Central European Journal of Energetic Materials, **2013**, *10*(4), 569-580
ISSN 1733-7178

Studies on FOX-7 Based Melt Cast High Explosive Formulations

Vijaya S. MISHRA*, Subbaraidu R. VADALI, Rakesh K. GARG, Vivek S. JOSHI, Rajbal D. WASNIK and Srinandan ASTHANA

High Energy Materials Research Laboratory,
Sutarwadi, Pune-411 021, India
**E-mail: mishravs_11@rediffmail.com*

Abstract: The key driving force in modern explosive research is the development of low vulnerable high explosive (LOVEX) compositions for future applications in insensitive munitions (IMs). The increasing demand for LOVEX has led to exhaustive studies on low vulnerable explosives as a replacement for conventional cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) in 2,4,6-trinitrotoluene (TNT) melt cast high explosive formulations. In the present study, 1,1-diamino-2,2-dinitroethene (FOX-7) has been evaluated as a possible RDX replacement in TNT based, non-aluminized as well as aluminized, melt cast formulation. FOX-7 based melt cast formulations were characterized for their sensitivity to mechanical/shock stimuli, velocity of detonation (VOD), blast parameters and thermal decomposition behavior. These characteristics are compared with the corresponding RDX based compositions as reference standard. The studies show that with little sacrifice on performance parameters, FOX-7 based, non-aluminized and aluminized, melt cast formulations are found to be less vulnerable, compared with the corresponding RDX based formulations.

Keywords: melt cast, FOX-7, LOVEX, shock sensitivity, VOD, impulse, IMs

Introduction

2,4,6-Trinitrotoluene (TNT) based, melt cast high explosive (HE) compositions occupy a premier position as fillings for warheads and projectiles due to extensive production facilities all over the globe, despite their limitations and the emergence of cast cured HE compositions. Composition B or RDX/TNT

(60/40) composition has been used for over 60 years as a filling in munitions due to its high performance parameters, ready availability and ease of processibility in standard melt cast facilities. This formulation finds application mainly in shaped charge and fragmentation type warheads. Aluminized melt cast formulations provide an enhanced blast effect due to the secondary combustion of aluminum (Al), extending the detonation zone. On initiation of an aluminized explosive composition, the reaction takes place in two stages. The detonation products of the CHNO explosive (CO, CO_2, H_2O, N_2 *etc.*) at high temperature react with aluminum, producing energy due to the exothermic reactions. The basic chemical processes involving Al in the explosion phenomenon, resulting in the blast effect, are summarized in a recently published review [1]. In air-blast, addition of aluminum up to 20% by weight is useful or adds to the destructive power. It increases the value of the impulse.

$2Al (s) + 3H_2O (g) \rightarrow Al_2O_3 (s) + 3H_2 (g) + 866$ kJ/mol
$2Al (s) + 3CO_2 (g) \rightarrow Al_2O_3 (s) + 3CO (g) + 741$ kJ/mol
$2Al (s) + 3CO (g) \rightarrow Al_2O_3 (s) + 3C (s) + 1251$ kJ/mol
$2Al (s) + N_2 (g) \rightarrow 2AlN (s) + 346$ kJ/mol
(The subscripts ‘s’ and ‘g’ refer to the solid and gas phases respectively).

Although 5-nitro-2,4-dihydro-1,2,4-triazol-3-one (NTO) based, melt cast compositions have been reported in the open literature, FOX-7 has not been explored to any significant extent as a component of this class of compositions. RDX is considerably cheaper than FOX-7, however increasing demand for low vulnerable explosives (LOVEX) for Insensitive Munitions (IMs) has led to the initiation of exhaustive applied research on high explosive formulations based on FOX-7, reported by many researchers to be a promising candidate. Lochert [2] has reported that FOX-7 is significantly less sensitive than RDX, particularly to impact and friction stimuli and is compatible in TNT based, melt cast compositions. The velocity of detonation and detonation pressure of FOX-7 charges are marginally higher than those for RDX charges and the detonation pressure shows a 5% increase [2]. Wild and Teipel [3] have also reported that the performance of FOX-7 is better than that of TNT and close to those of nitramines, with relatively insensitive characteristics. Helen Dorsett [4] has used first principles quantum chemical calculations to predict the initial steps of decomposition in FOX-7. Thus, FOX-7 could be an energy efficient replacement for RDX, meeting low sensitivity requirements without penalty on the energetics of the composition.

A plastic bonded explosive (PBX) formulation of FOX-7 with a poly Glyn binder has been reported by Karlsson *et al.* [5]. This formulation does not detonate up to a diameter of 25 mm in large-scale detonation and small-scale slow cook-off tests. The composition ignites at 220 °C on slow heating (3.3 °C/h) and burns without damage to the container [5]. A new formulation based on FOX-7 and HMX (called FOF-5), with the same theoretical performance as Composition B, has been developed by FOI Weapons and Protection Division, Swedish Defense Research Agency [6]. This composition has been tested with respect to its low sensitivity properties by applying fast heating, slow heating and bullet impact tests. The response of a FOF-5 loaded 40 mm gun munition (with an HNS II-based fuze) in the fast heating test was Type IV (deflagration), Type V/IV (fire/deflagration) in the slow heating test, and Type V (fire) in the bullet impact test. Composition B shows a detonation response in all of the above tests [6].

The above research has inspired to work in the field of LOVEX based on FOX-7 and TNT. In the present study, FOX-7 has been evaluated as a possible replacement for RDX in TNT based, non-aluminized as well as aluminized, melt cast formulations. In the present paper, the loading of FOX-7 in the formulations has been restricted to a maximum of 30% by weight in non-aluminized formulations and a maximum of 25% by weight in aluminized formulations. The formulations have been characterized for their thermal decomposition behaviour, sensitivity to mechanical/shock stimuli, velocity of detonation (VOD) and blast performance. The research was aimed at optimizing FOX-7 and TNT based, melt cast formulations and at generating initial data for exploring these formulations as insensitive high explosive formulations for future applications in insensitive munitions.

Experimental

Materials

The following materials were used for the preparation of the formulations:

Sl No.	Material	Source
1	FOX-7	Synthesized at HEMRL, Pune, India
2	TNT	HE Factory, Pune, India
3	RDX	Ordnance Factory, Bhandara, India
4	Aluminum powder	Metal Powder Company, Madurai, India

FOX-7 was synthesized in-house by the nitration of the precursor 2-methyl pyrimidine-4,6-Dione (MPD), followed by hydrolysis of the tetranitro intermediate (2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione) in water [7].

Explosive formulations

The FOX-7 based, melt cast, non-aluminized and aluminized formulations, namely FT and FTA respectively, as well as RDX based, melt cast, non-aluminized and aluminized formulations, namely RT and RTA respectively, which were studied are summarized in Table 1.

Table 1. Details of FOX-7 and RDX based formulations

Formulation	RDX	FOX-7	TNT	Al
FT	--	30	70	--
RT	30	--	70	--
FTA	--	25	60	15
RTA	25	--	60	15

Processing of the explosive formulations

The compositions were processed by the standard, melt-cast technique involving the addition of RDX or FOX-7 to molten TNT, with continuous stirring in a steam jacketed anchor blade mixer. This was followed by the addition of aluminum powder to the melt (in the aluminized formulations FTA and RTA). The mixture was stirred for about 10-15 minutes and then transferred to a mould. After cooling to ambient conditions, the charge was extracted and machined to the required dimensions.

Characterization / Evaluation

Thermal characterization

Thermal decomposition studies of FOX-7 and formulations FT, RT, FTA and RTA were carried out using a Differential Scanning Calorimeter (Perkin Elmer DSC-7). A sample weight of about 0.5 mg was taken for heating at 5 °C/min in the temperature range 50-350 °C for the determination of the decomposition temperature/exothermicity, and about 2.5-4.0 mg sample weight for heating at 10 °C/min in the temperature range 50-200 °C for phase change studies.

Determination of sensitivity parameters

Standard methods were used for the determination of the sensitivity and performance parameters. The sensitivity of explosive compositions to impact stimuli was determined using the fall hammer method (2 kg drop weight) using the Bruceton staircase approach and the results are given in terms of the statistically obtained 50% probability of explosion (h_{50}). Shock sensitivity − an important criterion for insensitive munitions, was determined by the card gap test in which cellulose acetate sheets were used as an attenuator. The thickness of cellulose sheets was varied until No-Go was observed on the witness plate. The shock sensitivity is reported in terms of the minimum pressure of the shock wave that can initiate detonation of the melt cast explosive composition. The critical pressure (P) in kbar, across the cellulose acetate sheets, by which the explosive composition can be detonated with 50% probability was determined from the relation:

$$P\ (\text{kbar}) = 105e^{-(0.0358x)}$$

where x is the thickness of the cellulose acetate attenuator in mm. The shock sensitivity results were confirmed by conducting 5 tests with consistent No-Go observations.

Determination of velocity of detonation (VOD)

The VOD was measured using the ionization probe technique. The pin type ionization probes (twisted enamel copper wire), were located in the charge at predetermined points for detecting the arrival time of the detonation wave. An oscilloscope (YOKOGAWA DL9140, 1GHz) was used for data acquisition. Three charges of each formulation were fired for the determination of the velocity of detonation. The reported VOD is an average of three trials.

Determination of blast parameters

The blast parameters, peak overpressure (P_{max}) and positive impulse (I_+) were measured at various distances from the point of explosion using free-field, blast-pressure transducers and the data was recorded on an oscilloscope. The cast, high explosive charges were mounted on a wooden stand of 2 m height. Three piezoelectric gauges were positioned at 1.5, 2.5 and 3.5 m distances in the horizontal plane, and aligned to the center of the charge. The sensing element in the transducer was a quartz crystal with an inbuilt driving amplifier of an aerodynamic design. The explosive charges were detonated by an RDX/Wax (95/5) booster in combination with an electric detonator. On detonation of the charge, the blast wave is generated and, as it crosses the blast pressure gauge, the piezoelectric crystal develops a charge which is amplified. The line power unit decouples the signals from the bias voltage and a pressure-time curve is obtained as a display on the data acquisition system. A multichannel, high speed data acquisition system, with a maximum sampling rate of 100 ns, was used to record the pressure-time history. The PC based system computed the peak overpressure, duration and positive impulse. Three charges, of each formulation FTA and RTA were fired for determining the blast characteristics. The charge was cylindrical in shape, of about 0.5 kg mass and having L/D ~ 1.

Results and Discussion

Thermal characteristics

Initially, sample weights of about 0.5-1.0 mg were run at 10 °C/min in the temperature range 50-350 °C for the decomposition studies of FOX-7, FT and RT formulations. During analysis of these DSC measurements, it was observed that the polymorphic phase transitions α → β and β → γ of FOX-7 reported by M.J. Crawford *et al*. [8] and J. Evers *et al*. [9] were not present. Subsequently, the sample weight was in the same range of 0.5 mg, but the samples were run at 5 °C/min. The results were the same, with no polymorphic phase transitions being observed. Further measurements with an increased sample weight of about 2-4 mg and a heating rate of 10 °C/min in the temperature range of 50-200 °C were carried out for FOX-7, FT and FTA. Table 2 gives details of the DSC measurements.

Table 2. DSC results of explosive compounds and formulations

Sl No.	Sample	Sample wt. (mg)	Heating rate (°C/min)	Temp. range (°C)	Peak Endo		Peak Exo	
					Temp (°C)	ΔH (J/g)	Temp (°C)	ΔH (J/g)
Decomposition studies								
1	FOX-7	0.496	5	50-350	---	---	264.2	1822.0
2	RDX	0.292	10	50-300	203.3	144.0	238.0	1988.2
3	FT	0.496	5	50-350	79.9	64.5	256.8	1545.8
4	RT	0.744	5	50-350	78.4	66.9	231.6	1676.9
5	FTA	0.954	5	50-500	78.7	49.4	252.4	962.9
6	RTA	1.160	5	50-500	78.4	59.9	231.3	2212.0
Phase change studies								
7	FOX-7	2.326	10	50-200	116.7 182.5	23.3 2.5	---	---
8	FT	2.556	10	50-200	81.0 114.8 175.3	68.4 2.9 3.7	---	---
9	FTA	3.044	10	50-200	80.7 117.7 183.3	57.2 3.5 3.7	---	---

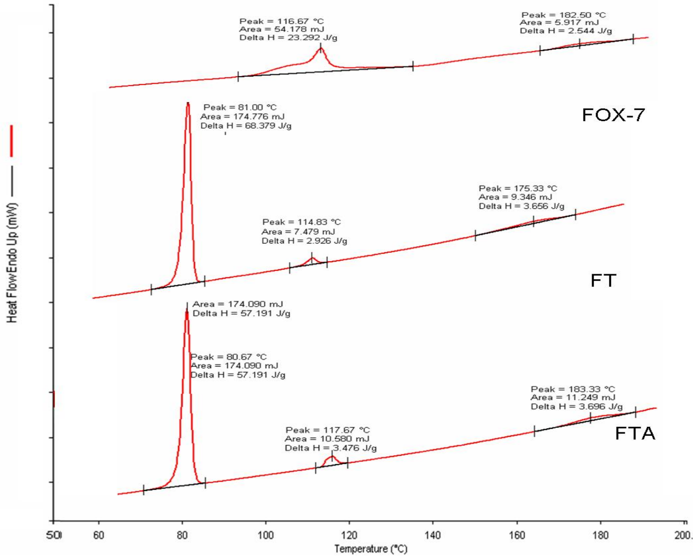

Figure 1. DSC curves of phase change studies of FOX-7, FT and FTA.

The DSC curves of the phase change studies of FOX-7, FT and FTA are shown in Figure 1. The curve of FOX-7 shows two endothermic peaks at 116.7 and 182.5 °C, the curve of FT shows two endothermic peaks at 114.8 and 175.3 °C, and the curve of FTA also shows two endothermic peaks at 117.7 and 183.3 °C, each corresponding to the α → β and β → γ polymorphic transitions respectively. The endothermic peaks at 116.7, 114.8 and 117.7 °C are distinct, sharp and smooth whilst the peaks at 182.5, 175.3 and 183.3 °C are broad and not sharp. The endothermic peaks at 116.7, 114.8 and 117.7 °C correspond to the α → β transition reported at 115 °C [8] and the β → γ transition reported at 119.7 °C [11]. The peaks at 182.5, 175.3 and 183.3 °C differ from the reported value corresponding to the β → γ transition at 162 °C [8] and γ → δ transition at 163.8 °C [11]. This difference can be attributed to possible impurities in the FOX-7. It is evident from these studies that the sample weight is an important factor in determining the phase changes of FOX-7. The ΔH values of the phase transitions of FOX-7 polymorphs α → β and β → γ observed were 23.3 and 2.5 J/g respectively. The ΔH value of 23.3 J/g for the phase transition α → β is of the same order as 21.5 J/g reported for β → γ by A.K. Burnham *et al.* [11] and ΔH of 18.1 J/g by M.J. Crawford *et al.* [8]. The ΔH value of 2.5 J/g for the phase transition β → γ is very low compared to the average ΔH of 20.0 J/g [8] and 18.7 J/g for γ → δ [11]. The ΔH values of the phase transitions α → β and β → γ for FOX-7 in FT were 2.9 and 3.7 J/g respectively, and in FTA were 3.5

and 3.7 J/g respectively. These ΔH values are also low in comparison to values reported by the above authors. Further investigations on these aspects are in progress. The DSC curves of the decomposition studies of FOX-7, FT, RT, FTA and RTA are shown in Figure 2. The endothermic peaks in the curves for these formulations in the temperature range 78.4-81 °C correspond to the melting of TNT. The exothermic peak for FOX-7 at 264.2 °C, FT at 256.8 °C, RT at 231.6 °C, FTA at 252.4 °C and RTA at 231.3 °C, correspond to decomposition of the formulations.

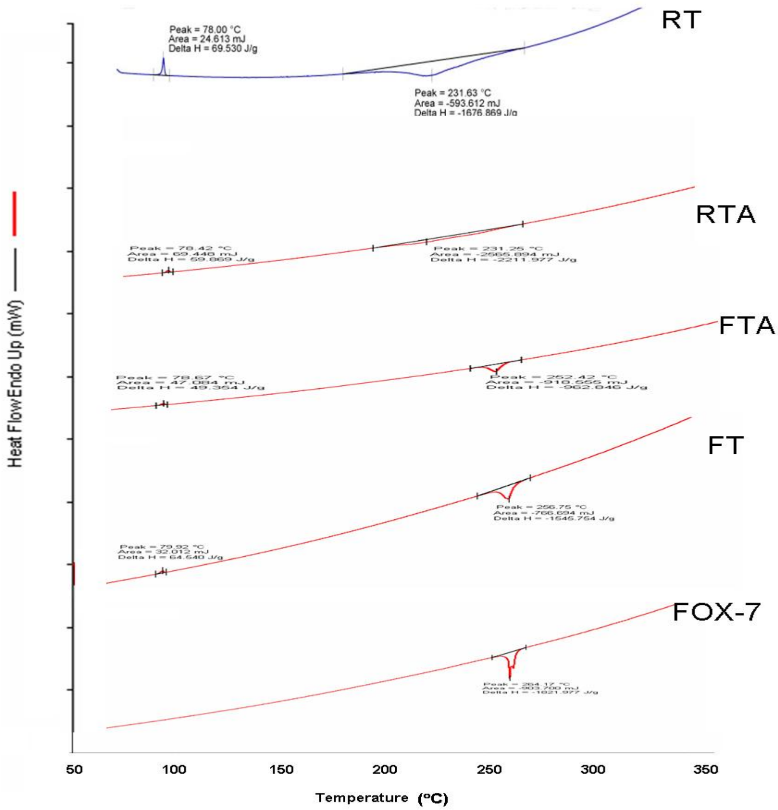

Figure 2. DSC curves of decomposition studies of FOX-7, FT, RT, FTA and RTA.

The decomposition of FOX-7 appears to occur in a single stage as reported by de Klerk *et al*. [10], whilst for the other systems, decomposition is also a single stage process. It may be inferred from the exothermic peak temperatures of the FT and FTA formulations that TNT and FOX-7 decompose as a mix at a temperature of about 256.8 °C, which is closer to the decomposition temperature of TNT at about 240 °C. On the other hand, RT and RTA decompose at about 231.6 °C, closer to the decomposition temperature of RDX at about 238 °C, which indicates greater thermal stability of FOX-7 based melt cast composition compared to the RDX based composition. From the exotherms it is seen that the heat energy (ΔH) evolved by FOX-7, FT and RT are 1822, 1545 and 1676.9 J/g respectively. A.K. Burnham *et.al*. [11] reported that two exotherms were observed for FOX-7 at a heating rate of 3 °C/min, first at 226.2 °C with ΔH 0.82 kJ/g and the second at 277.2 °C with ΔH 0.96 kJ/g, with a total ΔH of 1.82 kJ/g. The ΔH value observed in the present study for FOX-7 is also 1.82 kJ/g, but in a single exotherm with a peak temperature of 265 °C at a heating rate of 5 °C/min. The ΔH values observed for FT and RT, 1545 and 1676.9 J/g respectively, appear to be of the order of the ΔH values for FOX-7 and RDX respectively. The ΔH values observed for FTA and RTA were 963 and 2212 J/g respectively. The ΔH value observed for FTA, 963 J/g, appears to be very low, and further investigation is in progress.

Sensitivity characteristics and velocity of detonation

The results of the characteristics determined for these formulations compared to the standard explosive TNT are given in Table 3. The VOD of FOX-7 based formulation FT was found to be slightly lower than that for the RDX based formulation RT. As expected the VODs of aluminized mixtures were lower than those of the non-aluminized mixtures. The VODs of formulations FTA and RTA were found to be more or less the same. An optimization of the process parameters of the compositions should bridge the gap in VODs of the non-aluminized formulations. Despite having lower VODs, aluminized, TNT-based, melt cast high explosive compositions find application as high explosive fillings in various blast warheads and projectiles due to the overall enhanced energy release over an extended time. A comparative evaluation of blast parameters, peak over pressure and impulse of FOX-7 based aluminized formulation (FTA) and RDX based, aluminized formulation (RTA) was carried out. The FOX-7 based aluminized as well as non-aluminized, formulations were found to be more shock insensitive than the corresponding RDX based formulations. Impact sensitivity (in terms of the height of 50% explosion h_{50}) of FOX-7 based melt cast composition FT is also superior to the RDX based composition RT. This is in line with the reported sensitivity characteristics of both the compounds.

Table 3. VOD and sensitivity characteristics of the formulations

Formulation	Charge density (kg/m^3)	Percent TMD	VOD (m/s)	Sensitivity		
				Shock (GPa)	Impact h_{50} (m)	Friction (kg)
FT	1610	94	7061	2.1	1.57	36
RT	1640	97	7230	1.7	1.04	30
FTA	1700	94	6861	3.6	>1.70	36
RTA	1690	94	6908	3.0	>1.70	36
TNT	1590	96	6600	4.1	1.30	32.4

Blast parameters

The charges were placed at a height of 2 m on a wooden stand and evaluated for peak over pressure (P_{max}) and impulse (I_+) at distances of 1.5, 2.5 and 3.5 m. The plots of P_{max} vs. scaled distance and I_+ vs. scaled distance are shown in Figure 3 and Figure 4, respectively. Figure 3 indicates that initially P_{max} of FTA is lower than that of the RTA formulation, but gradually the difference narrows and becomes almost equal with increasing distance. Figure 4 indicates that initially I_+ of FTA is also lower than that of RTA, but gradually the difference narrows and becomes almost equal with increasing distance. This indicates that the blast effect of FTA lasts for a shorter duration than that of RTA.

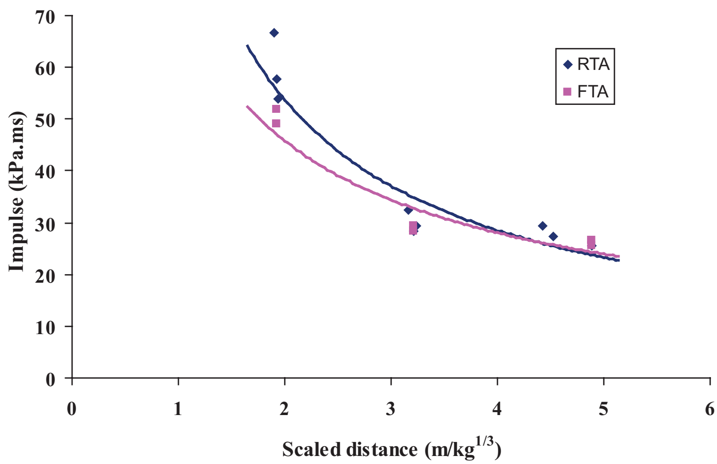

Figure 3. P_{max} (kPa) vs. scaled distance (m/kg$^{1/3}$).

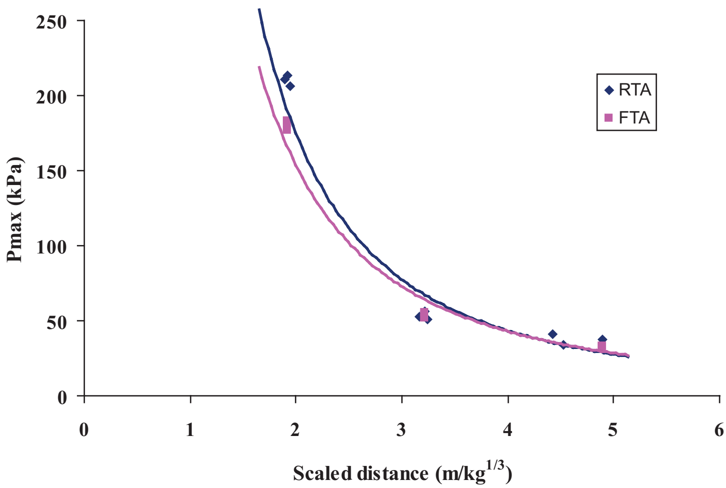

Figure 4. Impulse (kPa·ms) vs. scaled distance (m/kg$^{1/3}$).

Conclusion

Thermal decomposition studies by Differential Scanning Calorimetry indicate a greater thermal stability of formulation FOX-7/TNT (30/70) compared to RDX/TNT (30/70). TNT and FOX-7 decompose as a mix at a specific temperature in the composition. Shock sensitivity and impact sensitivity measurements of FOX-7 based, melt cast compositions are superior to the corresponding RDX based compositions. The VODs of FOX-7 based aluminized as well as the non-aluminized formulations are close to the analogous RDX based formulations. The blast effect of FOX-7 based aluminized formulation (FTA) lasts for a shorter duration than the corresponding RDX based aluminized formulation (RTA). Initial studies indicate the potential of FOX-7 as a replacement for RDX in TNT based melt cast formulations to achieve low vulnerability with little sacrifice in performance.

Acknowledgements

The authors are grateful to Outstanding Scientist and Director, HEMRL Shri Bikash Bhattacharya for his constant encouragement and valuable support in this technical work. The authors are thankful to S.W. Joshi, Technical officer ‘C’ and Shri R.S. Punekar, Technical officer ‘C’, for instrumentation support during the measurement of velocity of detonation and blast parameters. The authors are also thankful to Dr. A.K. Mandal, Sc. ‘E’ for his valuable suggestions. We are also thankful to Shri B.G. Polke, Scientist 'E' and his team during the measurement of impact sensitivities.

References

[1] Vadhe et al., Cast Aluminized Explosives, *Combust., Explos. Shock Waves (Engl. Transl.)*, **2008**, *44*, 461-467.

[2] Lochert I.J., *FOX-7 − a New Insensitive Explosive*, Weapons System Division, Aeronautical and Maritime Research Laboratory, DSTO-TR-1238, **2001**.

[3] Wild R., Teipel U., Characterization and Explosive Properties of FOX-7, *35th Int. Annu. Conf. of ICT*, 69, Karsruhe, Germany, **2004**.

[4] Dorsett H., *Computational Studies of FOX-7, a New Insensitive Explosive*, Weapons Systems Division, Aeronautical and Maritime Research Laboratory, DSTO-TR-1054, **2000**.

[5] Karlsson S. et al., *Detonation and Sensitivity Properties of FOX-7 and Formulations Containing FOX-7*, FOI Swedish Defence Research Agency, Grindsjöns Research Center, SE-147 25 Tumba, Sweden, **2002**.

[6] Progress Report Swedish Defence Research Agency, FOI-R--1611--SE ISSN 1650-1942, March **2005**.

[7] Nandi A.K., Paramsivan P., Singh S.K., Mandal A.K., Pandey R.K., Assay of the Insensitive High Explosive FOX-7 by Non-Aqueous Titration, *Cent. Eur. J. Energ. Mater.*, **2012**, *9*(4), 343-352.

[8] Crawford M.J., Evers J., Göbel M., Klapötke T.M., Mayer P., Oehlinger G., Welch J.M., γ-FOX-7: Structure of a High Energy Density Material Immediately Prior to Decomposition, *Propellants Explos. Pyrotech.*, **2007**, *32*, 478-495.

[9] Evers J., Klapötke T.M., Mayer P., Oehlinger G., Welch J., α and ß-FOX-7, Polymorphs of a High Energy Density Material, Studied by X-ray Single, Crystal and Powder Investigations in the Temperature Range from 200 to 423 K, *Inorg. Chem.*, **2006**, *45*, 4996-5007.

[10] de Klerk W.P.C., Popescu C., van der Heijden A.E.D.M., Study on Decomposition Kinetics of FOX-7 and HNF, *J. Therm. Anal. Cal.*, **2003**, *72*, 955-966.

[11] Burnham A.K., Weese R.K., Wang R., Kwok Q.S.M., Jones D.E.G., Thermal Properties of FOX-7, *36th Int. Annu. Conf. of ICT & 32nd International Pyrotechnics Seminar*, Karlsruhe, Germany, June 28 to July 01, **2005**.