but instead undergoes smooth thermal decomposition by what appears, from the DSC curves, to be a complex reaction.

The experiments reported here do not substantiate the conclusion drawn in previous reports (5,6) that 2 will burn to detonation even with a charge as large as 1.0 g, but a powerful explosion does occur. Detonation will occur when initiated by lead azide. The most disappointing aspect is that 2, when used as an initiating explosive, cannot cause even sensitive secondaries such as PETN, tetryl and RDX to detonate and this fact alone must put severe limitations on any practical uses. However, lead styphnate exhibits similar behaviour as an initiating explosive, and the ready ignition of 2 from hot wire or match head combined with its much lower sensitivity to electrostatic discharge than lead styphnate suggests that it could be a

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* The value of 45 mJ quoted in Figure 1, reference (10), seems to be in error.

possible replacement for this material in exploding devices. Another promising property of 2 is that explosion produces a large volume of gaseous products and it is a low melting purely organic compound; either might lead to specific future uses. Some stab sensitising ability is noted, but the enhancement is insufficient for practical application.

In comparison, although 1 has comparable mechanical sensitivity to 2, sensitivity to hot wire initiation is vastly lower. The results of Tarver et al. (6) give a more quantitative comparison; 2 will consistently initiate by capacitor discharge through nichrome wire using a 1.0 μF capacitor charged to 110 V (0.006 J) whereas 1 will initiate only 25% of the time when the capacitor is charged to 375 V (0.07 J). 1 also undergoes much slower thermal decomposition than 2, as evidenced from the DSC curves and the qualitative hot stage microscopy experiments. The reasons for these large differences are not immediately obvious; the suggestion (6) that hydrogen bonding between the methyl protons and the nitro group oxygens in 1, absent in 2 due to lack of spatial proximity, leads to enhanced stability seems highly unlikely. A more likely explanation is that the differing electron distribution in the tetrazole ring in 2 leads to significantly lower energy barriers for initiation than 1. This suggests that greater sensitivity to stimulae such as electrical and thermal shock represents an intrinsic feature of 2,5-substituted tetrazoles in comparison with their 1,5-substituted isomers. Clearly, a number of such systems would have to be prepared if this suggestion were to be further investigated.

The major drawbacks toward any projected use of 1 as an explosive, initiatory or otherwise, are its very low sensitivity to hot wire initiation plus low power output when initiated. There was, in addition, no indication that lead azide could initiate 1 to detonation and, even if a substantial booster could achieve detonation, the low melting point would be extremely unfavourable for fillings. No practical use of 1 can at this stage be envisaged.

5. EXPERIMENTAL

MATERIALS

1-Methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2) were prepared and purified as described previously (4). All other materials were commercially available. Lead azide was type RD1343, lead styphnate was type RD1303 and RDX was type RD1347. Reference to these three explosives in the text refers to these composition types only. PETN was type I.

SENSITIVITY MEASUREMENTS

The instruments used for Ball and Disc, Rotter Impact, the Electrostatic Spark Test and Temperature of Ignition measurements were constructed in this establishment to test specifications. Differential Scanning Calorimetry curves were recorded on a Perkin-Elmer DSC-1B under a flowing dry helium atmosphere, 20 cm^3/min, on aluminium pans using a scanning rate of 64°C/min. Sample sizes were approximately 0.5 mg.

MEASUREMENTS OF EXPLOSIVE PROPERTIES

(a) Initiation Using Match-Head Igniter

Experimental detonators were prepared by pressing weighed amounts of explosive into aluminium ICI detonator tubes, 5.57 mm i.d., using an Eltor press at a pressure of 90.7 MPa. A larger detonator was prepared by pressing 2 (1.0 g) in 0.2 g increments into a mild steel tube, 6.12 mm i.d., 9.47 mm o.d., at pressing pressure of 103.4 MPa.

The detonator tubes were then fitted with a match-head igniter and a brass witness block for the aluminium tubes and a brass plug for the steel tube, and fired remotely using an 18 V, 0.08 J capacitor discharge firing box.

(b) Initiation Using Hot Wire (Capacitor Discharge)

(i) Estimation of Initiating Ability of 1 and 2

Experimental detonators were prepared from detonator tubes constructed either of perspex or mild steel, 4.12 mm i.d., 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 platinum wire. A diagram of the entire assembly is shown in Figure 4 and photographs of perspex and mild steel detonators, unfilled, can be seen in Figures 3(a) and (b) respectively. Explosive charges were prepared by pressing weighed amounts of explosive into the detonator tubes using an Eltor press at 166 MPa pressure. Where two increments were used, the initiating charge was pressed first, then the secondary charge was added and pressed on top. The detonators prepared from 2 (400 mg) then RDX (100 mg) (Entry 10, Table 3) and lead azide (100 mg) and 2 (550 mg) (Entry 11, Table 4) were constructed from perspex tube, 5.57 mm i.d., to accommodate the larger mass, and pressed at 90.7 MPa.

Experimental firings were conducted from a capacitor discharge firing box, 18 V, 0.08 J; full details of the firing circuit are given in Figure 5(a) as circuit A.

(ii) Measurement of Function Times

Experimental detonators were prepared by pressing weighed amounts of 1 and 2 into 4.12 mm i.d. perspex tubes (Figure 4) at a pressure of 60.7 MPa. Cast charges were prepared by allowing pressed charges, prepared as above, to melt in an oven at 100°C and then cool slowly overnight. Charge lengths were measured with a depth gauge micrometer, taking the difference between filled and unfilled lengths. Lengths of cast charges were not measured owing to cavitation during cooling.

Experimental firings were conducted on a 282 V, 0.636 J firing circuit detailed in Figure 5(a) as circuit B. Ionisation probes, constructed from twisted enamelled copper wires, 0.41 mm diameter, inserted into a bakelite plug, 4.0 mm diameter, were fitted into the detonator tubes so that the plug was flush with the top of the charge. Details of the ionisation probe circuit are given in Figure 5(b). The function times were measured on a Hewlett-Packard 5302A Universal Counter in the time interval mode which was triggered by closing of the firing circuit and stopped by shorting the ionisation probe.

(c) Initiations Using Exploding Bridgewires

Experimental detonators were prepared by pressing 1 (400 mg) or 2 (350 mg) into 5.57 mm i.d. perspex detonator tubes fitted with a bridgewire device (Figure 4) at a pressure of 90.7 MPa. The respective densities were 1.75 g/cm^3 (1) and 1.77 g/cm^3 (2).

Firings were conducted on a high voltage capacitor discharge circuit using a 3000 V, 4.5 J output.

(d) Stab Sensitivity Measurements

Lead azide was mixed with finely powdered 1 and 2, 10% w/w, by brushing. Experimental detonators were made by pressing 100 mg of either lead azide or the 10% lead azide mixture with 1 or 2 into mild steel tubes, 3.2 mm i.d., 6.4 mm o.d., length 6.4 mm, using an Eltor press at 690 MPa pressure. The partly filled detonators were then back-filled with a pressing of lead monoxide (350 mg) at the same pressing load. Stab sensitivity was measured on an instrument designed and constructed in these laboratories (10) using a 200 g drop weight.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. Jenkins, J.M. and White, J.R. (1974). ERDE TR 172.

2. Gilligan, W.H. and Kamlet, M.J. (1976). NSWC/WOL/TR-76-146.

3. Bates, L.R. and Jenkins, J.M. (1976). ERDE TR 248. RESTRICTED.

4. Spear, R.J. (1979). MRL Report (Submitted).

5. von Herz, E. (1937). U.S. Patent 2,066,954.

6. Tarver, C.M., Goodale, T.C., Cowperthwaite, M. and Hill, M.E. (1977). "Structure/Property Correlations of Primary Explosives", Final Report 76-2 (Microfiche AD-A044 714).

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

8. Benson, F.R. (1967). In "Heterocyclic Compounds", (ed. R.D. Ederfield), vol. 8, chap. 1. New York: Wiley.

9. May, F.G.J. (1979). MRL (Unpublished results).

10. Bird, R. (1975). MRL Technical Note 362.

11. Spear, R.J. (1979). MRL (Unpublished results).

TABLE 1

MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY DATA FOR 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2)

Test	Result/Observation	
	1	2
Mechanical Sensitivity		
Ball and disc	No fires at 30 cm	No fires at 30 cm
Rotter F of I[a]	23 SD = 3.9 gas volume 12-27 cm^3, mean 23 cm^3	Recrystallised sample : 26 SD = 3.7 gas volume 20-27 cm^3, mean 25 cm^3 Sublimed sample : 22 SD = 1.2 gas volume 24-27 cm^3, mean 26 cm^3
Emery paper friction test[b]	Not performed	1.52 m/s 0/10 1.84 m/s 4/10 2.13 m/s 6/10 2.44 m/s 6/10
Electrostatic Sensitivity		
Electrostatic Spark Test	No ignitions at 4.5 J	Ignitions at 4.5 J No ignitions at 0.45 J
Thermal Sensitivity		
Temperature of Ignition	Did not ignite, volatilised 235-260°C	Did not ignite, volatilised 235-260°C
Qualitative Tests		
Drop on to hot plate at 300°C	Bubbles vigorously with slight evolution of smoke	Bubbles vigorously with slight evolution of smoke
Burn on filter paper	Burns with a yellow smoky flame, no explosion	Burns with a yellow smoky flame, no explosion

[a] Sample size 27 mg, 2 kg weight, drop heights varied from 30-110 cm. F of I relative to RDX = 80

[b] Data from Ref. 3, converted from the original ft/s.

TABLE 2

EXPLOSIVE DATA FOR PRESSED CHARGES OF 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2) INITIATED BY MATCH-HEAD IGNITER

Explosive	Mass (mg)	Witness Block	Result/Observation
1	125 [a]	-	Match-head ejected, tube not split.
1	250 [a]	brass	Tube casing split, witness block not dented.
2	125 [a]	brass	Tube fragmented into several pieces, no indentation of witness block.
Lead azide	125 [a]	brass	Tube fragmented into many pieces. Witness block dented and cratered.
2	1000 [b]	brass	Tube fragmented into many pieces but witness block not dented or cratered.

[a] Aluminium ICI detonator tubes, 5.57 mm i.d., pressing pressure 90.7 MPa

[b] Mild steel detonator tube, 6.12 mm i.d., 9.47 mm o.d., pressing pressure 103.4 MPa

TABLE 3

EXPLOSIVE DATA FOR 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2) PRESSED INTO PERSPEX TUBES [a] AND INITIATED BY CAPACITOR DISCHARGE [b]

Entry	Explosive Filling [c]		Witness Block	Result/Observation
	Initiating Charge (mg)	Secondary Filling (mg)		
1	1 (50)	-	-	No sound, charge undisturbed.
2	1 (100)	-	brass	No sound, charge pushed to top of tube, appears to be some thermal decomposition near bridgewire.
3	2 (50)	-	-	Loud noise, shattering of perspex tube.
4	2 (225)	-	brass	Loud noise, no indentation of witness block.
5	2 (50)	Lead azide (100)	brass	Cratering on witness block typical of primary explosive detonation.
6	2 (50)	RDX (100)	brass	Slight indentation on witness block.
7	2 (50)	RDX (225)	brass	No indentation on witness block, still appears to have unchanged RDX adhering to it.
8	2 (100)	RDX (100)	brass	No indentation on witness block.
9	2 (200)	RDX (75)	brass	No indentation on witness block.
10	2 (400) [d]	RDX (100)	brass	No indentation on witness block.
11	2 (50)	Tetryl (100)	brass	No indentation on witness block, still appears to have unchanged tetryl adhering to it.
12	2 (100)	Tetryl (100)	brass	As preceding entry.

TABLE 3

(Continued)

Entry	Explosive Filling [c]		Witness Block	Result/Observation
	Initiating Charge (mg)	Secondary Filling (mg)		
13	2 (50)	PETN (100)	brass	No identation on witness block.
14	2 (100)	PETN (100)	brass	Indentation on witness block. Repetition gave a smaller indentation. Neither approached the cratering typical of detonation of secondary explosives.
15	2 (50)	Lead monoxide (150)	brass	Indentation on witness block.
16	2 (100)	Lead monoxide (150)	brass	Slight indentation on witness block. Repeat experiment gave no indentation (two repeats).

a 4.12 mm i.d.

b 18 V, 0.08 J, discharged through 0.038 mm platinum bridgewire

c Pressing pressure = 166 MPa

d 5.57 mm i.d. tube, pressing pressure = 90.7 MPa.

TABLE 4

EXPERIMENTS DESIGNED TO INITIATE PRESSED [a] 2-METHYL-5-NITROTETRAZOLE (2) TO DETONATE UNDER HEAVY CONFINEMENT OR BY INITIATION FROM PRIMARY EXPLOSIVES

Experiment [b]	Result/Observation
1. Perspex tube, filling 2 (100 mg) then RDX (100 mg), brass plug wedged tightly in end.	Perspex tube shattered, plug undamaged, still appears to have unreacted RDX adhering.
2. Steel tube, filling 2 (100 mg) then lead azide (100 mg), brass witness block.	Witness block cratered, typical of primary explosive detonation. Steel tube scarred inside and outside cracked.
3. Steel tube, filling 2 (100 mg) then RDX (100 mg), brass witness block.	Witness block dented but not cratered. Steel tube essentially unaffected except for ejection of bridgewire device.
4. Steel tube, filling lead azide (100 mg) then RDX (100 mg), brass witness block.	Witness block severely cratered. Steel tube split into two pieces and severely distorted.
5. Steel tube,filling 2 (100 mg) then PETN (150 mg).	Witness block dented but not cratered. Steel tube flared at top but not split.
6. Brass tube, 4.12 mm i.d., 5.50 mm o.d., filled with 2 (100 mg) then RDX (60 mg) fitted with a glass to metal sealed bridgewire igniter, and the tube then sealed inside a brass block, 5.57 mm i.d., 17.8 mm o.d., length 20.0 mm.	Brass tube ejected, enlarged in diameter and badly flared. Brass block essentially unaffected, unreacted RDX can clearly be seen inside.
7. Brass tube as entry 6, filled with 2 (100 mg) then RDX (60 mg), brass witness block.	Tube split into two but witness block not dented.
8. Steel tube, filling lead styphnate (100 mg) then 2 (100 mg), brass witness block.	Tube undamaged apart from ejection of bridgewire device. Witness block dented but not cratered.
9. Steel tube, filling lead styphnate (100 mg) then lead azide (100 mg), brass witness block.	Tube scarred on the inside but not split. Witness block cratered typical of detonation.

TABLE 4

(Continued)

Experiment [b]	Result/Observation
10. Perspex tube, filling lead azide (100 mg) then 2 (250 mg), brass witness block.	Witness block dented, slight cratering.
11. Perspex tube [c], filling lead azide (100 mg) then 2 (550 mg), brass witness block.	Witness block cratered, typical of detonation.
12. Perspex tube, filling lead azide (100 mg) then 1 (265 mg), brass witness block.	Witness block not dented.

[a] Perspex, mild steel and brass tubes, 4.12 mm i.d., pressed at 166 MPa.

[b] Full details are given in the Experimental Section.

[c] 5.57 mm i.d., pressed at 90.7 MPa.

TABLE 5

QUANTITATIVE MEASUREMENTS OF FUNCTION TIMES FOR PRESSED CHARGES [a] OF 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2)

Isomer	Mass (mg)	Length (mm)	Density (g/cm^3)[b]	Function Time (μs)
1	25	1.20	1.56	Fail. Charge blown out but perspex holder intact. Probe not triggered.
1	50	2.56	1.47	As preceding entry.
1	100	4.80	1.56	20.25
1	100	4.79	1.57	197.0
1	150	7.64	1.47	702.5
2	25	1.27	1.48	Fail. Charge blown out but perspex holder intact. Probe not triggered.
2	50	2.57	1.46	34.4
2	75	3.72	1.51	43.4
2	100	4.82	1.56	443.9
2	100	5.05	1.49	642.9
2	125	6.11	1.53	37.2
2	150	7.40	1.52	5334.9
2	150	7.52	1.50	67.8
2	175	8.71	1.51	42.7
2	200	10.00	1.50	5305.0

[a] Pressing pressure = 60.7 MPa. Tubes i.d. = 4.12 mm.

[b] Average density : 1, 1.52 g/cm^3, 2, 1.51 g/cm^3.

TABLE 6

QUANTITATIVE MEASUREMENTS OF FUNCTION TIMES FOR CAST CHARGES [a] OF 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2)

Isomer	Mass (mg) [b]	Function Time (μs)
1	26	Fail. Some thermal decomposition of charge occurred as evidenced by bubbles near bridgewire, otherwise charge undisturbed.
1	50	As preceding entry.
1	100	As preceding entry.
1	150	As preceding entry.
2	26	8000
2	50	17.8
2	75	38.4
2	100	22.2
2	125	2507
2	150	18983

[a] Full details of casting procedure are given in the Experimental Section.

[b] Lengths of charges were not measured due to cavitation.

TABLE 7

MEASUREMENT [a] OF STAB SENSITIVITY OF LEAD AZIDE AND COMPOSITIONS PREPARED BY ADMIXTURE WITH 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2)

Drop Height (cm)	Explosive Material		
	Lead Azide	Lead Azide/1 (10:1)	Lead Azide/2 (10:1)
50.8	2/2	1/1	1/1
44.5	0/1		
38.1	0/1	1/1	
25.4	0/1	2/4	1/1
12.7		0/1	1/1
10.2			0/1
7.6			0/1
Stab Sensitivity (approx)	980 mJ	490 mJ	245 mJ

[a] 200 g drop weight. Full experimental details are given in Section 5.

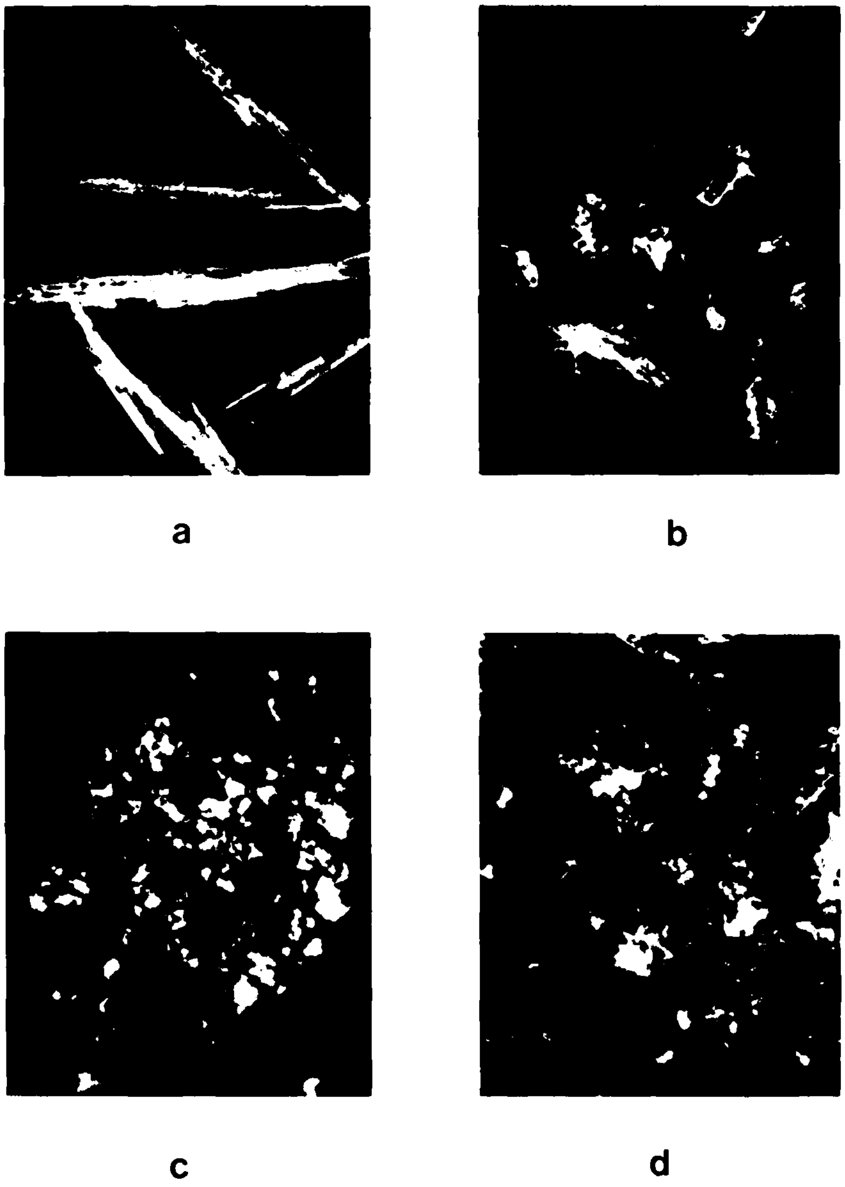

FIG. 1 - Photomicrographs of crystals of 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2), magnification x 7.5.

(a) 1, recrystallised as long needles.

(b) 1, recrystallised sample partially crushed.

(c) 2, recrystallised as fairly uniform clustered platelets.

(d) 2, sublimed as irregular platelets.

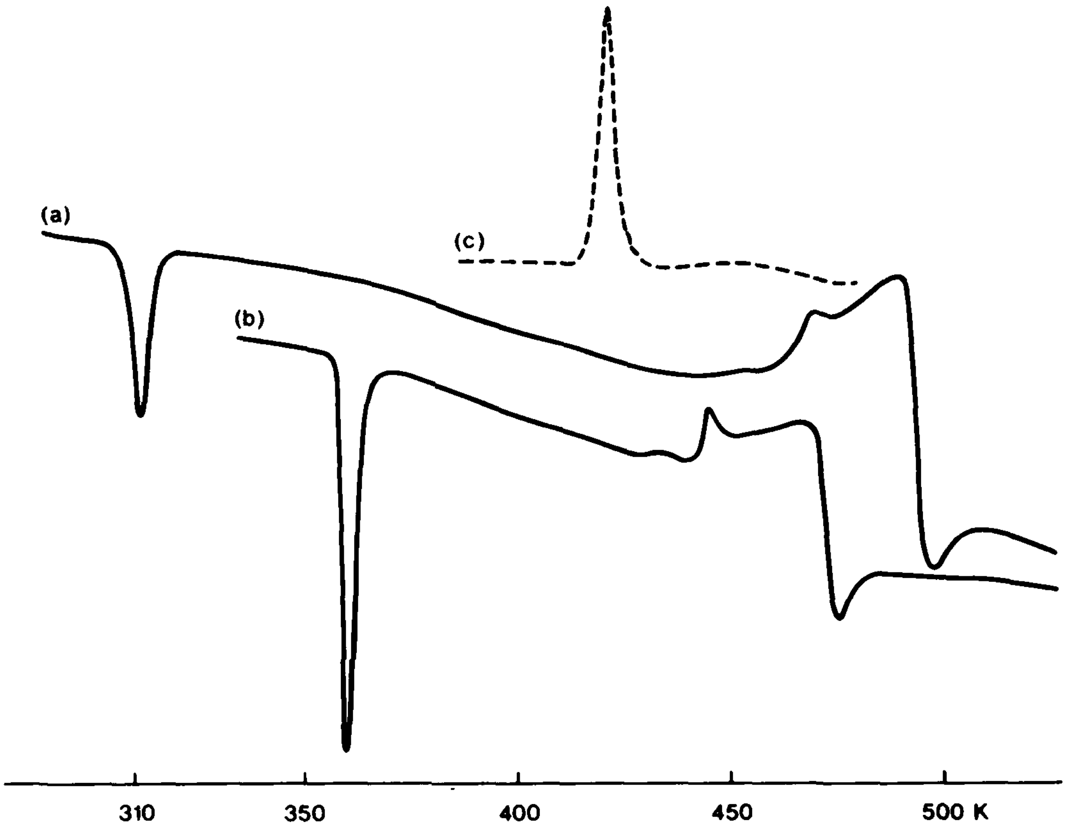

FIG. 2 - DSC curves recorded under flowing dry helium atmosphere using a scan rate of 64°C/min.

(a) 1-methyl-5-nitrotetrazole, 0.475 mg.

(b) 2-methyl-5-nitrotetrazole, 0.475 mg.

(c) (dotted line) tetrazene, 0.975 mg (data from Ref. 9).

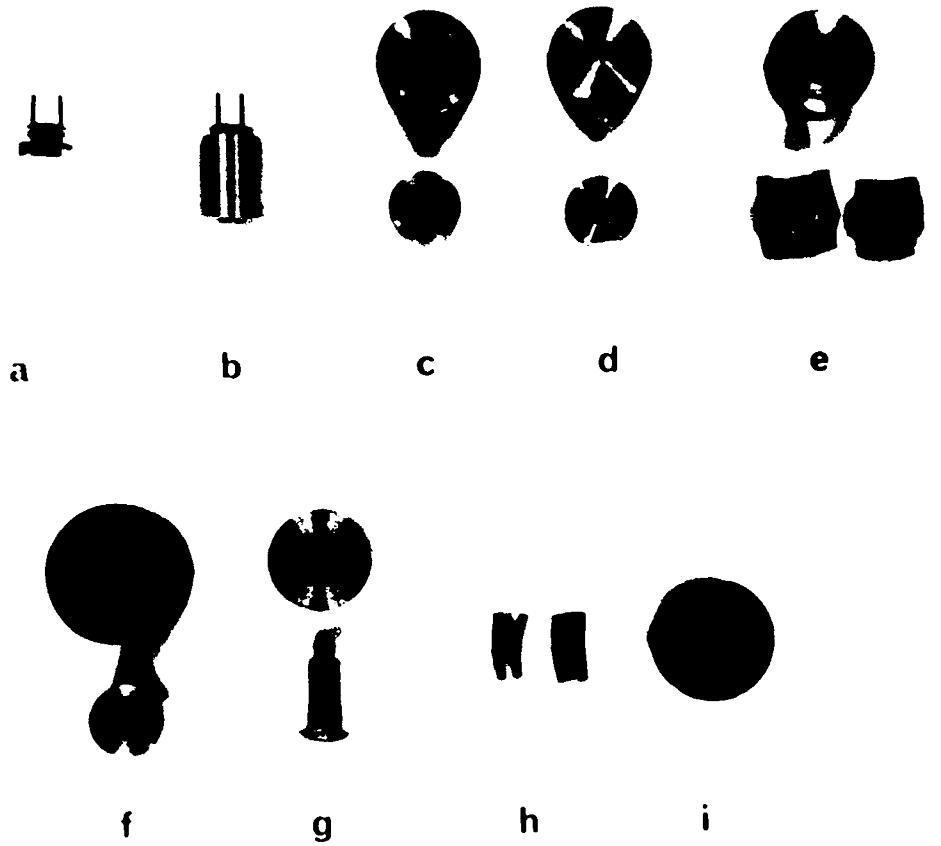

FIG. 3 - Test pieces from experimental firings of 2-methyl-5-nitrotetrazole (2). The corresponding entry in Table 4 is indicated below.

(a) Perspex detonator tube, 4.12 mm i.d., with bridgewire device, unfilled.

(b) Mild steel detonator tube, 4.12 mm i.d., with bridgewire device, unfilled.

(c-f) Brass witness block and mild steel detonator tube after firing of the following pressed charges; the order refers to the order of increment in the filling

(c) 2 (100 mg), lead azide (100 mg) (Entry 2).

(d) 2 (100 mg), RDX (100 mg) (Entry 3).

(e) Lead azide (100 mg), RDX (100 mg) (Entry 4).

(f) 2 (100 mg), PETN (150 mg) (Entry 5).

(g) Brass detonator tube and brass block, tube filled with 2 (100 mg) then RDX (60 mg) (Entry 6).

(h) Brass detonator tube filled with 2 (100 mg) and RDX (60 mg) (Entry 7).

(i) Brass witness block from perspex detonator tube, 5.57 mm i.d., filled with lead azide (100 mg) then 2 (550 mg) (Entry 11).

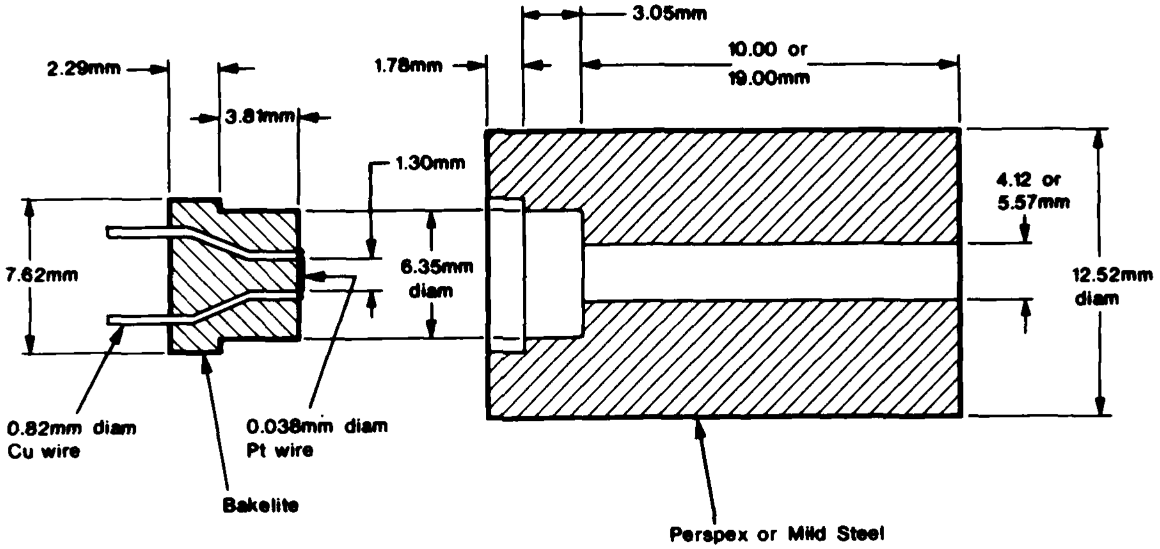

FIG. 4 - Schematic diagram of detonator tube and bridgewire device assembly used in experimental detonators.

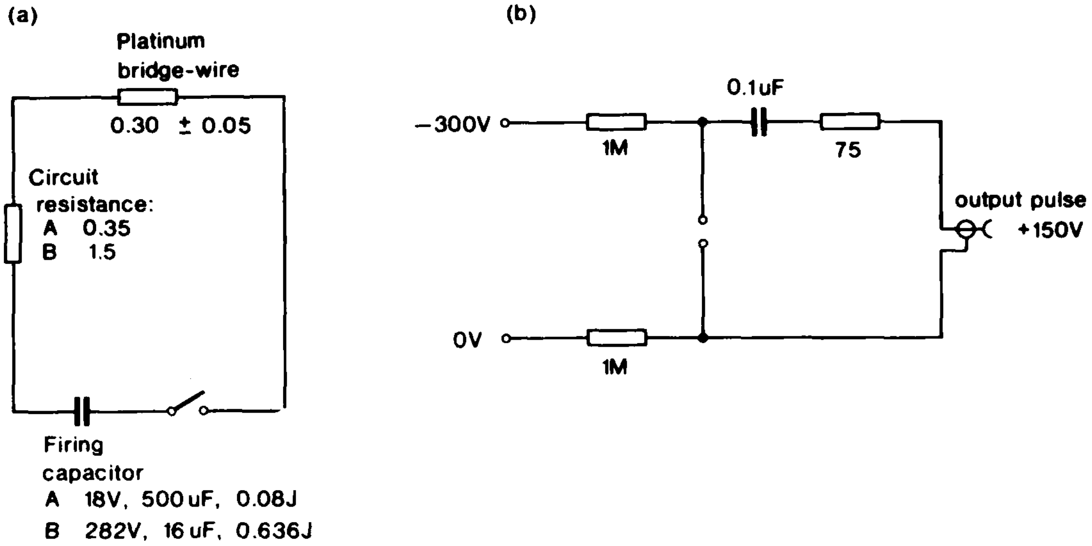

FIG. 5 - (a) Firing circuits used in experimental capacitor discharge firings.

A. Low voltage firing unit employed for firings designed to estimate the initiating ability of <u>1</u> and <u>2</u> (results in Tables 3 and 4).

B. Medium voltage firing unit employed for measurements of function times (results in Tables 5 and 6).

(b) Ionisation probe circuit used in conjunction with firing circuit B (above) for measurement of function times.

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