Journal of Hazardous Materials, 7 (1983) 199—210
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

SENSITIVITY CHARACTERISTICS OF MIXTURES OF MONO- AND DINITROTOLUENE WITH NITROGEN TETROXIDE AND TETRANITROMETHANE

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ABSTRACT

In the recovery of acids from the nitration of toluene to TNT, it is possible under certain conditions to obtain mixtures of nitroaromatic compounds, primarily mono- and dinitrotoluene with nitrogen tetroxide (N_2O_4) and/or tetranitromethane (TNM). Since these mixtures contain rather strong oxidizers and a fuel, they have the potential of being highly sensitive liquid explosives. Studies showed such mixtures are not exceptionally sensitive to mechanical impact and friction or thermal initiation. However, these mixtures at oxygen balanced proportions are extremely sensitive to induced shock and are capable of propagating explosive reactions at film thicknesses less than 0.5 mm. In the standard NOL card gap test, oxygen balanced mixtures of N_2O_4 with nitrobody exhibited an attenuator thickness of greater than 155 cm as compared to 3.8 cm for TNT.

Shock sensitive mixtures of N_2O_4 and nitrobody can collect in fume and acid recovery operations. It is suspected that such mixtures were the cause of some of the explosions in TNT acid recovery operations in the past which have been attributed to TNM.

INTRODUCTION

One problem associated with the recovery of nitric acid from TNT spent acids is the potential for forming sensitive mixtures of TNM or N_2O_4 with nitroaromatics. When proper environments prevail, such as low temperatures and process fluctuations, it is highly probable that sensitive mixtures can collect in weak nitric acid tanks and lines. Since these mixtures contain strong oxidizers and a fuel, they have the potential of being highly sensitive liquid explosives. Urbanski and other investigators describe the powerful explosive that TNM forms when mixed with nitroaromatics (Sprengel explosives) (refs. 1-4). Prior to this study, past explosions in TNT acid recovery had been attributed to TNM (refs. 5-7) when, in fact, it is now believed that some of these explosions were probably caused by N_2O_4-nitroaromatic mixtures.

0304-3894/83/0000—0000/$03.00

Because data were lacking, this study was undertaken to investigate and define the relative ease with which mixtures of N_2O_4 or TNM with mono- and dinitrotoluene are initiated by mechanical impact and friction stimuli. Also, the relative shock sensitivity and explosive propagation characteristics for these mixtures were investigated in the standard critical diameter and NOL card gap tests. Procedures and specific details for performing these sensitivity tests are found in reference 8.

The resultant data provide a sensitivity profile analysis for mixtures of N_2O_4 or TNM with nitrobody (NB) as a function of sample composition. These data have applications for assessing the initiation hazards and the explosion potential for such mixtures in fume recovery and spent acid recovery operations. Although 2-mononitrotoluene (2-MNT) was used almost exclusively in this investigation, similar test results should be expected of N_2O_4 or TNM in mixtures with any soluble nitroaromatic.

DISCUSSION

Initiation sensitivity

Individually, N_2O_4 or TNM are not sensitive to impact or friction mechanical stimulus. This is not surprising because both are strong oxidizing agents and should not be expected to exhibit explosive characteristics unless mixed with a suitable fuel. This is reflected by data in Table 1 which show N_2O_4 or TNM react (initiate) in the impact or friction test only when tested in combination with nitrobodies such as MNT, DNT, or TNT. Moreover, the mixture of N_2O_4/NB or TNM/NB is more easily initiated than MNT, DNT, or TNT. Although capable of initiation, the mixtures of N_2O_4/NB and TNM/NB are not considered to be unduly sensitive to impact or friction.

Mixtures of TNM/NB are shown to be more easily initiated than mixtures of N_2O_4/NB. Reasons for the differences observed between the impact threshold initiation limits for TNM and N_2O_4 are not apparent and believed to be attributed to sample volatility which is greater for N_2O_4 and which presented problems in the friction test. If during testing the N_2O_4 was vaporizing quickly, then the data for the N_2O_4 mixes are not representative of oxygen balanced but are, instead, samples of unknown compositions which could explain data variability.

TABLE 1

Sensitivity initiation characteristics

Mixture[1]	Threshold initiation level[2] Impact (J/sec x 10^{-4})	 Friction (KPa x 10^{-4} @ 2.4 m/s)
N_2O_4	$\geq$ 22.4	$\geq$ 131
N_2O_4/MNT	7.7	*
N_2O_4/DNT	18.5	*
N_2O_4/TNT	11.8	*
TNM	$\geq$ 22.4	$\geq$ 131
TNM/MNT	6.9	8
MNT	$\geq$ 22.4	$\geq$ 131
DNT	16.6	$\geq$ 51
TNT	8.4	36

[1] Mixtures oxygen balanced.

[2] Level above which initiation occurs; 20 consecutive failure level indicated. ($\geq$) represents upper limit of test equipment and/or test criteria.

*Sample volatility precluded testing on this apparatus.

Explosive reactivity

Critical diameter tests conducted on mixtures of N_2O_4 and TNM with 2-MNT characterized the mix explosive reactivity as a function of composition and determined minimum dimensions to propagate an explosion. As can be seen from data in Table 2, the explosive reactivity for the N_2O_4/2-MNT mixture is dependent on composition.

TABLE 2

Explosive propagation characteristics for N_2O_4/2-MNT and TNM mixtures

Composition	Weight ratio	Critical diameter[1,2] (mm)	Sample reaction
2-MNT/ N_2O_4	89:11	> 51	No reaction, ≃ 48 cm of container intact
	80:20	25.4	No reaction, ≃ 38 cm of container intact
	62:38	< 6.4	Explosion, container fragmented into small pieces
	28:72 (OB)[3]	< 6.4	Explosion, container fragmented into small pieces
	7:93	< 6.4	Explosion, container fragmented into small pieces
	5:95	> 51	Decaying reaction, ≃ 30 cm of test container intact
	3:97	> 51	No reaction, ≃ 41 cm of container intact
2-MNT/ TNM	59:41	< 6.4	Explosion, container fragmented into small pieces
	21:79 (OB)[3]	< 6.4	Explosion, container fragmented into small pieces
	7:93	< 6.4	Explosion, container fragmented into small pieces

[1] Defined as minimum dimension above which an explosive reaction can be propagated. Composition C-4 explosive donor having diameter equal to the test sample and a L:D of 3:1 plus 2.54 cm for blasting cap was employed.

[2] Confined in Schedule 40 steel and tested at ≃ 16°C.

[3] Oxygen balanced mixture.

Using critical diameter as an indicator for explosive reactivity, one readily observes a wide range where the mixtures propagate explosive reactions at dimensions less than 6.4 mm. Individually, N_2O_4 or 2-MNT would not be expected to react explosively. This is apparent from the composition profile in Figure 1 which shows that 2-MNT/N_2O_4 mixtures become increasingly more reactive with addition of N_2O_4 oxidizer. When assessed on the basis of oxygen balance, the data show that a wider range of explosive reactivity exists for N_2O_4/2-MNT mixtures which are oxygen deficient than for the oxygen rich mixtures.

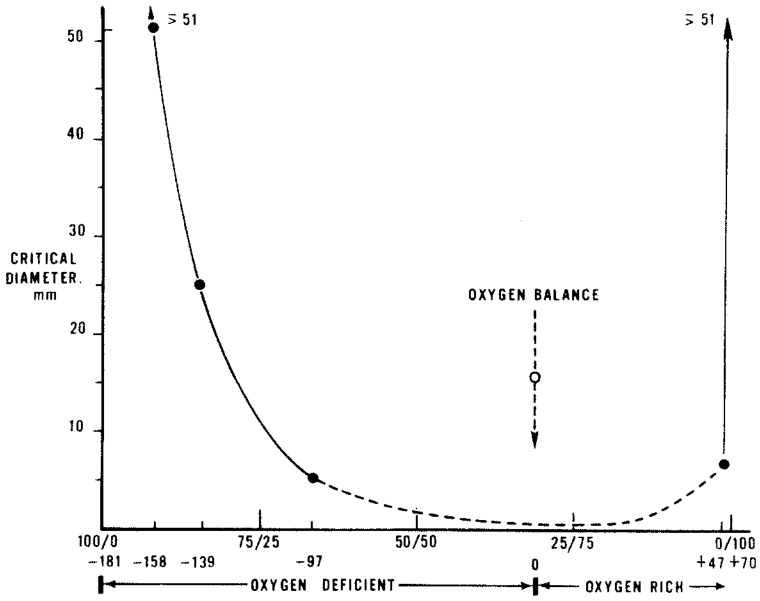

Fig. 1. Explosive shock propagation characteristics--2-MNT/N_2O_4 weight ratio.

Testing of mixtures in which TNM was substituted for N_2O_4 yielded an identical explosive propagation profile as obtained in the N_2O_4/2-MNT test series (see Table 2). It is expected that substituting other nitrobody, such as DNT, would yield a similar critical diameter sensitivity profile analysis.

The less than 6.4 mm critical diameter exhibited by N_2O_4/NB and TNM/NB mixtures necessitated investigating the explosive propagation characteristics of these mixtures as thin films using the test arrangement shown in Figure 2.

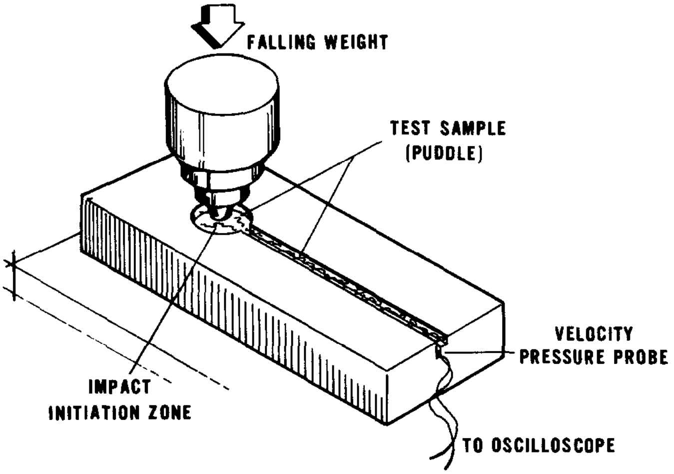

Fig. 2. Thin film explosive propagation test setup

Initial work was performed with TNM due to ease of handling versus the extreme volatility of N_2O_4. An oxygen balanced mixture of TNM and 2-MNT at a weight ratio of 79:21 was found to propagate an explosion at a layer thickness less than 0.5 mm (see Table 3). At this layer thickness and sample size (three grams), the force of the explosion destroyed the test vehicle. The data in Table 3 also reveals that similar reactions are obtained at oxygen rich and oxygen deficient mixture ratios covering a wide concentration range. The above information has particular applications for assessing the explosion hazard potential for thin films of N_2O_4/NB in fume and acid recovery storage and processing equipment.

TABLE 3

Thin film explosive propagation characteristics

Sample	Weight, percent	Oxygen balance, percent	Threshold thickness[1,2] (mm)
2-MNT/TNM	21:79	0 (oxygen balanced	< 0.5
	7:93	+112 (excess)	> 2.5
	38:62	-42.5 (deficient)	< 2.0

[1] Film thickness above which an explosive reaction can be propagated.
[2] Five failures obtained at the no reaction level at ambient temperature.

Sensitivity to Shock

The relative ease with which various mixtures of N_2O_4/2-MNT are initiated by shock stimulus was investigated in the NOL card gap test. Oxygen rich, oxygen deficient and oxygen balanced mixtures were tested.

As data in Figure 3 show, a wide N_2O_4/2-MNT weight-ratio range (80:20 to 10:90) is easily initiated by induced shock of two Pentolite explosive pellets. However, only a very narrow weight-ratio range was found to be extremely sensitive to shock, exhibiting a card gap value > 155 cm. The mixture composition exhibiting extreme sensitivity to shock occurs at oxygen balanced (72:28 N_2O_4/2-MNT); however, the shock sensitivity drops off quickly for oxygen rich and oxygen deficient mixtures.

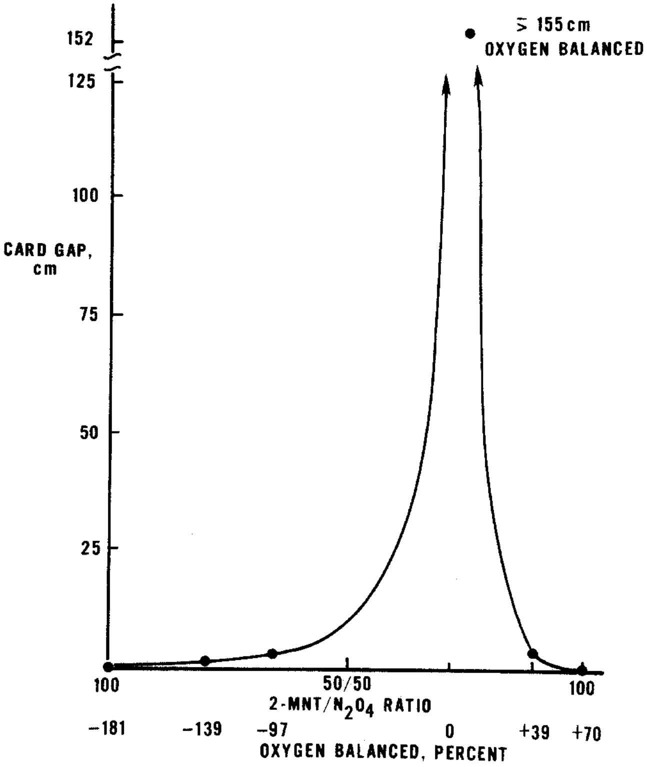

Fig. 3. Relative shock sensitivity of 2-MNT/N_2O_4 mixtures

When compared on the basis of shock pressures in Figure 4 (ref. 9), the relative shock sensitivity of the N_2O_4/2-MNT mixture (oxygen balanced) is greater than molten TNT by a factor of ≃ 190, i.e., > 155 cm versus 3.8 cm card gap value.

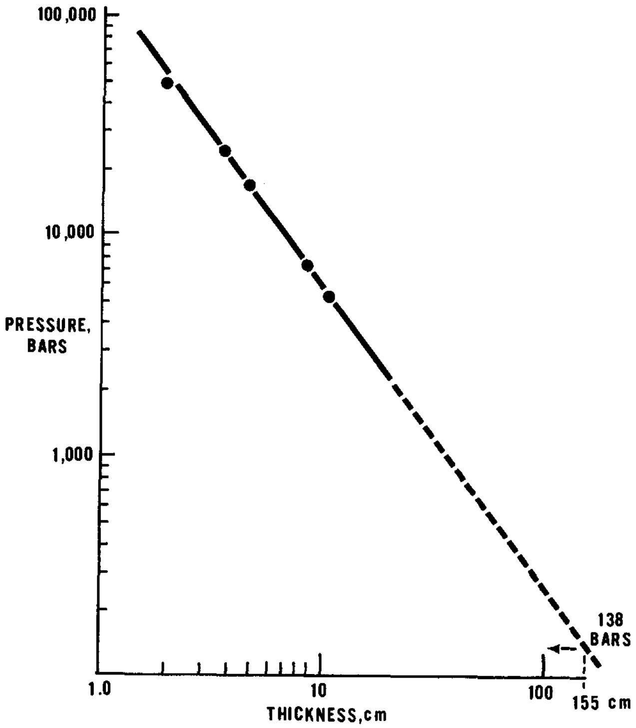

Fig. 4. Pressure as a function of card gap thickness

Hazards Analysis

The above sensitivity data for the N_2O_4 and TNM mixtures with nitrobody provide hazard information only from the relative viewpoint that the combustible response and reactivity to various stimuli can be compared on the basis of processing mixtures and/or chemical and physical properties. To quantitatively assess suspected initiation hazards and/or confirm the degree of safety in TNT operations, it was necessary to compare the data to the magnitude of initiation stimuli to which these materials are subjected during normal and accidental manufacturing operations. To this end, quantitative assessments were made of various compressors and pumps where exposure to TNM/NB or N_2O_4/NB could occur. Also, study findings are used to show a N_2O_4-nitrobody sensitive mixture as the most probable cause for an explosive incident in the TNT spent acid recovery operation at Radford AAP.

A complete characterization performed of the TNT spent acid recovery operation revealed that accumulations of potentially explosive mixtures could occur year round for most weather conditions. It was found that NB/N_2O_4 ratios in process samples obtained at 10°C and 0°C conditions ranged from near oxygen balanced (1:3) to oxygen rich (1:>3) to oxygen deficient (1:<3) mixtures. Chemical analysis of process samples in Table 4 showed a slight increase in the percentage of NB and N_2O_4 dissolved in the acid samples tested at temperatures of 0°C or below.

TABLE 4

N_2O_4, TNM and nitrobody found at acid recovery area[1]

	Temperature (°C)	Range (%)			No. Samples
		N_2O_4	NB	N_2O_4/NB ratio	
AOP tower	10	0.00 - 0.03	0.4 - 1.2	0.0 - 1:20	10
	0	0.03 - 0.08	0.91 - 1.3	1:16 - 1:30	6
Tanks	10	0.00 - 0.27	0.21 - 0.92	0.0 - 1:1	5
	0	0.07 - 2.42	1.05 -	1:1.4 - 1:15	6
Cooling condenser	10	1.33 - 3.0	0.33 - 3.38	1:2 - 7:1	5
	0	1.43 - 3.46	2.48 - 3.51	1:1 - 1:1.7	3
Nash compressor	10	0.82 - 2.15	0.13 - 2.59	1:2 - 16:1	5
	0	2.16 - 2.53	4.02 - 4.18	1:1.7 - 1:2	3
Surge pumps	10	3.48 - 9.50	0.52 - 1.00	4:1 - 19:1	4
	0	4.07 - 4.12	0.36 - 0.42	10:1 - 11:1	3

[1] No TNM found; sample analysis was by gas chromatograph, titration and/or infrared spectrophotometer techniques.

Because the potential exists for sensitive mixtures of N_2O_4/NB to be present at the acid recovery unit, quantitative hazards studies (ref. 8) were made of equipment and operations to ensure that hazardous energy potentials were not present. One such analysis carried out was concerned primarily with evaluating the initiation potential of oxidizer/fuel liquid mixtures under high rate, compression heating as might occur in various pumps and compressors.

Tests conducted in the fixture depicted in Figure 5 disclosed that TNM/MNT mixtures are capable of being initiated by compressional heating and exhibit a threshold initiation compression rate of 9.9 x 10^6 KPa/sec.

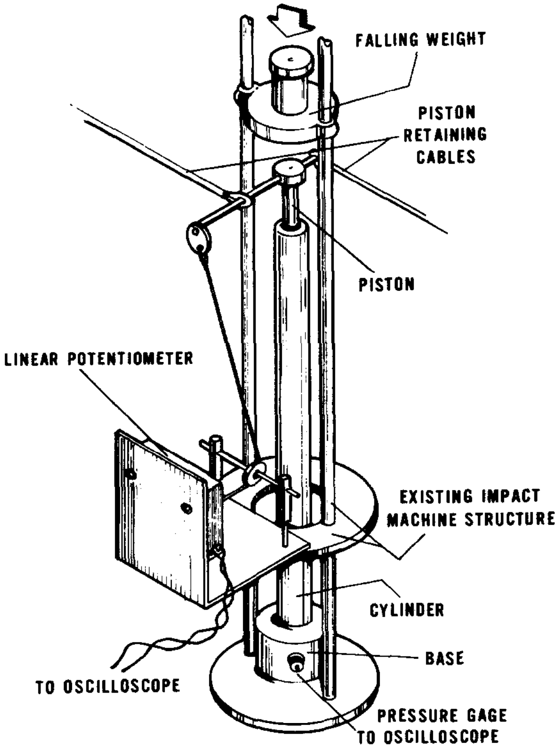

Fig. 5. Compression test apparatus

Equivalent pressure rates of rise at onset for sample initiation ranged from 9.9 to 11.2 x 10^6 KPa/sec (Table 5).

TABLE 5

High rate compression heating characteristics[1] for 2-MNT/TNM mixtures

Composition[2] (2-MNT/TNM)	Oxygen balance (%)	Pressure rate of rise (KPa/sec x 10^{-6}) Min	Max
21:79	0	11.2	18.8
7:93	+33	10.5	14.5
38:62	-38	9.9	27.9

[1] Test described in Unit Operating Procedure 4-29-9.
[2] Weight percent ratio.

After initiation, pressure rates of rise generally increased rapidly. Application of these data for assessing the initiation potential for N_2O_4/NB mixtures within the compressors and pumps listed in Table 6 show adequate safety margins ranging from > 17 to > 524. These assessments represent a more severe case since realistic high rate compression conditions are difficult to achieve in this equipment even if the pump or compressor outlets were operated closed. Other impact and friction potentials associated with the spent acid recovery operation which were hazards assessed are reported in reference 9.

TABLE 6

Safety assessment of spent acid and fume recovery pumps and compressors

Item being assessed	Initiation[1] mode	In-process potential (KPa/sec x 10^{-4})	Threshold initiation rate (KPa/sec x 10^{-4})	Safety margin
Nash compressor	High rate compression heating	2.1	1100	> 524
Spent acid pumps	High rate compression heating	7.9 to 64.5	1100	> 139 > 17
Weak nitric acid pumps	High rate compression heating	4.5	1100	> 244
Residual acid pumps	High rate compression heating	4.5	1100	> 244

[1] Assessed for initiation of N_2O_4 or TNM mixture with nitrobody.

Analysis of Incident

An explosion (ref. 10) occurred in the spent acid recovery storage tank outlet line which feeds reclaimed weak nitric acid to the day tanks adjacent to the nitration building. At the time, acid flowed by gravity from an elevation of ≃ 30 meters. Upon filling of the day tank, the closing of a fast-acting valve produced a hydraulic shock followed by a violent reaction at an acid storage tank some 122 meters away. Prior to the incident, evidence on hand showed the spent acids being sent to the acid recovery unit contained unusually high percentages of nitrobody and oxides in the acid.

Tetranitromethane was suspected at first; however, infrared analysis showed only traces of this compound present in a few of the many acid samples taken from various locations at the acid recovery unit and the nitration and purification buildings. Increasing evidence pointed to the presence of N_2O_4 because of plant process fluctuations prior to the incident and knowledge that N_2O_4 can form sensitive mixtures with nitroaromatics.

Subsequent sensitivity tests were performed and confirmed both laboratory-prepared N_2O_4-nitrobody-acid mixtures and TNT plant acid samples capable of explosive propagation reactions. Explosive reactions were most violent in tests employing high N_2O_4-nitrobody to acid ratios (ref. 10).

Calculations based on standard equations show the hydraulic shock could have transmitted a pressure pulse of ≃ 83 bars in the line or at the closed valve face. A temperature rise caused by adiabatic compression of an air bubble was calculated to approach ≃ 700°C. Greater localized pressures or temperatures could easily have existed for short durations due to wave reflections and rarefactions within this system. Data obtained in this recent study corroborated the earlier findings that the explosion was attributed to the presence of an N_2O_4-nitrobody mixture. As can be seen from data in Figure 4, shock pressure versus card gap thickness predict that an oxygen balanced N_2O_4/2-MNT mixture is initiated at less than 138 bars when extrapolated to a gap thickness of ≃ 155 cm. This low initiating shock pressure approximates the calculated hammer shock pressure of ≃ 83 bars possible during the valve closing operation in the RAAP acid recovery weak nitric acid tanks.

Processing changes made to eliminate or minimize formation of these mixtures from acid recovery unit include (1) reducing the NB content of the spent acid prior to acid recovery, (2) reducing the NO_x content of the cooler condenser acid through temperature control of this acid, and (3) bleaching the SAR absorption product and recycling a portion of this bleached acid through the tank which receives the cooler condenser acid and Nash compressor acid, and (4) elimination of fast-closing valves in TNT operations.

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