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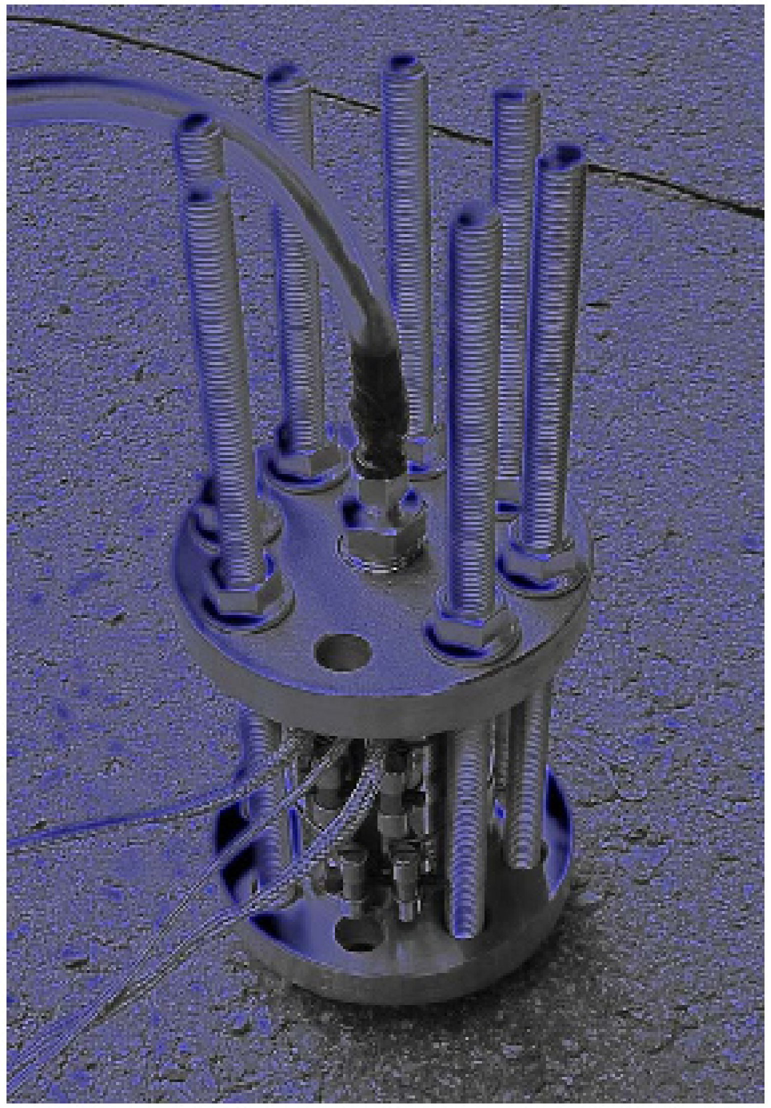

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Report title

N-GUANYLUREA DINITRAMIDE (FOX-12): PROPERTIES

Abstract

N-guanylurea-dinitramide (FOX-12 or GuDN) is a novel energetic material with low sensitivity and good potential for use as in propellants or in IM (insensitive munitions) explosives. This report presents some of its properties, including sensitivity, thermal stability and physical properties (bulk crystal density, ρ=1.7545 g/cm^3; heat of formation, ΔH_f = -355 kJ/mole; activation energy, E_a=277 kJ/mole).

The performance of FOX-12 has been calculated and measured experimentally. The detonation velocity was measured to 7970 m/s. This value is in the range between TNT and RDX. Initial measurements of shock sensitivity and sensitivity to slow heating have been performed and the result shows that FOX-12 is very insensitive (type V reaction in SCO test and 72-90 cards in LSGT).

The results in this report clearly show that FOX-12 is a very promising candidate ingredient for new insensitive munitions.

Keywords

N-Guanylurea dinitramide, FOX-12, GUDN, explosive, energetic material, properties, detonation velocity, slow cook-off, large scale gap test

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Rapportens titel

N-GUANYLUREA DINITRAMID (FOX-12): EGENSKAPER

Sammanfattning

N-guanylureadinitramid (FOX-12 eller GuDN) är ett nytt energetiskt material med låg känslighet och det har god potential som ingrediens i lågkänsligt krut eller som IM-sprängämne (IM=insensitive munition). Denna rapport beskriver ett antal av FOX-12:s egenskaper, såsom känslighet, termisk stabilitet och fysikaliska egenskaper (kristalldensitet (bulk), ρ=1.7545 g/cm^3; bildningsvärme, ΔH_f = -355 kJ/mol; aktiveringsenergi, E_a=277 kJ/mol).

Prestanda har beräknats och uppmätts experimentellt. Detonationshastigheten bestämdes till 7970m/s, vilket motsvarar ett värde mellan de för hexogen of trotyl. Inledande känslighetstest, med avseende på långsam upphettning (slow cook-off) och stötvågsinitiering (large scale gap test) visar att FOX-12 är mycket lågkänsligt (reaktion typ V (brand) i SCO och 72-90 cards i LSGT).

Resultaten presenterade i denna rapport visar tydlgt att FOX-12, som ingrediens, är en lovande kandidat för ny lågkänslig ammunition (Insensitive Munition).

Nyckelord

N-Guanylurea dinitramid, FOX-12, GUDN, sprängämne, energetiskt material, egenskaper, detonationshastighet, slow cook-off, large scale gap test

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Table of Content

1 Introduction

The purpose of the ongoing research on energetic materials in Sweden is to produce more powerful, safer and environmentally friendlier explosives that fit into the strategy of the defence forces. Hence, one line of research aims towards compositions with lower sensitivity, which improves the safety of ammunition. A problem with lower sensitivity energetic materials in munitions has been that insensitivity almost always has meant lower performance. With new energetic substances and energetic plasticizers and binders it might, however, not be so difficult to manufacture charges with low sensitivity and high performance.

In the search of new and safer high explosives, a number of low sensitive molecules have been identified (e.g. TATB, NTO[1,2] and FOX-7[3]). At FOI a new insensitive compound, N-guanylurea dinitramide[4] (FOX-12 or GuDN), has been developed. Due to its sensitivity combined with explosive properties, it could be of use for LOVA (Low Vulnerability Ammunition) gun propellant as well in melt-cast and PBX (Plastic Bonded eXplosives) high explosive formulations. N-guanylurea dinitramide, see Figure 1.

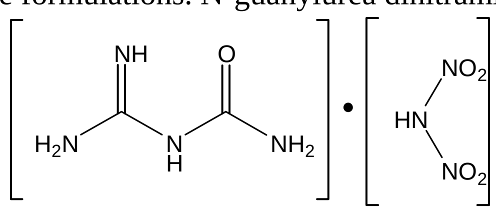

Figure 1. FOX-12 (N-guanylurea-dinitramide).

This report presents its properties, such as sensitivity, thermal stability, physical properties and explosion temperature. The performance has been estimated for pure FOX-12 as well as for IM melt castable formulations using the Cheetah 2[5] thermo-chemical code and the experimentally determined values of density and heat of formation. The report also present initial experimental detonation properties; detonation velocity, shock sensitivity and estimates the critical diameter.

2 Properties

The properties of FOX-12 have been determined with respect to stability, physical properties, performance and sensitivity. Parts of these results have been presented at the 13th International Detonation Symposium, Norfolk, VA, July 23-28, 2006.

2.1 Thermal Stability

The thermal stability of FOX-12 was measured with differential scanning calorimetry (DSC) using a Mettler 30 instrument. A typical DSC curve is shown in Figure 2. The samples were heated from room temperature with a heating rate of 0.5 - 10°C/min. FOX-12 has an onset at 214.8°C with a heating rate of 10°C/min. Figure 3 shows a plot of the heating rate versus the temperature at the peak of the exotherm. Using these data and the ASTM method E 698-79, the activation energy (E_a) was determined, see Table 1. Compared to both RDX[6] and ADN[7], FOX-12 has larger activation energy indicating higher thermal stability. The increased thermal stability, compared with ADN, shows that the dinitramide ion can be stabilized by hydrogen bonding and is not intrinsically unstable as was believed earlier. This is encouraging, as it seems likely that other low sensitivity dinitramide salts can be synthesized.

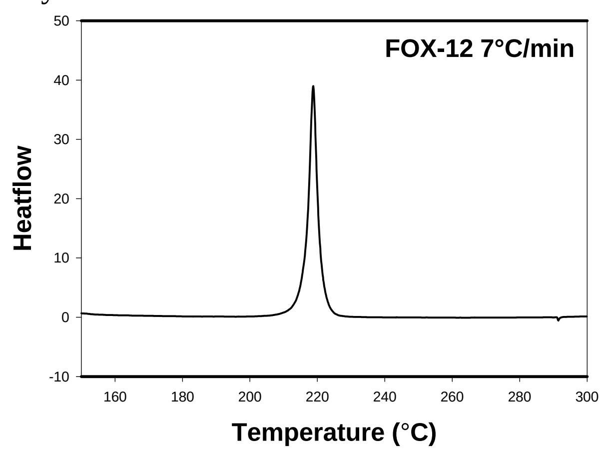

Figure 2. Typical DSC thermogram of FOX-12.

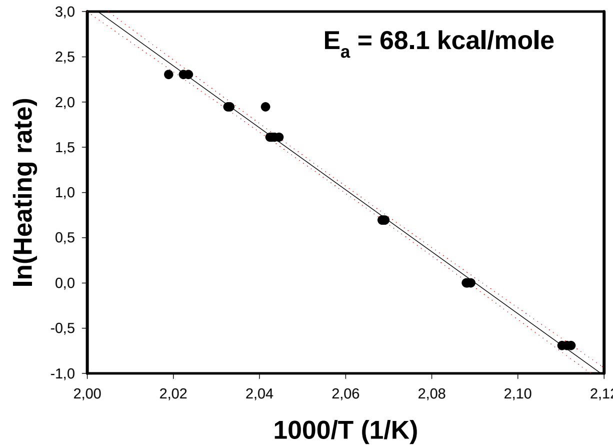

Figure 3. Plot of ln(heating rate) vs. 1/temperature. Temperature = the peak temperature of the exotherm of FOX-12, as measured by DSC.

Table 1. Kinetic parameters from thermal experiments on FOX-12. Comparison with ADN and RDX.

Explosive	E_a (kJ/mol)	Log(K_0) (s^{-1})	Temperature interval (°C)
FOX-12 (DSC)	277	29.4	200-225
FOX-12 (Wood)	149	-	190-240
ADN (DSC) [7]	158	15.8	
ADN (Wood)[7]	127	-	
RDX (DSC)[6]	201.5	18.8	

2.2 Physical Properties

2.2.1 Crystal Structure and Density

X-ray crystallographic studies of FOX-12 (single crystal X-ray density ρ=1.775(1) g/cm^3) show a special type of molecular packing in the crystal structure. The molecular packing in the crystal structure consists of two-dimensional planar sheets (see Figure 4) and the only molecular interactions present between these sheets are of the van der Waals type.

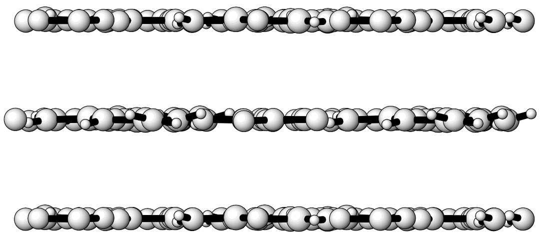

Figure 4. Drawing illustrating the layered packing in FOX-12. View along the a-axis with the b-axis across the paper and the c-axis down the paper.

Within the sheets, the molecules are held together by a large amount of intermolecular hydrogen bonds as shown in Figure 5. The molecular packing with intermolecular hydrogen bonds within the sheets and ordinary van der Waals interactions between the sheets is observed for the first time in FOX-12 among the group of dinitramide compounds.

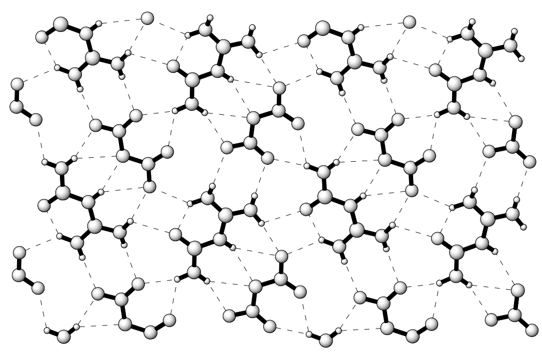

Figure 3. Drawing illustrating the layered packing in FOX-12 and the intra- and intermolecular hydrogen bonding within each layer where the hydrogen bonds are drawn as dashed lines. View along the c-axis with the a-axis across the paper and the b-axis down the paper.

The special molecular packing is of importance for several physical properties of FOX-12 such as low impact and friction sensitivity, absence of melting point and low water solubility. Other known high explosives with the same type of molecular packing in sheets are TATB[8], *β*-NTO[9] and FOX-7 (1,1-diamino-2,2-dinitroethylene)[10]. TATB, *β*-NTO and FOX-7 all show similar physical properties as FOX-12, indicating that this type of molecular packing is of large interest in the search for new insensitive high explosives. The single-crystal X-ray diffraction studies were complemented with powder X-ray diffraction measurements of the density, (ρ=1.7545(4) g/cm^3).

2.2.2 Heat of Formation

The heat of formation for FOX-12 was measured using an adiabatic bomb calorimeter (IKA C 4000). The calibration of the calorimeter was done by combustion of certified benzoic acid in oxygen atmosphere at a pressure of 3 MPa. The heat of formation was experimentally determined to be -355 kJ/mole (-85 kcal/mole). This rather low value of the heat of formation is probably due to the extensive hydrogen bonding

2.3 Performance

Detonation Velocity

The detonation velocity and cylinder expansion energy of FOX-12 was estimated by thermo-chemical calculations using the Cheetah 2 computer code[5]. These calculations were based on the measured powder diffraction density (ρ=1.7545 g/cm^3) and heat of formation (ΔH_f = -85 kcal/mole). The results are shown in Table 2.

Table 2. Calculated performance (BKW EOS, BKWC library Cheetah 2).

Explosive	**Density (g/cm^3)**	**VoD (m/s)**	**Detonation Pressure (GPa)**	**Cylinder Expansion Energy for V/V_0=4.10 ($HMX_{1.89}$=100)**
FOX-12	1.75	8210	25.7	64
TNT	1.65	6900	19.6	62
TATB	1.94	8420	30.9	76
RDX	1.81	8940	34.7	97
FOX-12/TNT (60/40)	1.71	7650	23.3	65
RDX/TNT (60/40)	1.74	8050	28.1	82

Figure 4. Setup for measuring the detonation velocity.

Uniaxial pressing of FOX-12 was used to prepare cylindrical charges (22 mm x 22.5 mm and 52.12 mm x 52.15 mm) to approximately 95% of the theoretical maximum density (TMD). The detonation velocity was measured using several of these charges with ionisation probes in between (see Figure 4). A PBXN-5 booster charge was used to initiate the 22 mm charges, whereas a PETN/FO booster charge was used to initiate the 52 mm charges. The arrival time of the detonation front was measured using ionization gauges. The 22 mm charges did not detonate. Using a booster with a weight of 60 g no steady detonation was observed with the 52 mm charges with the last four cylindrical charges left unreacted. With a booster weight of 375 g detonation was observed. The velocity was measured to 7870 m/s and it was very stable (7837-7896 m/s and Figure 5). The thermochemical calculation by Cheetah predicted a detonation velocity of 7810 m/s, for the same density, which is in good agreement with the experiments.

The initial detonation velocity measurement, as described above, was complemented with a more accurate detonation velocity measured using a plane wave ignition, this measurement showed equal stability and even higher detonation velocity (7970 m/s). A compilation of the detonation velocity measurements is shown in Table 3.

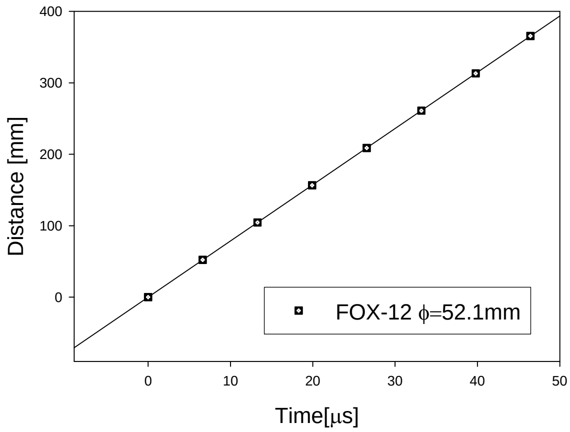

Figure 5. Detonation velocity of FOX-12 (VoD= 7870 m/s for ρ=1.66 g/cm^3)

Table 3. Measured and calculated detonation velocities for FOX-12 (ρ=1.66 g/cm^3).

Charge Diameter	Booster	Density (g/cm^3)	Detonation Velocity (m/s)	
			Measured	Calculated
22 mm	PBXN5 10g	1.67	No detonation	-
52.15 mm	PETN/FO 60g	1.66	No detonation	-
52.15 mm	PETN/FO 375g	1.66	7870	7810
60 mm (in copper tube shell thickness 6 mm)	Plane wave lens and 50 g Comp-B	1.666	7970	7835

2.3.1 Working Capacity

To characterize the working capacity of the explosive, cylinder tests were performed. A full-wall copper cylinder, (length 350 mm, inner diameter 60 mm, shell thickness 6 mm) filled with pressed FOX-12 was used. The detonation velocity was measured by measuring the arrival time to piezzo-pin transducers at 20 mm spacing over a length of 60 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 6. The selected streak speed was 4 mm/μs. As light source a cylindrically shaped ”argon flash bomb” was used.

The streak image was scanned in an optical flatbed scanner in transmission mode. The scanning resolution was 1600 dpi, giving a time resolution of 3.97 ns/pixel and a displacement resolution of 38 μm/pixel. The edge between the expanding cylinder and air was extracted by image processing and the radial displacement velocity was calculated with digital Savitzky-Golay filters[12].

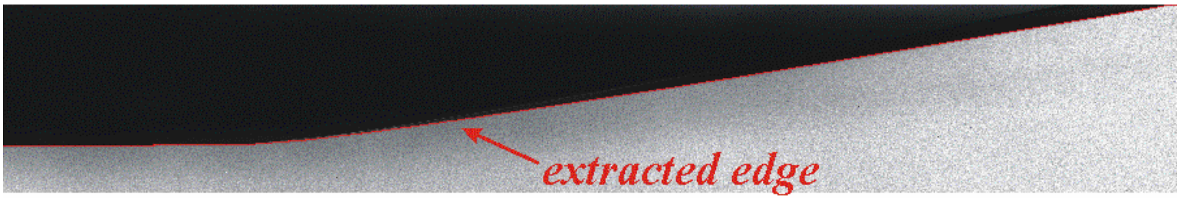

Figure 6. Streak recording of radial expansion of cylinder.

JWL-parameters for FOX-12 at density 1.666 g/cm^3 were calculated with Cheetah version 2.0 using the BKWC-library. The detonation velocity was close to the measured value 7966 m/s. The cylinder test was simulated using the HI-Dyna2D code and the radial displacement and velocity were sampled by the dynacyl-routine. There was a fair agreement between the streak recording and the simulated radial velocity using the Cheetah calculated JWL-parameters, but to increase the accuracy a re-parameterization was done. The new parameters are presented in Table 5 together with the Cheetah calculated parameters. The measured and calculated radial velocities for the two parameter sets are presented in Figure 7.

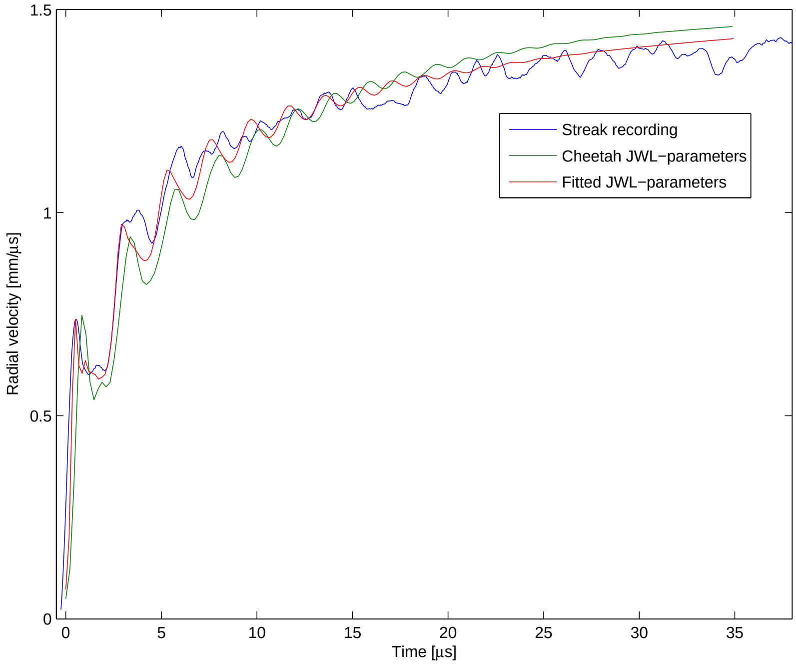

Figure 7. Measured and calculated radial velocity using HI-Dyna2D with JWL-parameters from Cheetah 2.0 and fitted to data.

Table 5. JWL-parameters for FOX-12 at density 1.666 g/cm^3. Calculated from Cheetah 2.0 with BKWC-library and fitted to measured detonation velocity and cylinder streak record.

	D (m/s)	**P_{CJ} (GPa)**	**A (GPa)**	**B (GPa)**	**R_1**	**R_2**	**ω**	**E_0 (MPa)**
Cheetah 2.0 BKWC	7 835	22.46	1061	7.048	5.178	1.064	0.385	6.796
Fit to exp. data	7 966	26.11	666.26	8.1308	4.55	1.46	0.385	6.800

2.4 Sensitivity

2.4.1 Friction and Impact Sensitivity

FOX-12 is very insensitive to friction, whereas the impact sensitivity is in line with RDX, see Table 6. It should, however, be noted that the impact and friction sensitivity may change depending on what recrystalisation method is used.

Table 6. Sensitivity data for FOX-12 in comparison with ADN, TNT and RDX.

Explosive	**Drop height (J)**	**Friction (N)**
FOX-12	12-31	>350
ADN (unprilled)	6-12	280-320
RDX	8-13	195
TNT	33	>350

2.4.2 Sensitivity to Slow Heating

In order to determine the sensitivity to slow heating, pressed charges were tested according to the Swedish Defence Standard, FSD, no. 0243 “Slow heating of explosives Model scale, 3.3 °C/h”[13]. FOX-12 was uniaxially pressed into two cylindrical charges (dimensions are shown in Table 7) to approximately 95% of the TMD. The charges were enclosed into steel cylinders described in the Swedish Defence Standard, FSD, no. 0244 “Model testing, sleeve for test explosive for low-sensitivity ammunition”[14]. The charge was prehetated to 45°C and then the heating rate was lowered to 3.3°C/hour. The temperature inside the charge was recorded during the experiment and cook-off occurred at 144°C. The reaction was a Type V, burning, with no fragmentation of the steel cylinder (Figure 9).

Table 7. Dimensions of pressed FOX-12 changes (ρ=1.66 g/cm^3).

	Charge 1	**Charge 2**
Height (mm)	51.52	47.02
Diameter (mm)	49.89	49.87
Weight (g)	166.92	153.76
Density (g/cm^3)	1.66	1.67

Figure 8. Slow cook-off test setup.

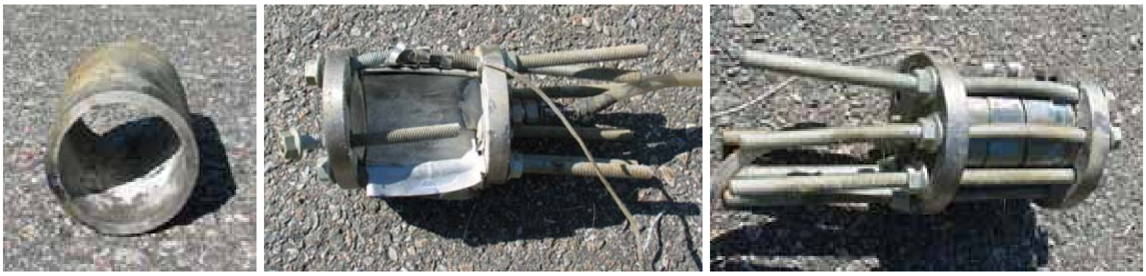

Figure 9. Test setup after cook-off: cylinder (left), setup showing the opened side of the heating band (middle) and setup showing the back side of the heating band (right).

2.4.3 Shock Sensitivity

Large scale gap test has been performed in order to determine the shock wave initiation sensitivity of pressed FOX-12. The method used is based on US NOL large scale gap test (MIL-STD-1751[15], method 1041), with the following exceptions: the donor charge consists of RDX pressed with 4% wax (ρ=1.66 g/cm^3); the thickness of the cylinder wall was 3.2 mm; and the thickness of the PMMA disks was 1.5 mm. The setup is shown in Figure 8 and 9.

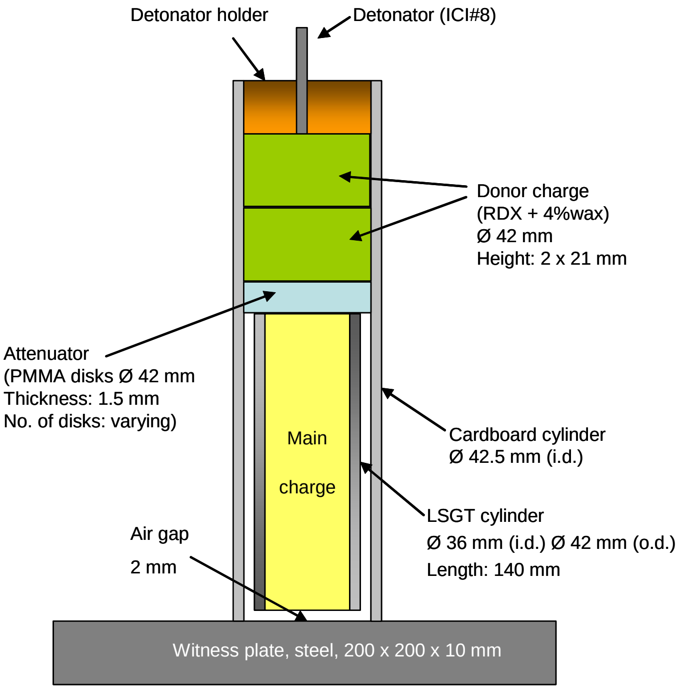

Figure 8. Large scale gap test setup.

Figure 9. Booster charge (top, left), cards (middle, left) and FOX-12 donor charge in a steel cylinder (bottom, left). Large scale gap test setup before test (right).

The gap test resulted in a sensitivity distance of 18 to 22.5 mm (corresponding to 72 - 90 cards). It was not possible to further specify the distance during this test due to lack of material. Corresponding literature values are shown in Table 8 and the result of FOX-12 is in line with pure TATB and the composition PBXW-115 in which I-RDX (desensitised RDX) is used. The result of large scale gap test clearly shows the potential of FOX-12 as an ingredient in future insensitive munitions.

Table 8. Literature values of shock sensitivity as measured by large scale gap test[16].

Name	Composition	Distance (50% probability point)
TATB	TATB	20 mm (78 cards)
RDX	RDX	82 mm (323 cards)
TNT	TNT	34[b] - 45[c] mm (133-175 cards)
Composition B	RDX/TNT	51[b] -61[c] mm (200-238 cards)
PBXN-109	RDX/Al/HTPB/DOA	47 mm (189 cards)
PBXN-109	I-RDX[a]/Al/HTPB/DOA	29 mm (113 cards)
PBXW-115	AP/Al/HTPB/I-RDX[a]	21 mm (84 cards)

a) SNPE densensitised RDX, called I-RDX. b) cast. c) pressed.

3 Discussion and Conclusions

The purpose of the ongoing research on energetic materials in Sweden is to produce more powerful, safer and environmentally friendlier explosives that fit into the strategy of the defence forces. Hence, one line of research aims towards compositions with lower sensitivity, which improves the safety of ammunition.

N-guanylurea-dinitramide (FOX-12 or GuDN) is a novel energetic material with low sensitivity. It shows no friction sensitivity, no sensitivity to slow heating and very low shock sensitivity as measured by large scale gap test.

The performance of FOX-12 has been calculated and measured experimentally. The detonation velocity was measured to 7970 m/s. This value is in the range between TNT and RDX.

The results in this report clearly show that FOX-12 is a very promising candidate ingredient for new insensitive munitions.

4 Acknowledgements

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