Lead-Free Initiator Materials for Small Electro-Explosive Devices for Medium Caliber Munitions: Final Report 04 June 2003

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Executive summary

Concerns over the hazard to health of using lead-containing initiatory compounds, both in their manufacture and use, has led to investigations on both sides of the Atlantic to identify suitable compounds, either known or novel and free of lead and other heavy metals, which could be used as replacements. Such compounds, broadly subdivided into those similar to lead azide (i.e. detonants) and those similar to lead styphnate (primary explosives), should possess similar characteristics (sensitiveness, explosiveness, stability etc.) to the particular compound they were required to replace. A survey report, based on open literature available world-wide and certain UK classified information, was published by QinetiQ in 1998 and identified twenty front-running candidate compounds.

Work has been progressed with funding from US SERDP (Strategic Environmental Research & Development Program) under the pollution prevention programme, where the synthesis and preliminary evaluation of eight of the front-running compounds, four similar to lead azide and four similar to lead styphnate, was undertaken.

In this work, of 12 months' duration, sufficient hazard and functional data were obtained to enable an assessment to be made with recommendations for compounds in the detonant category to be put forward for larger scale testing and ultimate incorporation into medium-large caliber ordnance systems. The two suitable candidates in the detonant category were both silver salts. In the primary explosive (i.e. lead styphnate replacement) category all of the candidates had shortcomings resulting in a need for further work to be done (see below).

Suggestions are made for future work in this area. The two lead azide replacement (i.e. detonant) candidates will be assessed rigorously for their environmental acceptability. From this assessment a recommendation as to whether they, or alternative candidates, are suitable for DoD use will be made and it is proposed that the successful candidates will enter a development phase where their formulation and functional testing will be studied. In the lead styphnate replacement (primary explosive) category further candidates are suggested which it is anticipated will overcome the shortcomings of the compounds studied here and be suitable to meet DoD requirements.

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1 Project Background

1.1 This work addressed the requirement to develop new explosive materials to replace lead azide and lead styphnate in detonators outlined in BAA Announcement, July 30, 2001, US Army Corps of Engineers, Humphreys Engineering Center Support Activity, SON Number: PPSON-02-07. A copy of the technical sections (objective, expected payoff and background) of this SON appears at Annex 1, and the project Fact Sheet is shown at Annex 2. Reference should be made to both these documents for further details of the project.

1.2 In essence, the project focussed on synthesizing and characterizing up to eight (8) replacement compounds for lead azide and lead styphnate, and as such, responded to the SON by putting forward for consideration new initiatory type compounds that possess the following desirable attributes:

1) They do not contain lead or other heavy metals known to be toxic.
2) The routes employed for their synthesis are anticipated to be adaptable in such a way that the use of toxic and/or carcinogenic materials in their manufacture may be avoided.

1.3 These compounds will nevertheless function in a similar way to the traditional compounds, displaying equivalent release of energy on application of a prescribed stimulus (in this case electrical discharge), and also resistance to environmental effects (temperature, humidity, compatibility with other chemicals present etc.).

1.4 The project was innovative in nature and yielded the data necessary to reduce inherent technical risks and prove the technical concept for replacement compounds for these lead-based initiators. QinetiQ has proposed additional phases of research with a U.S. or Canadian device manufacturer, as indicated in Section 7, to produce electro-explosive devices (EEDs) based on those compounds that satisfy the necessary performance, stability and cost criteria.

2 Objective of Project

2.1 The project focussed on synthesizing and characterizing, in two strands, up to eight (8) compounds (four possible replacements for lead azide and four possible replacements for lead styphnate). QinetiQ selected these compounds for their potential (e.g., performance - sensitiveness (F of I, $h_{50\%}$) and power (P_{CJ}) and stability - vacuum stability DSC, temperature of explosion) and from past experience in this area.

2.2 The program has two strands:

2.2.1 Strand 1: In the area of lead azide replacements, the synthesis and characterization of the following compounds was proposed (most desirable listed first; structures in Fig. 1):

Silver salt of 5-nitro-(*1H*)-tetrazole (CN_5O_2Ag, **I**)

Dinitroacetonitrile monopotassium salt ($C_2N_3O_4K$, **II**)

Ethylenedinitramine monocopper salt ($C_2H_4N_4O_4Cu$, **III**)

Silver azide (N_3Ag, **IV**).

These compounds have also been assessed on relative ease of synthesis (i.e. accessible and relatively cheap precursors).

2.2.2 Strand 2: As lead styphnate replacements, the synthesis and characterization of the following compounds was proposed (most desirable listed first):

5,5'-Hydrazodi-(*1H*)-tetrazole ($C_2H_4N_{10}$, **V**)

Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide ($C_6H_3N_4O_6K$, **VI)**

5-Picrylaminotetrazole ($C_7H_4N_8O_6$, **VII**)

5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate ($C_4H_{14}N_{16}O_7$, **VIII**)

It is believed that these candidates offer a combination of superior thermal stability (all stable at 200°C or above, with the possible exception of **VIII**) and ease of synthesis.

2.3 All products were subjected to small-scale hazard and thermal stability testing in accordance with the relevant NATO STANAG.

3 Technical Approach

3.1 Background

3.1.1 Introduction

3.1.1.1 A current aim in the science of initiators for explosive devices, both in the U.K. and the U.S., is the elimination of lead and other toxic heavy metals from the compositions required for these devices [1]. Constituents of compositions initiated by both mechanical action (e.g. stab-sensitive) and other means (e.g. flash-receptive compositions) [2] are surveyed. Applications of particular interest are devices used in small-arms and medium caliber ammunition, where volatilized heavy metals in the atmosphere can pose a health hazard for operatives under conditions of poor ventilation (e.g. in indoor practice ranges or self-propelled artillery pieces). Reduction of exposure to toxic heavy metals during manufacturing of initiator compounds is another aim of the project.

3.1.1.2 The objective of this project was a compilation of alternative compounds to lead azide or lead styphnate for use in initiator systems such as those mentioned above, primarily those which operate in the flash receptive mode. An over-riding criterion for the compounds was that they should be free of heavy metals in order to satisfy environmental requirements; for this purpose such metals are defined as those below the second row of the transition series (or the equivalent positions in the alkali metals or alkaline earths). Thus the following metals are excluded: Pb, Hg, Tl, Bi and Ba (but not Ag, Cd, Sr etc., though Cd is considered undesirable on account of its high toxicity).

3.1.1.3 Compounds are subdivided into three main classes:

a) Wholly inorganic compounds.
b) Metal derivatives of organic compounds: salts, organometallics etc.
c) Wholly organic compounds.

3.1.1.4 In general, detonant compounds (i.e. lead azide replacements) would be expected to fall into categories a) or b) (for reasons given below – see Section 3.1.2), while flash receptive initiators (i.e. lead styphnate replacements) would be in categories b) or c). The greatest benefit for low pollution initiatory devices would be gained if wholly organic compounds could be used in these applications (i.e. metals are completely absent).

3.1.1.5 Some mention should first be made of necessary attributes required by compounds to function effectively as initiators, which are not obvious at first sight. These important attributes are explained in Section 3.1.2 and are used in the selection process (see “Selection of Candidates”, Section 3.1.3). In the interests of brevity, full details of the candidates selected, using the selection criteria adopted (see “Initiator Criteria”, Section 3.1.2), are not given here but are recorded elsewhere [1]. For the purposes of the present report, attention is focussed on the eight candidates selected as lead azide and lead styphnate replacements.

3.1.2 Initiator Criteria

3.1.2.1 It is not intended to explain here the underlying science governing the operation of disruptive initiator compounds, as this has been adequately described elsewhere [3-7], but instead to focus attention on some crucial differences in the requirements for initiator compounds as opposed to high explosive (HE) main charges.

3.1.2.2 While the performance of HE compounds for a given application (e.g. metal-moving) can be fairly readily predicted from detonation parameters, particularly P_{CJ}, derived from relatively easily calculated or measured physical and thermodynamic data, the behavior of energetic compounds in the initiatory environment is much less well understood. Notably, the processes which occur as initial decomposition at a molecular level, instigated by an event such as mechanical impact/friction or by flash, develops into a detonation are not clearly understood [4,8].

3.1.2.3 The consequence of this lack of understanding is that it is difficult to predict, *a priori*, which compounds would make good initiators (or even function in this role at all). However, a few rules of thumb are fairly well established which allow some useful structural correlations to be made, and these are as follows:-

i) In general, the types of molecules having good initiatory behavior possess relatively simple structures (this assists the run up to detonation process).
ii) Conversely, molecules with complex structures, e.g. polycyclic compounds, are unlikely to function well as initiators (i.e. do not run up quickly to detonation).
iii) A high oxygen balance is not required - indeed some of the best initiatory compounds contain no oxygen at all!
iv) Certain molecular groupings are generally advantageous, e.g. multiple N-N bonds (as in azide, tetrazole etc.).

3.1.2.4 These attributes, together with the constraints on chemical constitution mentioned above, are now used in the selection of suitable candidate compounds as lead-free initiators (see below).

3.1.3 Selection of Candidates

3.1.3.1 Compounds are subdivided into three main classes:

a) Wholly inorganic compounds.
b) Metal derivatives of organic compounds: salts, organometallics etc.
c) Wholly organic compounds.

3.1.3.2 The following selection criteria were adopted, in order to generate a listing of manageable proportions:

i) Compounds containing proscribed elements (see Section 1.2) were excluded.
ii) Excessively sensitive, and also excessively insensitive compounds were excluded.

iii) Compounds which are unstable (heat, light, hydrolysis etc.) were excluded.
iv) Insufficiently powerful compounds were excluded.

3.1.3.3 Thus, criterion ii) was defined as follows: on the U.S. sensitivity scale (BRL), compounds with $h_{50\%}$ figures <10 cm or >45 cm were excluded, while compounds with U.K. F of I figures lying outside a range of 10 to 30 were disregarded. For criterion iii), a temperature of explosion of >175°C was required, and melting point >=150°C. The power criterion was more difficult to define and considerations previously discussed (see Section 3.1.2, above) were applied.

3.1.4 Literature Sources

3.1.4.1 Few up-to-date texts were available to facilitate the search: the early survey by Davis [9] and more recent (i.e. 1960s/70s) works by Urbanski [10] and Roth [2] cover the subject of initiators comprehensively but are heavily biased towards the use of heavy metal salts, i.e. compounds containing proscribed elements, particularly lead. The same consideration applies to Urbanski's update of the 1980s [11]. A different approach is taken in the book by Benson [12], where some purely organic materials of high nitrogen content are described, and of course the chemistry of azides and compounds derived from them (e.g. tetrazoles) is amply covered in the organic chemistry literature [13-15]. Specialist texts on tetrazoles are also available [16,17].

3.1.4.2 A number of internal publications and conference proceedings were of more relevance - these included the proceedings of an international conference held in the 1970s [18], technical reports by Haskins and others [4,5,19], and presented papers by Bates [20], Fronabarger [21] and McGuinness [22]; the last three cited articles are concerned with tetrazole chemistry. A series of reports and papers by Spear *et al*. in the early 1980s [23-27] is also of value, including work on benzofuroxans, as does a patent of Norris [28]. Finally, some recent work by Trudell [29-38] on other heterocyclic compounds merits attention.

3.1.4.3 Because of the wide distribution of information on initiators across the chemical and technical literature, a more concentrated source of data was sought, preferably where the information is presented in tabular form to assist comparison. Such sources were found in two specialized databases, the first and most comprehensive dating from the early 1960s [39] in which over 4,000 compounds from the whole spectrum of energetic materials are compiled. The second database [40], although more up-to-date, contained fewer references to initiators but was nevertheless useful. In addition, a keyword search was made of the general chemical database CASonline (Chemical Abstracts Service), whereby several articles (post-1975) were retrieved.

3.2 Methods

3.2.1 Selection of Lead-Free Initiator Candidates

3.2.1.1 A range of several hundred compounds identified from the sources above were put through a selection process described more fully elsewhere [1] to generate a selection of eight candidate compounds, four of which had lead azide-like properties and four of which had lead styphnate-like properties. These are now presented, subdivided as mentioned above, i.e.:

a) Wholly inorganic compounds.

b) Metal derivatives of organic compounds: salts, organometallics etc.

c) Wholly organic compounds.

3.2.1.2 Comments on the explosive properties of the compounds follow, and their categorization into lead azide-like or lead styphnate-like materials is shown in Table 1. The synthesis of the compounds is considered subsequently (see “Synthesis of Lead-Free Initiator Candidates”, Section 3.2.2).

3.2.1.3 In the inorganic compound category (a, above), of ten compounds originally put on the short list, only one – silver azide (**IV**) – satisfied both the rigorous selection criteria according to physical properties *and* the criteria of being easy to synthesize. Silver azide has already been recommended as a lead azide replacement, being markedly more stable to hydrolysis [41], and it should be seriously considered. Methods of sensitizing the compound to stab initiation have been described [42], and its reported [41] incompatibility with tetrazene should not be a problem with modern formulations.

3.2.1.4 Metal derivatives of organic compounds, including Meisenheimer complexes (products from the reaction or nitroaromatics with bases), comprised the largest category of candidates from the selection process, with four potential candidates selected (from a pre-selection of 27 candidates). These were:

i) Silver 5-nitrotetrazolate (**I**);

ii) The potassium salt of dinitroacetonitrile (**II**);

iii) The copper salt of ethylenedinitramine (**III**);

iv) The potassium salt (Meisenheimer complex) of 4-hydroxy-5,7-dinitrobenzofurazanide (**VI**).

3.2.1.5 Silver 5-nitrotetrazolate (**I**) [41] is the front-running candidate in this category, offering an optimum combination of high thermal stability (T_{exp} 340°C) and ease of synthesis (see below); the only possible drawback is the compound’s proneness to dead pressing [20]. Another highly promising candidate is the potassium salt of dinitroacetonitrile (**II**) [43] for which the only potential problem appears to be a variability in its impact sensitiveness (US $h_{50\%}$ figure 16-31 cm), indicating that there might be handling problems (although the lower figure is still acceptable). The detonation properties of this compound were also modeled [44]. Little data were available on the copper salt of ethylenedinitramine (**III**), save that its synthesis was reported in the 1940s [45], but it demonstrates high thermal stability (T_{exp} 350°C) and has the advantage of relative ease of synthesis (see below). The potassium salt (Meisenheimer complex) of 4-hydroxy-5,7-dinitrobenzofurazanide (**VI**) [27] is the most thermally stable of the Meisenheimer complexes of this type and was selected for this reason; its more complex synthesis could mitigate against it as a candidate for the final selection.

3.2.1.6 Finally, from the wholly organic compounds, a short list of twenty compounds was generated from which the following three were selected:

i) 5,5’-Hydrazodi-*1H*-tetrazole (**V**);

ii) Picrylaminotetrazole (**VII**);

iii) Guanylaminotetrazolium nitrate (**VIII**).

3.2.1.7 5,5'-Hydrazodi-*1H*-tetrazole (**V**) [46] showed the highest thermal stability of the compounds in the short list, and its detonation properties were modeled [44]. The calculated P_{CJ} came out at 401 kbar, based on a theoretical maximum density of 1.85 gcm^{-3}, suggesting that the compound will possess adequate power for the initiatory role. Thus of these compounds it would appear to be a front runner.

3.2.1.8 Picrylaminotetrazole (**VII**) [47], although not as thermally stable as **V**, nevertheless has a high density (1.91 gcm^{-3}) and should be considered as a candidate. Finally, 5-(guanylamino)tetrazolium nitrate monohydrate (**VIII**) [48,49] is a compound which, although exhibiting lower power output on account of its relatively low density (1.58 gcm^{-3}) nevertheless benefits from its ease of synthesis and relatively good thermal stability (for an organic initiator).

3.2.2 Synthesis of Lead-Free Initiator Candidates (Proposed)

3.2.2.1 The synthetic program, which forms the backbone of this research project, entails the synthesis, in sufficient quantity for preliminary evaluation, of the eight target compounds listed above and shown in Table 1 (structures shown in Figure 1). Where possible, cleaner organic chemistry techniques were employed in the syntheses, which will be suitable for cost-effective and environmentally friendly scale-up.

3.2.2.2 As an adjunct to the above activities, the compounds were fully characterized using modern analytical techniques – as appropriate: high field NMR, mass spectrometry, thermal behavior (differential scanning calorimetry and/or heat flow calorimetry).

3.2.2.3 The fully characterized products were assessed for hazard, with measurement of impact (F of I, Rotter or Ball and disc apparatus) and friction (Emery friction test apparatus) sensitiveness, electrostatic spark discharge (ESD) sensitivity, and temperature of ignition (T of I). These tests were carried out in accordance with the relevant NATO STANAG.

3.2.2.4 Concerning the syntheses of individual compounds, QinetiQ has based syntheses upon known methodologies with substitution of environmentally unfriendly precursors (e.g. toxic/carcinogenic solvents such as carbon tetrachloride, benzene etc.) with environmentally benign alternatives wherever possible. Thus the planned synthesis of the compounds was as follows:

i) Silver nitrotetrazolate (**I**) from 5-aminotetrazole monohydrate in two steps (via sodium nitrotetrazolate intermediate);

ii) Potassium dinitroacetonitrile salt (**II**): by a method yet to be determined;

iii) Ethylenedinitramine (EDNA) monocopper salt (**III**) from 2-imidazolidone in three steps (nitration/hydrolysis/salt formation);

iv) Silver azide (**IV**) in one step from sodium azide;

v) 5,5-Hydrazoditetrazole (**V**) in two steps from 5-aminotetrazole monohydrate;

vi) Potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (**VI**) in four steps from picryl chloride (via 4,6-dinitrobenzofuroxan)*;

vii) 5-Picrylaminotetrazole (**VII**) in one step from 5-aminotetrazole monohydrate and picryl chloride

viii) 5-Guanylaminotetrazolium nitrate monohydrate (**VIII**) in three steps from calcium cyanamide and 5-aminotetrazole monohydrate.

*In the event that **VI** is judged to be insufficiently powerful, an alternative compound – the potassium salt of 7-hydroxyamino-4,6-dinitro-4,7-dihydrobenzofuroxanide ($C_6H_4N_5O_7K$) – will be substituted.

4 Summary of Project Deliverables

4.1 CLIN 0001 AA

4.1.1 Synthesis and preliminary characterization of 2 lead azide and 2 lead styphnate replacement compounds.

4.1.2 Deliverable: Report on the synthesis and characterization of silver azide, silver 5-nitrotetrazolate, 5-picrylaminotetrazole and 5,5'-hydrazo-(1H)-tetrazole. Submit monthly reports tracking work progress and costs expended.

4.2 CLIN 0001 AB

4.2.1 Synthesis and preliminary characterization of 1 lead azide and 1 lead styphnate replacement compounds.

4.2.2 Deliverable: Report on the synthesis and characterization of ethylenedinitramine monocopper salt and 5-(guanylamino)tetrazolium nitrate, and the hazard characterization of the compounds mentioned in CLIN 0001 AA. Submit monthly reports tracking work progress and costs expended.

4.3 CLIN 0001 AC

4.3.1 Synthesis and preliminary characterization of 1 lead azide and 1 lead styphnate replacement compounds.

4.3.2 Deliverable: Report on the synthesis and characterization of dinitroacetonitrile monopotassium salt and potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide and the hazard characterization of the compounds mentioned in CLIN 0001 AB. Submit monthly reports tracking work progress and costs expended.

4.4 CLIN 0001AD

4.4.1 Final report. Deliverable: Report on the synthesis, characterization and hazard characterization of all compounds mentioned in CLIN 0001 AA-AC. Submit final month report tracking work progress and costs expended.

5 Project Accomplishments

5.1 Objectives

5.1.1 The project focussed on synthesizing and characterizing, in two strands, up to eight (8) compounds (four possible replacements for lead azide and four possible replacements for lead styphnate):

5.1.2 Strand 1: In the area of lead azide replacements, the synthesis and characterization of the following compounds was investigated (most desirable listed first; structures in Fig. 1):

Silver salt of 5-nitro-(*1H*)-tetrazole (CN_5O_2Ag, **I**)

Dinitroacetonitrile monopotassium salt ($C_2N_3O_4K$, **II**)

Ethylenedinitramine monocopper salt ($C_2H_4N_4O_4Cu$, **III**)

Silver azide (N_3Ag, **IV**).

5.1.3 Strand 2: As lead styphnate replacements, the synthesis and characterization of the following compounds was investigated (most desirable listed first):

5,5'-Hydrazodi-(*1H*)-tetrazole ($C_2H_4N_{10}$, **V**)

Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide ($C_6H_3N_4O_6K$, **VI)**

5-Picrylaminotetrazole ($C_7H_4N_8O_6$, **VII**)

5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate ($C_4H_{14}N_{16}O_7$, **VIII**)

5.1.4 Those compounds successfully synthesized, or acquired, were assessed for their utility in the respective initiatory roles by the procedures described below (Section 5.3).

5.2 Summary of Procedures

5.2.1 The chemical synthesis program, which forms the backbone of this research project, entails the synthesis, in sufficient quantity for preliminary evaluation, of the eight target compounds listed in Section 3.2.2 and shown in Table 1 (structures shown in Fig. 1).

5.2.2 The compounds were fully characterized using modern analytical techniques – as appropriate: high field NMR, elemental analysis, and thermal behavior (differential scanning calorimetry).

5.2.3 The fully characterized products were then assessed for hazard, with measurement of impact (F of I, Rotter apparatus or Ball-and-Disc test) and friction (Emery test apparatus) sensitiveness, electrostatic spark discharge (ESD) sensitiveness, and temperature of ignition (T of I). These tests were carried out in accordance with the relevant NATO STANAG.

5.2.4 The properties of the compounds tested are reported (Section 5.5) and recommendations are made as to their suitability for the proposed applications (i.e. as lead azide or as lead styphnate replacements).

5.3 Procedures: Synthesis

5.3.1 Lead Azide Replacements

N.B. The compounds are discussed in the order in which they were synthesized or otherwise procured (see Section 5.5 below), which differs somewhat from the order given in Section 2.

5.3.1.1 Silver azide (IV)

The compound is preparable by the double decomposition reaction of sodium azide and silver nitrate (Equation 1) [50]:

$$NaN_3 + AgNO_3 \text{ ----------> } AgN_3 + NaNO_3 \qquad \text{Equation 1}$$

Adjustment of the pH during reaction induces precipitation of the product in a form which is easily handlable. A commercially available product was used throughout this work (see Section 5.5.1.1).

5.3.1.2 Silver 5-Nitrotetrazolate (I)

Originally it was intended to use a route to **I** which required the isolation of sodium 5-nitrotetrazolate prior to its conversion to the silver salt (**I**, Equations 2 & 3) [51]:

$$AT + NaNO_2 + CuSO_4 \text{ ----------> } NaNT \qquad \text{Equation 2}$$

$$NaNT + AgNO_3 \text{ ----------> } AgNT\ (\mathbf{I}) \qquad \text{Equation 3}$$

Note: AT = 5-amino-(*1H*)-tetrazole; NT = 5-nitrotetrazolate

However, during the course of the synthetic investigation, an alternative method [52] which avoided the requirement to isolate this hazardous intermediate was discovered and this was employed instead. The route involves the isolation of a relatively insensitive ethylenediamine complex of copper 5-nitrotetrazolate (Equations 4 & 5):

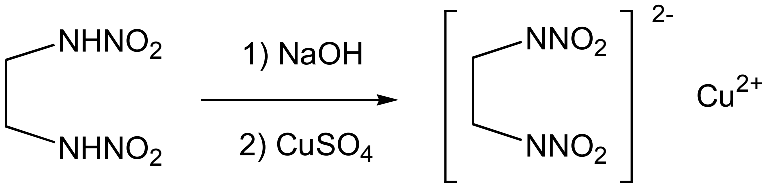
$$\left.\begin{array}{l} AT + NaNO_2 + CuSO_4 \longrightarrow CuHNT \\ CuHNT + \text{ethylenediamine} \longrightarrow Cu(\text{ethylenediamine})NT \end{array}\right\} \text{Equation 4}$$

$$Cu(\text{ethylenediamine})NT + AgNO_3 \text{ ----------> } AgNT \qquad \text{Equation 5}$$

Note: CuHNT = acid copper 5-nitrotetrazolate

5.3.1.3 Ethylenedinitramine Monocopper Salt (III)

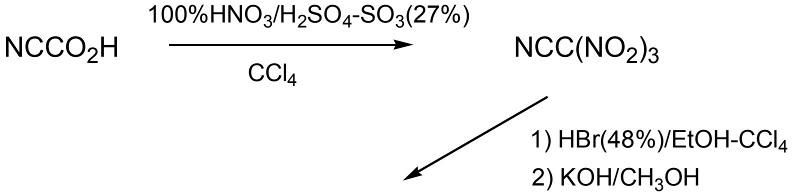
According to an early report [45], this compound can be made by reacting ethylenedinitramine (as its sodium salt) with copper sulfate, although no details were available owing to the inaccessibility of the report (see Scheme 1).



Scheme 1

5.3.1.4 Potassium Dinitroacetonitrile Salt (II)

The literature [53] route is shown at Scheme 2. It should be noted that both stages require the use of carbon tetrachloride as solvent, which is a proscribed substance under the Montreal Protocol.



$[NCC(NO_2)_2]^- \ K^+$ **II**

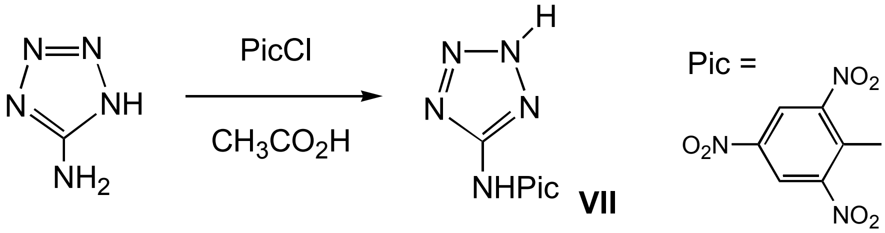
Scheme 2

5.3.2 Lead Styphnate Replacements

N.B. The compounds are discussed in the order in which they were synthesized or otherwise procured (see Section 5.5 below), which differs somewhat from the order given in Section 2.

5.3.2.1 5-(Picrylamino)tetrazole (VII)

The synthesis is reported [54] to occur in a facile manner by reaction of 5-amino-(*1H*)-tetrazole with picryl chloride (Scheme 3):

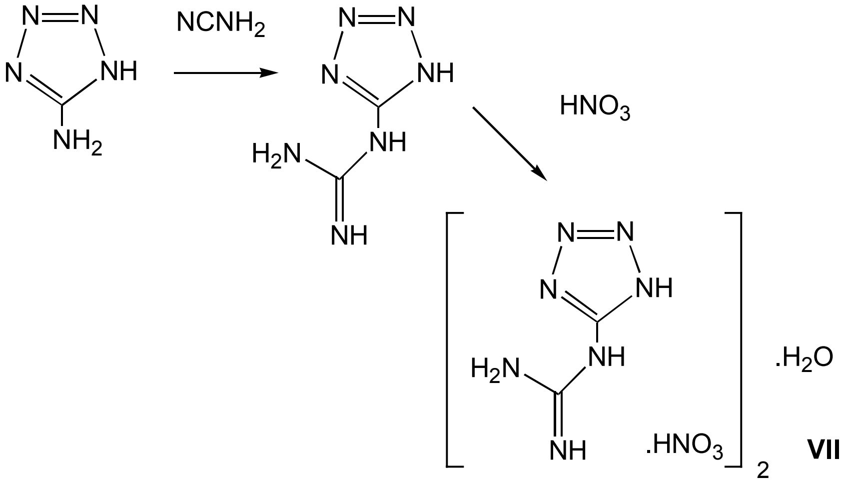


VII

Scheme 3

5.3.2.2 5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate (VIII)

The literature method [48] to prepare this compound is as shown (Scheme 4):

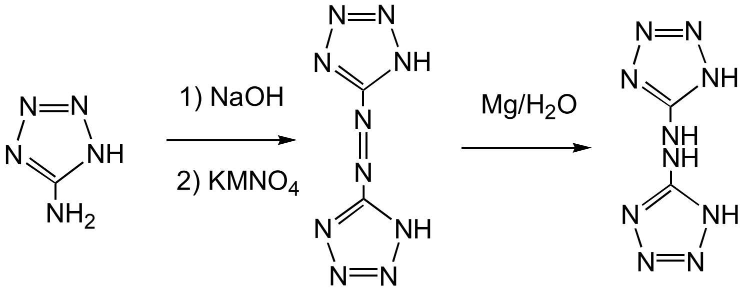


VIII

Scheme 4

5.3.2.3 5,5'-Hydrazodi-(*1H*)-tetrazole (V)

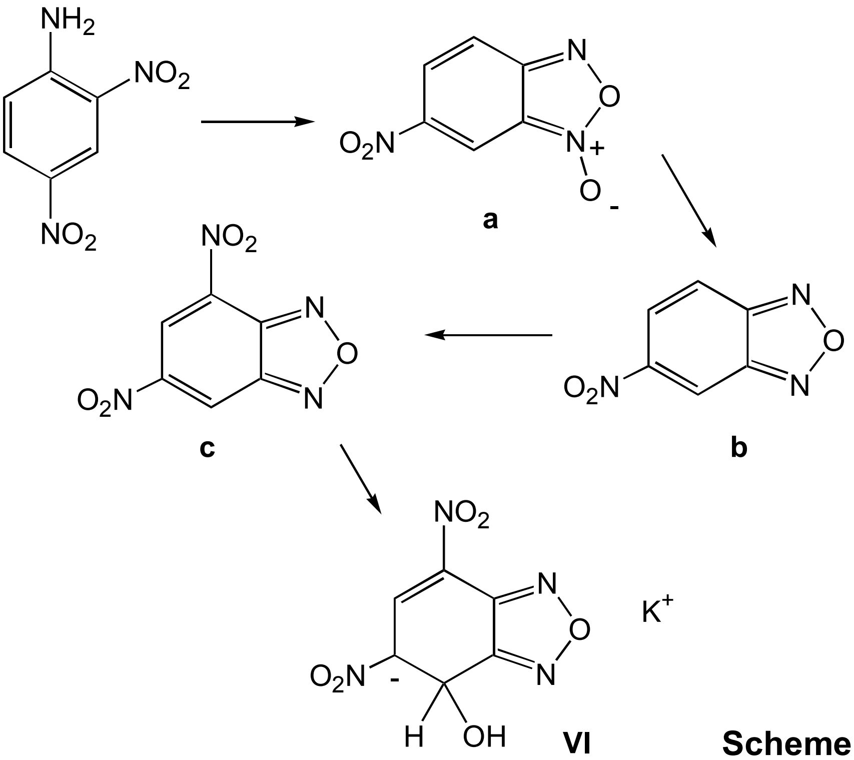
According to the literature [55], this compound can be readily synthesized in two steps from 5-amino-(*1H*)-tetrazole (Scheme 5):



V **Scheme 5**

5.3.2.4 Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, VI)

This compound is accessible by a 4-stage procedure, starting from 2,4-dinitroaniline (Scheme 6). In view of the toxicity of this aniline derivative, it is possible that 2,4-dinitrochlorobenzene could be used as a less toxic alternative, although time did not permit its investigation in the present project. The direct nitration of benzofuroxan cannot be employed as the intermediate obtained (5-nitrobenzofuroxan) is not further nitratable to the desired intermediate (compound **c**, Scheme 6). The successive steps to intermediates **a**, **b** and **c** are described in the literature [56,57,58 resp.], as is the conversion of **c** to **VI** [55].



Scheme 6

5.4 Procedures: Testing

5.4.1 Characterization

5.4.1.1 All samples prepared were characterized by melting point and at least one other identifier, in many cases IR or NMR spectra. Data were compared with literature values, where available.

5.4.2 Hazard Testing

5.4.2.1 Measurements of impact (F of I, Rotter apparatus or Ball-and-Disc test) and friction (Emery test apparatus) sensitiveness, electrostatic spark discharge (ESD) sensitiveness, and temperature of ignition (T of I) were carried out for each sample prepared or procured. These tests were carried out in accordance with the relevant NATO STANAG.

5.4.2.2 As these tests differ in some respects from those commonly employed in the U.S.A., an aid to comparison is included at Appendix D.

5.4.3 Thermal Testing

5.4.3.1 Differential scanning calorimetry (DSC) testing was carried out under the conditions described in Appendix C (Section C.1). Charts are shown in Appendix B (Section B2), and interpretation of the results is included, where appropriate, in the discussion of results for each compound (Section 5.5).

5.5 Results and Discussion

5.5.1 Lead Azide Replacements

5.5.1.1 Silver Azide (IV)

Synthesis

Whilst in the white paper proposal it was planned to synthesize this material, on commencement of work it was discovered that the material could be procured from an external source. Therefore 10 g of silver azide (**IV**) was obtained commercially from BAE Systems (designation RD1374), synthesized by reaction of silver nitrate with sodium azide in the presence of certain additives.

Test Results

Impact sensitivity: Ball & disc sensitiveness test: 47.4 cm

Friction sensitiveness (Emery paper test): 2.6 m/s

Temperature of ignition (T of I): 390°C (explodes)

Electric spark sensitivity: test no. 7: Ignitions at 0.21 µJ but not at 0.118 µJ (42 pF, 100 V and 42 pF, 75 V).

DSC onset: 303°C (see chart, Appendix B.2.1).

Discussion

These results show that this compound is suitable for further consideration as a lead-free initiator (detonant class).

Some comments on the DSC behavior: amongst detonants, silver azide is somewhat anomalous as it decomposes in the liquid phase, i.e. after the sharp endotherm oberved (303°C) which is associated with melting. Various temperatures have been reported for this phase change (251°C [59] or 300°C [60,61,62]) and the figure obtained is well documented as depending on sample size, sample purity, and rate of heating. The decomposition temperatures are partly dependent on sample history, in particular whether or not it has been exposed to light, as metallic silver nuclei are believed to influence the rate of decomposition. Hence variable results are quoted for the explosion temperature (e.g. 273°C [59], >340°C [60]) and 390°C was observed in this study.

5.5.1.2 Silver Salt of 5-Nitro-(*1H*)-tetrazole (Silver 5-Nitrotetrazolate, I)

Synthesis

To overcome some problems in the synthesis and handling of the sodium salt of 5-nitrotetrazole, which shows undesirable sensitivity to mechanical stimuli, a route which involves changing the reaction stoichiometry and the formation of an alternative intermediate based on a complex with ethylenediamine was investigated. The advantages of this route are primarily the removal of the need to isolate sodium nitrotetrazolate, the key intermediate. The sodium nitrotetrazolate is highly sensitive to initiation and is difficult to prepare with a reproducible purity level, and this has been shown to have a marked effect on the physical and explosive properties of the derived initiating salt [41,63]. Furthermore the salt is not a stable hydrate and the degree of hydration varies between 4 and 1 water molecules respectively.

An alternative route was to make the acid copper nitrotetrazolate salt by a variation of the method described [51]. This salt was then complexed with ethylenediamine to give a stable non-detonant intermediate which is safer to handle than the sodium nitrotetrazolate. The complex was then decomposed under controlled conditions to give silver 5-nitrotetrazolate (**I**) in a form which can be easily handled.

Test Results

Impact sensitivity: Ball & disc sensitiveness test: 22.7 cm

Friction sensitiveness (Emery paper test): 1.7 m/s

Temperature of ignition (T of I): 259°C (explodes)

Electric spark sensitivity: standard test: ignitions at 45 µJ

Electric spark sensitivity: test no. 7: ignition at 2.6 µJ but not at 1.9 µJ.

DSC onset: 254°C (see chart, Appendix B.2.2).

Discussion

These results show that this compound, like silver azide, is suitable for further consideration as a lead-free initiator (detonant class). It has a high sensitivity to electric spark, which should be taken into consideration in handling, both during its preparation and loading into devices.

5.5.1.3 Copper Salt of Ethylenedinitramine (III)

Synthesis

A synthesis of this compound was developed by treatment of the sodium salt of EDNA with copper(II) nitrate (details in experimental section).

Test Results

Impact sensitivity: Ball & disc sensitiveness test: >40 cm

Friction sensitiveness (Emery paper test): >3.7 m/s

Temperature of ignition (T of I): 196°C

Electric spark sensitivity: test no. 7: no ignitions at 40 μJ.

DSC onset: 162°C (see chart, Appendix B.2.3).

Discussion

This compound shows behaviour more akin to that of secondary explosives, particularly as it neither explodes in the T of I test nor ignites in the DSC test. In view of the greater suitability of earlier candidates **I** and **IV** it is therefore proposed that further work on this compound is curtailed.

5.5.1.4 Potassium salt of Dinitroacetonitrile (II)

Synthesis

The synthesis of dinitroacetonitrile monopotassium salt (**II**) was not carried out because the literature method required the use of carbon tetrachloride, a proscribed solvent. After some experimentation no appropriate substitute for this solvent could be found.

Test Results

As no sample of compound **II** could be prepared, there are no test results in this case.

5.5.2 Lead Styphnate Replacements

5.5.2.1 5-Picrylaminotetrazole (VII)

Synthesis

This compound was successfully synthesized from 5-aminotetrazole and picryl chloride by a literature method [54], with minor modifications (see Appendix C). Its physical data (m.pt., NMR and I.R. spectra) agree with literature figures (m.pt.) or are in accord with the predicted structures.

Test Results

Impact sensitivity: Ball & disc sensitiveness test: >50 cm

Friction sensitiveness (Emery paper test): >3.7 m/s

Temperature of ignition (T of I): 214°C

Electric spark sensitivity: standard test: ignitions at 0.45 J but not at 0.045 J.

Discussion

This compound shows behavior more akin to that of secondary explosives, particularly as it does not explode in the T of I test. For this reason it is proposed that further work on this compound is curtailed.

5.5.2.2 5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate (VIII)

Synthesis

The free base was successfully synthesized from 5-aminotetrazole and cyanamide and converted to the nitrate salt (title compound) by adaptation of a literature method (see Appendix C). The physical data (m.pt. and I.R. spectrum) agree with literature figures (m.pt.) or are in accord with the predicted structures.

Test Results

Impact sensitivity: Ball & disc sensitiveness test: >50 cm

Friction sensitiveness (Emery paper test): >3.7 m/s

Temperature of ignition (T of I): 166°C

Electric spark sensitivity: standard test: no ignitions at 4.5 J

DSC onset: 163°C (see chart, Appendix B.2.4). Ignition occurred at 186°C.

Discussion

As with compound **VII** above, this compound shows behaviour more akin to that of secondary explosives, particularly as it does not explode in the T of I test (although it does ignite in the DSC test). However, the temperature of ignition is too low for consideration in an initiatory application - it should be above 200°C. For these reasons it is proposed that further work on this compound is curtailed.

5.5.2.3 5,5'-Hydrazodi-(*1H*)-tetrazole (V)

Synthesis

Some problems were encountered in both the synthesis (lower yields were obtained than those reported in the literature) and handling (full second degree ESD precautions required) of this compound. A method which has been found to work satisfactorily (yield around 50%) for the preparation of the disodium salt intermediate is given in the experimental section.

The second stage of the synthesis, reduction of the disodium salt using magnesium turnings, is reported below (see Experimental section). Yields were variable but with optimized technique figures of around 30% were attainable.

Test Results

Impact sensitivity: Ball & disc sensitiveness test: >50 cm

Friction sensitiveness (Emery paper test): >3.7 m/s

Temperature of ignition (T of I): 215°C (explodes)

Electric spark sensitivity: standard test: ignitions at 0.045 J.

Electric spark sensitivity: test no. 7: ignition at 42 μJ but not at 32 μJ.

DSC onset: 218°C (see chart, Appendix B.2.5). Ignition occurred at 238°C.

Discussion

This compound shows an interesting combination of properties - although the sensitivity to mechanical stimuli is low and akin to that expected of secondary explosives, the thermal behavior resembles that of initiatories, with (in the DSC) a very rapid exotherm resulting in ignition (at 238°C). The compound also explodes in the T of I test (at 215°C). Although some problems were encountered in its synthesis (overall yield in the region of 15%), further optimization may raise this figure. The compound should be categorized as a "reserve" with respect to further investigation (see Conclusions, Section 6.2).

5.5.2.4 Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, VI)

Synthesis

The multi-stage synthesis of this compound proved problematic. As discussed above (Section 5.3.2.4), direct nitration of furoxan, which is commercially available, does not result in substitution in the desired positions of the benzene ring, and also the conditions required for workup after the deoxygenation reaction (i.e. sublimation) could not be applied to a polynitrated compound because of risk of explosion. Therefore the more complicated route involving ring synthesis (shown in Scheme 6, Section 5.3.2.4) had to be adopted. As a result, the overall yield of the product, **VI**, was very low (around 10%).

Test Results

Impact sensitivity: Ball & disc sensitiveness test: >50 cm

Friction sensitiveness (Emery paper test): >3.7

Temperature of Ignition (T of I): 179°C (explodes)

Electric spark sensitivity: standard test: No ignitions at 40 mJ (5 nF, 4 KV)

DSC onset: 118°C (see chart, Appendix B.2.6).

Discussion

Although this compound does explode in the T of I test, the temperature (179°C) is well below the value required for compounds to be used in initiatories (200°C). This finding is also at variance with the T of I figure of 223°C reported for **VI** in the literature [55]. The reason for this difference is unclear. However it is clear that **VI** is not a candidate compound suitable for further consideration as a lead-free initiator, mainly because of its excessively complex synthesis route. As mentioned in the background to the technical approach (Section 3.1), there are other compounds in the benzofuroxan class (e.g. KDNBF) which are easier to make, although with marginally acceptable T of I values for initiator use (e.g. 200°C for KDNBF).

6 Conclusions

6.1 Lead Azide Replacements

6.1.1 Two of the lead azide replacements - silver azide (**IV**) and silver 5-nitrotetrazolate (**I**) - which were synthesized or otherwise acquired appear promising as candidates for this application. Silver 5-nitrotetrazolate (**I**) could be prepared advantageously via the ethylenediamino complex. A potential drawback, however, is the very high electric spark (ESD) sensitivity of this compound.

6.1.2 Testing of the copper salt of EDNA (**III**) has indicated that, based on the hazard data given above, it appears insufficiently sensitive to impact or friction to function as an initiator. These findings are contrary to the literature data (shown in Section 3.2.1 and Table 1) which had indicated higher sensitivities. From the results obtained here, it was concluded that further consideration of **III** as a candidate in this role should be curtailed.

6.1.3 The final candidate compound for consideration as a lead azide replacement, dinitroacetonitrile monopotassium salt (**II**), did not prove amenable to synthesis owing to the necessity, noted above, of using carbon tetrachloride, a solvent proscribed under the Montreal Protocol, in its synthesis. The inaccessibility of this compound is not, however, felt to be detrimental to the program since two candidates for lead azide replacement, silver 5-nitrotetrazolate (**I**) and silver azide (**IV**), are still actively under consideration.

6.2 Lead Styphnate Replacements

6.2.1 Two of the lead styphnate replacement candidates were synthesized and tested - 5-(picrylamino)tetrazole (**VII**) and 5-(guanylamino)tetrazolium nitrate (**VIII**) - but further work on these compounds is not advocated. The compounds appear, from their hazard test results, to have much lower sensitivities to impact and friction than would be expected for primary explosives; also they did not explode in the T of I test. Thus their behavior is more akin to that of secondary explosives, and they are thus not suitable for the present application.

6.2.2 Of the remaining two candidate compounds - 5,5'-hydrazodi-(*1H*)-tetrazole (**V**) and the potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, **VI**) - compound **V** should be considered further but **VI** should be eliminated from consideration. Although both showed explosive behavior in the T of I test, one (**V**) also ignited in the DSC test. However, the synthesis of **VI** was too complex and low yielding, and it was also insufficiently thermally stable as evinced by its low T of I (179°C), so it is eliminated from further consideration. Compound **V** showed an intermediate type of behavior, with the low sensitiveness accorded to secondary explosives but a distinct initiatory behavior (rapid and complete decomposition once initiated), which indicates that it might be worth considering further as a lead styphnate replacement, subject to its satisfying other criteria (see Recommendations, Section 8).

6.3 Utility, Economic Feasibility and Attractiveness of Technology

6.3.1 In this work, of 12 months' duration, sufficient hazard and functional data were obtained to enable an assessment to be made with recommendations for compounds in each category - lead azide replacement (detonant) or lead styphnate replacement (primary explosive) - to be put forward for larger scale testing and ultimate incorporation into medium-large caliber ordnance systems. Two suitable candidates, both silver salts, were identified in the detonant category, but in the primary explosive (i.e. lead styphnate replacement) category all of the candidates had shortcomings resulting in a need for further work to be done (see Section 7.2.2).

6.3.2 The two lead azide replacement candidates are both viable economically - indeed silver azide is already in use in a number of U.K. munitions and sourcing of the material at competitive cost should not be a problem. Although silver 5-nitrotetrazolate is not, to the authors' knowledge, currently in use in munitions, related compounds which contain the nitrotetrazole ring, for instance BNCP (a perchlorate salt of a cobalt complex of 5-nitrotetrazole), are being manufactured and thus the economics of production appear promising.

6.3.3 The technology proposed here for replacing lead compounds in medium caliber munitions is attractive because, at least as far as lead azide replacements are concerned, it offers as real alternatives, compounds about which much is already known, thus providing a "fast track" to further development. The silver compounds recommended here possess good initiatory properties (e.g. silver azide is at least as effective a detonant as lead azide and is more resistant to hydrolysis), although their environmental impact will need to be evaluated thoroughly. Silver compounds would have gained more widespread use had it not been for troublesome compatibility problems with certain binder systems in use in the weapons systems of the post-war decades (notably Thiokol rubbers, where reaction with volatile sulfur compounds gave inert silver sulfide). A re-evaluation of factors such as these could conceivably reveal other compounds which were discarded earlier for reasons which are no longer valid.

7 Transition Plan

7.1 Aims

7.1.1 QinetiQ aims, with further SERDP funding, to develop devices which will meet the needs of the US military, namely: Environmentally benign small EEDs (detonators) which will result in a significant reduction in the release of hazardous materials -

- during manufacture,
- during use, and
- when demilitarized.

7.1.2 QinetiQ has established that two candidate compounds now exist as potential lead azide replacements, and intends, with additional SERDP funding, to progress studies aimed at demonstrating their suitability for use in detonators and this meet DoD needs. These studies, denoted "Project 1", are detailed below (Section 7.2.1).

7.1.3 Because of the unreliability of published data on initiatory explosives of the lead styphnate type, a follow-on program of research to identify suitable lead-free candidates for this role is therefore proposed, denoted "Project 2", as detailed below (Section 7.2.2).

7.2 Methods

Two follow-on projects are proposed:

7.2.1 Project 1: Lead azide replacements

7.2.1.1 QinetiQ proposes additional research, under SERDP funding, to investigate further the two proposed lead azide replacement candidates (silver azide and silver 5-nitrotetrazolate), according to the following work breakdown (see also critical path schematic, Fig. 3):

- Carry out an environmental assessment of the candidates for their suitability for US military use, particularly to establish the acceptability of silver residues in the environment.
- If the silver compounds are unsuitable, QinetiQ proposes to investigate other candidate compounds and to carry out a synthesis and characterization program along the lines of the work in this report (N. B. subsequent steps will depend on the analysis shown in the critical path schematic, Fig. 3).
- If the silver compounds are suitable, QinetiQ will complete safety tests of the compounds, including vacuum stability and compatibility, so that full hazard data sheets may be drawn up.
- Carry out investigations of the behavior of the compounds when pressed (to produce pellets) - aim is to find out optimum pressed density.
- Carry out filling of electro-explosive devices of a design used in US military hardware.
- Establish types of bridgewires which will be suitable to achieve initiation under the conditions prescribed in the SON.

- Develop a test vehicle which can assess the performance of the trial charges.
- Carry out functional testing (using the test vehicle).

7.2.1.2 Once the best candidate has been identified from the testing regime given above, the synthesis scale-up route will be identified to permit production of sufficient quantities for full scale device testing.

7.2.1.3 The rough cost of this work would be in the range $200-300k, depending on the results of the various assessments, and would be of around 2 years' duration.

7.2.2 Project 2: Lead styphnate replacements

7.2.2.1 QinetiQ has eliminated a number of possibilities in the present project and proposes, under SERDP funding, to investigate a further four candidate compounds for this role which will meet the requirements stated in the SON and thus satisfy DoD needs. The compounds, which may be those suggested below (Section 8.2) or a selection of these with other, as yet unidentified, candidates, will be evaluated by a process similar to that employed in the present project, although environmental assessment will be carried out at an earlier stage. Thus the processes will be:

- Final selection of candidates.
- Environmental assessment of candidates.
- Synthesis of trial quantities of candidates.
- Hazard evaluation of compounds.
- Thermal analysis of compounds.
- Report on preferred candidates.

7.2.2.2 Successful candidates would then be progressed in follow-on work analogous to that given above (section 7.2.1), although in the case of the lead styphnate replacements evaluation would not include pressing studies (as they are applied to the bridgewire as a paste).

7.2.2.3 The rough cost of this work would be $60-90k, duration 12 months.

7.3 Transition of work to industry

7.3.1 QinetiQ has relations with a U.S. munitions manufacturer and is in early stage dialog with a Canadian device manufacturer with a view to expediting initiator technology, and anticipates that fully qualified heavy metal-free initiatory devices suitable for DoD (and possibly also civil) hardware can be developed in a short (<5 year) timespan.

7.3.2 QinetiQ will draw upon its proven record of accomplishment in successfully transferring pilot processes and materials into full-scale production with an appropriate industrial partner - for example, QinetiQ's team has successfully transferred a range of SR compositions for pyrotechnics and initiatories from our R&D programs through the Royal Ordnance factories into UK service use. For example, a large number (>100) of compositions have been progressed in this way for the following applications: pyrotechnic delays, igniters, thermal devices, signals (colored flares), illuminating flares, I.R. countermeasures, tracer (artillery and small arms) and smokes (visual marine markers).

8 Recommendations

8.1 Lead Azide Replacements

8.1.1 Two lead azide replacement candidates (silver azide and silver 5-nitrotetrazolate) have been assessed as suitable compounds for further study. Their explosive properties match or exceed the requirements of the proposed application in electro-explosive devices (as outlined in the SON, Annex 1). In the proposal for this project, silver compounds were felt to meet the SERDP requirements and be less environmentally harmful than lead. However the project review meeting in April highlighted some concerns over the environmental impact of silver and this would need to be assessed as the first part of any follow on work to further develop these compounds.

8.1.2 QinetiQ advocates some further studies to gain further information, particularly for silver 5-nitrotetrazolate (**I**), which will enable full qualification of the compounds to be achieved. Such studies should include X-ray diffraction studies of **I**, which is known [20] to exist in different polymorphic forms, to verify which polymorph has been formed and evaluated in this study. This knowledge, in conjunction with further laboratory scale synthetic studies, will permit the consistent production of this particular polymorph for a subsequent scale-up phase. As assessment of the robustness of the synthetic method adopted will form part of these studies.

8.1.3 Scale-up of the production of these two candidate compounds, to a sufficient level for filling trials to be carried out, will form an integral part of development work. An aim of these studies would be to enable production of the compounds ultimately to be carried out in the explosives industry to ensure supply for long-term system needs.

8.2 Lead Styphnate Replacements

8.2.1 As problems (particularly low yields) were encountered in the synthesis of the one compound (5,5'-hydrazodi-(*1H*)-tetrazole, **V**) which merited consideration for use as a lead styphnate replacement, further study of this compound is not recommended. Therefore QinetiQ advocates further studies to synthesize and carry out preliminary evaluation of additional lead styphnate candidates selected from previous literature surveys. A list of four such compounds, evaluated by the process already described (Section 3.2) is shown at Table 2. A program to establish the best synthetic routes to these compounds, and to measure their hazard and explosive properties, would form a major part of this follow-on work.

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10 Glossary

Ag	Silver
Asym.	Asymmetrical
Ba	Barium
BAM	Bundesanstalt fuer Materialprufung
Bi	Bismuth
b.pt.	Boiling point
br.	Broad
BRL	Ballistic Research Laboratory
ca.	*circa* (i.e. approximately)
Cd	Cadmium
dec.	with decomposition
diam.	diameter
DoD	Department of Defense
DSC	Differential scanning calorimetry
EDNA	Ethylenedinitramine
EED	Electro-explosive device
ESD	Electrostatic Discharge
ESTCP	Environmental Security Technology Certification Program
F of I	Figure of insensitiveness (from Rotter impact sensitivity test)
HE	High explosive
^1H	Proton (for NMR)
Hg	Mercury
I.R.	Infra-Red (spectroscopy)
J	Joule
KDNBFZ	Potassium 4-hydroxy-5,7-dinitrobenzofurazanide
Lit.	Literature
m.pt.	melting point
MHz	Megaherz
NMR	Nuclear Magnetic Resonance (spectroscopy)
Pb	Lead
P_{CJ}	Detonation pressure
PETN	Pentaerythritol tetranitrate
pF	Picofarad (unit of electrical capacitance)
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine [syn. hexogen, cyclonite]
RDxxxx	Research Department (British) explosive compound/formulation number
s.g.	specific gravity
SERDP	Strategic Environmental Research & Development Program

SON	Statement of need
Sr	Strontium
Sym.	Symmetrical
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
T_{exp}	Temperature of explosion
T of I	Temperature of ignition
Tl	Thallium
µF	Microfarad (unit of electrical capacitance)
W/w	Weight/weight (measurement)
W/v	Weight/volume (measurement)

11 Annex 1: Statement of Need PPSON-02-07 (Objective, Expected Payoff and Background)

SON Number: PPSON-02-07 DATE: 30 July 2001

STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM
STATEMENT OF NEED FOR FY02
POLLUTION PREVENTION NEW START

ENVIRONMENTALLY-ACCEPTABLE SMALL ELECTRO-EXPLOSIVE DEVICES
FOR MEDIUM CALIBER MUNITIONS

1. OBJECTIVE OF PROPOSED WORK

The objective of this Statement of Need is to develop environmentally benign, small, electro-explosive devices (EEDs) (detonators). These small EEDs (detonators) are to be sized such that they will be compatible (volume, weight and power) with the newest fuzes being developed for medium caliber (20-60 mm) ammunition and have sufficient output energy to initiate lead and main charges containing "insensitive" explosives. These detonators currently use lead styphnate, lead azide and HMX in their construction and all of these are considered to be hazardous/toxic materials. This project is to identify an alternate chemistry to eliminate or minimize their use. The new EEDs must also provide the same level of affordability as current designs (depending on quantity produced, $3-9 per EED).

2. EXPECTED PAYOFF OF PROPOSED WORK

The development of environmentally benign small EEDs (detonators) will result in the significant reduction of the release of hazardous materials during manufacture, use and demilitarization of medium caliber fuzes.

3. BACKGROUND

Current medium caliber high explosive munitions are functioned by initiating an impact sensitive (stab) detonator. This requires the projectile to strike an object with sufficient force to rapidly push a firing pin into an initiating mix. The next generation of fuzes for medium caliber rounds is seeking to selectively function the round in at least three modes: 1) at a pre-determined location in space without impact, 2) upon impact with the target but within the protective covering of the target or 3) immediately upon impact with the target. To have this flexibility in the design, the fuze must have a selection of the functioning mode prior to shot start and then a method of initiating the round when the detonation conditions are satisfied. The current impact initiated detonators require a relatively large impact energy to initiate, an energy that would have to be created by an onboard mechanism in the case of no target impact. Weight and space constraints prohibit the incorporation of his type of device. Instead small EEDs are being utlilized in these new design concepts to accomplish this initiation. With a small EED, the detonator can be functioned electrically, regardless of the fuze functioning mode. The only available EEDs that will meet the functional requirements are the M100 detonator and variants of the M100 (e.g. PA537, etc.). The M100 no fire requirement is the energy discharged from a 100 μF capacitor charged to 0.7 Volt potential. The 99% reliability with 99% confidence all fire requirement is dependent upon the circuit design. The all fire circuit range for the M100 is a 0.1 μF capacitor charged to 30.4 Volt potential (462 ergs) up to a 100 μF capacitor charged to a 1.7 Volt potential (1445 ergs).

The M100 and its variants are all functioned by electrically initiating (bridge wire) a spot charge of Lead Styphnate that outputs into a transfer charge of Lead Azide. The lead charge consists of 0.0008 grams of pure Lead Styphnate place on a bridge wire lead. The bridge wire is then placed into 0.014 grams of pure special purpose Lead Azide. The Lead Azide then detonates a base charge of 0.016 grams of Grade B, Class 3 HMX. The variations on the M100 achieve smaller lengths by having less or no base charge.

12 Annex 2: Project PP1306 Fact Sheet

Title: Lead-Free Initiator Materials for Small, Electro-Explosive Devices for Medium Caliber Munitions

SERDP Reference: PP1306

Background:

The United States Department of Defense (DoD) recognizes that heavy metal contaminants are a critical environmental problem and has committed to reduce its use of lead (Pb) in medium caliber munitions. In collaboration with SERDP, the DoD has therefore issued SON Number: PPSON-02-07, with the goal of eliminating the use of lead azide, lead styphnate, and HMX in small, electro-explosive devices (EEDs).

Objective:

QinetiQ's proposed project will focus on synthesizing and characterizing up to eight (8) compounds (four possible replacements for lead azide and four possible replacements for lead styphnate) believed, based on an examination of explosives literature, to have the potential to replace lead azide and lead styphnate. Further, QinetiQ scientists will synthesize sufficient quantities of these compounds to conduct preliminary characterization and hazard assessments of each of them during the course of the project. A substantial proportion of the work will be of an innovative nature, and the thrust behind the project is proof of concept, since no heavy metal-free compounds have previously been used in the initiatory categories mentioned above. QinetiQ will propose additional phases of research to produce EEDs based on those compounds that satisfy the necessary performance, stability and cost criteria.

Summary of Process/Technology:

The compounds proposed for examination fall into three categories – inorganics, light metal derivatives of organics (salts & Meisenheimer complexes), and metal-free organic compounds. QinetiQ will devise routes for the synthesis of these compounds, which, where possible, avoid the use of toxic and/or carcinogenic reagents, intermediates and solvents. The candidate compounds thus synthesized will be characterized fully by spectroscopic and thermal analysis, and checked for polymorphism by X-ray diffraction. After these analyses, QinetiQ will assess the compounds for hazard (impact, friction, electrostatic discharge and ignition temperature) before making recommendations as to which are suitable for the next phase of the project.

Benefit:

The primary outcome of this research will be to make available to SERDP and DoD initiatory compounds which do not release toxic heavy metals (particularly lead) when they function in a munition or civilian blast application (e.g. demolition). The major benefits of substituting such compounds in EEDs for medium caliber munitions include: (1.) Reduced health risks to workers during production processes; (2.) Reduced environmental risks during the production process; (3.) Reduced health and environmental risks to operational users; (4.) Cost avoidance through reduced clean-up at both manufacturing and operational sites, and thus a lower Total Ownership Cost for DoD acquisitions.

Accomplishments:

This is a FY 2002 new start project.

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Table1: Final Selection of Potential New Initiators – Summary of Properties

Entry	Name (Short)	Formula	$h_{50\%}$ (cm)	Density (gcm^{-3})	Explosion Temp. °C	Power (P_{CJ})kbar	Vac. Stab.**	Figure No.
A <u>Lead azide-like compounds</u>								
1	5-nitro-(1*H*)-tetrazole, silver salt	CN_5O_2Ag	n/r	n/r	340	-	n/r	**I**
2	dinitroacetonitrile monopotassium salt[‡]	$C_2N_3O_4K$	16-31	2.013[†]	388	336.5	0.1[a]	**II**
3	ethylenedinitramine monocopper salt[‡]	$C_2H_4N_4O_4Cu$	17	n/r	350	-	n/r	**III**
4	silver azide[‡]	N_3Ag	10(FofI)	5.1	300	-	n/r	**IV**
B <u>Lead styphnate-like compounds</u>								
5	5,5'-hydrazodi-(1*H*)-tetrazole)[‡]	$C_2H_4N_{10}$	20	1.85[†]	229	401.6	6.9[b]	**V**
6	KDNBFZ[§]	$C_6H_3N_4O_6K$	n/r	n/r	223	-	n/r	**VI**
7	5-picrylaminotetrazole	$C_7H_4N_8O_6$	36	1.91	210*	-	n/r	**VII**
8	5-(guanylamino)-tetrazolium nitrate[‡]	$C_4H_{12}N_{16}O_6.H_2O$	10 in.	1.58	n/r	-	0.35[a]	**VIII**

*DTA [†]calculated [‡]compound listed in *The Explosives Catalogue* [39]
[§]full name: potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide
n/r = not recorded **Vacuum stability test at: [a]120°C/48 hr; [b]120°C/40 hr

Table 2: Potential Alternate Lead Styphnate Replacements (Suggested for Future Investigation)

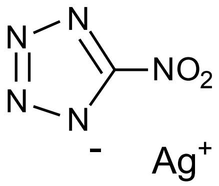
Entry	Name (Short)	Formula	$h_{50\%}$ (cm)	Density (gcm^{-3})	Explosion Temp. °C	Power (P_{CJ})kbar	Vac. Stab.	Figure No.
1	KDNBF*	$C_6H_3N_4O_7K$	n/r	n/r	200	-	n/r	**IX**
2	1-picryl-1,2,3-(*1H*)-triazole	$C_8H_4N_6O_6$	11	1.695	218**	-	0.5⁺	**X**
3	5-chloro-(*1H*)-tetrazole copper salt	$C_2N_8Cl_2Cu$	1 in.	n/r	300	-	n/r	**XI**
4	5-nitrotetrazolatopenta-amminecobalt(III) perchlorate	$CH_{15}N_{11}O_{10}Cl_2Co$	n/r	n/r	n/r	-	n/r	**XII**

*Full name: potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide-3-oxide (or potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofuroxan)

**DSC measurement

⁺At 120 for 48 h.

Figure 1: Lead-Free Initiator Structures



I

$[(NC)C(NO_2)_2]^- \; K^+$

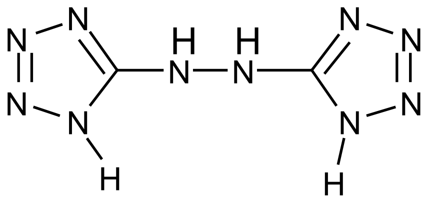
II

$[\;NNO_2(CH_2)_2NNO_2\;]^{2-} \; Cu^{2+}$

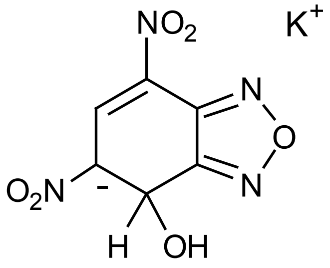
III

AgN_3

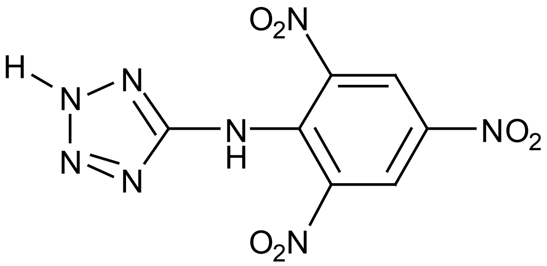
IV



V



VI



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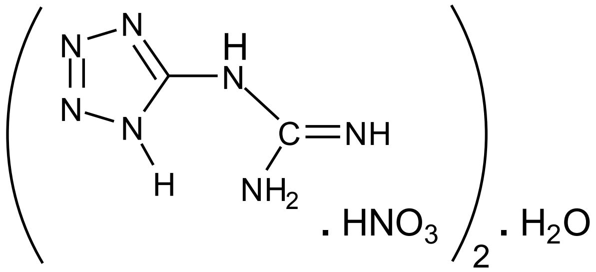
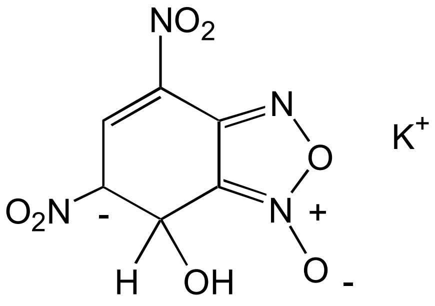
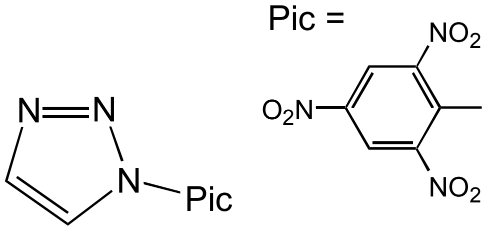


VIII

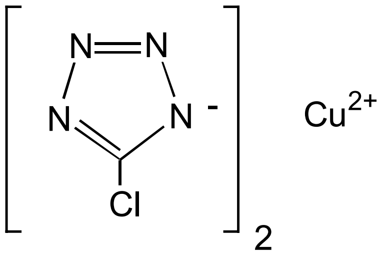
Figure 2: Potential Alternate Lead Styphnate Replacements (Compounds IX-XII)



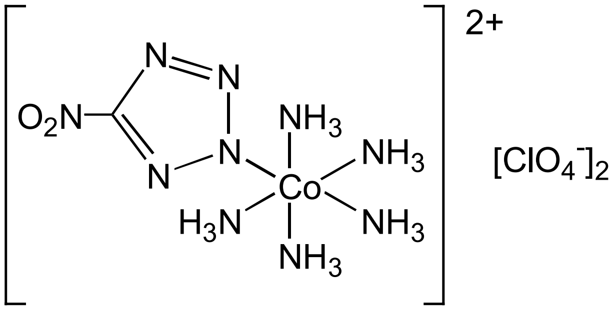
IX



X



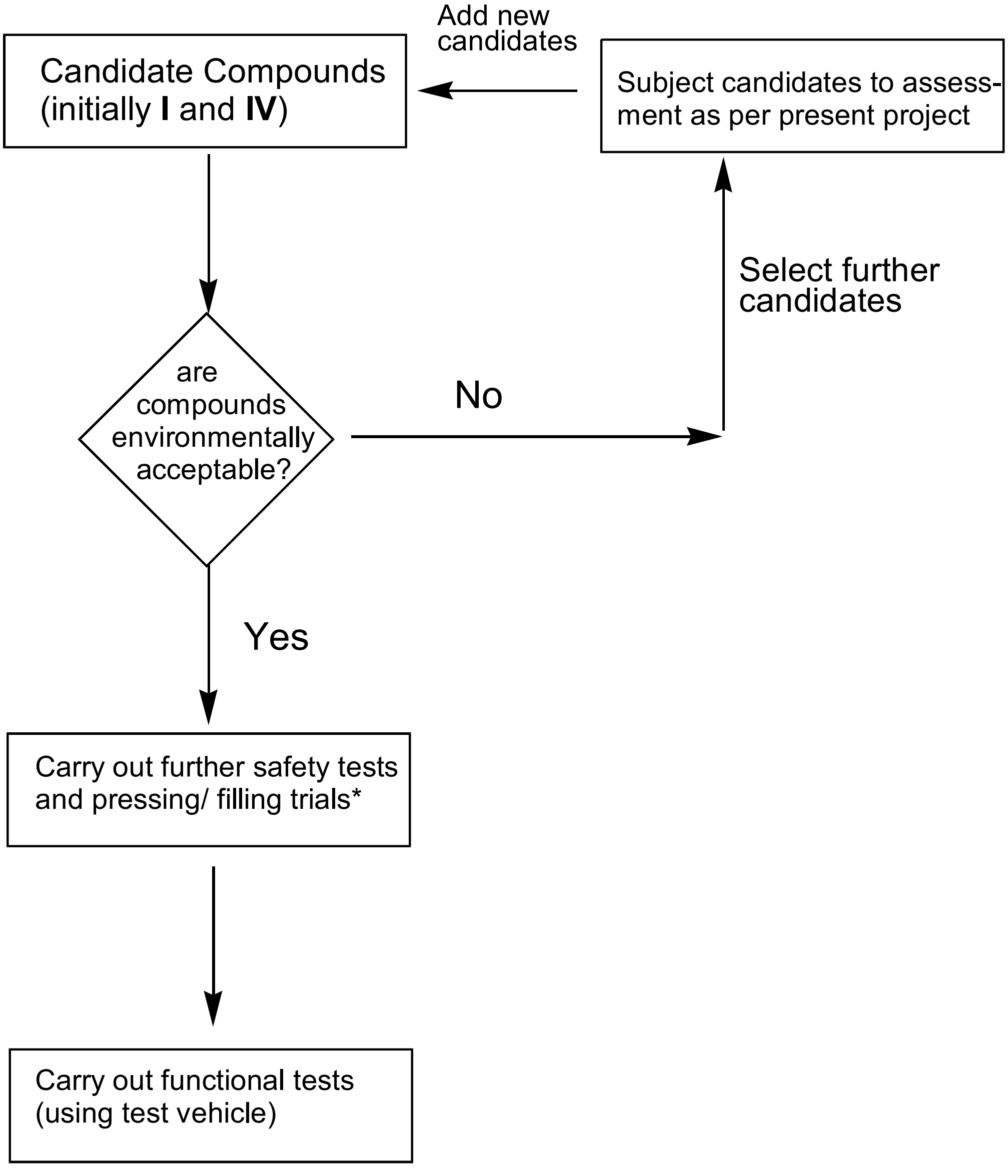
XI



XII

Figure 3

Critical Path Schematic: Lead Azide Replacements



*As described in Section 7.2.1.1

A Appendix: Publications

"Lead-Free Initiator Materials for Small Electro-Explosive Devices for Medium Caliber Munitions", R. W. Millar & J. Hamid, Abstract for poster (no. 201) presented at SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, Marriott Wardman Park Hotel, Washington DC, 3-5 December 2002.

B Appendix: Tabulated Data and Charts

B.1 Data from Hazard Tests

B.1.1 Lead Azide Replacements: Hazard Test Results

Compound	Impact Test[1]	Friction Test[2]	Temp.of Ignition	Electrostatic	(Spark) Test
	cm	ms^{-1}	°C	Standard test	Advanced test (no.7)
I	22.7	1.7	259 (explodes)	45 μJ ign.	2.6 μJ ign., not 1.9 μJ
II	-	-	-	-	-
III	>40	>3.7	196	>40 mJ	-
IV	47.4 30 (F of I)	2.6 V. Sens.	390 (explodes)	-	0.21 μJ ign., not 0.118 μJ
Lead azide[3]	19 (F of I 29)	1.2	319 (explodes)	-	2.5 μJ (520 pF)

[1] Ball and Disc Test (compound **IV** & lead azide: F of I (Rotter Test) also given)
[2] Emery Friction Test (compound **IV**: categorization by mallet test also given)
[3] Service composition RD1343 (pptd. from sodium carboxymethylcellulose/sodium hydroxide)

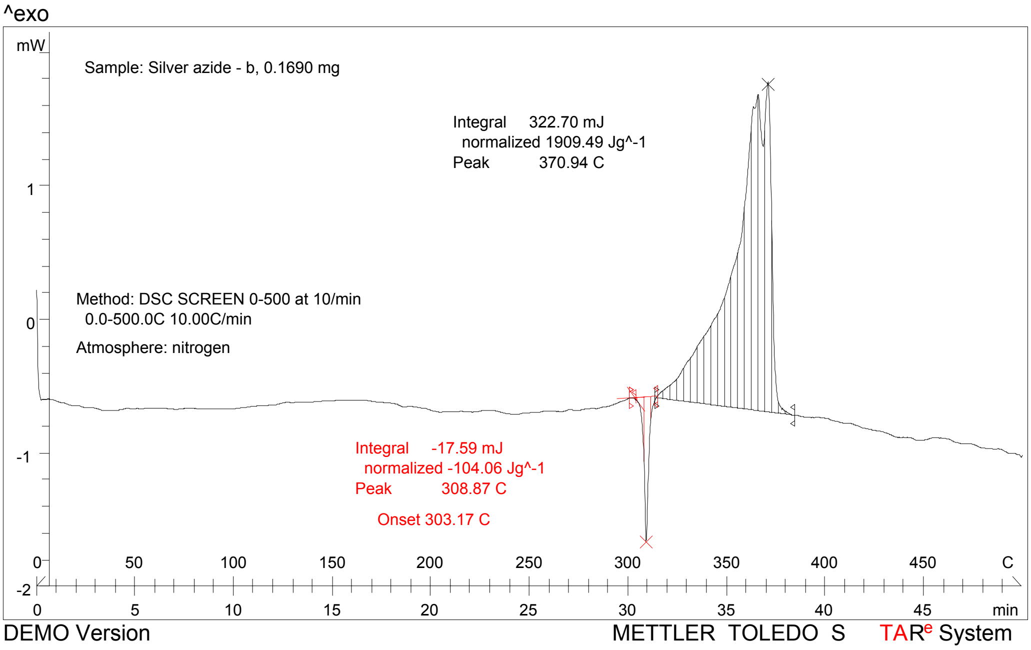
B.1.2 Lead Styphnate Replacements: Hazard Test Results

Compound	Impact Test[1]	Friction Test[2]	Temp.of Ignition	Electrostatic	(Spark) Test
	cm	ms^{-1}	°C	Standard test	Advanced test (no.7)
V	>50	>3.7	215 (explodes)	0.045 J ign.	42 μJ ign., not 32 μJ
VI	>50	>3.7	179 (explodes)	> 40 mJ	
VII	>50	>3.7	214	0.45 J ign.	-
VIII	>50	>3.7	166	>4.5 J	-
Lead styphnate[3]	11 (F of I 20)	1.8	269 (explodes)	-	7 μJ (520 pF)

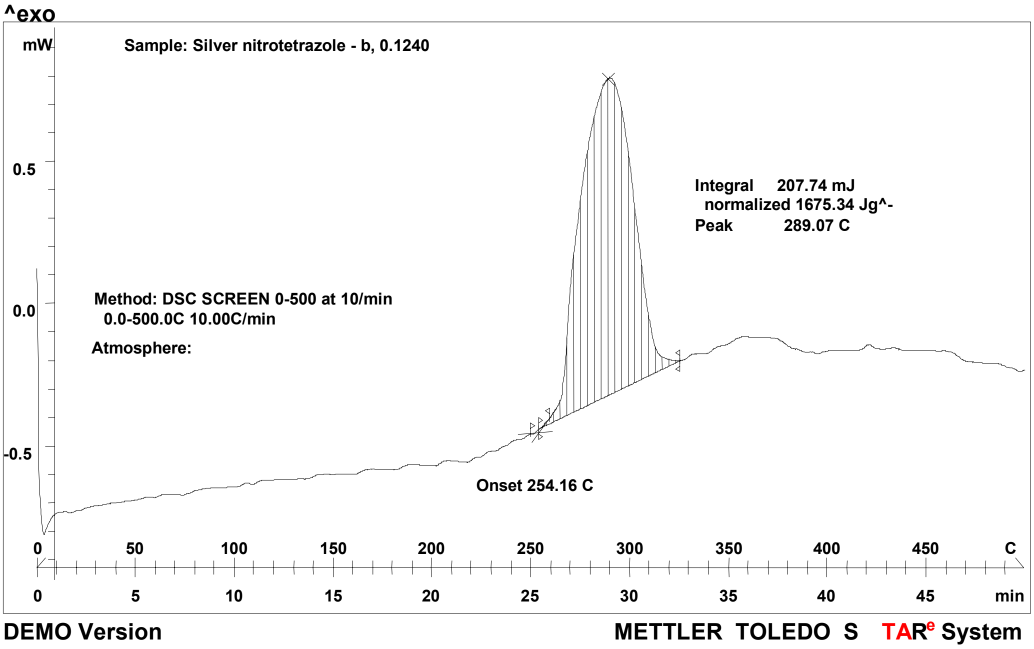
[1] Ball and Disc Test
[2] Emery Friction Test
[3] Service material RD1303.

B.2 DSC Data

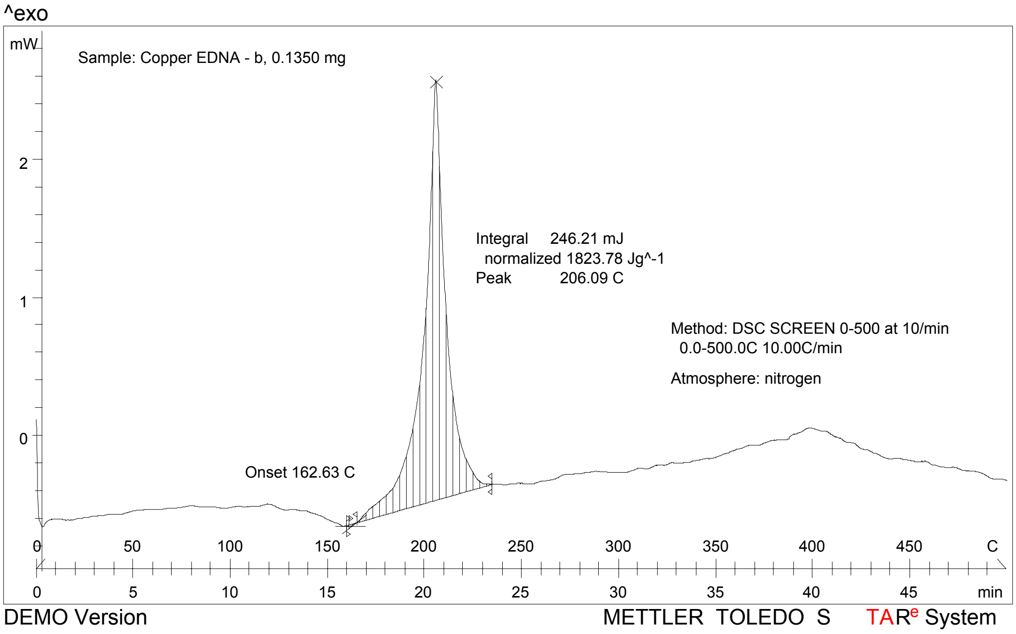
B.2.1 Silver Azide (**IV**)



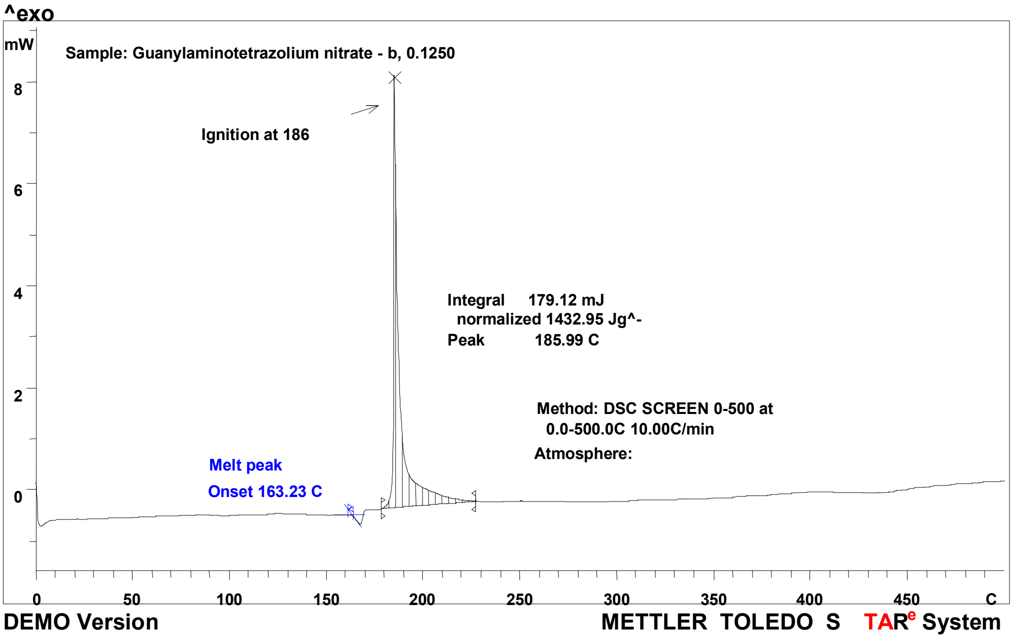
B.2.2 Silver 5-Nitrotetrazolate (**I**)



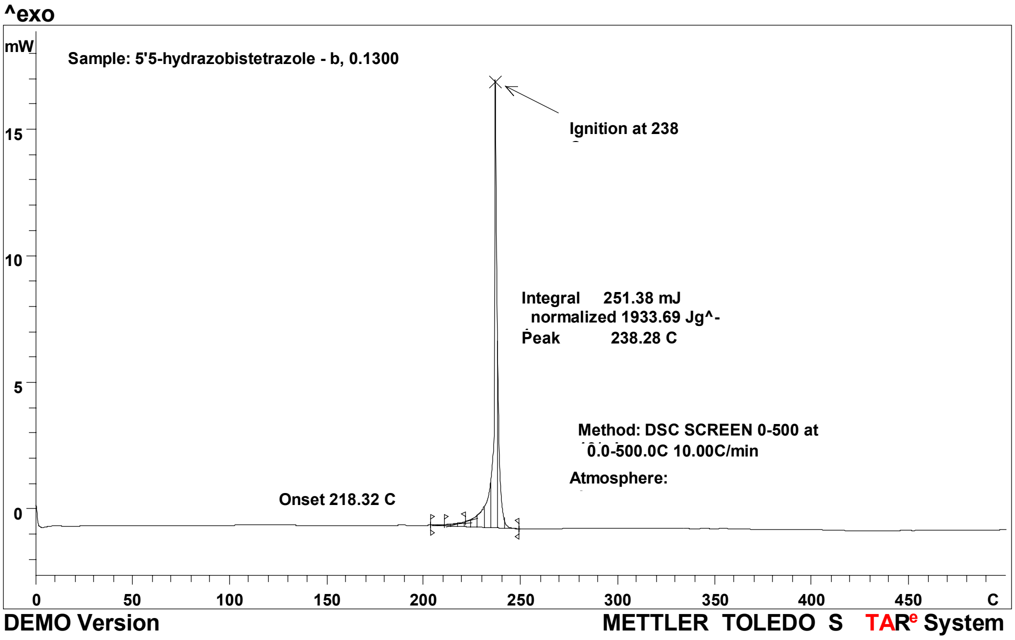
B.2.3 Copper Salt of Ethylenedinitramine (**III**)



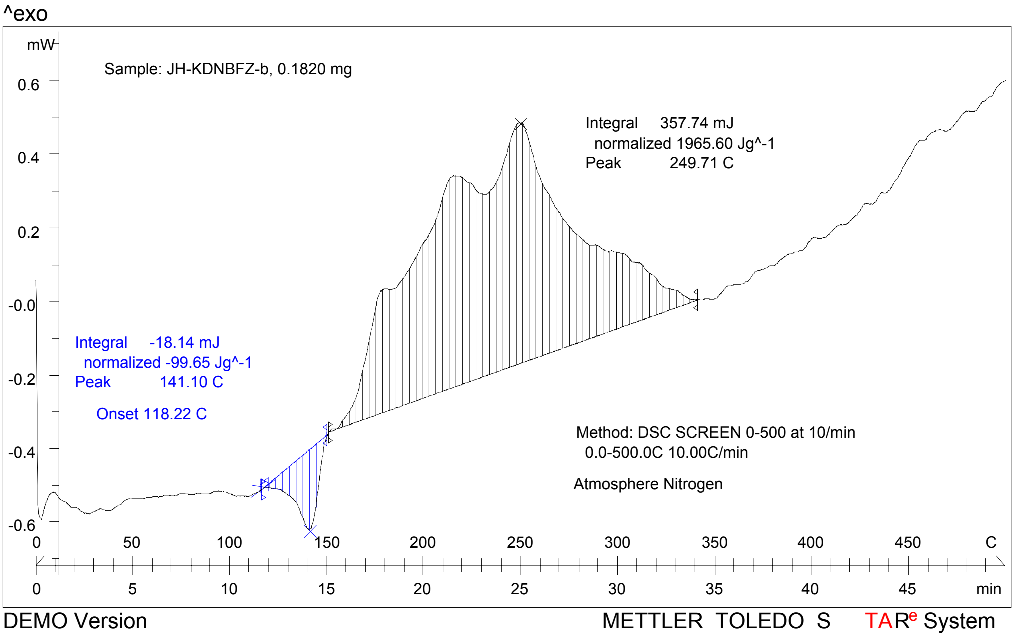
B.2.4 5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate (**VIII**)



B.2.5 5,5'-Hydrazodi-(*1H*)-tetrazole (**V**)



B.2.6 Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, **VI**)



C Appendix: Experimental Methods

Note: Many of the compounds described subsequently are explosive and appropriate precautions should be taken. Where precautions are necessary against electrostatic discharge this has been indicated.

C.1 Materials and Apparatus

C.1.1 Chemicals

C.1.1.1 All materials were used as received unless otherwise stated. Chemicals were supplied as follows:- organic/inorganic chemicals and solvents by Aldrich Chemical Co. Ltd., Merck (UK) Ltd and Fluka (UK) Ltd.

C.1.2 Apparatus

C.1.2.1 All experiments, except those where non-explosive precursors were prepared, were carried out in armoured cupboards. Explosives were handled under conducting conditions (with conducting surfaces) to minimise the effects of static electricity. More stringent precautions were adopted in the handling of those compounds (noted in the text) where secondary ESD precautions were required.

C.1.2.2 IR spectra were recorded on a Nicolet 760 Magna series spectrometer, either between KBr disks (liquids) or as Nujol mulls (solids). ^{1}H NMR measurements were obtained on a Bruker 400 Avance spectrometer operating at 400 MHz using a 5 mm QMP probe.

C.1.2.3 Hazard testing of explosive samples (ball-and disc, emery friction, temp. of ignition and ESD tests) was carried out on equipment approved for STANAG testing on-site at Fort Halstead. An aid to interpreting the figures from these tests is appended (Appendix D).

C.1.2.4 DSC testing was carried out on a Mettler Toledo STAR DSC instrument. Samples were contained in a 40 μl aluminum pan covered with an aluminum lid which had been perforated with a single pinhole. Scans were carried out under the following conditions:

Initial temperature: 0°C
Final temperature: 500°C
Heating rate: 10°C/min
Purge gas: Nitrogen.
The instrument was calibrated against indium or tin standards.

C.2 Lead Azide Replacements

C.2.1 Silver Azide (IV)

As explained in the text (Section 5.4), a sample of this compound (designation RD1374, prepared according to specification TS 50232) was procured from BAE Systems Ltd., Chorley, U.K.

C.2.2 Silver 5-Nitrotetrazolate (I)

C.2.2.1 Preparation of Acid Copper Nitrotetrazolate salt

Sodium nitrate (15.4 g) in water (100 ml) was added to 25 ml of copper (II) sulfate solution (prepared by dissolution of copper (II) sulfate pentahydrate (25 g) in 100 ml water) in a 1L jacketed vessel containing a thermometer and magnetic stirrer at a temperature of 15°C. To this solution was added dropwise 300 ml of an aqueous solution containing 5-aminotetrazole monohydrate (10.3 g), copper (II) sulfate pentahydrate (6.25 g) and 2.5*M* sulfuric acid (23 ml). The solution was added below the surface of the mixture using a dip pipe over a 50 min. time period while keeping the temperature below 20°C. After the addition, the mixture was allowed to stir for a further 20 min. at 18°C and then a 1:1 sulfuric acid:water mixture (18 ml) was added. After a further hr of stirring the light blue mixture was filtered on a Buchner funnel, washed with water (150 ml) and allowed to dry in air to give the acid copper salt (9.1 g). (Please note that this compound is a sensitive primary explosive which was only dried for yield analysis.)

M.pt.: explodes at 237°C.

C.2.2.2 Preparation of Bis(ethylenediamino) Copper (II) 5-Nitrotetrazolate

A damp cake of the acid copper nitrotetrazolate (20 g, containing 9.1 g (dry weight) of material) was added to water (70 ml) at 60°C in a 150 ml beaker followed by a solution containing copper (II) sulfate pentahydrate (2.37 g) and ethylenediamine (3.98 g) in water (6 ml). The dark purple mixture was stirred until all the copper nitrotetrazolate was in solution and then allowed to cool. The precipitated solid was filtered under vacuum and washed with a little ice-cold water before being allowed to air dry to give the purple ethylenediamino complex (7.67 g).

M.pt.: explodes at 204°C.

C.2.2.3 Preparation of Silver 5-Nitrotetrazolate (**I**)

N.B. Full secondary ESD precautions were employed during this synthesis.

The above ethylenediamino complex (6.6 g) was stirred with a solution of sodium nitrite (4.23 g) in water (65 ml) at 25°C in a 200 ml beaker. 2.5*M* nitric acid (32.5 ml) was added dropwise over 15 min. and the mixture allowed to stir for a further 15 min. The solution was then heated to 95°C for 15 min. to drive off any gases from the solution then allowed to cool to 60°C before dropwise addition of a solution of silver nitrate (5.4 g) in water (32.5 ml) over a further 15 min. The mixture was allowed to stir for a further 10 min., then filtered under gravity and the creamy tan solid was allowed to dry in air to give silver nitrotetrazolate (6.44 g). The cake was suspended in 100 ml of petroleum ether (b.pt. 40-60°C) and gently broken up using a glass rod and then filtered again and allowed to dry in air overnight to give a free flowing powder.

M.pt.: explodes at 262°C (lit. [52] 262°C).

C.2.3 Copper Salt of Ethylenedinitramine (III)

The method in ref. 52 was adapted.

Copper(II) nitrate hemipentahydrate (2.5 g) in water (20 ml) was added dropwise to a hot solution (50°C) of disodium ethylene dinitramine salt obtained from ethylene dinitramine [64] (0.75 g) and sodium hydroxide (0.8 g) in water (80 ml). After addition of the copper salt (approx. 5 min.) the blue/green precipitate that had been formed was gravity filtered and washed with water (30 ml) and then allowed to air dry overnight to give a blue/green solid (1.10 g), M.Pt.: explodes 234°C. Generally the solid dried out to a solid mass which was treated as follows to give a powder suitable for characterization: the salt was added to toluene and gently ground in solvent using a glass rod, filtered and the residual solvent allowed to evaporate under vacuum to leave the powdered material.

I.R. spectrum (KBr disk, cm^{-1}): 3375, 2940 and 2862 (CH_2), 1390 (NNO_2, sym.), 1297 (NNO_2, asym.), 1076 and 1036 (C-N).

C.2.4 Potassium salt of Dinitroacetonitrile (II)

As explained in the text (Section 5.4) this compound could not be prepared owing to the necessity of using carbon tetrachloride, a solvent banned under the Montreal Protocol. Despite attempts to find alternative solvents - several chlorinated hydrocarbon solvents were tried - no suitable substitute for this solvent was found.

C.3 Lead Styphnate Replacements

C.3.1 5-Picrylaminotetrazole (VII)

After R. Stolle & O. Roser [54].

Picryl chloride (6 g, 24 mmol) and 5-aminotetrazole (2.46 g, 24 mmol) in glacial acetic acid (50 ml) were heated under reflux for 2 h. Crystals separated during the reaction and subsequent cooling. The product was filtered off and recrystallized from glacial acetic acid, giving a light yellow powder with m.pt. 232°C (chars), lit.[54] m.pt. 224°C, yield: 2.4 g (30%). A similar product was obtained when a more concentrated mixture of picryl chloride and 5-aminotetrazole was heated for a shorter time at 110 °C.

I.R. spectrum, KBr disc (cm^{-1}): 3087 (CH), 2935 (CH), 1615, 1541 (NO_2), 1345 (NO_2), 1081, 720.

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.07, s, 2H, (NH), 9.2, s, 2H, (Ar).

^{13}C NMR: δ 127.3, ($C_{2,4}$), 136.8, ($C_{1,5}$), 140.5, (C_6), 141.6, (C_3) and 157.5, (C_4, tetrazole ring).

C.3.2 5-(Guanylamino)-*1H*-tetrazolium nitrate monohydrate (VIII)

A.1.1.1 Preparation of cyanamide solution (aqueous solution method)

Crude (~60%) calcium cyanamide (300 g) was made into a slurry with water (300 ml). The slurry was transferred to a 7 in. diam. Buchner funnel connected to a long efficient reflux condenser connected in turn to a 4 l flask immersed in an ice bath. Warm (70°C) water (1.8 l) was poured through the slurry at such a rate as to leave a thin layer of water above the slurry (application of a weak vacuum was necessary). The solution in the flask was treated with 20% w/v sulfuric acid until the pH reached 5 (*ca*. 1 l of the sulfuric acid was required). The precipitated calcium sulfate was removed by filtration. The resulting cyanamide solution was concentrated to 300 ml by evaporation through a 10 cm fractionating column (Dufton spiral) at 10-12 mm Hg. The yield was around 42 g (1 mol) cyanamide.

C.3.2.2 Preparation of 5-(Guanylamino)tetrazole

Approximately one fifth of the cyanamide solution (prepared as shown above) was neutralized to pH 7 with dilute ammonia solution. 5-Aminotetrazole monohydrate (20 g, 194 mmol) was added and the mixture was immersed in a boiling water bath and heated with stirring for 5 h. After initial dissolution of the starting material (within 30 min.), precipitation of the product occurred progressively throughout the reaction period. The crude product was filtered off from the hot reaction mixture, and dilution of the mother liquor with water followed by concentration and filtration gave further product. The total product obtained was 18 g (81%) of the title compound as a colorless crystalline solid. The product was purified by recrystallization from water at 85°C (800 ml required per 10 g product) and had m.pt. >290 °C. Yield: 16 g (72%).

I.R. spectrum (cm^{-1}): 3384, 2649 (br), 1652, 1456, 1062.

C.3.2.3 Preparation of 5-(Guanylamino)tetrazolium Nitrate (**VIII**)

Pure 5-(guanylamino)tetrazole (10 g) was dissolved with stirring in hot 3*M* nitric acid (150 ml). The hot solution was filtered and white platelets of the nitrate crystallized on cooling. The product was filtered off, washed in sequence with water, ethanol and ether, and dried at 80°C. It had m.pt. 185°C (dec., violent), lit.[48] m.pt. 183°C (dec.). Yield: 7.9 g (49%).

I.R. spectrum, KBr disc (cm^{-1}): 3357 (NH), 2663 (br), 1699, 1627 (N=N), 1385 (NO_3^-), 1306, 1050, 840 (NO_3^-).

C.3.3 5,5'-Hydrazodi-(*1H*)-tetrazole (V)

C.3.3.1 Disodium salt of 5,5'- azodi-(1*H*)-tetrazole (after Spear and Elischer [55]).

N.B. Full secondary ESD precautions were employed during this synthesis.

5-Aminotetrazole hydrate (10 g) was added to a solution of 15% sodium hydroxide (100 ml) in a two neck round bottom flask and the mixture heated to 100°C. Powdered potassium permanganate was added portionwise slowly to the mixture with vigorous stirring (exothermic reaction!) until further addition of potassium permanganate gave no discernible reaction (approx. 12-13 g). Several drops of ethanol were then added to the still hot solution to destroy any excess permanganate and the mixture hot filtered to remove the precipitated manganese dioxide. On cooling the disodium salt crystallized as a yellow solid. This was filtered and dried to give 5.31 g of material (M.Pt.: explodes above 270°C).

C.3.3.2 Reduction of the disodium salt of 5,5'- azodi-(1*H*)-tetrazole

A suspension of the disodium salt (7.0 g) and magnesium turnings (3.5 g) in water (300 ml) was heated at reflux for 24 h. The slightly yellow resultant solution containing a white suspension was quickly filtered under suction at 80°C and the filtrate acidified with 25% aqueous nitric acid (8 ml). Upon cooling crystals of 5,5'-Hydrazo-bis-(1H)-tetrazole separated out and were filtered off under suction and dried to give 2.85 g of 5,5'-hydrazodi-(*1H*)-tetrazole (**V**). M.pt. 217°C (explodes) (lit.[55] 228, 229, 230°C; [65] 206, 208°C).

I.R. spectrum, KBr disc (cm^{-1}): 3122, 3208 and 3285 (NH), 1654 (C=N), 1627 (N=N), 1526 (C=N), 1386 (C-N aryl), 1278 (C-N aryl).

C.3.4 Potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, VI)

C.3.4.1 Preparation of 5(6)-nitrobenzofuroxan

After Mallory & Varimbi [56].

2,4-Dinitroaniline (22 g) was added to acetic acid (175 ml) with stirring in a 500 ml beaker with stirring and cooling (cardice/acetone) to 15°C. 98% sulfuric acid (88 ml) was then added slowly while keeping the temperature between 15-20°C over 5 min. The solution was then cooled to 5°C and a solution of sodium nitrite (9.8 g) in water (50 ml) was added dropwise over 15 min. while keeping the temperature between 5-8°C. After the addition the mixture was allowed to warm to room temperature and stirred for 2 hr before being transferred to a 1 L beaker.

Sodium azide (17.6 g) in water (50 ml) was then added dropwise while keeping the temperature below 25°C (much gassing and frothing occurs). After the addition (20 min.) the mixture was stirred for a further 30 min. and then filtered under vacuum to give a yellow solid which was washed with water (150 ml) and then allowed to dry under suction. The crude azidodinitrobenzene was suspended in water (100 ml) and heated to 95°C with stirring for 3 hr and then allowed to cool. The solid was filtered off, washed with water and dried to give the crude nitrobenzofuroxan (14.97 g). Sublimation under vacuum gave 5(6)-nitrobenzofuroxan as a yellow solid (10.71 g).

M.pt.: 71°C (lit.[56] 72°C).

C.3.4.2 Deoxygenation of 5(6)-nitrobenzofuroxan (to give 5-nitrobenzofurazan)

5(6)-Nitrobenzofuroxan (9.1 g, 0.05 mol) and triphenylphosphine (14.4 g, 0.055 mol) were dissolved in xylene (500 ml) and the dark red mixture was refluxed for 4 hours. The solvent was then removed under vacuum and the residue sublimed to give 5-nitrobenzofurazan (5.3 g), m.pt. 65°C.

C.3.4.3 Nitration of 5-nitrobenzofurazan

The method used was that of Read *et al* [58]. 5-Nitrobenzofurazan (6.0 g) was dissolved in conc. sulphuric acid (30 ml) and fuming nitric acid (18 ml) was added dropwise over 10 min. with cooling. The solution was then warmed to about 90°C over 1 hour and then maintained at that temperature for a further 1 hour, cooled and then poured on ice. The precipitate was filtered, washed with ice-water and dried under suction to give a yellow powder which after recrystallization from dichloromethane/hexane to give 4,6-dinitrobenzofurazan as yellow crystals (3.20 g), m.pt. 131°C (lit.[58] m.pt. 131-132.5°C).

C.3.4.4 Reaction of dinitrobenzofurazan with base [to give potassium salt of 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide (KDNBFZ, **VI**)]

4,6-Dinitrobenzofurazan (2.0 g) was added in one portion to aqueous potassium bicarbonate solution (50 ml) with stirring. The solid dissolved with gas evolution and the solution became dark in colour. The mixture was stirred for a further 3 h then cooled to 0°C and the precipitated yellow solid was suction filtered. The solid was washed with a little cold methanol (10 ml) and allowed to dry in air to give the potassium salt **VI** (1.95 g). The solid turned red above 115°C and darkened further around 180°C (the same melting behavior was noted in the literature [58]).

I.R. spectrum, KBr disc (cm^{-1}): 3565, 3210, 1603, 1580, 1492, 1380, 1338, 1250, 1091, 998, 878 and 825.

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.70 s, 1H, 6.16, s, br,1H and OH, 2.51, s, solvent, 3.31, s, H_2O.

The I.R. and NMR spectra matched the values quoted in the literature [58].

D Notes to Assist Interpretation of Hazard Test Data

Drop-weight Impact Tests

Rotter test: F of I (Figure of Insensitiveness): measured using UK Rotter apparatus, where a 5 kg drop weight impacts via intermediate components onto a sample (30μl, no grit) on a hardened steel anvil and the height required for a 50% probability of ignition is determined (up-and-down method). Assessment of fire/no fire is by a gas evolution criterion.

Figures for typical explosives: (>90: comparatively insensitive; <90 but >30: sensitive; <30 very sensitive):
TATB: >200; RDX: 80; PETN: 50; Lead Azide: 30; Lead Styphnate: 20.

Thus most common secondary explosives are "sensitive"; all primary explosives tend to be "very sensitive". Primary explosives may be defined as energetic solids that explode when heated unconfined.

Ball-and-Disc test: A more discriminatory test for primary explosives, where a 95 g steel ball is dropped from a measured height via an intermediate striker onto approximately 6μl of the explosive covered by a brass disc. Assessment of fire/no fire is by audible report; height for 50% probability of ignitions is found as above.

Figures for typical explosives (cm):
Lead azide: 19; Lead Styphnate: 11.

Explosives which do not respond in this test (i.e. figure >50 cm) behave more as secondary explosives, though they may retain some of the characteristics of primary explosives

Friction Test

Emery Paper Friction Test: A more discriminatory friction test for primary explosives. 6μl of the explosive is sandwiched between two abrasive (emery paper) coated steel surfaces, under light pressure from a lever arm, and the two surfaces are moved sideways relative to each other by impact from a pendulum weight, which has swung through a measured angle. The results are quoted as the pendulum velocity required to produce a 50% probability of ignition (audible report and scorching of the emery paper).

Figures for typical explosives (m/s):
Lead azide: 1.2; Lead Styphnate: 1.8. Note the reversal in the order of sensitivities cf. above.

Explosives which do not respond at velocities below 3.7 m/s (the maximum for the apparatus) are relatively insensitive to this stimulus and may not show the behaviour expected of primary explosives.

Electrostatic (Spark) Tests

Standard Test: To determine if the compound is sensitive to a spark resulting from the charge which can be accumulated on the human body (typically 20 mJ). Conventional initiatory compounds fall into this category. Compounds which are sensitive to discharges of 45 mJ are subjected to further testing (Test No. 7, below).

Test for sensitive explosives (No. 7): The extent of the testing depends on the behavior of the sample. Using a specific electrode configuration and selecting from a range of capacitance and test voltage, the lowest value (in μJ) at which ignition does not occur is found (in 50 trials) - this value is quoted together with the next highest value at which ignitions start to occur. For example:

"2.5 μJ ignition, not 2.0 μJ". The test result is used to define the appropriate level of ESD precaution that should be taken in operations involving the handling of the explosive.

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Report documentation page

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7a. Report Title:	Lead-Free Initiator Materials for Small Electro-Explosive Devices for Medium Caliber Munitions

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10a. Abstract. (An abstract should aim to give an informative and concise summary of the report in up to 300 words).

Concerns over the hazard to health of using lead-containing initiatory compounds, both in their manufacture and use, has led to investigations to identify suitable compounds, either known or novel and free of lead and other heavy metals, which could be used as replacements. Such compounds, broadly subdivided into those similar to lead azide (i.e. detonants) and those similar to lead styphnate (primary explosives), should possess similar characteristics (sensitiveness, explosiveness, stability etc.) to the particular compound they were required to replace. A survey report, based on open literature available world-wide and certain UK classified information, was published by QinetiQ in 1998 and identified twenty front-running candidate compounds. Work has been progressed with funding from US SERDP (Strategic Environmental Research & Development Program) under the pollution prevention programme, where the synthesis and preliminary evaluation of eight of the front-running compounds, four similar to lead azide and four similar to lead styphnate, was undertaken. In this work, of 12 months' duration, sufficient hazard and functional data were obtained to enable an assessment to be made with recommendations for compounds in each category to be put forward for larger scale testing and ultimate incorporation into medium-large calibre ordnance systems. Two suitable candidates, both silver salts, were identified in the detonant category, but none of the four candidates synthesized in the primary explosive (i.e. lead styphnate replacement) category was recommended. Suggestions are made for future work in this area.

10b. Abstract classification: Unlimited	FORM MEETS DRIC 1000 ISSUE 5

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