Central European Journal of Energetic Materials, **2013**, *10*(3), 351-358
ISSN 1733-7178

Erythritol Tetranitrate as a Sensitizer in Ammonium Nitrate Based Explosives*)

Martin KÜNZEL, Ondřej NĚMEC and Robert MATYÁŠ

Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 95, Pardubice, 532 10, Czech Republic
E-mail: gunarex@gmail.com

Abstract: This paper focuses on ammonium nitrate based explosives sensitized with erythritol tetranitrate. Erythritol tetranitrate (ETN) is an ester of nitric acid and erythritol. It is a low melting crystalline solid with explosive properties similar to those of pentaerythritol tetranitrate. Experiments were conducted in order to determine any sensitizing effect this compound might have on three basic types of ammonium nitrate based mixtures – powdered, slurry and emulsion explosives. According to the results obtained, erythritol tetranitrate acts as a sensitizer giving detonator sensitivity to ammonium nitrate based explosives when incorporated therein in quantities from 10 to 20 percent.

Keywords: erythritol tetranitrate, improvised explosive, ammonium nitrate, slurry, emulsion

Introduction

Erythritol tetranitrate (ETN) is a simple nitrate ester which was first synthesized in 1843 by Stenhouse [1]. In recent years, ETN has become a popular explosive for amateurs, since erythritol was first released onto the market as a sugar substitute (sweetener) [2]. Some basic properties of ETN were published recently by Oxley [3]. Because of its sensitivity and highly explosive nature, ETN can be used as a sensitizing component in mixed explosives, mainly those

*) Part of this paper was presented at the *2nd Korean International Symposium on High Energy Materials* (*KISHEM-2*), held in September 2012, Incheon, South Korea.

based on ammonium nitrate (AN). Addition of ETN to powdered ammonium nitrate explosives was first proposed by Bergeim in his patent [4].

Although most of the detonation parameters of such mixed explosives are reduced in comparison with pure ETN, these mixed explosives are available and thus should also be taken into account by law enforcement forces. Ammonium nitrate based explosives are the cheapest and the most frequently used commercial explosives. There are three main types of AN explosives, *i.e*. simple powdered, slurry and emulsion explosives. Powdered explosives are simple mixtures of ammonium nitrate and fuel oil (ANFO). Slurry explosives are fluids or gels with the consistency of mud. They usually consist of a liquid phase of an AN (or other nitrate) solution mixed with a soluble or dispersed fuel and a solid phase of powdered AN with the possible addition of other solid fuels. Emulsion explosives are reversed water-in-oil emulsions of a supersaturated AN solution as a discontinuous phase dispersed in a continuous phase which consists of a mixture of hydrocarbon fuels with a high performance emulsifier.

The above described explosives cannot be detonated by means of a standard detonator and some sensitizer has to be added when this property is required. At present hollow glass microspheres are the usual sensitizer of choice for emulsion explosives [5]. The density of the explosive is thus lowered and hot spots are provided to support the detonation wave, but the density and thus the volume energy concentration is reduced. Flake aluminum with a large surface area is one of the oldest sensitizers of AN based explosives and it is also a quite efficient one. Aluminum is able to enhance both the sensitivity and the performance characteristics and to lower the critical diameter to a few millimeters, but its use is limited due to stability and cost issues [6]. The addition of a high explosive presents another method of sensitization. Finely powdered pentaerythritol tetranitrate (PETN) was suggested as a sensitizer for slurry explosives by Forrest [7]. PETN can ensure detonator sensitivity when incorporated in amounts of more than 20%, and at the same time can lower the critical diameter even more than aluminum. In this study, we decided to examine the sensitizing effect of ETN on particular examples of AN based explosives.

Material and Methods

Chemicals

Erythritol with declared purity of 99.5% was obtained from a local pharmacy (Extra-linie trademark) and the other chemicals used for ETN synthesis were of analytical purity (p.a.). Ammonium nitrate and sodium nitrate were purchased

from Explosia Company in technical quality, as they are used for the production of commercial explosives. The moisture content of ammonium nitrate was declared to be less than 0.5%. Pentaerythritol tetranitrate (PETN) designated NS (particle size under 0.2 mm) was also obtained from Explosia Company.

Synthesis of ETN

Caution: No problems have occurred during the synthesis and handling of erythritol tetranitrate, but the material is still a high explosive. Laboratories and personnel should be properly grounded and safety equipment such as protective gloves, shields, and ear plugs should be used, even when working with small-scale reactions.

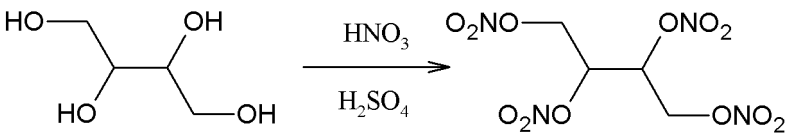

Figure 1. Scheme for erythritol tetranitrate preparation.

The compound was prepared according to the method patented by Bergeim [8] (Figure 1). Erythritol (150 g; 1.23 mol) was dissolved in 96% sulfuric acid (450 mL; 8.5 mol) at a temperature not exceeding 40 °C, which was ensured by using a cold water bath. The resulting yellowish solution was transferred to a dropping funnel and slowly added to a beaker of rapidly stirred fuming nitric acid (720 mL; 16.8 mol) whilst the temperature increased from 20 to 40 °C. The reaction was only slightly exothermic and cooling was not necessary. The reaction mixture was stirred at 45 °C for a further 30 minutes and then slowly cooled to 10 °C, with continued vigorous stirring. During this time, ETN precipitated out and solidified in granular form. The reaction mixture was then filtered and the filtrate was discarded. The product was transferred from the filter into a beaker containing an aqueous solution of sodium bicarbonate and was stirred for 30 minutes. After further filtration and drying at room temperature, the yield was 347 g (94%) of crude erythritol tetranitrate (m.p. 56-58 °C). The crude product was then dissolved in ethanol (ca. 800 mL) at 55 °C, neutralized with ammonium carbonate and crystallized by cooling, giving a yield of 331 g (89%) of ETN. The melting point of the recrystallized product was 59-60 °C. Elemental analysis: Calc. C 15.90, H 2.00, N 18.55; Found C 16.66, H 2.48, N 17.78 %.

Preparation of samples

Three different mixtures based on ammonium nitrate were used for the evaluation of the sensitizing effect of ETN. The mixtures were designed with respect to ease of preparation, simplicity of composition, adequate storage stability and neutrality of oxygen balance. The compositions of these mixtures are shown in Table 1.

Table 1. Composition of selected ammonium nitrate based explosives

	Powdered	Slurry I	Slurry II	Emulsion
ammonium nitrate	94.5	76.0	60.0	63.5
calcium nitrate tetrahydrate			14.5	
sodium nitrate				13.5
water		5.0	5.0	15.0
urea		18.5	20.0	3.0
diesel fuel	5.5			
motor oil				3.0
emulsifier				2.0
guar gum		0.5	0.5	

Ammonium nitrate was first sieved through a 1 mm sieve in order to exclude agglomerates. The powdered explosive was then prepared by hand mixing of powdered AN with diesel fuel in a beaker for 10 minutes.

Slurry I was prepared by proper mixing of ammonium nitrate, urea and water at a temperature of 80 °C. A yellowish solution was formed which was then cooled to room temperature. Finely powdered guar gum was then added with vigorous stirring to obtain a gel-like slurry.

In the case of slurry II, two thirds of powdered AN mass (40% total mass) were mixed with fine guar gum in a large beaker. The remaining ingredients, including one third of AN (20% total mass), were mixed in another beaker and heated with stirring on a hot-plate until all of the solids had dissolved at a temperature of about 80 °C. This solution was then cooled to room temperature and mixed with the powdered components in the large beaker. After 10 minutes of hand mixing, a thick suspension was formed.

The emulsion explosive was prepared according to our usual laboratory method. The discontinuous phase constituents (AN, sodium nitrate, urea and water) were mixed in a stainless steel pot and heated on a hot-plate until all of the solids had dissolved at a temperature of about 95 °C. The continuous phase constituents (fuel oil and emulsifier) were mixed in a cylindrical stainless steel

vessel and heated to 95 °C. The discontinuous phase solution was then poured into the continuous phase vessel with vigorous stirring at 2000 rpm. After 5 minutes a thick translucent emulsion was formed.

The above stated mixtures were doped with appropriate amounts of ETN (or PETN) and mixed manually for 5 minutes. Plastic foil tubes were then filled with the help of a piston in order to prepare homogeneous and void-less samples. The weight of the charges varied from 280 to 320 g. The density of the charges was measured using the hydrostatic weighing method.

Detonation velocity measurement

Measurement of the detonation velocity was conducted by the discontinuous method using fiber optic probes, optoelectronic receivers and a digital counter with the frequency of 50 MHz. The measured charges had a length of at least 200 mm and a diameter of 37 mm, with a negligible confinement layer (plastic foil). At the end of each fiber optic probe there was a small air pocket covered by aluminum tape. The measured length (the distance between the optical probes) was 100 mm in all cases. A distance between the detonator/booster and the first optic probe of about two charge diameters was used in order to stabilize the detonation front. This distance also ensures that actuation of the first probe cannot be caused by the booster alone, in cases where the main charge does not detonate at all. Two charges of each mixture were fired, the first initiated with a standard industrial detonator with aluminum cup (720 mg PETN base charge) and the second with a booster charge of 10 g of Semtex 1A plastic explosive.

Results and Discussion

The measured values of densities and detonation velocities for all charges of the ammonium nitrate based explosives sensitized with ETN are summarized in Table 2. Table 3 shows the same parameters for slurry explosives sensitized with PETN as a comparison.

Table 2. Experimental results for ETN sensitized bulk explosives

Base	ETN content [%]	Charge density [g·cm^{-3}]	Detonation velocity [m·s^{-1}]	Probes actuated	Initiation[1]
powdered	5	1.10		0	D
		1.10		0	D
	10	1.12		1	D
		1.12	2630	2	B
	15	1.18	3800	2	D
		1.16	3700	2	D
slurry I	15	1.40		0	D
		1.42		0	D
	20	1.47		0	D
		1.47	5150	2	B
	25	1.44		1	D
		1.50	6020	2	B
slurry II	10	1.38		0	D
		1.42		1	B
	15	1.39		1	D
		1.39	3850	2	B
	20	1.37	4120	2	D
		1.38	4310	2	B
emulsion	10	1.40		1	D
		1.40	1900	2	B
	15	1.42		1	D
		1.40	3490	2	B
	20	1.42	4400	2	D
		1.41	4960	2	B

[1] D = detonator, B = detonator + 10 g Semtex 1A booster.

Table 3. Experimental results for PETN sensitized slurry explosives

Base	PETN content [%]	Charge density [g·cm^{-3}]	Detonation velocity [m·s^{-1}]	Probes actuated	Initiation[1]
slurry II	15	1.38		0	D
		1.38	4510	2	B
	20	1.44	5560	2	D
		1.46	5610	2	B

[1] D = detonator, B = detonator + 10 g Semtex 1A booster.

The powdered explosive becomes sensitive to a detonator after the addition of 15% ETN whilst the slurry and emulsion matrices need 20% of ETN. Booster sensitivity is reached with 10% of ETN in the cases of the powdered and the emulsion explosives and 15% in the case of the slurry explosive. In those cases where only the first probe was actuated, incomplete detonation probably occurred. If the charge diameter were increased or the ETN particle size reduced, the ETN content needed to reach detonator sensitivity will probably be reduced.

In comparison with PETN sensitized slurries, ETN slurries exhibit as much as 1300 $m \cdot s^{-1}$ lower detonation velocities, but about the same level of initiation sensitivity. The sensitivity to initiation of our PETN sensitized slurries is also consistent with the findings of Forrest [7]. The reason for the higher detonation velocity could be mostly due to the fine particle size of the PETN used.

Conclusions

Ammonium nitrate explosives can be sensitized by the addition of crystalline erythritol tetranitrate. For powdered explosives, ETN is not very useful while its sensitizing effect is poor, compared to flake aluminum. In the case of slurry explosives, ETN sensitized explosives may attain a higher density and detonation velocity than those with flake aluminum [6]. For emulsion and slurry explosives, ETN provides sensitization without a significant density decrease compared to hollow glass microspheres, but only at a higher sensitizer content. Generally, detonation was achieved when more than 10% of ETN was incorporated in such explosives and detonator sensitivity was reached with 20% of ETN, which is the same level as in the case of PETN sensitization. ETN may provide an even higher sensitizing effect when tailored with respect to particle size and shape, as can be seen from the incomplete detonations.

Acknowledgement

The work in this paper was carried out as part of the Ministry of Interior of the Czech Republic Project No. VG20102014032.

References

[1] Stenhouse J., About some Constituents of Lichens (in German)*, Justus Liebigs Annalen der Chemie*, **1849,** *70*(2), 218-228.

[2] Nehasilová D., Erythritol as a Sweetener (in Czech), **2008**, 21.1.2011; Available

from: http://www.bezpecnostpotravin.cz/Index.aspx?ch=552&typ=1&val=71658&ids=3587.

[3] Oxley J.C., *et al*., Characterization and Analysis of Tetranitrate Esters*, Propellants Explos. Pyrotech.*, **2012**, *37*(1), 24-39.

[4] Bergeim F.H., *Blasting Explosive*, US 1751436, **1930**, DuPont de Nemours Company, Delaware, USA.

[5] Němec O., *et al*., Fortification of W/O Emulsions by Demilitarized Explosives. Part I. Use of TNT, *Cent. Eur. J. Energ. Mater.*, **2011**, *8*(3), 193-207.

[6] Zygmunt B., Detonation Parameters of Mixtures Containing Ammonium Nitrate and Aluminium, *Cent. Eur. J. Energ. Mater.*, **2009**, *6*(1), 57-66.

[7] Forrest C.D., *Super Fine PETN Thin Layer Slurry Explosive*, US 4012246, **1977**, Teledyne Industries, Inc., California, USA.

[8] Bergeim F.H., *Production of Erythritol Tetranitrate*, US 1691954, **1928**, DuPont de Nemours Company, Delaware, USA.