

AN INVESTIGATION OF THE MATERIAL HAZARD

AR-006-375

Vm

ROBERT J. SPEAR AND LUCIANA MONTELLI

MRL-TR-91-22



APPROVED

FOR PUBLIC RELEASE



An Investigation of the Material Hazard of Some Insensitive High Explosives

Robert J. Spear and Luciana Montelli

MRL Technical Report MRL-TR-91-22

Abstract

A number of insensitive high explosives (IHE) and formulations which were determined to have unexpectedly high sensitiveness by Rotter impact testing (F of I 60-110) were further assessed by Rotter powder explosiveness testing. Analysis shows that the hazard as reflected by the ability to propagate following ignition, was low. Risk, defined as the product of hazard and frequency (F of I), was similar to assessment based on US impact test data for these materials. An assessment of both the usefulness and the quantitative nature of powder explosiveness testing is made. Guidelines for using Rotter data for deciding relative risk from handling of relatively small quantities of IHEs in R & D are given. The desirability of carrying out charge hazard testing to support these risk assessments is stressed.



91 12 4 069

MATERIALS RESEARCH LABORATORY

Published by

Materials Research Laboratory Cordite Avenue, Maribyrnong Victoria, 3032 Australia

Telephone: (03) 319 3887 Fax: (03) 318 4536

© Commonwealth of Australia 1991 AR No. 006-375

APPROVED FOR PUBLIC RELEASE

Authors

Robert J. Spear



Robert Spear graduated BSc (Hons) in Organic Chemistry from University of Melbourne in 1969. His PhD was conferred in 1973 by University of Sydney for studies on the use of nuclear magnetic resonance spectroscopy to define molecular structure. After post-doctoral studies for two years in the USA he taught in the Department of Organic Chemistry at University of Melbourne for three years. He joined MRL in 1978 and has worked exclusively on explosives and their applications. His current position is Research Leader Energetic Materials.



Luciana Montelli

Lucianna Montelli graduated BAppSc in Chemistry in 1987 from Royal Melbourne Institute of Technology. She was then recruited to MRL where she has conducted R & D into a number of aspects of explosives technology including polymer bonded explosives formulation and thermally stable high explosives for initiating devices.





Contents

1. INTRODUCTION 7

2. GENERAL COMMENTS ON IMPACT SENSITIVENESS/SENSITIVITY OF EXPLOSIVES 8

- 3. SENSITIVENESS, EXPLOSIVENESS AND CRITERIA THEREOF 9
- 4. EXPERIMENTAL 10
- 4.1 Materials 10
- 4.2 Method 11

5. RESULTS 11

- 6. DISCUSSION 16
- 6.1 Rotter Impact Data 16
- 6.2 Calculation of Powder Explosiveness 17
- 6.3 Comparison of Explosiveness Data 19

7. CONCLUSION 20

- 8. ACKNOWLEDGEMENTS 20
- 9. REFERENCES 21

新潟

An Investigation of the Material Hazard of Some Insensitive High Explosives

1. Introduction

Basic R & D to identify new or improved explosive formulations which can lead to reduced munition vulnerability is being conducted at MRL using a number of strategies:

- (i) Cast-cured polymer bonded explosives (PBX) for fragmentation and underwater warhead main charge fillings [1].
- (ii) PBX moulding powders for pressed boosters for low vulnerability fuzes [2, 3].
- (iii) New energetic but insensitive explosive molecules [4], or improved forms of currently used explosives [5, 6], which have potential for use in (i), (ii) or TNT-based melt-cast explosives.

With any of these types of materials, the initial assessment of their risk commences with their sensitiveness to impact. We use the UK Rotter method [7, 8a], which requires only 1 to 2 g of material and provides good guidance for safety in handling via an extensive data base accumulated over many years. Risk is a product of hazard and frequency. The Rotter data are converted to a Figure of Insensitiveness (F of I) which correlates with frequency, i.e. the likelihood of an initiation/ignition. It should be stressed that the F of I relates only to loose explosive at low masses and provides background for experimental work and small-scale production; it cannot be read across to either charge or munition hazard.

We were therefore very surprised to find that a number of the "insensitive" explosives on which we were carrying out basic R & D had F of I values similar to the booster explosive tetryl. For example, the high explosive 3-nitro-1,2,A-triazol-5-one (NTO) was found to have impact sensitiveness equal to tetryl [4]; while US data obtained on ERL impact machines [9] rated NTO as very much less sensitive [10, 11]. We found high surface area hexanitrostilbene (HINS) to be more sensitive than tetryl [6]. Also a previous comparative study on booster explosives including the US insensitive booster formulation PBXW-7 (RDX/TATB/Viton A 35:60:5) had identified Rotter impact sensitivity equal to or greater than tetryl in contrast to published US data [12].

This study investigates the impact response of a number of "insensitive" high explosives and formulations in detail, primarily to provide a measure of the risk to R & D personnel in handling these materials. The usefulness of explosiveness tests to supplement impact data is then discussed. The experimental investigations have concentrated on materials which have yielded unexpectedly low F of I values; NTO, HNS, nitroguanidine (NQ), 7-amino-4,6-dinitrobenzofuroxan (ADNBF) and PBXW-7, and suitable reference explosives. More limited data are given for a range of other explosives.

2. General Comments on Impact Sensitiveness/Sensitivity¹ of Explosives

The lack of correspondence between Australian and US impact sensitiveness¹ data was not altogether unexpected since there is generally poor agreement between results from different types of impact machine. Hornby and Merrick [15] noted poor correlation between Rotter F of I and ERL $h_{50\%}$ data, while Smith [16] published a careful study of a range of explosives from PETN to Explosive D and found a plot of F of I versus $h_{50\%}$ to be a "scattergram with a correlation coefficient of 0.19!" More recently Mullenger has demonstrated poor reproducibility between Rotter and the European BAM impact test results [17].

Coffey *et al.* [18], in a detailed critique of impact testing, have bluntly suggested that the standard 50% point (F of I, h_{506} etc.) reveals as much or more about the impact response of the particular impact machine as it does about the impact ignition response of the material being tested. Afanas'ev and Babolev [19] have analysed in great detail the machine parameters which affect test results. On the positive side, it should be stressed that understanding of the physical processes leading to ignition under impact has been very substantially improved, particularly through studies conducted at the Cavendish Laboratory [20].

¹ Sensitiveness is the terminology used in Australia and the UK to denote "ease of ignition". The US use sensitivity; we consider this to be initiation through the design mode, e.g. shock sensitivity. Sensitiveness is used throughout the text whether referring to US or any other impact data.

8

These differences in impact data are not merely academic. Fuze safety design criteria used by Australia and her allies [21-24] have as one of the fundamental tenets that no explosives of higher sensitiveness than tetryl may be used below the shutter or unshuttered in a fuze train. A key input to this judgement is impact sensitiveness data, and acceptable US [21] and UK [25] explosives have been defined. A measure of the concern felt by the UK Ordnance Board can be seen from their sponsorship of the study described in reference [17].

3. Sensitiveness, Explosiveness and Criteria Thereof

Determination of the impact sensitiveness of an energetic material is reliant upon having a defined criterion of ignition/initiation. The criterion for the Rotter method is either 1 mL of gas produced from a 27 mg sample following impact, or 0.5 mL of gas coupled with evidence of burning/smoke when the sample is subsequently inspected [8a]. For some pyrotechnic formulations which produce very little gas even when totally consumed, only evidence of combustion is necessary. A high explosive such as RDX will typically give 16 to 20 mL of gas for complete reaction under impact.

The ERL criterion is to use a noisemeter zeroed at the noise level produced by impact on an inert substance, in conjunction with visual cues such as flash and smoke noted by the operator [9]. The noisemeters can be set to detect only 5% reaction [26], which would make it roughly equivalent to the Rotter criterion for initiation described in the preceding paragraph, but in general are probably set to higher thresholds. Thus samples which react but propagate poorly, i.e. give low gas or smoke output, will be rated as less sensitive than samples which react at the same impact level but propagate well. Another key point of difference between the Rotter and ERL methods is that the sample for Rotter testing is confined on a polished steel anvil, whereas the ERL Type 12B test (for which most data are available) has the sample unconfined on sandpaper or garnet paper.²

It is not the object of this investigation to identify the physical causes of differences between the Rotter and ERL methods; this would just be reworking old ground [9, 15, 16, 26]. The summary from the extensive experimental study by Hornby and Merrick [15] will suffice; "not only the criterion but the experimental method leads to differences in ease of initiation and also the manner of initiation and its resultant buildup to reaction." What we do possess is sufficient knowledge to rationalize where differences may occur in specific circumstances, and this will be brought out in the following sections.

² The difference is not solely due to the presence of grit, i.e. sand or garnet. The US Type 12 test has the explosive under test placed on a flat steel surface, i.e. similar to the Rotter, but the data trends are similar to those for Type 12B testing. Type 12 data was not quoted because data are not available for several of the explosives cited in the text.

The Rotter test is therefore a test of the ease of ignition to produce gas under impact, the assumption being that any observed reaction, however small, constitutes a potential risk. The evolved gas volume can range from 0.5 mL at the threshold criterion to 20 mL or more. Since there is no differentiation on the basis of gas production above 0.5 mL, the ability to propagate following ignition does not form part of the basic assessment [8a].

That the evolved gas could yield important information about the hazard of the material under test was recognized by Rotter himself, and he devised a complicated assessment procedure based upon gas evolved at various drop heights [15, 27]. Although Whitbread stated in 1960 that for high explosives the volume of gas evolved yields no more information than that the shot has fired or failed [28], by 1963 other UK researchers had extensively investigated the volume of gas produced by a range of explosives at a range of drop heights and strongly concluded that they were important [15, 27]. This led to the suggestion that evolved gas volume is a direct measure of propagation ability [7].

More recently, Mullenger derived a new experimental Rotter method utilizing gas volumes evolved under impact to measure explosiveness of energetic materials [29]. This has now been incorporated as an official SCC test [8b].

Since most of the explosives which we observed to give unexpectedly low F of I values also gave low to very low evolved gas volumes (0.5 to 7 mL compared to RDX at about 18 mL), we decided to approach the experimental study by initially subjecting selected explosives to the test method described in reference [8b]. This method had not been used at MRL previously.

4. Experimental

4.1 Materials

RDX was grade A supplied by Albion Explosives Factory. The wet material was dried under suction and in air at ambient temperature prior to use.

HNS was type IIB, batch NSWC X580 Lot 11138-20, and PBXW-7 was type II, batch NSWC ID #3409; both were donated by NSWC White Oak for a previous study [12].

NTO was prepared at MRL for a previous investigation [4]. The sub 850 μ m material was as described in that report, i.e. recrystallized from water and sieved dry through an 850 μ m sieve. The sub 150 μ m material was further sieved dry through a 150 μ m sieve.

ADNBF was prepared at MRL by nitration of chlorobenzofuroxan followed by reaction with ammonia, using the method described by Norris [30]. Recrystallization was from ethyl acetate.

NQ was propellant grade ex Nigu Chemie, lot 6, donated by Explosives Factory Maribymong. Spherical NQ (SNQ) was obtained from ICT in Germany and also produced at MRL [5].

TATB was Type A donated by RARDE, UK for previous studies.

DATB was prepared from resorcinol dimethylether via 2,4-dimethoxy-1,3,5trinitrobenzene (DiOMeTNB) for a study on insensitive booster explosives.

All explosives were used as received or prepared as described above.

4.2 Method

and the second se

The experimental Rotter method was substantially the same as described in the SCC Manual [8] except the samples were accurately weighed to 27 mg rather than a fixed volume used. Initially a 25 drop run was carried out using the Bruceton method to obtain a height for 50% initiation probability (h_{508}). The criterion used for initiation was 1 mL gas evolved or 0.5 mL accompanied by smoke or evidence of burning in the sample.

For each sample 20 drops were typically carried out at each of 0.75, 1.0, 1.5 and 2.0 h_{508} . Drops at 0.67 and 2.5 h_{508} were also recorded for some samples. The maximum drop height available is about 3.0 m, and at these heights considerable damage to the anvils occurs. This limited testing to 2.0 h_{508} for most samples, and to only 10 drops at greater heights to minimize anvil consumption. At each height the number of goes (ignitions) and the gas evolution (to 0.1 mL) for each go were recorded. Comparative data for the method standard, lead azide RD1343, were not obtained; the UK data were used instead. This decision was made because lead azide usually detonates under impact test and a large number of anvils would have been required to merely reproduce UK tests.

Theoretical total gas volume evolved for complete sample reaction was calculated using the NASA-Lewis code [31]. This differs from that described in the UK method [8b, 29].

5. Results

Rotter impact data (F of I, evolved gas) are listed in Table 1 for a range of commonly used explosives; lead azide to TNT. This broadly covers the sensitivity range of explosives used in Australian ordnance. Data are listed also for a number of "insensitive high explosives", some chemically related materials and precursors, as well as the formulations Comp A-3 and PBXW-7.

US impact sensitivity data are listed in the final two columns of Table 1. This is not an exhaustive compilation such as can be found, for example, in reference [13] for some of these materials. Instead the data are chosen from a minimum number of references (see footnotes to Table 1) to give a direct comparison both internally to the laboratory involved (NSWC or NWC) and externally to the Rotter data. NSWC and NWC use different impact machines (but of a similar design) and it was necessary to use both sets of data to cover the entire range of explosives chosen for our study.

Table 2 details data for 20 drop experiments conducted at a series of drop heights commencing at 0.67 h_{500} and extending in most instances to 2.0 or

11

2.5 h_{son} (h_{son} , the median drop height, is listed for each explosive in the first column). Each 20 drop experiment has the number of ignitions out of 20 (n_g) (or otherwise as noted in brackets), the fraction of ignitions (P_g), average gas volume evolved per ignition (V_g) and calculated powder explosiveness at each level (X).

	Rotter in	spect Data	US Data		
Evergetic Material	F of I	Gas* evolved (mL)	NSWC/NOL: ERL Type 12*	NWC: Bureau of Mines Type 12	
Lead azide RD1343	20	13	12		
PEIN	50	12	12	12	
RDX	80	17.9	24	19	
Tetryl	90-110 *	12-15	38	30, 25 ⁴	
Comp. B (RDX/TNT 60:40)	140-170	- 12	60	36	
TNT	150-200	- 2	157	74, 98 ⁴	
Comp. A-3 (RDX/wax 91:9)	1 40 *	1	81		
PBXW-7 (RDX/TATE/Viton 35:60:5)	90 °	4	52 *		
DATB	170	0.5	320	> 200 4	
TATB Type A	> 200	0.5	> 320 [est. 500]	> 200 ^d	
Hexanitrobiphenyl	110 •	14.1	85	70 *	
DIPAM	80*	6.0	132	67 *	
Dimethoxytrinitrobenzene	> 200		251		
HNS Type I Type II	90 * 90 *	7 12	54		
NTO	80-90 *	3-5	75-104 ^s		
NQ (picrite) (spherical)	100-105 ^b 120-180	1-2 1	> 320, 70-100 *		
DNBF	90 ¹	19.8		18 ¹ , 76 ⁴	
ADNBF	60	13.0		53 ×, 100 4	

 Table 1: Rotter Impact Sensitivity Data for a Range of Explosives and Comparison with US Data

a. Average value for all positive events

b. Data from Ref. 34 unless indicated otherwise

c. Deta from Ref. 12

d. Data from Ref. 36

e. Data from Ref. 32

f. Data from Ref. 4

g. Data from Ref. 35

h. Data from Ref. 5

i. Dets from Ref. 33

k. Data from Ref. 30

Table 2: Rotter Explosiveness Results for Materials Tested

Material	Drop height multiple of h _{sen}	Number of fires out of 20 drops (n _s)	$P_g = n_g/20$	Average gas evolved V _s (mL)	Explosivenes at each level X (%)
Lead azide RD1343 *	0.67	0	0	0	0
(h _{om} = 31.5 cm)	0.75	3	0.15	13.4 (8.5)	100
	1.0	8	0.40	13.1 (8.3)	100
	1.5	12	0.60	12.9 (8.2)	100
	2.0	[10/10]	1.0	12.0 (7.6)	100
RDX Grade A	0.67	1	0.05	17.0	62.3
(h _{sea} = 105 cm)	0.75	1	0.05	18.0	63.3
	1.0	10	0.5	14.0	50.4
	1.5	20	1.0	13.1	47.8
	2.0	[10/10]	1.0	13.7	53.9
HINS Type IIB	0.67	Э	0	0	0
(h _{see} = 120 cm)	0.75	2	0.1	7.0	20.3
	1.0	11	0.55	12.0	35.6
	1.25	20	1.0	13.1	39.2
	15	20	1.0	12.8	38.6
	1.75 *	20	1.0	12.5	38.9
ADNBF	0.67	0	0	0	0
(h _{sen} = 82 cm)	0.75	1	0.05	4.6	12.9
	1.0	18	0.9	5.7	18.1
	1.5	20	1	12.4	36.1
	2.0	20	1	14.8	44.4
	2.5	20	1	14.3	44.8
PBXW-7 Type II	0.75	0	0	0	0
(h ₃₉₅ = 116 cm)	1.0	11	0.55	1.1	3.1
	1.5	20	1	5.2	15.0
	2.0	20	1	5.7	1 7 .6
	2.5	20	1	5.5	16.8
NTO sub 850 µm	0.67	0	0	0	0
(h ₃₉₆ = 128 cm)	0.75	[3/40]	0.075	3.1	10.6
	1.0	13	0.65	2.9	10.1
	15	20	1.0	7.8	27.7
	2.0	[10/10]	1.0	10.0	38.2
NTO sub 150 µm	0.67	0	0	0	0
(h _{ses} = 114 cm)	0.75	[3/30]	0.10	3.7	12.7
	1.0	16	0.80	3.4	11.8
	1.5	18	0.90	11.0	39.1
	2.0	[10/10]	1.0	8.0	34.4
NQ Picrite, propellant	0.67	0	0	0	0
grade	0.75	0	0	0	0
(h _{sen} = 135 cm)	1.0	5	0.25	1.7	5.1
	1.5	19	0.95	1.1	3.3
	2.0	[10/10]	1.0	0.9	2.9
SNQ	0.67	0	0	0	0
(han = 164 cm)	0.75	0	0	0	0
	1.0	2	0.10	0.6	1.8
	15	[3/10]	0.3	0.6	1.8
	1.75	[5/10]	0.5	0.6	1.8

a. Data from Ref. 17 for 42.4 mg sample. V_s values in brackets have been converted to 27 mg sample for direct comparison with our data.

b. Maximum height precluded 2.0 hass at that time.

In Table 3 is listed the theoretical maximum gas evolved for complete reaction of 27 mg of all explosives listed in Table 2 plus a further five for comparison. This was obtained using the NASA-Lewis code [31] assuming standard temperature and pressure (STP). Data are also given for a further five explosives for comparison. Experimental volumes for detonation of 27 mg samples, calculated from the data of Ornellas [37], are also shown for comparison. Reaction products calculated for three explosives (TNT, RDX and NTO) are listed in Table 4.

Average powder explosiveness (X*) and hazard index (HI) calculated from the data in Tables 2 and 3 are listed in Table 5. Also shown are UK data for tetryl, RDX Grade 1, BX4 (the UK version of PBXW-7), RDX/wax 99:1 and ammonium perchlorate (AP).

Matania)	Gas Evolved for Complete Reaction (mL			
Material	Combustion	Detonation *		
Lead Azide RD1343	6.2			
RDX	20.0	15.65		
HNS	23.9	15.1		
ADNBF	25.2			
PBXW-7 Type II	25.8			
NTO	20.4			
NQ	24.2			
Lead styphnate	11.4			
PETN	16.1	14.6		
НМХ	20.0	19.7		
Ammonium Perchlorate (AP)	9.1			
TNT	26.7	14.6		

Table 3: Gas Evolved (mL) for Complete Reaction of 27 mg of Each Sample as Calculated Using NASA-Lewis Code and Compared to Experimental Detonation Gas Volumes

a. Data obtained from Ref. 37.

Table 4: Mole Fractions of Reaction Products Calculated to be Formed fromCombustion and Detonation using the NASA-Lewis Code. Experimental DetonationProducts are shown for Comparison.

	Calculated * Exoti.*		RDX			NTO		
Reaction Products *			Expti.	Calculated		Exptl.	Calculated	
FIGURE	Combustion	Detonation	Detonation	Combustion	Detonation	Detonation	Combustion	Detonation
c	0.0883	0.1892	0.341			0.052		
CH,		0.0509	0.0092		0.0035	0.005		0.0168
со	0.5468	0.3720	0.1847	0.2440	0.2201	0.129	0.3191	0.2693
CO		0.0905	0.1166	0.0740	0.1089	0.163	0.0789	0.1250
н	0.0007			0.0372	0.0003		0.0072	
Ha	0.2260	0.0454	0.0429	0.0907	0.0611	0.04	0.0771	0.0368
H L O		0.0723	0.149	0.1959	0.2445	0.275	0.1171	0.1130
HCN	0.0025	0.0084	0.0187		0.0048	0.003		0.0059
NH,		0.0089	0.0149		0.0158	0.003		0.0129
N ₂	0.1355	0.1478	0.123	0.3157	0.3327	0.329	0.3978	0.4140
ОН				0.0258	0.0005		0.0023	

a. Mole fractions at STP. Minor products (< 0.002) are not listed.

b. Experimental results not available.

c. Calculated using NASA-Lewis code [31]. Combustion refers to STP, detonation to reaction at the experimental detonation pressure.

d. Data from Ref. [37].

Material	F of I	Powder Explosiveness X*	Hazard Index HI (m ⁻¹)
Lead azide RD1343	20	100	423
Tetryl •	90	61	
RDX Grade A	80	51	88.5
Grade 1 ^b	80	85.3	100
HINS Type IIB	90	38.1	29.7
ADNBF	60	36.4	29.3
PBXW-7 Type II	90	13.1	8.6
BX4 • (RDX °/TATB/Teflon 35:60:5)	90	24	
NTO sub 850 µm	90	25.3	14.9
sub 150 µm		28.4	22.9
NQ Picrite	100-105	3.8	3.8
SNQ	120-180	1.8	1.1
RDX/wax 99.1 b	85	81.6	71
AP b	80	29.9	23

Table 5: F of I Powder Explosiveness and Hazard Index Figures for Materials Examined and Related Materials for Comparison

a. Data from Ref. [41].

b. Data from Ref. [29]. UK Grade 1 is identical with Australian Grade A.

c. RDX contains 10% HMX. This is a UK version of PBXW-7 Type I.

6. Discussion

6.1 Rotter Impact Data

The data for the first six entries of Table 1, covering lead azide through TNT, show a consistent trend from either Rotter, US ERL or Bureau of Mines (BOM) impact machines. The relative values are consistent with the generally accepted propensity of these materials to ignite when mechanically stressed during handling. However, the data for a number of the other explosives in Table 1 clearly reinforce the statements made in the Introduction. PBXW-7, DIPAM, HNS and NTO are rated RDX/tetryl sensitiveness via Rotter F of I, but Comp B/TNT sensitiveness from US data. The most extreme divergence occurs for the last entry in the Table, ADNBF.

The Rotter explosiveness data (Table 2) show some informative trends both for initiation probability (P_g) and average gas volume evolved at ignition (V_g) versus drop height as a multiple of $h_{50\%}$ for the nine samples listed. A plot of V_g versus $h_{50\%}$ multiple is given for five of the samples in Figure 1, and shows in general an increase in V_g to a maximum then a small decrease³. This small decrease has been noted previously [29] in Rotter testing, as well as for emitted light from some samples during drop weight testing [38] and for frequency of explosion versus energy in BAM impact testing [39]. The lower gas volume and decreased light output may reflect a changing reaction mechanism at the higher pressures (see later).

Reference to the data in Table 2 and Figure 1 gives an immediate qualitative picture of the explosiveness of the materials examined. High explosiveness materials such as lead azide and RDX show an abrupt transition from zero response to maximum evolved gas upon ignition, with the maximum occurring at or below 1.0 $h_{50\%}$. Decreasing explosiveness is evidenced by a less steep rise up to maximum evolved gas which occurs at an increasing multiple of $h_{50\%}$, e.g. HNS, ADNBF, PBXW-7 in Figure 1. Very low explosiveness is represented by NQ and SNQ which give evolved gas volume at the minimum for definition of reaction at all heights over 1.0 $h_{50\%}$. The n_g values for SNQ (Table 2) suggest that $h_{50\%}$ has been underestimated, i.e. n_g of 5/10 does not occur till 1.75 $h_{50\%}$. However the standard 25 shot Rotter was carried out prior to the more extensive explosiveness tests, to give the accurate $h_{50\%}$ value.

It is worth noting that PBXW-7 gives only about 40% of the evolved gas for RDX at $h_{50\%}$ and above. Since PBXW-7 is 35% RDX, this suggests that only the RDX and possibly the Viton A binder are reacting. Reaction of the TATB would presumably occur only at much greater drop heights (refer to data in Table 1).

³ The data for RDX grade A are atypical, showing a sharp decrease in V_g at 1.0 h₅₀₅ and above. This differs from the data in reference [29]. However, the V_g results at 0.67 and 0.75 h₅₀₅ represent a single event out of 20.



Figure 1: A plot of average gas evolved per ignition (V_g, mL) versus drop height as a multiple of $h_{50\%}$ for five samples subjected to Rotter explosiveness testing.

6.2 Calculation of Powder Explosiveness

The conversion of the qualitative assessment of the previous section into a more "quantitative" comparison was carried out according to the procedure of Mullenger [8b, 29]. The procedure is to convert the raw values of V_g in Table 2 to a powder explosiveness figure (X) for each test level, i.e. multiple of $h_{50\%}$, using the formula

$$X = V_{s} m_{s} V_{s} / V_{m} m V$$

where the subscript s refers to the data for the lead azide standard (Table 2). In our measurements a constant sample mass of 27 mg was used, hence m is always 0.027 while m, is 0.0424 [29].

Calculation of V and V_{\bullet} , the volume of gas for complete reaction, is carried out in the UK using an "in-house" program written in the mid 1960s [8b, 40]. Although we were able to obtain a copy of the program, kindly donated by RARDE/WA, it required extensive reformatting to be compatible with our systems. As a consequence we decided to use the NASA-Lewis code; this is more modern and is used extensively throughout the Western energetic materials community for calculating combustion products. We have had considerable experience with its successful use for pyrotechnic formulations. While it could be argued that a high explosive code should have been used, the processes occurring under impact initiation result from combustion (with the exception of lead azide, which detonates) at pressures which are low relative to detonation. The recommended code for the test procedure [8b] is a propellant code [40] which also generates equilibrium products, as does NASA-Lewis [31].

Calculated values of V at STP for complete combustion (V_s for lead azide) are listed in Table 3 for the explosives from Table 2 together with some other common explosives for comparison. It could be asked why explosiveness (equating to hazard in risk equation) cannot simply be related to V_g/V , where explosiveness would be the % of reaction under impact. Perhaps the lead azide standard was included to smooth out errors introduced by inability to accurately calculate V.

Increasing pressure, up to detonation, results in decreasing total gas volume [37]; this is particularly marked for HNS and TNT (Table 3) and results both from formation of more carbon and water (not gases at STP) and less hydrogen. Comparison of data for TNT, NTO and RDX amply illustrates this (Table 4). Reduction in gaseous products at increasing pressure is a possible answer for the small decrease in evolved gas at increasing drop heights, e.g. HINS in Figure 1.

Two additional numbers were calculated for each material tested using the methods described in references [8b, 29]. These were:

Average Powder Explosiveness (X^*) = average of all X values for test levels nh_{505} , where $n \ge 1$.

> Hazard Index (HI) = maximum value of the ratio X/height (m) for all test levels.

These two numbers for each material tested, together with UK data for a few materials for comparison, are listed in Table 5. Rotter F of I data are relisted for reference.

It should be noted that whereas X* is derived from only X values at or above $h_{50\%}$, HI can be from any level. For example the HI for lead azide derives from the 0.75 $h_{50\%}$ result, and RDX grade A from the 0.67 $h_{50\%}$ result. Some comment on this will be made in the following section.

6.3 Comparison of Explosiveness Data

Before commenting on each individual explosive, we first will refer to the somewhat large difference between the UK and MRL results for RDX. The grades of RDX are equivalent. The lower number for X* obtained by us can be seen to arise from the relatively small experimental evolved gas volume (approximately 14 mL) compared to the 20.0 mL calculated using the NASA-Lewis code. The higher gas volumes obtained by us at 0.67 and 0.75 $h_{50\%}$ do not count in calculating X*, which exhibits the greatest difference from the UK result. The HI value arises from the 0.67 $h_{50\%}$ figure and accordingly is much closer to the UK result.

Nonetheless the measurements were very carefully performed and repeated in a number of instances where doubt existed. The fact that we use a different program to calculate V will introduce differences. However, the object was never to exactly reproduce the UK figures but rather to assess the usefulness of the method and in doing so to generate an indigenous data base. The authors therefore conclude that relative comparison of explosives should avoid a single parameter such as X^* (in particular), but use relative data such as the plots in Figure 1. The HI results would appear to give a better basis for comparison.

The extended data (Tables 2 and 5) confirm that the risk associated with handling small quantities of HNS, ADNBF and NTO as loose powder in a laboratory situation is low. While the probability/frequency of a hazardous event is equal to tetryl, for which we have substantial handling experience, the outcome (hazard) of this event is likely to be incomplete propagation/low order. PBXW-7 has an even lower HI value but this is biased by the fact that the TATB does not appear to be reacting; V_g is therefore only about 35% of V. NQ in powder form exhibits very poor ability to propagate, i.e. low explosiveness as reflected in low X*/HI values. These assessments very much more closely correspond with the US h_{50%} rather than Rotter F of I data (Table 1).

The Rotter method was designed for, and traditionally used on, explosives of high explosiveness; thus, F of I could be equated with risk because the probability of propagation from initiation to explosion was close to 1. Explosives which propagate poorly (low hazard) but where the relative frequency of an event is rated high (low F of I) cause a problem. The conservative approach is to assume that risk is high if either sensitiveness or explosiveness is high. Compounding the problem is the difficulty of determining a criterion for an ignition, which is crucial for determining sensitiveness. To give an extreme example for the relatively insensitive commercial explosive ANFO (ammonium nitrate - fuel oil), the apparent sensitivity of ANFO varies by nearly one order of magnitude depending on the criterion being used to assign positives, e.g. scorch marks through to flame production [42].

The authors tender the following advice as a guideline for people carrying out research on new high explosives and formulations. When initial Rotter testing has indicated relative sensitiveness, e.g. F of I < 110, charge hazard tests should be carried out. However since these tests are expensive and time-consuming, determination of X, X^{*} and HI can afford additional assessment of the risk of handling the material, this particularly applies where Rotter testing has given

average evolved gas volume upon ignition of > 5 mL. However neither the X^{*} nor HI value should in any way be considered to be a quantitative measure of hazard (explosiveness) or risk.

7. Conclusion

Extended Rotter impact testing to determine powder explosiveness according to UK procedures [8b, 29] has been carried out on a number of "insensitive" high explosives currently being considered for low vulnerability fillings in Australian ordnance. These explosives were selected because initial Rotter impact screening had indicated relative sensitiveness; F of I 60 to 110. Powder impact explosiveness data is consistent with relatively low hazard, and more closely corresponds to risk assessments based on US ERL and BOM impact test data.

An attempt has been made to give broad "rule of thumb" directions to help in assessing relative risk for these types of explosives. Where the F of I is < 110 and average gas evolution is moderate, say > 5 mL, relative hazard should be assessed by determining powder explosiveness to give greater confidence in risk assessment. It cannot be stressed too strongly, particularly for development studies where charges are being handled, that charge hazard tests should be performed to obtain an accurate assessment of risk.

It is the authors' opinion that the powder explosiveness test [8b, 29], as an adjunct to routine Rotter impact testing, can serve a useful purpose for further defining material hazard. However, the relatively poor correlation between X* and HI values generated for RDX at MRL and in the UK suggests that the method does not yield quantitative comparison.

8. Acknowledgements

The authors particularly wish to thank Mr Ewan Wanat for the large amount of testing he performed during the course of this study. Mrs Jo Pinson and Mrs Branka Pletikapa also provided technical support.

Mr John Pisani and Mr Oscar Fullinfaw provided assistance through a number of discussions on testing strategy.

9. References

- Spear, R.J., Nanut, V. and Bocksteiner, G. (1989). Insensitive polymer bonded main charge explosive PBXN-107: Binder and formulation studies (MRL Technical Report MRL-TR-89-12) (Confidential). Maribyrnong, Vic.: Materials Research Laboratory.
- Dagley, I.J., Spencer, H.J., Louey, C.N. and Parker, R.P. (1989). An evaluation of ethylene-vinyl acetate copolymers as desensitizers for RDX in insensitive booster compositions prepared by the slurry coating technique (MRL Technical Report MRL-TR-89-33). Maribyrnong, Vic.: Materials Research Laboratory.
- Dagley, I.J., Montelli, L., Parker, R.P. and Louey, C.N. (1989). Preparation, characterization and cookoff behaviour of booster compositions prepared from RDX and acrylic or ethylene-vinyl acetate dispersions (MRL Technical Report MRL-TR-89-44). Maribyrnong, Vic.: Materials Research Laboratory.
- Spear, R.J., Louey, C.N. and Wolfson, M.G. (1989). A preliminary assessment of 3-nitro-1,2,4-triazol-5-one (NTO) as an insensitive high explosive (MRL Technical Report MRL-TR-89-18). Maribyrnong, Vic.: Materials Research Laboratory.
- Spear, R.J. and Redman, L.D. (1991). Production and characterization of spherical nitroguanidine, an insensitive explosive filler for melt-cast TNT formulations (MRL Technical Report MRL-TR-91-). Maribyrnong, Vic.: Materials Research Laboratory.
- Montelli, L. and Spear, R.J. (1989). An improved method for preparation of high surface area hexanitrostilbene suitable for slapper detonators (MRL Technical Report MRL-TR-89-43) (Commercial-in-Confidence). Maribyrnong, Vic.: Materials Research Laboratory.
- 7. Mortlock, H.N. and Wilby, J. (1966). Explosivstoffe, 3, 49.
- 8. Royal Armament Research and Development Establishment (1988). Sensitiveness collaboration committee, manual of tests, (a) Test No. 1A, (b) Test No. 1D.
- Federoff, B.T., Sheffield, O.E. and Kaye, S.M. (1975). Encyclopedia of explosives and related items, PATR 2700, Vol. 7, p. 135. Dover, NJ: Picatinny Arsenal.

- Lee, K-Y. and Coburn, M.D. (1985).
 3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive (LA-10302-MS). Los Alamos, NM: Los Alamos National Laboratory; Lee, K-Y., Chapman, L.B. and Coburn, M.D. (1987). Journal of Energetic Materials, 5, 27.
- 11. Personal communication (1988). Unpublished data from Naval Surface Warfare Center, White Oak, MD, USA.
- Spear, R.J. and Nanut, V. (1987). A comparative assessment of US and UK explosives qualified as replacements for tetryl (MRL Report MRL-R-1094). Maribyrnong, Vic.: Materials Research Laboratory.
- Dobratz, B.M. and Crawford, P.C. (1985).
 LLNL explosives handbook. Properties of chemical explosives and explosive simulants (UCRL-52997, Change 2), Section 9.1. Livermore, CA: Lawrence Livermore National Laboratory.
- 14. Drimmer, B.E. (1983). Navy bank of explosives data (NAVBED) volume III (NSWC MP 83-230). White Oak, MD: Naval Surface Warfare Center.
- Hornby, G. and Merrick, W. (1963). The use of gas evolution measurements in the assessment of impact sensitiveness of HE powders. *Proceedings of the International Conference on Sensitivity and Hazards of Explosives*, ERDE, London, UK, Paper 5.6.

16. Smith, L.C. (1977).

On the problem of evaluating the safety of an explosive. Conference on Standardization of Safety and Performance Tests for Energetic Materials, L. Avrami, H.V. Matsaguma and R.F. Walker (eds.), ARLCD-SP-77004, ARCDC, Dover, NJ. Vol. 1, p. 397.

- Mullenger, D.C. (1989).
 European impact sensitiveness assessment of solid energetic materials.
 14th International Pyrotechnics Seminar, Jersey Island, p. 293.
- Coffey, C.S., De Vost, V.F. and Woody, D.L. (1989). Towards developing the capability to predict the hazard response of energetic materials subjected to impact. 9th Symposium (International) on Detonation, Portland, OR. Preprints p. 965.
- 19. Afanas'ev, G.T. and Bobolev, V.K. (1971). Initiation of solid explosives by impact, Israeli Program for Scientific Translations, Tel Aviv.
- 20. Field, J.E., Swallowe, G.M. and Heavans, S.N. (1982). Proceedings of the Royal Society of London, A382, 231.

- US Department of Defense (1984). Military standard. Fuze, design, safety, criteria for, MIL-STD-1316C.
- 22. UK Ordnance Board (1982). Principles for the design of fuzing systems, OB Proceeding 42202.
- North Atlantic Treaty Organisation ().
 Fuzing systems Design safety requirements, STANAG 4187.
- 24. Australian Ordnance Council (1990). Principles and criteria for the assessment of explosives initiation systems for safety and suitability for service, AOC Proceeding 174.90.
- 25. UK Ordnance Board (1984). Explosive compositions Debrix 1 and Debrix 2, OB Proceeding 42293, Annex A (UK Restricted).
- Smith, L.C. (1987).
 Los Alamos National Laboratory explosives orientation course: Sensitivity and sensitivity tests (LA-11010-MS) [Microfiche DE87 011261]. Los Alamos, NM: Los Alamos National Laboratory.
- 27. Wilby, J. and Mortlock, H.N. (1963). The Rotter apparatus for the determination of impact sensitiveness. Proceedings of the International Conference on Sensitivity and Hazards of Explosives, ERDE, London, UK. Paper 5.5.

Whitbread, E.G. (1960). Sensitiveness testing and its relation to the properties of explosives. Proceedings of 3rd Symposium (International) on Detonation, Princeton, NJ, p. 695.

- Mullenger, D.C. (1984).
 A powder explosiveness test for energetic materials. ICT Internationale Jahrestagung, Karlsruhe, FRG, p. 683.
- Norris, W.P. (1984).
 7-Amino-4,6-dinitrobenzofuroxan, an insensitive high explosive (NWC-TP-6522). China Lake, CA: Naval Weapons Center.
- 31. Gordon, S. and McBride, B. (1976). Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouguet detonations (NASA Report SP-273). National Aeronautics and Space Administration, USA.
- 32. Bell, A.J., Eadie, E., Read, R.W., Skelton, B.W. and White, A.H. (1987). Australian Journal of Chemistry, 40, 175.

- Spear, R.J., Norris, W.P. and Read, R.W. (1983).
 4,6-Dinitrobenzofuroxan, an important explosive intermediate (MRL Technical Note MRL-TN-470). Maribyrnong, Vic.: Materials Research Laboratory.
- Storm, C.B. and Stine, J.R. (1986). The estimation of impact sensitivity in energetic materials. ONR Workshop on Energetic Materials, LANL, Los Alamos, NM, Oct 14 [LA-UR-86-1393].
- Stosz, M., Collignon, S., Gotzmer, C. and Leahy, J. (1987). An insensitive explosive containing NTO. Energetic Materials for Munitions, Proceedings, Vol. II, p. 585, Eglin, AFB, FL.
- Wilson, W.S., Bliss, D.E., Christian, S.L. and Knight, D.J. (1990). Explosive properties of polynitroaromatics (NWC TP 7073). China Lake, CA: Naval Weapons Center.
- Ornellas, D.L. (1982).
 Calorimetric determinations of the heat and products of detonation for explosives: October 1961 to April 1982 (UCRL-52821). Livermore, CA: Lawrence Livermore National Laboratory.
- Buntain, G.A., McKinney, T.L., Rivera, T. and Taylor, G.W. (1989).
 Decomposition of energetic materials on the drop-weight-impact machine. 9th Symposium (International) on Detonation, Portland, OR. Preprints p. 434.
- Janswoude, I.J.J. (1978). Survey of the activities concerning sensitivity test methods for explosives (PML-1979-20) [Microfiche N80-11253 H2/C]. Rijswijk, Neth.: Prins Maurits Laboratory TNO.
- 40. Harper, M.J. and Scrivener, J. (1967). Theoretical specific impulses of plastic propellant (ERDE 8/M/67). Waltham Abbey: Explosives Research and Development Establishment (now RARDE).
- 41. Bent, D.V. (1990). Private communication of unpublished data.
- 42. Turcotte, R. and Mohanty, B. (1990). Problems associated with relating sensitivity of reactive materials under mechanical stimuli to quantification of hazards. *Proceedings of 14th Symposium on Explosives and Pyrotechnics*, Feb. 13-15, San Francisco, CA, Paper 12.
- 43. Hutchinson, C.D. (1985). The response of intermediate explosives to thermal and shock stimuli, PhD thesis, University of Cambridge, UK, Chapter 8.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

DOCUMENT CONTROL DATA SHEET

· · · · · · · · · · · · · · · · · · ·		
REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-TR-91-22	AR-006-375	Unclassified

TITLE

An investigation of the material hazard of some insensitive high explosives

AUTHOR(S) Robert J. Spear and Luciana	Montelli	CORPORATE AUTHOR Materials Research Laboratory PO Box 50 Ascot Vale Victoria 3032
REPORT DATE July, 1991	TASK NO. DST 88/090	SPONSOR DSTO
FILE NO. G6/4/8-4027	REFERENCES 43	PAGES 25
CLASSIFICATION/LIMITATION R	EVIEW DATE	CLASSIFICATION/RELEASE AUTHORITY Chief, Explosives Division
SECONDARY DISTRIBUTION		
	Approved for public re	elease
ANNOUNCEMENT		
	Announcement of this report	is unlimited
KEYWORDS		······································

Impact Sensitiveness Rotter Impact Test Explosiveness
Powder Explosiveness

ABSTRACT

A number of insensitive high explosives (IHE) and formulations which were determined to have unexpectedly high sensitiveness by Rotter impact testing (F of I 60-110) were further assessed by Rotter powder explosiveness testing. Analysis shows that the hazard as reflected by the ability to propagate following ignition, was low. Risk, defined as the product of hazard and frequency (F of I), was similar to assessment based on US impact test data for these materials. An assessment of both the usefulness and the quantitative nature of powder explosiveness testing is made. Guidelines for using Rotter data for deciding relative risk from handling of relatively small quantities of IHEs in R & D are given. The desirability of carrying out charge hazard testing to support these risk assessments is stressed.

SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED