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Explosive Properties of Melt Cast Erythritol Tetranitrate (ETN)

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Abstract: Erythritol tetranitrate (ETN) is a low melting, solid, nitrate ester with significant explosive properties. The increased availability of its precursor (erythritol), which is now used as a sweetener, has attracted attention to the possible misuse of ETN as an improvised explosive. However, ETN also has some potential to be used as a component of military explosives or propellants. This article focuses on the properties of melt-cast ETN. The sensitivity of the compound towards impact and friction was tested. The explosive performance was evaluated, based on cylinder expansion tests and detonation velocity measurements. The impact energy and friction force required for 50% probability of initiation was 3.79 J and 47.7 N, respectively. A Gurney velocity value of G = 2771 $m \cdot s^{-1}$ and a detonation velocity of 8027 $m \cdot s^{-1}$ at a charge density of 1.700 $g \cdot cm^{-3}$, were found for the melt-cast material. The sensitivity characteristics of melt-cast ETN does not differ significantly from either literature values or the authors' data measured using the crystalline material. The explosive performance properties were found to be close to those of PETN.

Keywords: sensitivity, detonation velocity, melt-cast, erythritol tetranitrate, Gurney velocity

1 Introduction

Erythritol tetranitrate (ETN) is a solid, four-carbon unbranched ester of nitric acid, structurally similar to the two-carbon ethyleneglycol dinitrate and the three-carbon nitroglycerine. Although ETN is an easily synthesized powerful explosive, it has not really attracted the attention of scientists as a useful

explosive [1], the high cost of erythritol, a necessary starting material for ETN, being one of the main reasons for this lack of interest. Early books in the field of explosives simply mention its basic explosive parameters [2-4]. However new technology for erythritol production has been developed recently [5] and the price of erythritol has thus been significantly reduced. The consequent current availability and affordability of erythritol has led to recent extensive research into the explosive properties of ETN.

The first paper was published by Oxley *et al*. [6], who presented some analytical and thermoanalytical data for ETN. Manner *et al*. [7] focused on analytical data and the influence of crystal morphology on the sensitivity of ETN to mechanical stimuli. Our research group investigated the fundamental physical properties of ETN [1] and recently some analytical properties of ETN [8]. Yan *et al*. [9] studied the thermal behaviour and decomposition kinetics of pure ETN and its mixtures with both pentaerythritol tetranitrate (PETN) and hexogen (1,3,5-trinitro-1,3,5-triazinane, RDX). We also investigated the explosive properties of mixtures based on ammonium nitrate sensitized with erythritol tetranitrate [10]. Manner *et al*. recently reported the detonation parameters of pressed ETN, determined by cylinder expansion tests [11].

All of the studies on the explosive properties of ETN have focused on the crystalline material, in the form in which it is obtained from synthesis or recrystallization. ETN is a compound with a low melting point, 61 °C [2, 3], substantially lower than the temperature at which exothermic decomposition occurs (158 °C) [9]. This significant difference between the melting and decomposition temperatures allows ETN to be melt-cast. To the best of our knowledge, the properties of melt-cast ETN have not been published before, and therefore we have focused on research into the sensitivity and performance of melt-cast ETN.

2 Materials and Methods

Caution: No problems have occurred during the synthesis and handling of erythritol tetranitrate, but the material is still an explosive. Laboratories and personnel should be properly prepared and safety equipment such as protective gloves, shields, and ear plugs should be used, even when working with small quantities of this substance.

2.1 Materials

Erythritol tetranitrate was prepared according to the method patented by Bergeim [12] and recently described in detail [10]. Erythritol (meso form −

(2R,3S)-butane-1,2,3,4-tetraol), with a declared purity of 99.5%, was obtained from a local pharmacy (trade name Extra-linie). Other chemicals used were of analytical purity (p.a.). The ETN was recrystallized from ethanol and resulted in a crystalline powder consisting of needle-like crystals of average length 230 μm and a length to width ratio of 6.5. The product analysis, yield, crystal size and shape of ETN have already been described in detail in our previous work [1]. Melt-cast ETN samples were prepared in the form of small pellets by dropping molten ETN onto a cold tile – the appearance of the samples is shown in Figure 1.

Figure 1. Shape and size of crystalline ETN (left) and melt-cast ETN pellets (right). The fine-scale divisions are in millimeters

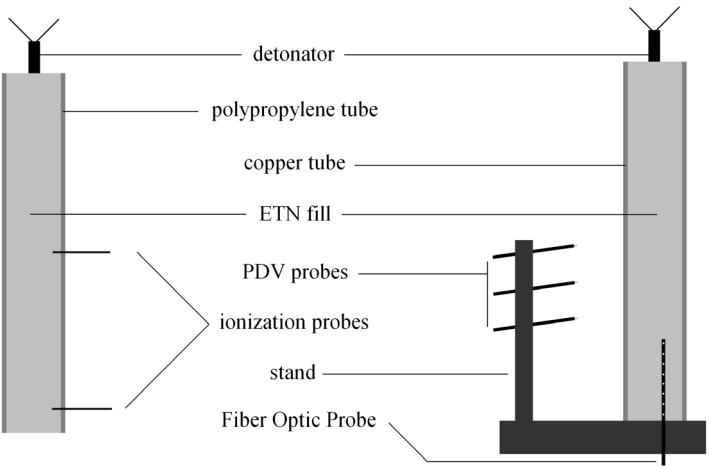

Figure 2. Cross-sections of the measurement arrangements: detonation velocity (left) and cylinder test (right)

Mercury fulminate (MF), pentaerythritol tetranitrate (PETN) and hexogen (RDX) were used as reference explosives for comparisons with ETN's sensitivity. The preparation of brown mercury fulminate, its crystal size and shape have been published in our previous paper [13]. PETN, with particles smaller than 200 μm, was provided by Explosia a. s. (Czech Republic) under the trade name "Pentrit NS", and RDX was sourced from Chemko Strazske (Slovakia).

2.2 Impact sensitivity

Impact sensitivities were measured using a Kast fall hammer, produced by OZM Research, as were the pistons (BFH-SR) and cylinders (BFH-SC). A 0.5 kg hammer was used for MF, a 1 kg one for PETN and ETN, and a 2 kg hammer for RDX. Probit analysis [14] was used for the evaluation of the data and for the construction of sensitivity curves. Each sample was tested at five energy levels with fifteen trials at each level. One pellet of ETN with weight ~20 mg was used for each trial. Crystalline ETN and other explosives were used in the powdered state in volumes of 40 mm^3 for each trial.

2.3 Friction sensitivity

Sensitivity to friction was determined using an FKSM-08 BAM device supplied by OZM Research. BFST-Pt-100S type test plates and BFST-Pn-200 pestles were used, all produced by OZM Research. Each sample was measured at five energy levels with fifteen trials at each level. Probit analysis was again used for evaluation of the data obtained and for the construction of sensitivity curves. Melt-cast ETN samples were prepared by directly dropping of molten ETN onto a rough test plate and allowed to solidify. Other explosives were used in their crystalline state.

2.4 Gurney velocity

Four reduced scale cylinder tests were performed to determine the Gurney velocity of melt-cast ETN. Copper tubes, 200 mm in length, with a 15 mm internal diameter and a wall thickness of 1.4 mm, were used. The exact dimensions of the tubes were measured within 0.01 mm accuracy to produce the actual metal to explosive mass (*M/C*) ratio. The tubes in a vertical position were gradually filled with molten ETN at 75 °C to obtain homogeneous charges without cavities. The final charge densities were 1.700 ± 0.003 $g \cdot cm^{-3}$. The expansion of the tubes was recorded photographically using a UHSi 12/24 high-speed framing camera (Invisible Vision). Back lighting was provided by an argon flash bomb. The expanding wall velocities were measured by a first generation photonic Doppler velocimeter (PDV, prototype device produced by

OZM Research) with three active channels and bare fibre probes [15]. Original voltage-time oscilloscope records were evaluated using short-time Fourier transform (STFT) in a MATLAB based software to obtain the velocity *vs*. time profiles in a way which is described in detail in [16]. The PDV probes were fixed in positions of about 120 mm, 135 mm and 150 mm from the upper end of the tube with the probes' axes angled to the copper surface normal by 5° towards the detonator. The distance of the probes from the cylinder surface was kept at 11.5 mm, which allowed undisturbed observation of a seven-fold cylinder volume expansion ($V/V_0 \approx 7$). The wall velocity at $V/V_0 \approx 7$ is sometimes referred to as the terminal velocity (v) in the case of the standard copper cylinder test, with reference values available in the literature [17-19]. Using the terminal expansion velocity, the Gurney velocity (G) for ETN was calculated according to the Gurney equation for cylindrical charges [20]:

$$\frac{v}{G} = \left(\frac{M}{C} + \frac{1}{2} \right)^{-1/2}$$

2.5 Detonation velocity

The detonation velocity of erythritol tetranitrate was measured using ionization probes and a digital oscilloscope. The ionization probes were prepared from 0.1 mm twisted copper wire. Four charges of erythritol tetranitrate were prepared by filling polypropylene tubes having an internal diameter of 16.6 mm and wall thickness of 4.2 mm. Two of these tubes were filled by careful hand pressing of ETN crystalline powder, which resulted in charge densities of 0.83 $g \cdot cm^{-3}$ and 0.86 $g \cdot cm^{-3}$. Fine powder was added in small increments in order to achieve a regular density distribution along the charge. The remaining two tubes were filled with molten ETN, in the same way as for the cylinder test charges, and resulted in charge densities of 1.64 $g \cdot cm^{-3}$ and 1.66 $g \cdot cm^{-3}$.

The detonation velocity was also measured in four cylinder expansion tests using the fibre optical probe method (FOP) [21]. The probes were prepared by perpendicular drilling of 8 holes with a diameter of 0.3 mm into a plastic optical fibre with 1 mm core diameter and 2.2 mm outer diameter. The FOP was inserted into the last 40 mm of the charge parallel with the charge axis. Air cavities in the holes are compressed by the passing detonation wave which causes them to produce a bright flash of light. The light signal is transported by the fibre to an optoelectronic receiver and is then recorded by a digital oscilloscope. A typical raw signal and the data evaluation methods are presented in Figure 3.

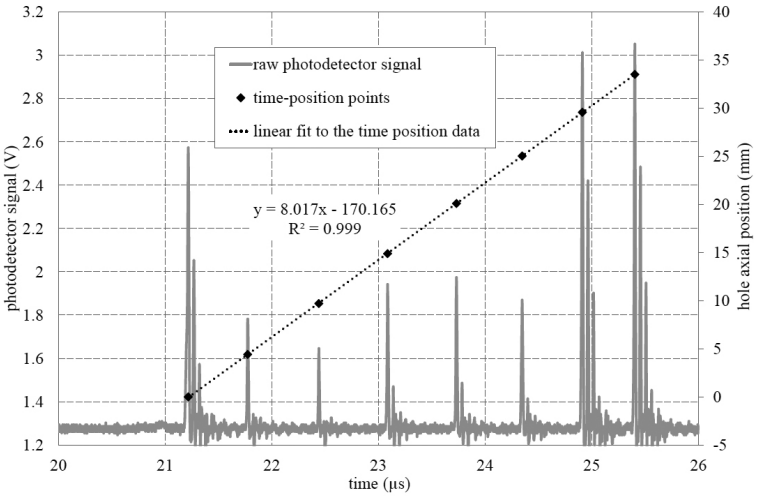

Figure 3. FOP raw signal and detonation velocity evaluation. The peak times taken from the raw signals are plotted against the positions of the holes. The slope of the regression line is the velocity of detonation ($mm \cdot \mu s^{-1}$)

2.6 Calculation of detonation parameters

The detonation parameters of ETN were calculated using the Explo5 V6.03 thermochemical code. The semi-empirical Becker-Kistiakowsky-Wilson (BKW) equation of state was used with the BKWN set of parameters as follows ($\alpha = 0.5$; $\beta = 0.38$; $\kappa = 9.32$; $\theta = 4120$), which is useful for thermochemical calculations of the properties of high explosives in a wide range of densities [22, 23].

3 Results and Discussion

3.1 Sensitivity to mechanical stimuli

The impact sensitivity of ETN was evaluated using probit analysis [14]. The resulting sensitivity curves for crystalline and melt cast ETN are presented in Figure 4. We compared the friction sensitivity of ETN with the sensitivities of MF, PETN and RDX (using the same method). The values for 50% probability of initiation (taken from the sensitivity curves) for all of the explosives measured are summarized in Table 1.

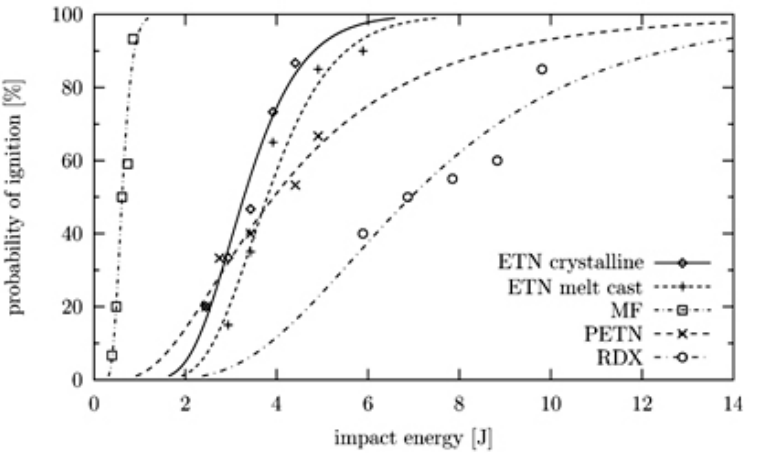

Figure 4. Comparison of the impact sensitivity of ETN with that of MF, PETN and RDX

The form of ETN does not significantly affect the sensitivity to impact. Crystalline ETN is only slightly more sensitive than melt-cast ETN. The impact sensitivity of ETN is about the same as that of PETN and higher than that of RDX. A similar result for crystalline ETN was obtained by Oxley *et al*. [6], while Manner *et al*. [7] reported an impact sensitivity for crystalline ETN nearly twice as high as that for PETN. However, our absolute values differ from the values obtained by Oxley *et al*. [6] and Manner *et al*. [7]. This can be explained by the use of a different apparatus and evaluation method. Consequently, our sensitivity data for the reference explosives are also shown for comparison.

Table 1. Sensitivity to impact and friction

	Impact energy for 50% probability of initiation [J]	Friction force for 50% probability of initiation [N]
MF	0.62	5.3
ETN (crystalline)	3.28	38.9
ETN (melt-cast)	3.79	47.7
PETN	3.93	75.1
RDX	6.94	127

The values of the impact sensitivity for the reference explosives (PETN and RDX) in this study differ significantly from our previously published data [24]. The probable reason for this difference is the use of older types of pistons and

cylinders in the earlier measurements. Older types of pistons and cylinders were out of the range of the diameter tolerance demanded by today's use of STANAG 4489. Other conditions of measurement, methodology and measuring apparatus were the same as in our earlier study.

The friction sensitivity was also evaluated using probit analysis. The resulting sensitivity curves for crystalline and melt-cast ETN are presented in Figure 5 and the values for 50% probability of initiation (taken from the sensitivity curves) for all of the explosives are summarized in Table 1.

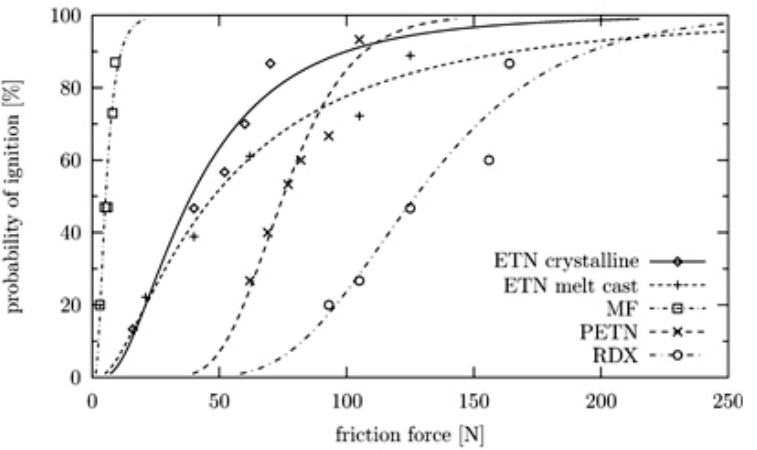

Figure 5. Comparison of the friction sensitivity of ETN with that of MF, PETN and RDX

The form of ETN does not have a significant effect on its friction sensitivity. The experiments showed that the friction sensitivity of melt-cast ETN is slightly higher than that of crystalline ETN. The sensitivities of both forms of ETN exceed the sensitivity of PETN. The result for crystalline ETN is in agreement with the friction sensitivity previously published by Manner *et al*. [7].

3.2 Explosive properties

Copper tube cylinder expansion tests were performed to characterize the metal accelerating ability of melt-cast ETN. A wall velocity for ETN of 1694 ± 8 m·s^{-1} ($V/V_0 = 7$; density 1.700 ± 0.003 g·cm^{-3}) was obtained using cylinder tests, as the average of 11 available results from the total number of 12 PDV probes. The resulting standard deviation corresponds to a 0.5% variability of results, which is caused by slight variations in the cylinder dimensions and the materials' lack of homogeneity. The average Gurney velocity value, $G = 2771 \pm 8$ m·s^{-1},

was calculated from the Gurney equation using the measured wall velocity. In this case, the variability of the results is only 0.3%, partly because the slight differences in tube dimensions were taken into account in the calculation. For comparison, the wall velocity data presented for the two cylinder tests on pressed ETN were extracted from Figure 2 in [11] and the corresponding Gurney velocities for $V/V_0 = 7$ were calculated. These results differ from ours by less than 1.5%. The wall velocity profiles and tube expansions obtained by the three PDV probes in one of the cylinder tests, are shown in Figure 6. The shadow photographs of the expanding charge casing show that some ruptures appeared at $V/V_0 = 6.5$, but none of them influenced the signal of the PDV probes. It can be seen that the expansion of the tubes was fairly symmetrical (Figure 7).

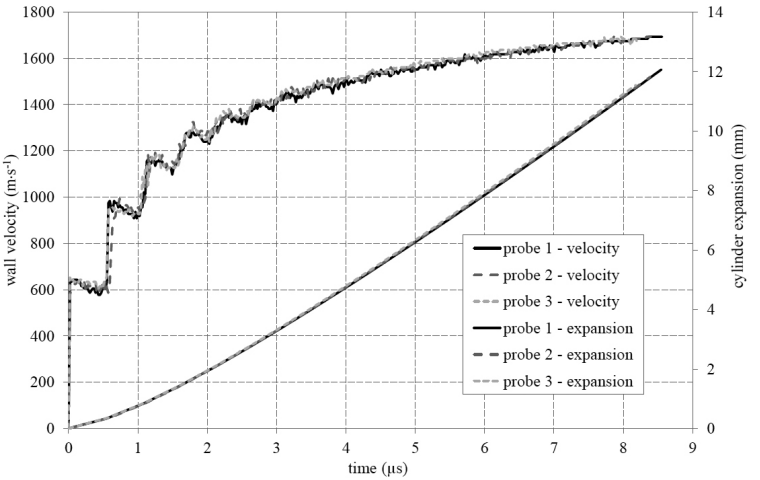

Figure 6. Example of the wall velocity and expansion profiles obtained by a cylinder expansion test of melt-cast ETN

The detonation parameters for pressed ETN have been published recently [11]. The detonation velocities of crystalline hand-pressed ETN and melt-cast ETN were measured at a charge diameter of about 16 mm, which should be enough to exclude diameter effects according to [11]. The peak detonation velocity of 8027 ± 27 m·s^{-1} at a charge density of 1.700 ± 0.003 g·cm^{-3} was determined in four cylinder expansion tests. All of the measured values are summarized in Table 2, where the available values are compared with the literature data for PETN [26] and the values of ETN and PETN computed using the Explo5 thermochemical code. Both measured and calculated detonation velocities of ETN at high densities are 1% lower than those for PETN. The

observed values are in agreement with Manner *et al*. [11], with the differences being lower than 1% at the same densities.

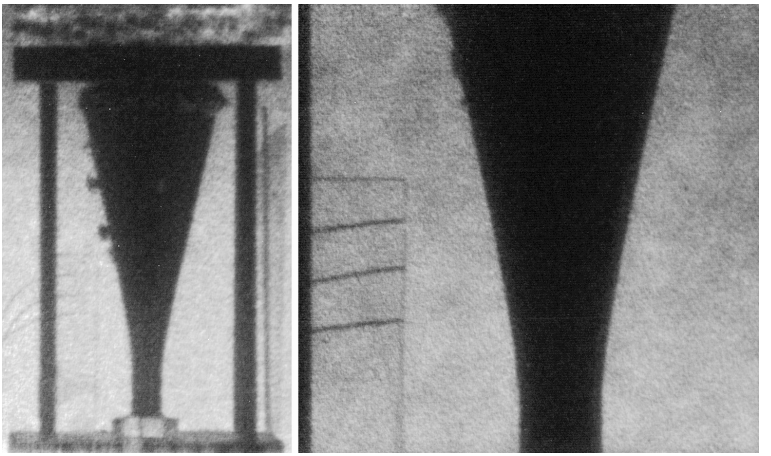

Figure 7. High-speed camera shadow photographs of the expanding cylindrical charge (overall on the left and a detailed view on the right)

Table 2. Detonation velocities of ETN. All values are rounded to the nearest ten

	Detonation velocity [m·s^{-1}]			
Density [g·cm^{-3}]	0.83	0.86	1.65	1.70
ETN experimental	4420[a]	4630[a]	7940[b]	8030[b]
ETN calculated	4800	4900	7890	8100
PETN [26]	4890	5000	7930	8110
PETN calculated	5040	5150	7970	8150

[a] hand-pressed crystalline powder
[b] melt-cast

4 Conclusions

The sensitivity and performance properties of erythritol tetranitrate were determined for powdered and melt-cast material. Probability curves, which describe the sensitivity of ETN towards impact and friction, were measured and compared with those of well-known explosives. The frictional force required for ETN initiation was found to be nearly half of that required for PETN. However, no significant difference was found between powdered and melt-cast material. The Gurney velocity and detonation velocity of melt-cast ETN were found to

agree with the literature values of pressed samples at similar densities. The detonation velocity of melt-cast ETN was found to be 1% lower than that of PETN at the same density.

Acknowledgement
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