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DETONATION AND SENSITIVITY PROPERTIES OF FOX-7 AND FORMULATIONS CONTAINING FOX-7

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1,1-diamino-2,2-dinitroethylene (FOX-7) is known to be a new energetic material with promising properties as a IM ingredient in high explosive formulations. Drophammer (BAM) tests shows a value of 63 - 79 cm and no reaction in the friction test (> 340 N). A cylinder test has been performed to determine an equation of state (JWL) for pure FOX-7, and to compare the thermochemical calculations.

Thermochemical calculations show that PBX's based on FOX-7 and energetic binders could serve as a replacement of Comp B even at rather low solid loadings. A castable composition of FOX-7 and polyGlyN has been made (LIS-2). Small-scale safety tests show that the compositions were not sensitive to friction and the thermal stability at 65°C was excellent. Larger-scale detonation tests and small-scale slow cook-off tests show that the FOX-7 based PBX did not detonate at a diameter of 25 mm and upon slow heating (3.3°C/hour) it ignites at 220°C and burns without damage to the container or the surroundings.

INTRODUCTION

Composition B has been used for over 50 years in a wide range of explosive applications. This well known explosive has very good performance, is readily processed using standard melt cast facilities and utilizes low cost materials. However, it suffers from several problems such as cure shrinkage, which results in cracks and voids, relatively poor impact sensitivity and somewhat violent reaction during cook-off [1]. Because of these deficiencies the ongoing research in Sweden is concentrated on developing new explosives with much improved cook-off response, lower sensitivity and maintained performance.
The purpose of this paper was to develop detonative data as well as a PBX formulation based on FOX-7 and an energetic binder. The sensitivity of the selected formulation was then tested and compared with Comp. B. Some thermal stability data of FOX-7 is also presented.

THERMAL PROPERTIES AND DECOMPOSITION

The basic thermal stability of FOX-7 was measured by DSC (Differential Scanning Calorimetry), TG (thermogravimetry) and by Wood´s metal bath technique. The DSC spectrum of FOX-7 shows a complex structure with two exothermal peaks, one at 238 °C and another one at 281 °C and activation energy for FOX-7 was measured to be 56 kcal/mole which if compared to RDX (40 kcal/mole) and HMX (35 kcal/mole) shows that FOX-7 is more thermally stable than RDX and HMX.

The TG curve shows at least two, possibly four steps. This indicates that a two-step decomposition characterizes the initial decomposition of FOX-7, where the initial intermediate has a low thermal stability. The number of steps in the curve can possibly explain the two peaks in the DSC spectra.

The initial mass study was done on a conventional magnetic sector mass spectrometer. A very significant observation is that with electron impact ionization of 70 eV, FOX-7 exhibits a very strong molecular peak (*m/z* 148). This indicates that the molecule is very stable compared to RDX and HMX. Earlier work has shown that NTO and TNT have small molecular peaks at 70 eV [2]. Another interesting observation is that one of the decomposition paths is water elimination, indicated by the simultaneous observation of *m/z* 18 and *m/z* 130. This is similar to the accepted thermal decomposition of TATB. Evidence of the other possible decomposition path, the elimination of NO_2 is also present.

To improve the time resolution and to be able to vary the heating rate and type of heating, a new Time of Flight (TOF) mass spectrometer has been developed, see Figure 1. This set up is a development of an earlier technique that combines laser decomposition with mass spectrometer detection [3]. The time resolution is 20 000 scans/second at 2-300 amu. Possible heating methods are electrical heating, CO_2 – laser heating and fast YAG –laser "heating". This enables us to vary the degree of reaction from a very slow thermal decomposition to a pure shock initiation and acquire mass data in near real time. This instrument was applied for a more detailed study of the thermal decomposition.

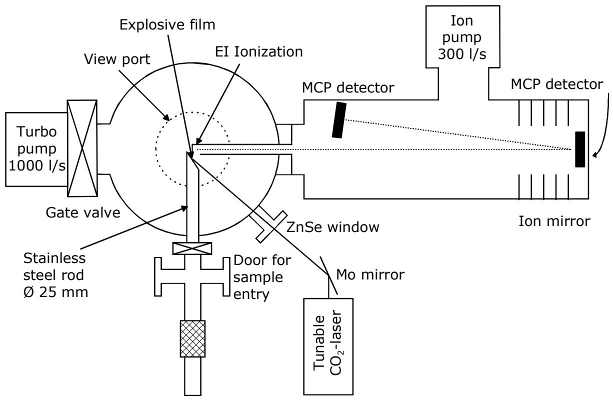

FIGURE 1. TIME OF FLIGHT (TOF) MASS SPECTROMETER FOR DECOMPOSITION STUDIES BY MEANS OF CO_2-LASER HEATING

This new mass spectrometer was applied to the study of FOX-7 decomposition. An example of a mass spectrum of FOX-7 is shown in Figure 2. By comparing a pure EI-spectrum with a spectrum from CO_2-laser induced decomposition it is possible to some degree separate thermal from ionic decomposition. For instance the peak *m/z* 86 is only present in the laser induced decomposition spectrum, which points towards a thermal origin. A proposed assignment is $C_2H_2N_2O_2$ (e.g. NH_2-C≡C-NO_2) or less likely C_2NO_3. Another interesting feature is the presence of NO and NO_2 that could indicate that one possible decomposition mechanism is the C-NO_2 bond breakage as proposed by Karle [4].

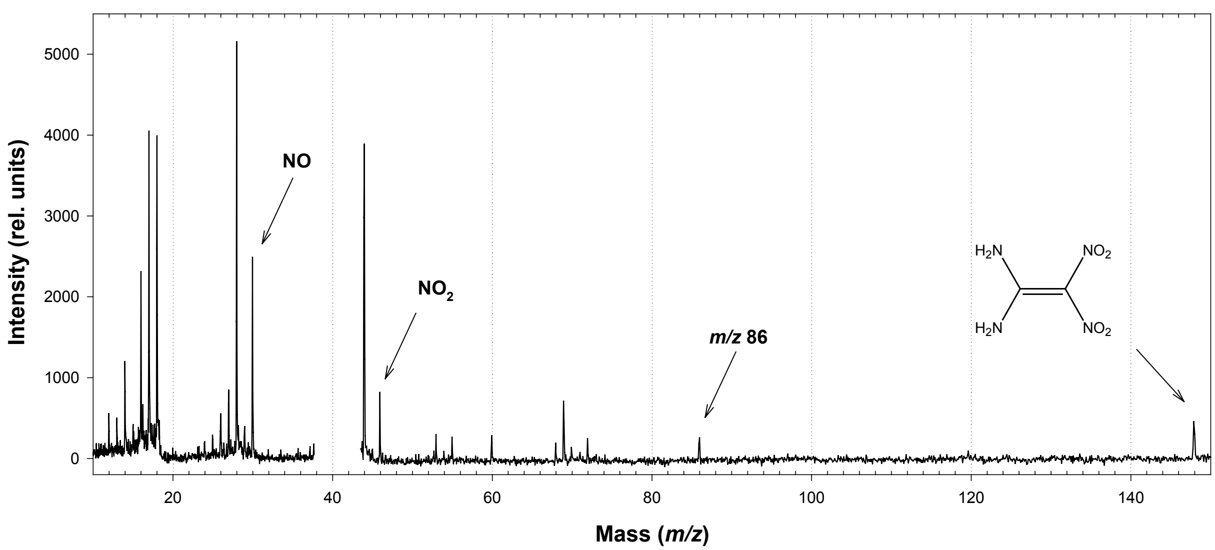

FIGURE 2. CO_2-LASER INDUCED THERMAL DECOMPOSITION MASS SPECTRUM OF FOX-7, 100 W 80 MS. (THE REGION BETWEEN *m/z* 38 AND 42 IS ENTIRELY DOMINATED BY SOLVENT PEAKS AND HAS THEREFORE BEEN REMOVED).

CYLINDER TEST

Experimental technique

Cylinder tests were performed to characterize the explosive. A copper cylinder, (length 300 mm, diameter 30.2 mm, shell thickness 2.52 mm) filled with FOX-7 (1.5 w% wax), δ=1.756 g/cm^3 was used. The detonation velocity was measured by measuring the arrival time to piezo-pin transducers at 10 mm spacing over a length of 50 mm along the cylinder axis. A Cordin rotating mirror camera, model 116, was used in streak mode to measure the radial displacement and thereby, indirectly the velocity of the detonating cylinder, see Figure 3. The selected streak speed was 4 mm/µs with a total recording time of 77.5 µs. As light source a cylindrically shaped ”argon flash bomb” was used. The duration of the argon flash was 20 µs or longer.

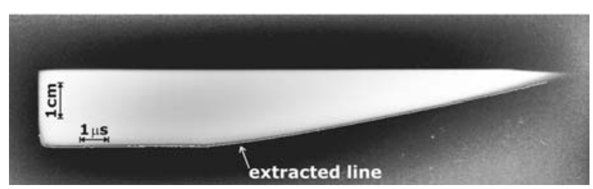

FIGURE 3. STREAK RECORDING OF RADIAL EXPANSION OF THE CYLINDER WALL.

In order to make the result available for computer-aided evaluation, the streak image was scanned in an optical flatbed scanner in transmission mode. The scanning resolution was 1200 dpi, giving a time resolution of

5.3 ns/pixel (corresponding to 189 MHz sampling frequency) and a displacement resolution of 40 μm/pixel. The bandwidth of the streak recording was estimated to 34 MHz. The standard deviation of the noise of the displacement was estimated to 30 μm from the initial (zero-displacement) part of the signal.

The evaluation was done in two steps:

(1) The edge between the expanding cylinder and air was extracted by image processing

(2) The radial displacement velocity was calculated with digital Savitzky-Golay filters.

To achieve a reliable result when extracting the edge, the main difficulties that had to be overcame were the varying intensity of the argon flash during the exposure and the disturbance of the edge image from the air shock-wave front. The edge is therefor extracted by convolution of the image with a manually sampled representative contrast level crossing. By this, the algorithm becomes sensitive for the shape of the contrast profile of the edge and not its quantitative values, which are ambiguous in this case.

Since the instantaneous velocity should be evaluated, numerical smoothing and derivation had to be performed. This was done using Savitzky-Golay filtering which is a least square method for smoothing and calculation of derivatives of noisy signals using local polynoms [5,6]. To estimate the derivative, a fourth order polynom filter was used. The local standard deviations of the derivatives (i.e. the fitted coefficients) were also estimated using well-known regression formulas. The standard deviation of the noise of the filtered velocity signal was estimated to 0.07 mm/μs from the initial (zero-velocity) part of the signal. The bandwidth of the Savitzky-Golay velocity filter was 5 MHz.

Computer modeling

HI-Dyna2d modeling was used for comparison with the experimentally derived cylinder wall motion. This was done using a 40 by 370 grid for the HE and 16 by 740 elements for the cylinder wall. A rigid boundary condition was applied to one end of the cylinder where also the HE was ignited, using programmed burn. Simultaneous ignition over the full radius was used. The copper cylinder was modeled with Johnson & Cook material model and a equation of state on Grüneisen form. The specially written subroutine for this purpose in HI-Dyna2D *Dynacyl* was used to monitor the appropriate node 70 mm from the initiation end. The extracted data used was the radial displacement ($r-r_0$) and radial velocity versus time. These data are directly comparable to the experimental data derived from the streak-camera records.

Cheetah 2.0 was used to calculate a first approximate for the coefficients of the CJ isentrope, see Table 1.

TABLE 1. CALCULATED DATA FOR FOX-7 + 1.5 W% WAX, δ=1.756 G/CM^3.

Pcj GPa	E0 KJ/cc	A GPa	B GPa	R1	R2	ω
27.9	8.663	998.578	8.778	4.928	1.119	0.401

Experimental results

The detonation velocity was estimated to 8.335 ± 0.025 mm/μs. The ± intervals are the 95% confidence limits for the least square fit. A Cheetah calculation, BKWC, gave a velocity of 8.266 mm/μs, which is in good agreement with the experimental value.

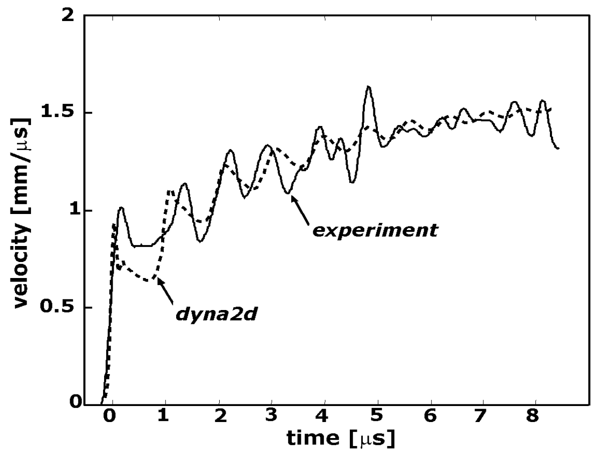

FIGURE 4. EVALUATED RADIAL VELOCITIES

In Figure 2 the result of the radial velocity evaluations are shown, where the solid line is the experimentally evaluated result, while the dotted line is the HI-Dyna2d calculated velocity.

The asymptotic velocity was estimated to 1.527 ± 0.003 mm/μs by least square fitting the curve between 8-12 μs (not shown in the figure).

The results showed good agreement (as regards amplitude and periodicity) with the HI-Dyna2d numerical simulations of the explosive, as evident from Figure 2. The deviation around 5 μs could be explained by a local defect due to film development.

FORMULATION

Recrystallisation of FOX-7

FOX-7 as-received from synthesis is not usable in a formulation since the particle size is much too small. Therefore, FOX-7 was recrystallised in a mixture of N-methylpyrrolidone and water. Cubic shaped particles at a rather broad size distribution (approx. 30-800 μm) was obtained. The particles are shown in Figure 3.

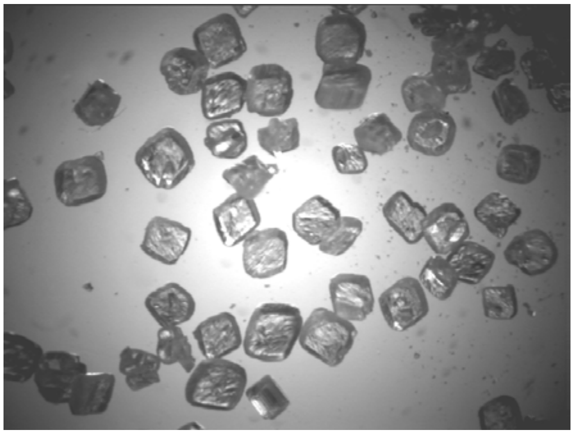

FIGURE 5. RECRYSTALLISED FOX-7.

Thermochemical calculations have shown that the use of an energetic prepolymer in the binder will make it possible to obtain a PBX formulation with comparable performance of Comp. B. Figure 4 shows the calculated detonation velocity of a mixture of FOX-7 and different energetic prepolymers. PolyGLYN is the best choice followed by GAP and AMMO/BAMO.

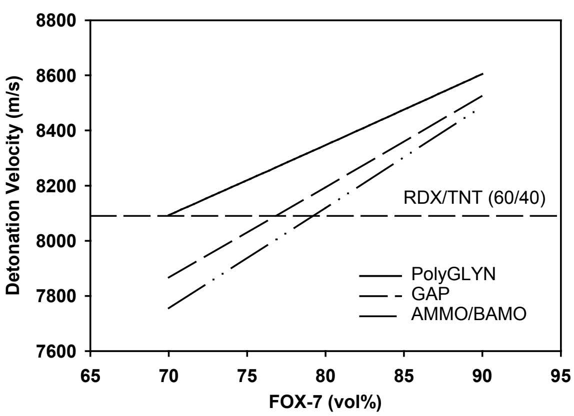

FIGURE 6. CALCULATED DETONATION VELOCITY OF DIFFERENT FOX-7 BASED MIXTURES WITH ENERGETIC PREPOLYMERS (CODE: CHEETAH 2.0).

The composition of the formulation (LIS-2) used for further studies is shown in Table 2.

TABLE 2. COMPOSITION OF THE CHOSEN FOX-7 BASED FORMULATION (LIS-2).

Component	Amount (weight)
FOX-7 (250-355 μm)	50 %
FOX-7 (< 70 μm)	20 %
PolyGlyN	21 %
Bu-NENA	5 %
H_{12}MDI (Desmodur-W)	4 %
DBTDL	cat. amounts

Cured for 24 hours at 50°C.

The chemical compatibility of the binder ingredients and FOX-7 have been investigated by microcalorimetry at 65°C and no exothermal reactions were observed. The thermal stability of the cured FOX-7 based formulation was studied by microcalorimetry for 14 days at 65°C and the formulation was thermally stable.

Sensitivity testing

The impact and friction sensitivity of this formulation and its components is summarized in Table 3. No friction sensitivity was observed, but the formulation was sensitive to impact. Surprisingly, the ingredients itself had a lower impact sensitivity than the formulation and further investigation of this phenomenon is needed to fully understand these results.

TABLE 3. IMPACT AND FRICTION SENSITIVITY OF THE SELECTED FORMULATION AND ITS COMPONENTS.

Sample	Drop height[a] (cm)	Min. load (N)
FOX-7 (recryst., 250-355 μm)	79	-
FOX-7 (recryst., < 70 μm)	63	-
Binder[b]	159	-
LIS-2 (70% FOX-7)	40	> 340

a) The highest drop height where no reaction occurs. Drop weight = 2 kg.
b) The composition of the binder is shown in Table 2.

A detonation test [7] was performed to investigate if the selected formulation was sensitive to a detonation shock wave. The diameter of the tubes was 25 mm and sodium chloride and Comp. B (RDX/TNT 60/40) was used as reference materials.

The results of the detonation test are summarized in Table 4. It was shown that the selected FOX-7 based formulation did not detonate in steel tubes of a diameter of 25 mm. The inert reference material (sodium chloride) did not detonate, whereas the Comp. B reference did and the steel tube was fragmented.

TABLE 4. PROPAGATION/FRAGMENTATION.

Formulation	Propagation	Fragmentation
NaCl (inert)	No propagation	No fragmentation
Comp. B	Propagation	Fragmentation
LIS-2, test 1	No propagation	No fragmentation
LIS-2, test 2	No propagation	No fragmentation

FIGURE 7. TEST TUBE AFTER THE DETONATION TEST.

Small-scale cook-off test

A small-scale slow cook-off test was performed to investigate how the selected formulation reacts to slow heating (3.3°C/hour). The reaction was classified according to the STANAG 4382 (Ed 1) "Slow heating tests for munitions" [8]. Comp. B (RDX/TNT 60/40) was used as a reference material. The results from the slow cook-off test are summarized in Table 5 and Figure 6.

It was shown that the selected FOX-7 based formulation did not detonate during slow heating. The formulation ignited at 220°C and burned non-violently. The bomb did not split open during the reaction and no fire was spread. The Comp. B reference ignited at 207°C and reacted violently. The bomb was extensively fragmented and all the energetic material was consumed.

TABLE 5. RESULTS OF THE SMALL-SCALE SLOW COOK-OFF TEST.

Formulation	Type of reaction	Cook-off temperature
Comp. B	Type I	207°C
LIS-2	Type V	220°C

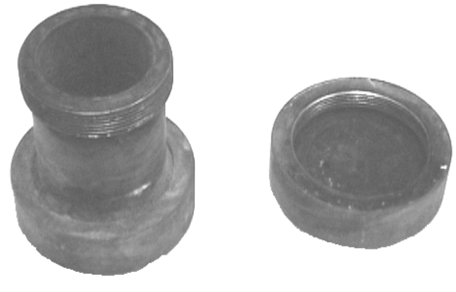

FIGURE 8. THE BOMB AFTER THE SLOW COOK-OFF TEST.

CONCLUSIONS

1,1-diamino-2,2-dinitroethylene (FOX-7) is known to be a new energetic material with promising properties as a IM explosive. Thermochemical calculations show that PBX's based on FOX-7 and energetic binders could serve as a replacement of Comp B even at rather low solid loadings. A plastic bound explosive based on FOX-7 and an energetic binder have been prepared, LIS-2. The energetic binder consisted of polyGLYN, Bu-NENA and $H_{12}MDI$. The formulation showed no friction sensitivity but it was more sensitive to impact than its respective components. The formulation did not propagate to detonation during a detonation test in steel tubes with a diameter of 25 mm. The formulation did neither react violently during slow heating (3.3°C/hour). It ignited at 220°C and burned without damage to the bomb or the surroundings. Compared to the Comp. B (RDX/TNT 60/40) reference material, FOX-7 based formulations have a very promising future for use in insensitive munitions and as a possible replacement of Comp. B.

REFERENCES

1. Doll D. W., Hanks J. M., Niles J. H. "Insensitive Composition B Replacement". Proc. of 1999 Insensitive Munitions and Energetic Materials Technology Symposium, Tampa, Florida, USA, November 29 – December 2, **1999**, p. 264.

2. Asta Gindulytė, Lou Massa, Lulu Huang and Jerome Karle, "Proposed Mechanism of 1,1-Diamino-Dinitroethylene Decomposition: A Density Functional Theory Study", *J. Phys. Chem.* **103** (1999): 11045-11051.

3. Henric Östmark, Helena Bergman and Göran Åqvist, "The chemistry of 3-nitro-1,2,4-triazol-5-one (NTO): thermal decomposition", *Thermochimica Acta*, **213** (1993): 165-175.

4. Henric Östmark, Helena Bergman and Katrin Ekvall, "Laser pyrolysis of explosives combined with mass spectral studies of the ignition zone", *Journal of Analytical and Applied Pyrolysis*, **24** (1992): 163-178.

5. Savitzky A., Golay M.J.E., "Smoothing and differentiation of data by simplified least squares procedures," Anal. Chem., **36**(8), pp.1627-1639, (1964)

6. Tsai F., Philpot W., "Derivative analysis of hyperspectral data," Remote Sens. Environ, **66,** pp.41-51, (1998)

7. SÄIFS 1986:1. Sprängämnesinspektionens författningssamling. Sprängämnesinspektionens allmänna råd om känslighetsprovning av explosivämnen. June 6, 1986. Ch. 12, p. 83-89. (In swedish).

8. STANAG 4382 (Ed 1) Slow heating tests for munitions. Military Agency for Standardization. AC/310-D/100. June 1992.