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PII: S0304-3894(18)31259-7
DOI: https://doi.org/10.1016/j.jhazmat.2018.12.110
Reference: HAZMAT 20144

To appear in: *Journal of Hazardous Materials*

Received date: 5 October 2018
Revised date: 11 December 2018
Accepted date: 27 December 2018

Please cite this article as: Lease N, Kay L, Chavez DE, Robbins D, Manner VW, Increased Handling Sensitivity of Molten Erythritol Tetranitrate (ETN), *Journal of Hazardous Materials* (2018), https://doi.org/10.1016/j.jhazmat.2018.12.110

Increased Handling Sensitivity of Molten Erythritol Tetranitrate (ETN)

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Highlights

- Erythritol tetranitrate has been analyzed for impact sensitivity in the solid and molten state
- Dramatically increased handling sensitivity of ETN was observed in the molten state
- The change in sensitivity in the liquid state was found to be reversible upon solidification

Abstract: Erythritol tetranitrate (ETN) is a well-studied homemade explosive (HME), which is known for its ability to be melt-cast at a fairly low temperature. We have observed dramatically increased handling sensitivity of ETN in the molten state, using temperature controlled drop-weight impact sensitivity measurements. Impact testing was performed using ERL Type 12 drop hammer equipment using a 2.5 kilogram weight, a 0.8 kilogram striker, an anvil and sound detection equipment. Most experiments were performed in the absence of standard grit paper, due to the elevated temperature measurements with a liquid. At room temperature, ETN exhibited an impact sensitivity of 14.7 ± 3.4 cm, which changed to 1.0 ± 0.6 cm in the liquid state at 65 °C. The change in sensitivity in the liquid state was found to be reversible upon solidification, and did not appear to correlate with temperature. Control experiments were performed in the same setup using standard explosives pentaerythritol tetranitrate (PETN) and triacetone triperoxide (TATP). This is the most sensitive material that we have been able to measure using our instrumentation, and indicates that ETN be handled with extreme caution during the melt-casting process.

Keywords: Explosive, ETN, Sensitivity, Impact, Melt-cast

1 Introduction

ETN has attracted recent interest as an explosive due to its ease of synthesis, high performance capabilities and its ability to be melt-casted. Due to the accessibility of the starting materials, the simple synthetic method, and the ability to melt-cast at 62 °C, ETN has been extensively studied as a potential

homemade explosive [1]. Erythritol tetranitrate (ETN) was first synthesized in 1849 [2] by Stenhouse, and is a nitrate ester akin to nitroglycerine and PETN (pentaerythritol tetranitrate), all of which are vasodilators and have been studied for their medicinal properties [3]. It is only recently that the explosive properties of ETN have been investigated thoroughly. This increased interest in ETN coincided with improved manufacturing capabilities of its starting material erythritol [4], dramatically reducing its price.

Explosive and physical properties[5] of ETN such as critical diameter and detonation velocity[6], as well as blast wave and fragmentation velocity[7] have recently been reported. Sensitivity studies have shown that ETN is more sensitive to drop-weight impact and friction testing than PETN [8], which is typically regarded as one of the more sensitive secondary explosives. Additionally, recent studies on (one polymorph of) ETN have shown that particle size does not influence the impact sensitivity[8]. However there have been no reports on the sensitivity of molten ETN, which is of particular importance for safety reasons due to the recent rise in melt casting of ETN. Herein we report impact test studies showing that in its molten phase the sensitivity of ETN is increased dramatically and should be handled with extreme caution.

2 Experimental Section

Caution: Erythritol tetranitrate is a very sensitive explosive that has been involved in multiple explosive accidents [9]. ETN should only be handled in approved explosives facilities.

2.1 Materials and Methods

Ethanol, nitric acid (70%) and sulfuric acid (fuming) were purchased from Sigma Aldrich and Amresco and were used as received. Erythritol marketed by Now Foods was used as received. Deuterated solvents (acetonitrile d_3) were purchased from Acros chemical and used as received. ^{1}H NMR was recorded on a 400-MHz Bruker spectrometer. ^{1}H NMR signals were referenced using residual solvent signals. Erythritol tetranitrate (ETN) was prepared using the mixed acid method (nitric and sulfuric acid) according to literature procedures [**Error! Bookmark not defined.**]. Samples were synthesized on a 50 gram scale, and crude ETN was purified by dissolution in hot ethanol followed by precipitation in water. The purity of each ETN batch was verified by NMR (see Supporting Information).

2.2 Impact Testing
2.2.1 General Information

Impact testing was performed using ERL Type 12 drop hammer equipment using a 2.5 kilogram weight, a 0.8 kilogram striker, an anvil and sound detection equipment. For each run 40 mg of material was used either with grit paper or directly on the smooth (bare) anvil and was impacted using the drop weight from various heights. A go was defined as a 120 average decibel level from two sound detectors. The parameter reported is the DH_{50}, which is defined as the height from which 50% of the drops are a go. The DH_{50} values were calculated using the Neyer D-Optimal method for which the higher the DH_{50} value corresponds to lower sensitivity to initiation.

To ensure that experimental setup was not a factor in the observed results, two anvils were used during the course of the impact testing and both yielded similar results. For solid samples the striker was placed gently on top of the sample. For liquid samples, a ~1 mm gap was imposed between the striker and the anvil, using a plastic spacer (the striker was held loosely in place with magnets) to prevent dispersion of the liquid between the anvil and striker. In this configuration, the top surface of the liquid was in contact with the striker. Impact testing at elevated temperatures was performed using an aluminum collar around the anvil that was heated and cooled using ethylene glycol in a circulating bath. Temperatures of the anvil were confirmed using a thermocouple attached to the center of the anvil before drops were conducted. Strikers were heated in a furnace to the appropriate temperature prior to use. One striker was used per test before returning to the oven to ensure the temperature of the striker remained within 65 – 67 °C.

2.2.2 Molten ETN Impact Testing

The ETN sample was loaded onto the heated bare anvil (65 – 67 °C) and was allowed to sit for 2 – 3 min to ensure melting had gone to completion. Upon melting, bubbles could generally be observed at the top and bottom surface of the liquid. A flashlight was used to confirm that no solid remained in the sample. Upon completion of the melting process, a hot striker (~67 °C) was placed in the apparatus. An approximate time of 2 minutes was observed between removal of the striker from the oven and completion of the impact test, during which time minimal cooling of the striker was observed (< 2 °C).

2.2.3 Impact testing of Re-solidified ETN

The ETN sample was loaded onto the heated bare anvil (65 – 67 °C) and allowed to completely melt. Upon completion of melting, the anvil was cooled to allow the sample to re-solidify into a hard, opaque, glass-like pellet over the course of approximately 5 – 10 minutes (Figure 1). When solidification did not occur within this time frame, a small amount of the liquid was gently removed, allowed to solidify, and then replaced into the liquid in order to seed the crystallization process. Once solidification was complete, impact testing of the sample was then performed using the method for solid samples as described above. Several samples of the solidified ETN were collected from the anvil for analysis by NMR, to ensure no decomposition had occurred in the heating and cooling process (see Supporting Information). NMR spectra indicated that the ETN samples were > 99% pure after this process. Generally the anvil had cooled to a temperature of ~40 °C by the time the sample had solidified, and a room temperature striker was used for the test. Upon completion of one run, the anvil was cleaned and reheated to 65°C to prepare for the next sample.

3 Results and Discussion

In order to accurately access the sensitivity of molten ETN, baseline measurements of solid ETN were recorded at both ambient and elevated temperatures. Impact testing at elevated temperatures were performed directly on the anvil with no grit paper. Unlike the standardized method, grit paper was not used in most of our tests in this study, as testing impact sensitivity at elevated temperatures resulted in the grit paper curling, making it unusable. Impact tests resulted in a DH_{50} value of 14.7 ± 3.4 cm for ETN at ambient temperature with no grit paper (Table 1). This is a significant drop in sensitivity from the typical value of 5 – 6 cm with grit paper, likely due to the loss of a source of high melting point grit.

To test the impact sensitivity of molten ETN, both the anvil and striker were heated to 65 – 67 °C, several degrees above ETN's melting point. Melting is observed almost immediately after the sample is placed on the anvil, with no solid remaining after approximately 1 minute. During the melting process, very small bubbles can be seen forming on the top and sometimes bottom surface of the molten ETN. Impact tests were only performed once there was visual confirmation that all the solid had melted. It is important to ensure no solid remains as other nitrate esters such as nitroglycerin have shown that mixtures of solids and liquids can exhibit sensitivities that are different from the pure solid or liquid [10]. Impact testing results for molten ETN showed dramatically increased sensitivity. The DH_{50} value for molten ETN was observed at 1.0 ± 0.6 cm, a 13.7 cm decrease from the ambient ETN impact tests. It is known that liquid explosives can be more sensitive than solid explosives based on factors such as cavitation[11,12].

Impact testing at elevated temperatures was performed to determine if the increased impact sensitivity of molten ETN is due to the temperature of the sample, or the change in phase. To do this, a temperature just under ETN's melting point (62 °C) was chosen. ETN samples were prepared and placed on an anvil heated to 55 °C, and given time (2 – 3 minutes) to equilibrate. While on the anvil no visible change was observed in the solid. Impact testing with a striker heated to 55 °C showed that ETN at 55°C has DH_{50} values ranging from 17.8 ± 4.2 – 19.9 ± 4.0 cm, slightly larger, but within error of the impact sensitivity at room temperature. These results suggest that the higher temperatures used in this study are not the cause of the increased impact sensitivity of ETN. To further probe the effect of temperature on a related material, we performed analogous tests on PETN with no grit paper at 24 °C, 55 °C, and 65 °C (significantly below the melting point for PETN). Table 1 shows that PETN becomes less sensitive with temperature, potentially due to a reduction in density at the higher temperatures.

Table 1. Drop-weight impact test results for solid and molten ETN (**ETN$_m$**), along with PETN and TATP control experiments. [a]

Material (conditions)	Impact DH_{50} (cm)	Material (conditions)	Impact DH_{50} (cm)
ETN (24°C, b)	14.7 ± 3.4	ETN (24°C, g)	5.4 ± 1.0
ETN (55°C, b)	17.8 ± 4.2	PETN (24°C, g)	10.2 ± 0.9
ETN (55°C, b) rep[b]	19.9 ± 4.0	PETN (24°C, b)	20.8 ± 4.3
ETN$_m$ (65°C, b)	1.0 ± 0.6	PETN (55°C, b)	24.8 ± 2.2
ETN$_m$ (65°C, b) rep[b,d]	1.0 ± N/A	PETN (65°C, b)	27.3 ± 5.2
ETN (65°C→cool, b)[c,d]	12.0 ± N/A	TATP (24°C, b)	2.7 ± 0.5

[a] Each drop-weight impact test was performed using ERL Type 12 drop hammer equipment using a 2.5 kilogram weight, a 0.8 kilogram striker, an anvil and sound detection equipment, and evaluated using the Neyer D-Optimal method. Both anvil and striker were heated to the specified temperatures. "g" indicates that standard grit paper was used for samples, and "b" indicates that samples were placed directly on the anvil. [b] ***"rep"*** indicates that repeat measurements were conducted using a new anvil, to ensure that a new impact test setup would not significantly influence results. [c] The solid ETN was allowed to melt on the anvil at ~65 °C, then the setup was cooled to allow for solidification of the ETN before striking with a room temperature striker. [d] For the tests with no standard deviation assigned, there was no crossover, ie. the lowest "go" was higher than or equal to the highest "no go" (see Supporting Information for more detail).

Because of the well-known variability of impact test results, we collected data with a well-known primary explosive, using an identical setup for the solid and molten ETN. Impact testing of triacetone triperoxide (TATP) was conducted at room temperature with no grit paper, resulting in a DH_{50} value of 2.7 ± 0.5 cm. This data indicates that TATP is slightly less sensitive than molten ETN (though close to within error), highlighting the importance of using increased safety measures when handling molten ETN.

In order to ensure that the increased sensitivity was not due to sample decomposition leading to formation of a new explosive species, samples of ETN were melted on the anvil at 65 – 67 °C. After the entire sample had melted, the anvil was cooled to 30 – 40 °C causing the sample to re-solidify, or melt-cast, onto the anvil into a hard, opaque, glass-like pellet. In some cases, a small amount of solid was needed to seed the crystallization. Impact testing of the re-solidified material had a DH_{50} value of ~12 cm, close to the value of the room temperature solid. The slight increase in sensitivity of the re-solidified material compared to the standard powder could be a result of the increased density of the melt-cast material. This is in agreement with literature reports that show no increased sensitivity in melt-casted ETN,[13] or variations in impact sensitivity with different particle sizes of ETN [**Error! Bookmark not defined.**]. Additionally, the re-solidified material was collected from the anvil and analyzed by nuclear magnetic resonance (NMR), and found to be identical to the initial pure material. There are not many nitrate esters that can be safely studied in both the solid and molten state. However, the increase in sensitivity observed with molten ETN relative to the solid has been observed with other materials, such as nitroglycerin[14] and an analogous nitrate ester with an extra methylene group at the 2-position [15].

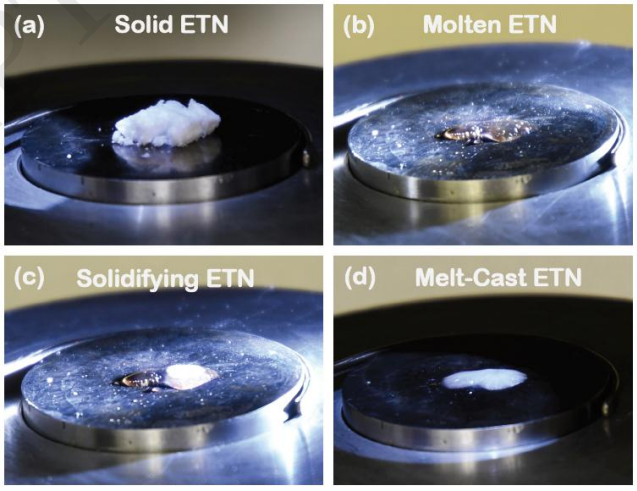

Figure 1. (a) 40 mg of ETN placed on the bare anvil set to 65 – 67 °C, (b) Molten ETN after approximately 1 minute on the heated anvil, (c) ETN re-solidifying after cooling the anvil to approximately 40 °C, and (d) completely re-solidified ETN (melt-cast), showing a visible reduction in volume.

4 Conclusion

In conclusion, we have observed that ETN exhibits dramatically increased sensitivity in the molten state. This is the most sensitive material that we have been able to measure using our instrumentation, and it should be handled with extreme caution. TATP, a notably sensitive primary explosive that has been involved in numerous accidents [16,17], exhibits slightly lower impact sensitivity than molten ETN on our apparatus. In this study, no chemical change occurred during the melting process, which was observed to be completely reversible. The change in phase to the liquid state appears to be the cause for the significant increase in sensitivity for molten ETN. The formation of bubbles and cavitation are potential reasons for the observed increase in sensitivity for molten ETN, and further work is underway to understand these effects and other sensitivity properties of molten ETN.

Acknowledgements

This work was supported by the US Department of Energy through the Los Alamos National Laboratory. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (Contract DEAC52-06NA25396). The authors would like to acknowledge Geoff Brown, Jacqueline M. Veauthier, Brent A. Faulkner, Thuy-Ai D. Nguyen, and Robert J. Houlton for use of the aluminum collar for temperature-controlled impact measurements, supported by the Laboratory Directed Research and Development program of Los Alamos National Laboratory under 20180369ER.

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