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REPORT

MRL-R-918

**A THERMAL STABILITY TEST FOR PRIMARY EXPLOSIVE STAB
 SENSITIZERS: STUDY OF THE THERMAL AND HYDROLYTIC
 STABILITY OF 2-PICRYL-5-NITROTETRAZOLE**

Paul P. Elischer & Robert J. Spear

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TITLE

A THERMAL STABILITY TEST FOR PRIMARY EXPLOSIVE STAB SENSITIZERS: STUDY OF THE THERMAL AND HYDROLYTIC STABILITY OF 2-PICRYL-5-NITROTETRAZOLE

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ABSTRACT

A simple screening test for determining thermal stability of primary explosives being considered as replacements for tetrazene has been developed. In this test, at 89°C, 2-picryl-5-nitrotetrazole (PNT) has a half life 4-5 times longer than tetrazene. Both materials have adequate hydrolytic stability and replacement of tetrazene by PNT in stab and percussion sensitive mixes should enhance shelf life. Thermal decomposition of tetrazene is approximately exponential while PNT exhibits autocatalysis.

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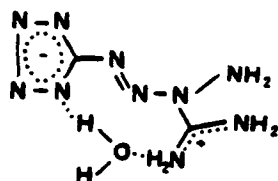
1. INTRODUCTION

The inadequate performance of many of the primary explosive fillings currently used in military stores has long been recognised. One area of particular concern is fillings containing the primary explosive tetrazene; stab and percussion sensitive mixes contain 2-5% by weight of tetrazene which functions as a sensitizing agent. The poor thermal stability of tetrazene, degradation of which leads to dudding of the detonator or primer, limits both shelf life and conditions under which stores containing these compositions can be used. At MRL we have been engaged for a number of years in a programme aimed at examining new materials with the potential to replace tetrazene in stab and percussion sensitive mixes. Some of the material properties which are important for providing adequate sensitization have been identified [1] and a number of new materials which afford high sensitization have been prepared [1,2,3].

This exploratory approach has concentrated on explosive properties, ie, basic sensitivity testing of materials being assessed as tetrazene replacements followed by determination of their ability to sensitize the primary explosive lead azide to stab initiation. However, assessment of a new material must involve examination of a number of other properties, the most important being development of a preparation method which reproducibly affords the right physical form and determination of stability and compatibility. In the case of new materials being considered as replacements for tetrazene, stability must be assessed at an early stage before further development proceeds. Significantly enhanced thermal stability (over tetrazene) would have to be demonstrated to warrant further study.

The aim of the investigation reported here was to develop a simple and reproducible screening test for thermal stability of new primary explosives. The approach chosen was to directly compare one of the promising new primary explosives with tetrazene under conditions which gave a conclusive result in 1-2 months. Other materials could subsequently be tested without having to re-run tetrazene on each occasion. The material chosen for

assessment was 2-picryl-5-nitrotetrazole (PNT). PNT has been shown previously to confer a high degree of sensitivity to stab initiation of lead azide [1,2]. PNT will also ignite readily from hot-wire and subsequently initiate RDX to detonation in a typical detonator geometry [2]. In order that a complete assessment of the stability of PNT be undertaken, a concurrent study on hydrolytic stability was also carried out. PNT has been reported to possess poor hydrolytic stability [4], although our own work does not support this claim [2].



TETRAZENE



PNT

2. EXPERIMENTAL APPROACH

2.1 Thermal Stability

There is considerable variation in the published decomposition rates for the thermal decomposition of tetrazene [5-8]. Norwitz et al [5] studied two different commercial batches of tetrazene and found one batch "deteriorated" in 5 weeks at 60°C, 8 days at 75°C and 3 h at 100°C, while the corresponding values for the other batch were >13 weeks, 14 days and 7.5 h respectively. In contrast Bird et al [7,8] stated that tetrazene decomposes too slowly at 60°C for short-term experimentation, can withstand 75-80°C for short periods, while at 90°C decomposition is complete within one week. Reitsma [9] has reported that tetrazene is recovered unchanged after 91 days at 65°C.

In order that the test be complete within 1-2 months, it was necessary to study the decomposition at a temperature towards the upper end of the temperature limits quoted above. A temperature of about 90°C was accordingly chosen; complete decomposition of tetrazene should be expected within 1 month, and any enhanced thermal stability of other materials should thus be readily apparent.

Both "small" and "large" samples were examined. The "large" samples consisted of PNT and tetrazene, each 1.25 g, which were placed in covered glass petri dishes in the oven. Each sample was mixed every 2-3 days to ensure uniform exposure and representative sampling for analysis. The sample size was chosen so that removal of material for analysis would have a minimal

effect on the total mass, since it has been suggested previously [8] that the rate of thermal decomposition of tetrazene is mass dependent. Obviously a mass larger than 1.25 g would have been preferable but would have constituted an unwarranted safety hazard from the possibility of a runaway thermal decomposition/explosion in the oven. Preliminary experiments suggested that neither PNT nor tetrazene constituted a significant safety hazard at mass 1.25 g under our test conditions. The "small" samples were each about 0.2 mg accurately weighed directly into differential scanning calorimetry (DSC) sample pans, then placed in numbered racks which were put in the oven on the same shelf as the large samples in petri dishes. This is much safer than the large samples and has the added advantage that weight loss could be quantitatively determined, but limits analysis to a single method, ie DSC. Although it was suggested that thermal stability testing should be carried out on pressed experimental stab compositions, we ruled out this approach because it essentially would correspond to an accelerated compatibility test between the sensitizer and the other component(s) in the mix.

2.2 Hydrolytic Stability

Tetrazene is reported to be "stable at ordinary temperatures when wet" [10] and in fact is often transported in bulk under water. Further confirmation of the adequate hydrolytic stability of tetrazene is that the standard production method of drying is heating at 45-55°C [10]. Although the usual method for destruction of tetrazene wastes is treatment with boiling water, where decomposition is extremely rapid with formation of two molecules of nitrogen per mole [10], this largely reflects a combination of thermal processes and the much higher hydrolytic rates at 100°C. A number of products formed via acid and base catalysed hydrolysis have been identified [11] but no detailed kinetic studies have been reported, probably owing to the very limited solubility of tetrazene in most solvents. In contrast, PNT has been reported to be "of doubtful hydrolytic stability" [4], although no experimental details were given. Results from our earlier study [2] did not support this view.

The test chosen for initial screening of tetrazene and PNT was exposure of 1.25 g of each material in a glass petri dish stored in a closed vessel containing a saturated solution of ammonium chloride, which gives a humidity of 78-80% at ambient pressure over a temperature range of 15-25°C [12]. The room temperature was controlled at 20°C. Each sample was mixed every 2-3 days to ensure uniform exposure and representative sampling for analysis.

A second test was subsequently carried out (see text) in which samples of PNT and tetrazene, about 10 mg, were accurately weighed into glass sample tubes, covered with water and stoppered. The tubes were stored at 20°C and the samples were subsequently recovered by filtration followed by drying in air overnight.

Tetrazene should be stable to both the above tests for many months, and both tests were chosen with the aim of discriminating against materials with poor hydrolytic stability. It was anticipated that a period of perhaps 6 months might be required for the test. The authors ruled out testing at

higher temperatures, say 40-50°C, because of the presence of a thermal component in addition to hydrolysis. We readily admit that such a test may be more appropriate to the conditions likely to be experienced by ordnance items, and indeed may be developed in the future. However the principal aim of this work was to develop a thermal stability test, and hydrolytic stability was only examined because of specific doubts expressed about PNT [4].

2.3 Analysis of PNT and Tetrazene Samples

Two methods were used for analysis.

2.3.1 Differential Scanning Calorimetry (DSC)

The DSC thermograms for both PNT and tetrazene consist of exotherms corresponding to ignition. In the case of tetrazene, the area under the exotherm is proportional to sample weight [13] and this method has been used for quantitative determination of tetrazene in primer mixes [14]. The exotherm peak area for the PNT thermogram was determined on a number of samples ranging in mass from 0.025 - 0.30 mg and an excellent linear correlation (Fig. 1) was also obtained. DSC was therefore used for quantitative determination of PNT and tetrazene in the samples under examination.

2.3.2 Stab Sensitivity of Pressed 1:20 Admixtures with Lead Azide RD1343

Samples of PNT and tetrazene taken from the large sample batches were mixed with lead azide RD1343 in the ratio 1:20 by weight. The mixes were then compacted at 560 MPa into experimental stab detonators and stab initiation energies were determined for the 50% level using standard Bruceton analysis [15]. This test has the advantage that it more closely approaches the practical use of such sensitizers, but suffers from the disadvantage that both PNT and tetrazene still afford high sensitization (low stab initiation energies) to lead azide when present at only 0.5% by weight [1,2,16]. The results are therefore useful for detecting substantial deterioration but can only provide a qualitative measure of the degree of deterioration of the sensitizer.

3. RESULTS AND DISCUSSION

3.1 Thermal Stability

Analysis results for tetrazene and PNT samples undergoing thermal degradation at 89°C are detailed in Tables 1 and 2 respectively. Stab initiation energies for 1:20 admixtures with lead azide RD1343 are listed in Table 3.

The results for tetrazene amply illustrate its susceptibility to thermal decomposition. The residual tetrazene content of the small samples decreases steadily with time and after 6 weeks only 20% of the original tetrazene remains (Table 1, figures not in parentheses). Mass loss over this time is also considerable, with almost 50% lost by decomposition into volatile products. Decomposition of the large sample is considerably faster and after only 5 weeks residual content is down to 3%*; mass loss on this sample is unknown. These figures support the earlier conclusion [8] that the rate of decomposition is mass dependent, being faster with increase in mass. A typical DSC trace for pure tetrazene and a portion from the large sample, after 5 weeks at 89°C, can be seen in Figure 2a. The broadening and diminishing of the first exotherm relative to the second exotherm can clearly be seen. The second exotherm is believed to correspond to thermal decomposition of the initial products of ignition [6].

PNT, in contrast, decomposed much more slowly (Table 2). No mass loss was observed for the small samples till 6 weeks had elapsed, and the PNT content was still 87.3% of original. At the completion of the trial at 10 weeks, PNT content was 65.6% and mass loss only 13%. As was the case with tetrazene, the large sample decomposed significantly faster (Table 2, compare with numbers in parentheses for small sample) and after 9 weeks had completely decomposed. Typical DSC traces for pure PNT and a portion taken from the large sample after 7 weeks at 89°C are shown in Figure 2b.

The relative decomposition rates of the tetrazene and PNT samples can be seen in the plots in Figure 3. The substantially enhanced thermal stability of PNT relative to tetrazene is clearly evident, as is also the higher decomposition rates of the large samples in each case. Note that whereas tetrazene exhibits a typical exponential-like decay, the PNT large sample decomposes slowly for about 35 days followed by an acceleratory period. This latter behaviour is typical of autocatalysis where, in this case, PNT would form decomposition products which catalyse further decomposition. Further evidence to support this conclusion can be seen in the exotherm peak maxima temperatures, shown in Tables 1 and 2 as T_{max} . The T_{max} for tetrazene gradually declines from approx. 150°C to approx. 148°C after 5 weeks for the small sample and to slightly lower for the large sample (Table 1). In contrast, T_{max} for the PNT small samples changes from approx. 173°C to approx. 163°C after 10 weeks, and even more substantially for the large sample (Table 2 and see Figure 2b). Although decomposition of the PNT small sample has not reached the stage of accelerated decomposition after 10 weeks, the decrease in T_{max} (Table 2) would suggest that this point has almost been reached.

Stab initiation energies for pressed 1:20 admixtures of tetrazene and PNT with lead azide are consistent with the DSC results. The sensitizing ability of tetrazene declines gradually, then more rapidly, to be minimal at

* Note that these figures are for tetrazene content as a percent of residual mass, not total original mass. A direct comparison with the small sample can be obtained from the numbers in parentheses, Table 1.

the end of 6 weeks. For comparison, lead azide containing only 0.25% pure tetrazene (i.e. a 1:250 admixture) has a 50% stab initiation energy of 5.4 mJ. In contrast, the sensitizing ability of PNT shows no change over the first 4 weeks, within experimental error, and is still substantial after 6 weeks.

The decreasing sensitization afforded by tetrazene as decomposition progresses results both from loss of purity and buildup of decomposition products on the surface of the particles. The latter is apparent even after 1 week at 89°C, where a few colourless prisms could be seen, by optical microscopy, growing out from the almost spherical tetrazene particles. After 3 weeks the number of prisms and colourless needles had increased markedly, and at 6 weeks had grown together to form continuous clumps. This surface contamination and accompanying agglomeration presumably led to the poor mixing with the lead azide and deterioration in the sensitizing ability. When a portion of the tetrazene large sample held at 89°C for 2 weeks was treated overnight with methanol then filtered and allowed to dry, the colourless prisms were removed from the particle surfaces. This restored the excellent mixing properties with lead azide and the admixture had 50% stab initiation energy of 3.9 mJ, compared with 6.6 mJ for the untreated material (Table 3).

The physical changes associated with PNT decomposition were an initial darkening of the crystals within 1 day, but no surface changes could be observed microscopically. Mixing with lead azide remained excellent till the fifth week, and the deterioration in this property is the most likely explanation for the increase in stab initiation energy at this time (Table 3). Other changes observed at 5-6 weeks included the appearance of some needles, presumably decomposition product, and a tendency for the remaining PNT particles to agglomerate. Physical properties deteriorated further after this time and at 9 weeks the remaining material was dark-brown and intractable.

3.2 Hydrolytic Stability

The samples of tetrazene and PNT were held at 78-80% humidity, 20°C, and portions were removed for analysis at 3 months, 6 months and 12 months. After air drying overnight, analysis by DSC revealed >99% purity of all samples. Stab initiation energies determined on 1:10 admixtures* with lead azide RD1343 are detailed in Table 3. As expected from the above DSC results, tetrazene shows minimal activity loss. The small gradual increase in stab initiation energies most likely results from surface contamination by slow buildup of very small amounts of hydrolysis products, and suggests that while this analysis method may be crude it can detect surface deterioration at a time when total decomposition is still very low. The corresponding figures

* We typically use 1:10 admixtures for exploratory testing of sensitization. These tests were performed before the corresponding thermal stability testing, at which stage it was decided to use 1:20 admixtures to more quickly detect deterioration in sensitization.

for PNT (Table 3) likewise increase slightly (with the "hiccup" at 3 months) over the period of study.

Both materials are obviously of adequate stability under the above conditions. As a more severe test both were suspended in water at 20°C, then samples recovered by filtration after 2 weeks, then 2 months. After overnight air drying, samples were analysed by DSC which showed >99% purity in all cases. Mass loss in all samples was negligible, although the water above the PNT samples had taken on a distinct yellow colour.

Under these tests, both materials are hydrolytically stable. If a requirement existed to "rank" their hydrolytic stability, a more severe test would be required (see comments in Section 2.2).

4. CONCLUSIONS

PNT has significantly greater thermal stability than tetrazene. The half-life at 89°C (w.r.t. original material, i.e. taking into account mass loss and not just decrease in residual content to 50%) for the small samples is >10 weeks for PNT and about 16 days for tetrazene. The corresponding times for the large samples are approximately 7 weeks and 10 days respectively, estimated by taking account of mass loss data for the small samples. Both materials show adequate hydrolytic stability. Replacement of tetrazene by PNT in stab and percussion sensitive mixes would be expected to significantly increase shelf life. Whereas thermal decomposition of tetrazene follows a typical exponential decay, PNT appears to be subject to autocatalysis. Clearly this would have to be further examined if service qualification of PNT were to proceed.

A number of other new sensitizing materials developed at MRL are currently awaiting assessment of their thermal stability. The recommendation from this study is that initial screening should be done using the "small sample" method described here; the obvious advantages are that minimal amounts of material are required, significantly increasing safety, and mass losses are more easily determined. Such a test also probably corresponds more closely to the situation in pressed stab and percussion mixes, where the sensitizer particles are largely separated by dispersal throughout the more thermally stable components which comprise 95-98% of the total mass. The "large sample" method tested here would tend more to model bulk storage of production batches. It is also suggested that testing should include stab initiation of admixtures after the initial "small sample" screening tests. This would specifically search for deterioration of mixing and sensitizing ability by buildup of decomposition products on the particle surfaces, at a stage where decomposition was at a very low level relative to total mass: see comments in Section 3.2.

5. EXPERIMENTAL

5.1 *Materials*

PNT was prepared by reaction of sodium 5-nitrotetrazole with picryl chloride and recrystallised from acetone-hexane. Full experimental details have been described previously [2]. The actual batch used was designated Batch D and was identical to that referred to as Batch C in Reference [2].

Tetrazene was type RD1357 prepared at Materials Research Laboratories. The batch used was designated Batch 10/83(A).

Lead Azide was type RD1343 and was obtained as a single batch (Batch 12) from Munitions Filling Factory, St. Marys, NSW.

Both PNT and tetrazene were initially sieved remotely through a 300 μ m sieve to break up any crystal aggregates and to ensure reasonable homogeneity of particle size.

5.2 *Procedures for Thermal and Hydrolytic Stability Testing*

Thermal stability was investigated using a Qualtex Solidstat oven, model OG18SZ. The oven settings were adjusted to an average temperature of 89.0°C. Measurements with a pre-calibrated digital thermometer positioned on the same shelf as the experimental samples showed that the temperature cycled each 3.7 ± 0.15 min over a maximum temperature range of 88.4 - 89.6°C, with a typical temperature range of 88.6 - 89.4°C.

The thermal stability of both "small" and "large" samples of tetrazene and PNT was investigated. The small samples consisted of about 0.2 mg weighed accurately (to 0.001 mg), using a Mettler ME 30 Microbalance, directly into aluminium DSC sample pans. Each pan was then placed in a numbered position in an aluminium sample holder which held 20-30 pans. The holders were each loosely covered with a cardboard sheet and placed in the oven. Large samples consisted of 1.25 g weighed directly into a 6.5 cm diam. glass petri dish. The material was spread evenly to maximise the exposed surface area, the loose fitting petri dish lid was fitted then the petri dishes were placed in the oven. Samples were removed at regular intervals (see text) for analysis, and were analysed on the day of sampling.

Hydrolytic stability was determined on samples of 1.25 g in glass petri dishes. Each sample was placed in a desiccator containing a saturated solution of ammonium chloride. Samples were then taken at three monthly intervals, allowed to dry overnight then analysed the following day. When no degradation was observed using this test, samples of about 10 mg of both PNT and tetrazene were accurately weighed into sample tubes, covered with water and stoppered. After a period of two weeks, the remaining material was filtered off, allowed to dry overnight, then analysed the following day. A second sampling was repeated after a time interval of two months.

5.2.1 Analysis Using Differential Scanning Calorimetry (DSC)

DSC thermograms were recorded on a Perkin Elmer DSC-2 Differential Scanning Calorimeter equipped with Scanning Auto Zero accessory. Experimental conditions were vented aluminium pans under a flowing nitrogen atmosphere (15 ml/min), heating rate 20°C/min. In the case of the "small" samples in the DSC pans, the pans were removed from the oven, allowed to cool, then reweighed on the Microbalance. Aluminium lids were then placed (but not crimped) on the pans and the thermograms were recorded using an identical but empty aluminium pan as reference. The large batches were sampled and about 0.2 mg was accurately weighed into an aluminium DSC pan. The thermogram was recorded as above. All measurements were made in duplicate. Peak areas were determined by digitization on a Calcomp Model 622 Digitizer. In the case of tetrazene, where two exotherms are present, only the lower temperature exotherm was used for area determination. Masses of (residual) PNT and tetrazene were determined from the calibration charts (c.f. Fig. 1); standard samples of pure PNT and tetrazene were recorded with each analysis to check calibration.

5.2.2 Analysis by Determination of Stab Sensitization

5.2.2.1 Preparation of Lead Azide Admixtures

The PNT or tetrazene sample (40 mg) was added to lead azide RD1343 (0.8 g) and fold-mixed on a sheet of paper behind a safety screen. Mixing was continued until the composition had achieved optimum homogeneity. In the case of the thermally aged tetrazene and PNT samples, mixing was poor (see text). The hydrolytic stability samples were tested using 1:10 admixtures.

5.2.2.2 Preparation of Experimental Detonators

Experimental detonators were prepared in mild steel tubes, 6 mm o.d., 3.2 mm i.d., length 6 mm, prepared from commercially available tubing. A back filling of lead monoxide (280 mg) was first pressed into the tube using a remotely controlled Pongrass press at a pressure of 560 MPa. The experimental composition (50 mg) was then added on top and the unit repressed at 560 MPa.

5.2.2.3 Determination of Stab Initiation Energies

The experimental set up, consisting of a drop tower test rig fitted with a quick release mechanism, has previously been described in detail [17]. The free falling striker weighed 14.5 g except for the composition prepared using tetrazene which had been at 89°C for 6 weeks, where a 55.2 g striker was used. The striker body was refitted with a new needle after every test whether or not a fire occurred. The needle was silver steel hardened to 640 HV with a 0.08-0.20 mm flat on the tip. In each experiment the striker was released from a pre-set height to impact on the experimental detonator supported in an aluminium holder held in a mild steel base. Each testing was assessed as fire or no fire by sound (very loud for a positive fire) and

visual inspection of the detonator tubes. A no fire resulted only in an obvious indentation into the compacted explosive. The detonators were not retested after a no fire but were destroyed chemically.

Preliminary determinations were conducted at a number of heights to obtain an approximate 50% fire level. The drop height was then varied using regular intervals of approximately 10% of this level. 15 detonators were tested for each experimental composition prepared from the thermally or hydrolytically aged samples. Measurements on compositions prepared from the pure (non-aged) tetrazene and PNT samples were recorded on 25 samples of each. All testing used the Bruceton staircase method and the results for the 50% fire levels were obtained by standard Bruceton statistical analysis [15].

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7. REFERENCES

1. Spear, R.J. and Elischer, P.P. (1982). Aust. J. Chem., 35, 1 and earlier references cited therein.
2. Spear, R.J. and Elischer, P.P. (1982). MRL-R-859.
3. Norris, W.P. and Spear, R.J. (1983). MRL-R-870.
4. Bates, L.R. and Jenkins, J.M. (1975). "Search for New Detonants" in Proc. Int. Conf. on Primary Explosives, ERDE, Waltham Abbey, UK.
5. Norwitz, G., Everett, M.E. and Gurbarg, M.T. (1975). Thermochim. Acta, 12, 227.
6. Patel, R.G. and Chaudhri, M.M. (1976). "Thermal Decomposition of Tetracene" in Proc. 4th. Symp. on Chem. Prob. Conn. with Stab. of Explos., ed. J. Hansson, Molle, Sweden, p. 347 and earlier studies cited therein.
7. Bird, R. and Power, A.J. (1978). MRL-R-710.
8. Bird, R., May, F.G.J. and Warren, M.D. (1975). "Tetrazole and Tetracene Studies", 5th. Quadrupartite Ammunition Conf., Canberra, Oct. 2-3.
9. Reitsma, H.J. (1977). "Investigations into the Compatibility of a few Primary Explosives/Polymer Combinations", Institut fur Chemie der Trieb-und Explosivstoffe, I.C.T., Int. Jahrestag., Karlsruhe, Ger., p. 249.
10. Urbanski, T. (1967). "Chemistry and Technology of Explosives", Pergamon Press, London, Vol. 3, p. 206.
11. Patinkin, S.H., Horwitz, J.P. and Lieber, E. (1955). J. Am. Chem. Soc., 77, 562, and earlier studies cited therein.
12. CRC Handbook of Chemistry and Physics (1976), R.C. Weast, ed., CRC Press, Ohio, 56th edition, p. E-46.
13. Krien, G. (1976). "Uber die Thermische Zersetzung von Tetrazen" in Proc. 4th. Symp. on Chem. Prob. Conn. with Stab. of Explos., ed. J. Hansson, Molle, Sweden, p. 371.
14. Krien, G. (1979). Propellants Explos., 4, 53.
15. Culling, H.P. (1953). NAVORD Report 2101, US Naval Ordnance Laboratory, Whiteoak, Maryland.
16. Bird, R. (1975). MRL-TN-362.
17. Bentley, J.R. and Elischer, P.P. (1981). MRL-R-776.

TABLE 1

Analysis results ^a for Tetrazene samples undergoing thermal degradation at 89°C.

Time Elapsed	Small Samples ^b			Large Sample ^c	
	Mass Loss (% of total)	Residual tetrazene content (%) ^d	Thermogram T _{max} (°C)	Residual tetrazene content (%) ^e	Thermogram T _{max} (°C)
0	0.0	100.0 (100.0)		100.0	
1 day	0.6	95.6 (95.7)	149.9	95.7	150.4
4 days	2.6	82.7 (84.6)	148.8	90.1	149.1
7 days	5.0	71.7 (77.4)	148.1	80.5	148.2
10 days	10.4	62.3 (72.3)	148.4	60.4	148.6
14 days	19.5	55.1 (67.1)	148.8	45.6	148.1
18 days	24.5	41.6 (54.7)	148.7	32.9	148.7
3 weeks	27.5	44.9 (60.9)	148.7	32.7	148.2
4 weeks	35.1	33.8 (51.3)	148.3	13.0	147.5 ^f
5 weeks	42.7	17.1 (29.7)	148.5	~3	~146 ^f
6 weeks	46.9	20.0 (36.5)	149.6	<3	~147 ^f

^a All measurements were made in duplicate and represent mean values.

^b Samples weighed directly into DSC pans and stored at 89°C.

^c Sample originally 1.25 g, stored in covered petri dish at 89°C.

^d As a percent of the total original mass. Numbers in parenthesis are percent in remaining mass to afford a direct comparison with results for large sample.

^e As a percent of the total mass of sample removed for analysis. This does not take into account mass losses by volatilization of decomposition products.

^f Very broad, difficult to measure T_{max}.

TABLE 2

Analysis results^a for PNT samples undergoing thermal degradation at 89°C.

Time Elapsed	Small Samples ^b			Large Sample ^c		
	Mass Loss (% of total)	Residual PNT content (%) ^d	Thermogram T _{max} (°C)	Residual PNT content (%) ^e	Thermogram T _{max} (°C)	
0	0.0	100.0	(100.0)	100.0		
1 day	- 2.4 ^f	102.0	(100.3)	173.2	95.9	171.4
4 days	2.3	100.6	(102.8)	171.7	101.6	171.9
7 days	2.0	95.4	(97.2)	172.4	95.4	172.0
10 days	- 1.8 ^f	95.3	(93.8)	172.2	97.2	171.9
14 days	0.2	100.3	(100.6)	172.0	95.6	171.6
18 days	0.8	96.1	(97.0)	171.5	90.3	171.1
3 weeks	1.4	92.7	(94.2)	171.5	89.9	170.3
4 weeks	- 0.9 ^f	93.7	(92.7)	170.3	88.3	168.7
5 weeks	1.9	91.0	(92.6)	170.0	85.2	166.8
6 weeks	3.1	87.3	(90.1)	170.1	73.4	164.6
7 weeks	3.9	85.3	(89.0)	168.8	50.1	~162 ^g
8 weeks	8.0	78.5	(85.4)	165.1	~4	~161 ^g
9 weeks	13.0	65.8	(75.4)	164.5	<1	~158 ^g
10 weeks	12.9	65.6	(74.8)	163.2	<u>h</u>	<u>h</u>

a All measurements were made in duplicate and represent mean values.

b Samples weighed directly into DSC pans and stored at 89°C.

c Sample originally 1.25 g, stored in covered petri dish at 89°C.

d As a percent of the total original mass. Numbers in parenthesis are percent in remaining mass to afford a direct comparison with results for Large sample.

e As a percent of the total mass of sample removed for analysis. This does not take into account mass losses by volatilization of decomposition products.

f Apparent gain in weight.

g Very broad, difficult to measure T_{max}.

h Not determined.

TABLE 3

Stab initiation energies^a for admixtures of lead azide with tetrazene and PNT samples which had been subjected to thermal and hydrolytic stability studies.

Test/Time Elapsed	Stab Initiation Energies (mJ) ^a	
	Tetrazene	PNT
1. Thermal Stability at 89°C		
0 ^{b,c}	3.6	7.3
1 week ^c	3.9	8.3
2 weeks	6.6	7.2
3 weeks	6.9	7.2
4 weeks	10.2	6.8
5 weeks	20	18
6 weeks	110	18
2. Hydrolytic Stability ^{d,e}		
0	3.3	11.1
3 months	3.5	19.1
6 months	4.1	11.7
3. Pure lead azide RD1343	approx. 1000 ^f	

- a 50% fire levels obtained by standard Bruceton analysis [15].
- b 25 detonators tested, all other results refer to test samples of 15 detonators.
- c Lead azide : tetrazene or PNT = 20:1, pressed at 560 MPa.
- d 78-80% humidity, 20°C.
- e Lead azide : tetrazene or PNT = 10:1, pressed at 560 MPa.
- f Ref. 1, quoted for comparison.

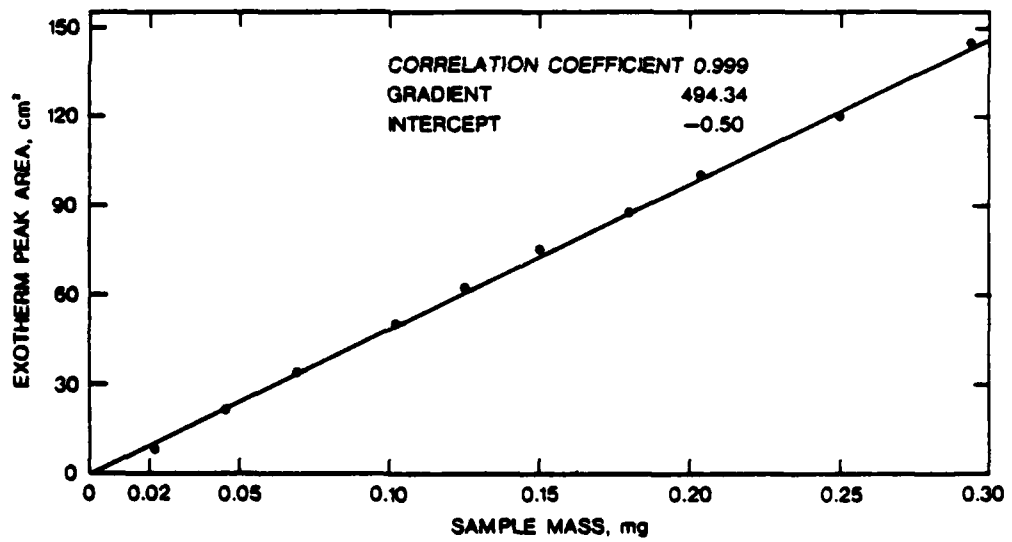


FIGURE 1. A plot of exotherm peak area vs. sample mass for PNT DSC thermograms.

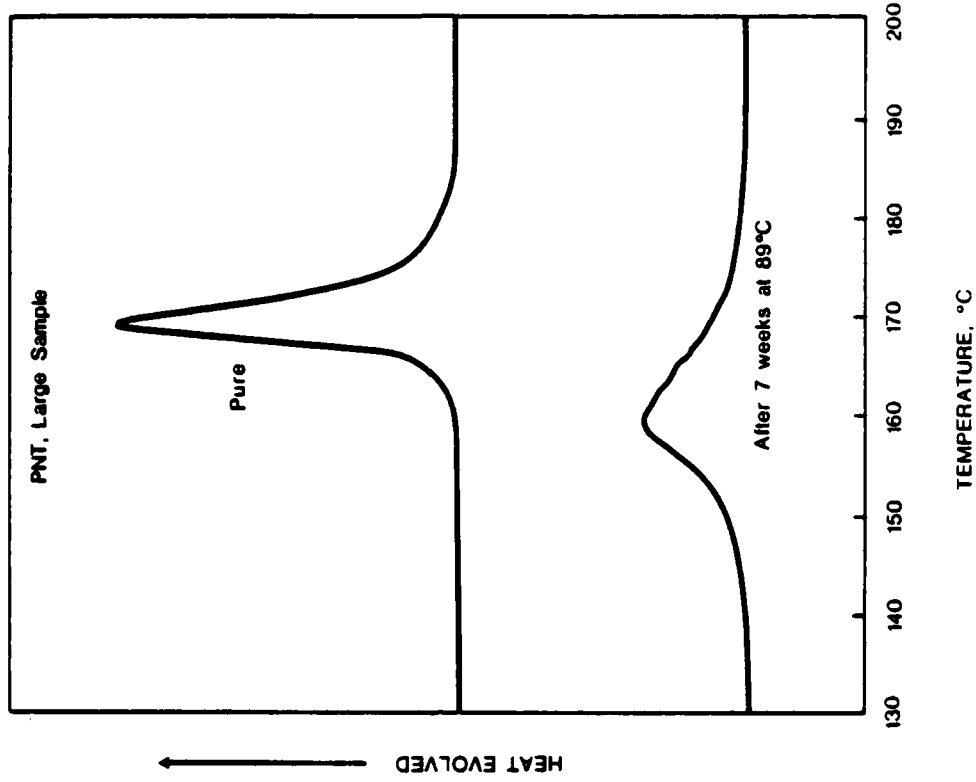


Fig. 2b

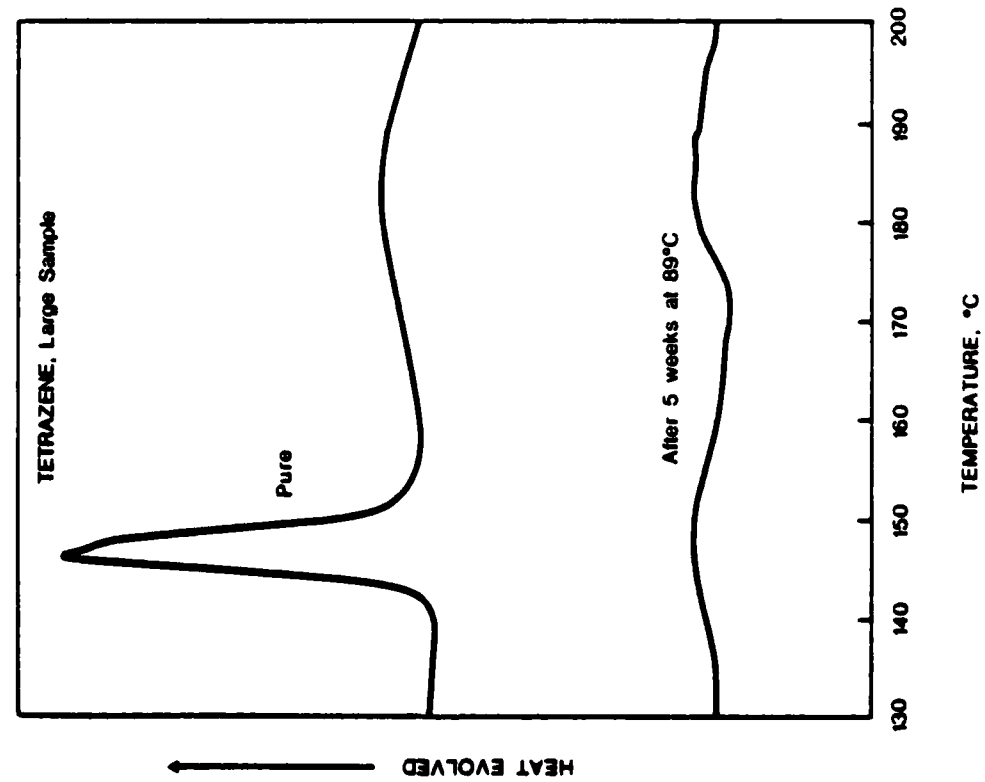


Fig. 2a

FIGURE 2. DSC thermograms for tetrazene and PNT, both large batches, heating rate 20°C/min, showing the effect of storage at 89°C. The lower trace in each figure was recorded at higher gain.

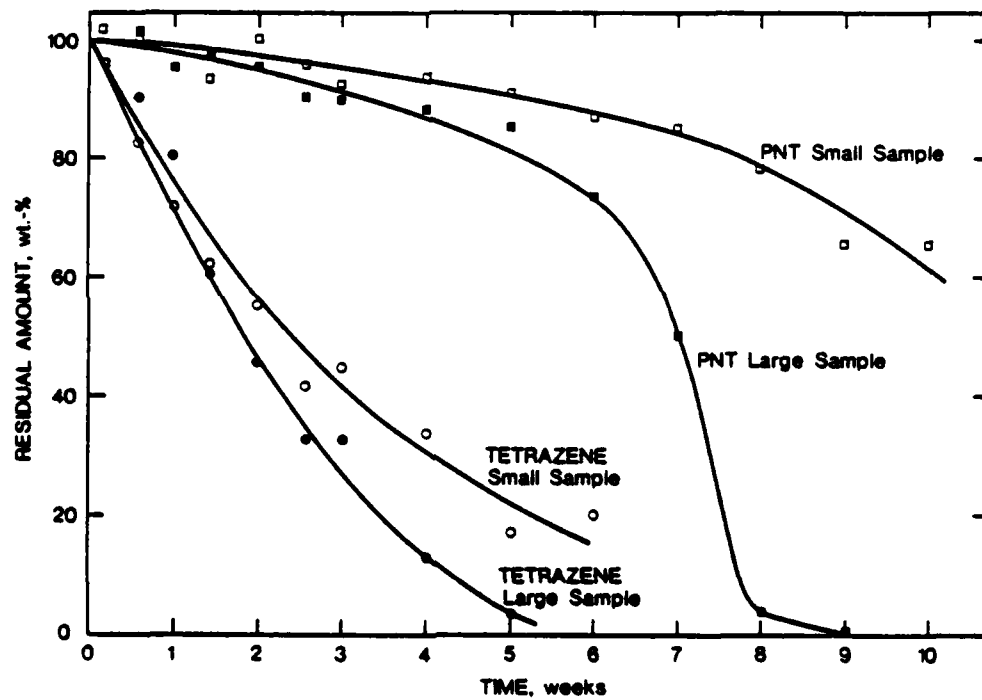


FIGURE 3. Residual amount vs. time for tetrazene and PNT samples held at 89°C.

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