Central European Journal of Energetic Materials, **2014**, *11*(4), 501-513
ISSN 2353-1843

Characteristics of Melt Cast Compositions Based on *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5 d] imidazole (BCHMX)/TNT

Ahmed ELBEIH[1,*], Svatopluk ZEMAN[2]

[1] *Military Technical College, Kobry Elkobbah, Cairo, Egypt*
[2] *Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*
[*] *E-mail: elbeih.czech@gmail.com*

Abstract: *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5 d]imidazole (BCHMX) is a new bicyclic nitramine which has been prepared using a two-stage synthetic method. In this work, a new melt cast composition based on BCHMX/TNT (60/40 by wt.) was prepared. For comparison purposes, Composition B based on RDX (1,3,5-trinitro-1,3,5-triazacyclohexane)/TNT (60/40 by wt.), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)/TNT (60/40 by wt.) were also studied. Impact and friction sensitivities of these compositions and of the individual explosives were determined. The detonation velocities were measured experimentally. The performance of the compositions prepared was studied by measuring the brisance using the Kast method. The detonation parameters of the compositions and the individual explosives were calculated using the EXPLO5 thermodynamic code. The results show that mixing these nitramines with TNT decreases their sensitivities. BCHMX/TNT is more sensitive to impact and friction than Composition B while it has higher detonation parameters, at the same level as HMX/TNT. In comparison, BCHMX/TNT has the highest relative brisance of the compositions studied. It is postulated that the higher performance characteristics of BCHMX and compositions based on it, in comparison with those of HMX, are due to a higher positive heat of formation for this nitramine.

Keywords: nitramines, BCHMX, sensitivity, detonation, brisance

1 Introduction

2,4,6-Trinitrotoluene (TNT) is considered the most available explosive throughout the world and it is widely used in the formation of the melt cast explosives used in mortars, grenades, artillery shells, warheads and anti-personnel mines. TNT is chemically very stable, is moderately sensitive to impact and friction and has a melting point of 80-82 °C, which allows it to be melted with the addition of other explosives and poured into artillery shells and mines [1]. Composition B is a mixture of 60% RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and 40% TNT and is the most generally employed explosive composition in mortars and projectiles. There are several melt cast formulations based on TNT which have military and civilian applications, and further formulations are in the research stages [2-5]. These current research activities are aimed at finding a melt cast composition more powerful than Composition B. *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5 d]imidazole (BCHMX) is a new attractive polycyclic nitramine which has been prepared at the Institute of Energetic Materials (IEM), University of Pardubice, using a two-stage synthetic method [6]. BCHMX has been studied as a plastic explosive based on C4, Semtex and acrylate matrices, for which the detonation parameters have been determined [7-10]. It has also been investigated as a highly pressed plastic bonded explosive using Viton A and Fluorel binders [11, 12]. The effect of different polymeric matrices on the sensitivity, performance and detonation characteristics of BCHMX has been studied [13-17]. The thermal stability and decomposition kinetics of BCHMX bonded by different polymeric matrices have been studied using different techniques [18-24] and the low temperature thermolytic behaviour has been evaluated using the STABIL method [25, 26]. In the present work, a melt cast composition based on BCHMX/TNT (60/40 by wt.) was prepared and studied. For comparison purposes, Composition B and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)/TNT (60/40 by wt.) were also investigated. The impact and friction sensitivities were determined, the detonation velocities of the compositions were measured and the detonation parameters were calculated by the thermodynamic code EXPLO5. Performance was studied using the brisance test.

2 Experimental

2.1 Materials

RDX and HMX were products supplied by Eurenco, Paris, France. TNT and BCHMX were prepared in our laboratories. BCHMX was prepared by a two-stage synthetic process according to the Czech patented method [6]. RDX, HMX and BCHMX had mean particle sizes of 64, 42 and 18 µm, respectively.

2.2 Preparation of the melt cast explosive compositions

The preparation process was based on melting TNT at 90 °C for 30 min, with continuous stirring, followed by addition of the desired weight of the individual nitramine. Stirring of the mixture was continued for 30 min after the complete addition of the nitramine to obtain a thoroughly mixed composition. A part of each prepared mixture was poured into PVC (polyvinyl chloride) tubes closed at one end, with a diameter of 19 mm and a length of 250 mm. Three tubes containing the explosive compositions were prepared for each composition for the experimental measurement of the detonation velocity. The remainder of each mixture was poured into a Teflon mould and left to cool. In this work, the compositions obtained were BCHMX/TNT, HMX/TNT and RDX/TNT with 60/40 by wt. in each case and are designated as BC-TNT, HMX-TNT and Composition B, respectively.

2.3 Impact sensitivity measurements

A standard impact tester with exchangeable anvil (Julius Peters [27]) was used with a 2 kg drop hammer; the amount of substance tested was 50 mm^3. Probit analysis [28] was used to determine the probability levels for initiation. The sensitivity obtained was expressed as the drop energy, E_{dr}, versus percentage of initiation. Only the 50% probability of initiation has been used in this article and is reported in Table 1.

2.4 Friction sensitivity measurements

A BAM friction test apparatus was used to determine the sensitivity to friction using the standard test conditions [27]. The sensitivity to friction was determined by spreading about 0.01 g of the studied explosive on the surface of the porcelain plate in the form of a thin layer. Different loads were used to change the normal force between the porcelain pistil and the plate. Sample initiation was observed through sound, smoke appearance, or by the characteristic smell of the decomposition products. Using the Probit analysis [28], only the normal force at which 50% of initiations occurred is reported in Table 1 as the friction sensitivity.

2.5 Detonation velocity measurements

The detonation velocity of the compositions prepared was measured by an EXPLOMET-FO-2000 produced by KONTINITRO AG. The compositions tested were 19 mm in diameter and 250 mm in length inside PVC cylinders. Three optical sensors were placed in each charge, with the first sensor being placed at a distance of 50 mm from the booster. Each of the other two sensors was placed at a distance of 80 mm from the previous one. Charges were set off using a booster charge based on PETN and a detonator No. 8. For each composition, three measurements were performed and the mean value (max. ±120) for each is reported in Table 2.

Table 1. Results of the experimental measurements on the samples studied

No.	Code designation*	Impact sensitivity [J]	Friction sensitivity [N]	Relative brisance (%TNT)
1	TNT cryst.	39.2**	342	100
2	RDX cryst.	5.6	120	-
3	HMX cryst.	6.4	95	-
4	BCHMX cryst.	3.2	88	-
5	Comp. B	12.1	232	129
6	HMX-TNT	12.5	210	130
7	BC-TNT	10.8	181	133

Note: *) Each code designation is described in the experimental part under subheading 2.2 'Preparation of the melt cast explosive compositions'.
**) Data taken from Ref. [29].

2.6 Performance determination

Brisance, measured by the Kast method produced by OZM Company, was used to determine the relative performance of the prepared compositions [27]. The deformation of a standard copper crusher (7 mm diameter and 10.5 mm high) was used to estimate the brisance of each composition studied. 2 g of each composition was cast in an aluminum tube 30 mm high, 12 mm internal diameter and 4 mm wall thickness. The aluminum tube was placed on a solid steel cylinder which served as a counter weight for the copper crusher. The charges were initiated by electric detonator. The deformation (final lengths) of the copper crushers was determined and recorded as a relative brisance (with respect to TNT as reference sample) in Table 1.

2.7 Calculation of detonation parameters

The theoretical detonation characteristics (detonation velocity, D, heat of detonation, Q, and detonation pressure, P) of the prepared compositions, as well as those of the individual explosives, were calculated by the EXPLO5 code version 4 [30]. The following BKWN set of parameters was used: $\alpha = 0.5$, $\beta = 0.186$, $\kappa = 14.61$, $\Theta = 6620$ [30]. The heat of explosion is the heat released in a constant volume explosion and is determined by subtracting the heats of formation of the explosive (reactants) from the sum of the heats of formation of the detonation gases (products) in the Chapman-Jouguet (CJ) state. The calculated detonation characteristics of all of the explosives studied are reported in Table 2.

Table 2. Detonation parameters of the samples studied

Sample		Experimental		EXPLO5 code			
No.	Code designation	Density, ρ [g·cm^{-3}]	Detonation velocity D_{exp} [m·s^{-1}]	Detonation velocity calc. D_{calc} [m·s^{-1}]	D_{calc}-D_{exp} D_{exp}/100 [%]	Detonation pressure P [GPa]	Heat of detonation Q [kJ·kg^{-1}]
1	TNT	1.60*	6900*	7126	+3.27	19.5	5101
2	RDX	1.80*	8750*	8718	-0.36	32.12	6085
3	HMX	1.90*	9100*	9225	+1.37	38.00	6075
4	BCHMX	1.79**	8650**	8840	+2.19	33.95	6447
5	Comp. B	1.71	7920	8105	+2.33	26.9	5698
6	HMX-TNT	1.74	8112	8203	+1.08	27.8	5673
7	BC-TNT	1.73	8088	8187	+1.22	28.0	5891

Note: *) Data taken from Ref. [32]
**) Data taken from Ref. [33]

3 Results and Discussion

The orders of the impact and friction sensitivities of the explosives investigated correspond with the generally accepted theory [12, 13, 34] that an increase in the explosive strength (performance) is usually accompanied by an increase in the sensitivity, and, therefore, an insensitive explosive will not exhibit a high level of explosive strength. However, it was pointed out by Licht [34] that it is not possible to prove this theory − some exceptions exist (it is partially exemplified in Figure 1 by the dotted line, taken from a more complex relationship [35]) which needs further research and explanation [34, 35]. In the paper [12] it was shown that the performance can be expressed as a volume heat of detonation (*i.e.* by a product of the heat of explosion and the corresponding loading density − both quantities taken from Table 2). A relationship between the impact sensitivity and the volume heat of detonation of the explosives in this study is presented here in Figure 1. A similar, but linear relationship generally exists in the case of friction sensitivity [13]. Therefore, it is not surprising that impact and friction sensitivities correlate well in a semi-logarithmic relationship [13, 36], in this case presented in Figure 2.

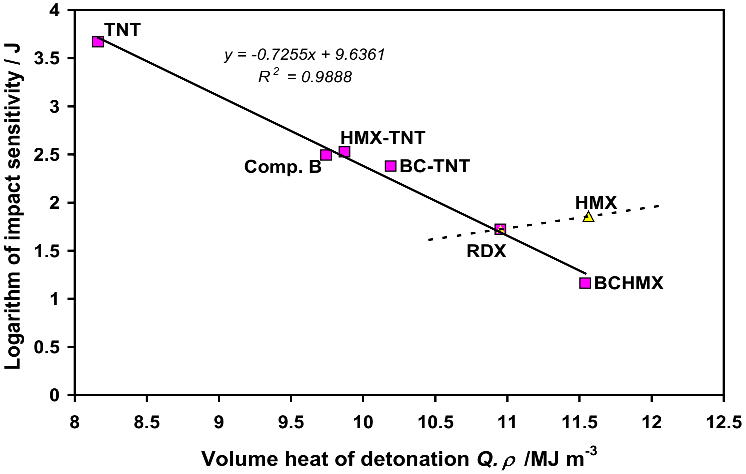

Figure 1. Semi-logarithmic relationship between impact sensitivity and volume heat of explosion; the dotted line indicates exceptions from the general rule for a series of highly explosive nitramines (a more detailed explanation is given in paper [35]), which is the subject of further research [35].

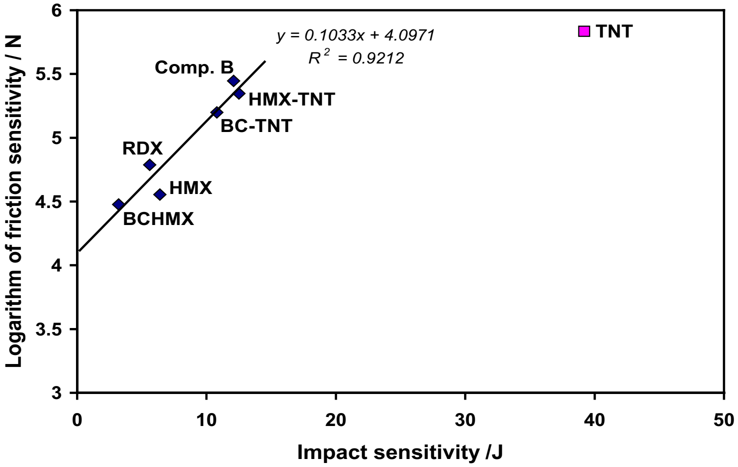

Figure 2. Semi-logarithmic relationship between friction and impact sensitivities. These sensitivities are determined by the nitramine sensitivities, and therefore the data for TNT lie outside the relationship.

The difference between initiation by impact (uni-axial compression) and initiation by friction (shear slide with a fixed volume) is pointed out in the theoretical paper by Zhang [37] concerning the influence of the desensitizing mechanism of olefins; these admixtures reduce the shear stress of explosives in both kinds of initiation because of the reduction in the explosive particle's degree of contact [37]. A relatively soft energetic binder, in our case TNT, operates measurably as a lubricant (the area of the nitramine particle's contact is reduced).

Another approach to the evaluation of the performance for the TNT-explosives is to compare their relative brisance and calculated detonation pressures as presented in Figure 3. As in Figure 1 (and also data in Table 1), it is shown here that BCHMX and its mixture with TNT have higher heats of explosion compared with Composition B and HMX-TNT. This fact was found also in the case of plastic bonded explosives (PBXs) using these nitramines [7, 8, 11-14] and was also confirmed by the relative explosive strengths of these PBXs measured using a ballistic mortar [16]. The reason for this finding lies in the positive heat of formation of BCHMX being three times greater than that of HMX (236.5 kJ·mol^{-1} against 77.3 kJ·mol^{-1}) [8, 11]; the spatially angular BCHMX molecule is sterically crowded [33], which means a greater energy content. However, the armour-piercing effect of shaped explosive charges containing these PBXs as the explosive filling, already corresponds to the detonation velocities of these explosives [38], *i.e.* HMX-PBXs are more effective.

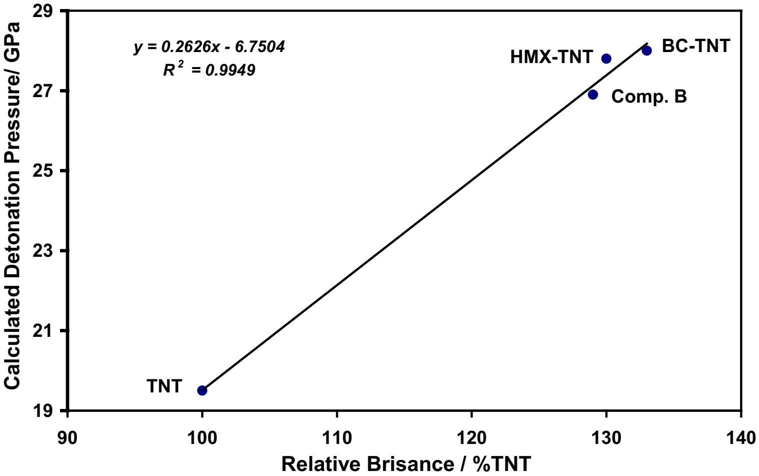

Figure 3. Relationship between the calculated detonation pressure and relative brisance.

The trends in performance of the explosives in this study can also be shown by comparing the calculated detonation pressures with the products of the square of the experimental detonation velocities and the loading densities, as presented in Figure 4; these products can be taken as representative of the pressures. Figure 4 confirms the compatibility of the calculated results with the experimental measurements. It is clear that the detonation pressure of BC-TNT is in the same range as that for HMX-TNT and higher than that for Composition B.

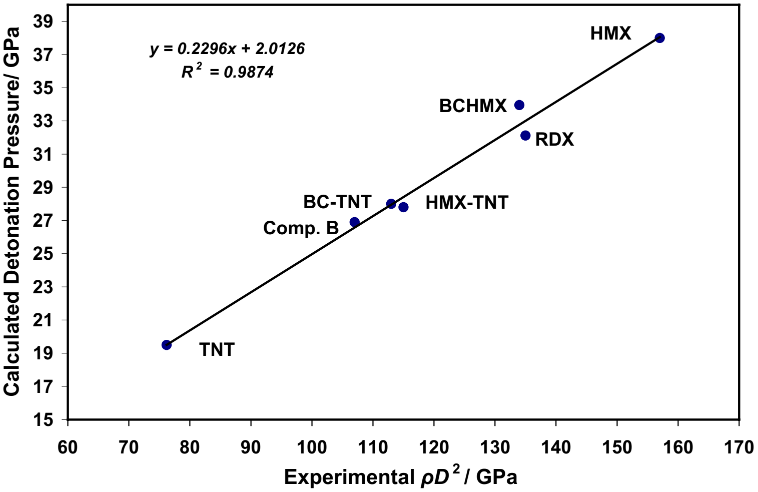

Figure 4. Relationship between calculated detonation pressure and the square of the experimental detonation velocity multiplied by the loading density.

Figure 5 represents the well-known dependence of detonation velocity on loading density. From Figure 5 it is clear that the detonation velocity of BC-TNT is higher than that for Composition B and at the same level as that for HMX-TNT. BCHMX (3% Viton B) appeared to have a lower detonation velocity than pure RDX. Actually it was unsafe to press crystalline BCHMX to a high loading density, and as a result we bound and de-sensitized BCHMX with 3% Viton B [33].

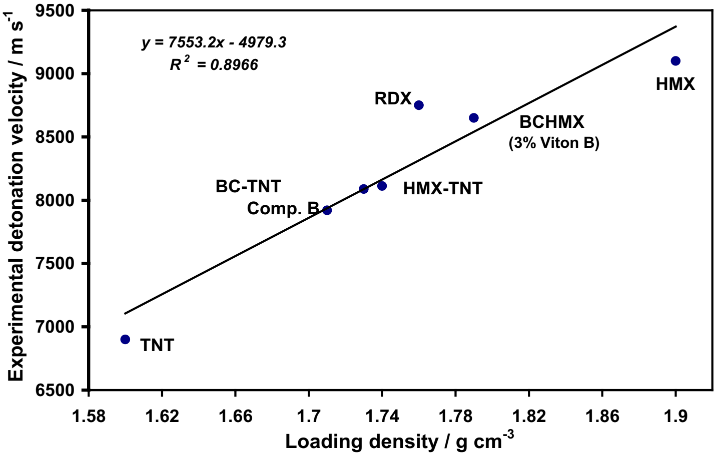

Figure 5. Relationship between the experimental detonation velocity and the loading density of the explosives studied.

In order to confirm our predictions based on the application of the EXPLO5 code, a comparison of the calculated detonation velocities with the measured ones is presented in Figure 6. The dotted line in Figure 6 represents the ideal correlation of both sets of results. It is clear that most of the points are shifted to the right, which means that the calculated results have slightly higher values than the measured ones.

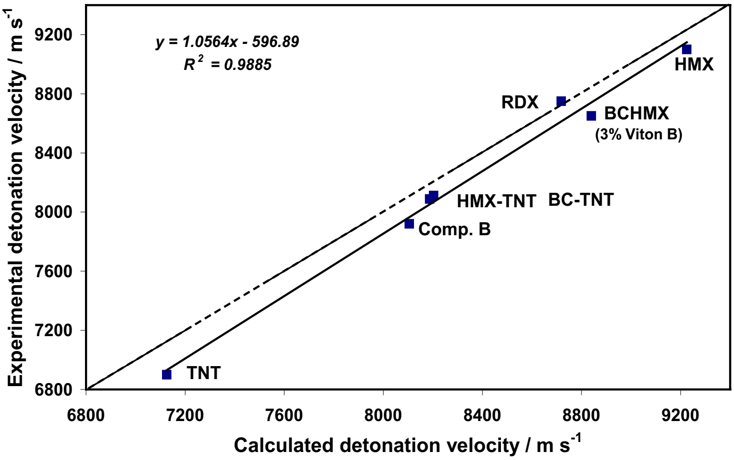

Figure 6. Relationship between calculated and experimental detonation velocities.

4 Conclusions

The newly prepared composition based on BCHMX/TNT has sensitivities to impact and to friction which are higher than Composition B and lower than all of the pure nitramines studied; a semi-logarithmic relationship exists between the impact and friction sensitivities of the evaluated nitramine explosives. The measured detonation velocity of BCHMX/TNT is higher than that for Composition B and in the same range as that for HMX/TNT. The calculated heat of detonation and detonation pressure of BCHMX/TNT are higher than those for Composition B and HMX/TNT. Furthermore, the nitramine explosives in this study fall within the general rule concerning the inverse proportionality relationship between impact and friction sensitivity, on the one hand, and the heat of explosion (generally performance), on the other. The performance test shows that BCHMX/TNT has the highest relative brisance of all of the explosive compositions under evaluation. It is postulated that the higher performance characteristics of BCHMX and those compositions based on it, in comparison with those of HMX, are due to the positive heat of formation for this nitramine being three times greater than that of HMX. The detonation parameters calculated using the EXPLO5 code are compatible with the measured values and confirm the relationships of the physics of explosion.

5 References

[1] Weckert S., Anderson C., *A Preliminary Comparison between TNT and PE4 Landmines*, Weapons Systems Division, DSTO-TN-0723, Australia, **2006**.

[2] Nemec O., Jungova M., Marecek R., Novotny M., Zeman S., Selesovsky J., Fortification of W/O Emulsions by Demilitarized Explosives, Part I. Use of TNT, *Cent. Eur. J. Energ. Mater.*, **2011**, *8*(3), 193.

[3] Brousseau P., Thiboutot S., Ampleman G., Behaviour of CL20 in TNT Based Explosives, *38th Int. Annu. Conf. ICT*, V 27, Karlsruhe, Germany, **2007**.

[4] Mishra V., Vadali S., Garg R., Joshi V., Wasnik R., Asthana S., Studies on FOX-7 Based Melt Cast High Explosive Formulations, *Cent. Eur. J. Energ. Mater.*, **2013**, *10*(4), 569.

[5] Ravi P., Badgujar D., Gore G., Tewari S., Sikder A., Review on Melt Cast Explosives, *Propellants Explos. Pyrotech.*, **2011**, *36*(5), 393.

[6] Klasovitý D., Zeman S., Process for Preparation of *cis*-1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]imidazole, Czech Patent CZ 302068, B6 20100922, University of Pardubice, **2010**.

[7] Elbeih A., Pachman J., Trzcinski W., Zeman S., Akstein Z., Selesovsky J., Study of Plastic Explosives Based on Attractive Cyclic Nitramines, Part I: Detonation

Characteristics of Explosives with PIB Binder, *Propellants Explos. Pyrotech.*, **2011**, *36*(5), 433.

[8] Elbeih A., Pachman J., Zeman S., Vavra P., Trzcinski W., Akstein Z., Detonation Characteristics of Plastic Explosives Based on Attractive Nitramines with Polyisobutylene and Poly(methyl methacrylate) Binders, *J. Energ. Mater.*, **2011**, *30*(4), 358.

[9] Elbeih A., Pachman J., Zeman S., Akštein Z., Replacement of PETN by BicycloHMX in Semtex 10, *Problems of Mechatronics*, **2010**, *2*(2), 7.

[10] Elbeih A., Pachman J., Zeman S., Trzciński W.A., Akštein Z., Advanced Plastic Explosive Based on BCHMX Compared with Composition C4 and Semtex 10, *New Trends Res. Energ. Mater., Proc. Semin., 14th*, Czech Republic, **2011**, 119.

[11] Elbeih A., Pachman J., Zeman S., Trzciński W.A., Suceska M., Study of Plastic Explosives Based on Attractive Cyclic Nitramines, Part II: Detonation Characteristics of Explosives with Polyfluorinated Binders, *Propellants Explos. Pyrotech.*, **2013**, *38*(2), 238.

[12] Elbeih A., Zeman, S., Jungova M., Vavra P., Attractive Nitramines and Related PBXs, *Propellants Explos. Pyrotech.*, **2013**, *38*(3), 379.

[13] Elbeih A., Zeman, S., Jungova M., Akstein Z., Effect of Different Polymeric Matrices on Sensitivity and Performance of Interesting Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2012**, *9*(2), 17.

[14] Elbeih A., Zeman S., Jungova M., Vavra P., Akstein Z., Effect of Different Polymeric Matrices on Some Properties of Plastic Bonded Explosives, *Propellants Explos. Pyrotech.*, **2012**, *37*(6), 676.

[15] Elbeih A., Zeman, S., Pachman J., Effect of Polar Plasticizers on the Characteristics of Selected Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2013**, *10*(3), 339.

[16] Elbeih A., Jungova M., Zeman S., Vavra P., Akstein Z., Explosive Strength and Impact Sensitivity of Several PBXs Based on Attractive Cyclic Nitramines, *Propellants Explos. Pyrotech.*, **2012**, *37*(3), 329.

[17] Zeman S., Elbeih A., Akštein Z., Preliminary Study of Several Plastic Bonded Explosives Based on Cyclic Nitramines, *Chin. J. Energ. Mater. (HanNeng CaiLiao)*, **2011**, *19*(1), 8.

[18] Yan Q., Zeman S., Selesovsky J. Svoboda R., Elbeih A., Thermal Behaviour and Decomposition Kinetics of Formex-bonded Explosives Containing Different Cyclic Nitramines, *J. Therm. Anal. Calorim.*, **2013**, *111*, 1419.

[19] Yan Q.-L., Zeman S., Elbeih A., Svoboda R., Thermodynamic Properties, Decomposition Kinetics and Reaction Models of BCHMX and Its Formex Bonded Explosive, *Thermochim. Acta*, **2012**, *547*, 150.

[20] Yan Q.-L., Zeman S., Elbeih A., Recent Advances in Thermal Analysis and Stability Evaluation of Insensitive Plastic Bonded Explosives (PBXs), *Thermochim. Acta*, **2012**, *537*, 1.

[21] Yan Q.-L., Zeman S., Zhao F.-Q., Elbeih A., Non-isothermal Analysis of C4 Bonded Explosives Containing Different Cyclic Nitramines, *Thermochim. Acta*, **2013**, *556*, 6.

[22] Yan Q.-L., Zeman S., Elbeih A., Thermal Behavior and Decomposition Kinetics of Viton A Bonded Explosives Containing Attractive Cyclic Nitramines, *Thermochim. Acta*, **2013**, *562*, 56.

[23] Yan Q.-L., Zeman S., Zang T.-L., Elbeih A., Non-isothermal Decomposition Behaviour of Fluorel Bonded Explosives Containing Attractive Cyclic Nitramines, *Thermochim. Acta*, **2013**, *574*, 10.

[24] Yan Q.-L., Zeman S., Elbeih A., Zbynek A., The Influence of the Semtex Matrix on the Thermal Behaviour and Decomposition Kinetics of Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2013**, *10*(4), 509.

[25] Zeman S., Elbeih A., Yan Q.-L., Note on the Use of the Vacuum Stability Test in the Study of Initiation Reactivity of Attractive Cyclic Nitramines in Formex P1 Matrix, *J. Therm. Anal. Calorim.*, **2013**, *111*, 1503.

[26] Zeman S., Elbeih A., Yan Q.-L., Notes on the Use of the Vacuum Stability Test in the Study of Initiation Reactivity of Attractive Cyclic Nitramines in the C4 Matrix, *J. Therm. Anal. Calorim.*, **2013**, *112*, 1433.

[27] Sućeska M., *Test Methods for Explosives*, Springer, Heideleberg, **1995**.

[28] Šelešovský J., Pachman J., Probit Analysis – a Promising Tool for Evaluation of Explosive's Sensitivity, *Cent. Eur. J. Energ. Mater.*, **2010**, *7*(3), 269.

[29] Storm C.B., Stine J.R., Kramer J.F., Sensitivity Relationships in Energetic Materials, in: *Chemistry and Physics of Energetic Materials*, (Bulusu S.N., Ed.), Kluwer Acad. Publs., Dordrecht, **1990**, pp. 605-639.

[30] Sućeska M., Calculation of Detonation Parameters by EXPLO5 Computer Program, *Materials Science Forum*, **2004**, *465* (Explosion, Shock Wave and Hypervelocity Phenomena in Materials), 325.

[31] Elbeih A., Pachman J., Zeman, S., Trzcinski W., Akstein Z., Suceska M., Thermal Stability and Detonation Characteristics of Pressed and Elastic Explosives on the Basis of Selected Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2010**, *7*(3), 217.

[32] Meyer R., Kohler J., Homburg A., *Explosives,* 5th ed., Wiley-VCH & Co. KGaA, Weinheim, **2007**.

[33] Klasovitý D., Zeman S., Růžicka A., Jungová M., Roháč M., *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), Its Properties and Initiation Reactivity, *J. Hazard. Mater.*, **2009**, *164*, 954-961.

[34] Licht H.-H., Performance and Sensitivity of Explosives, *Propellants Explos. Pyrotech.*, **2005**, *25*, 126-132.

[35] Zeman S., Study of the Initiation Reactivity of Energetic Materials, Ch. 8, in: *Energetics Science and Technology in Central Europe*, (Armstrong R.W., Short J.M., Kavetsky R.A., Anand D.K., Eds.), CECDS, University of Maryland, College Park, Maryland, **2012**, pp. 131-167.

[36] Jungová M., Zeman S., Husarová A., Friction Sensitivity of Nitramines. Part I: Comparison with Impact Sensitivity and Heat of Fusion, *Chin. J. Energ. Mater. (Hanneng Cailiao)*, **2011**, *19*(6), 603-606.

[37] Zhang C., Understanding the Desensitizing Mechanism of Olefin in Explosives Versus External Mechanical Stimuli, **2010**, *J. Phys. Chem.*, *C 114*, 5068-5072.

[38] Elbeih A., Zeman S., Jungová M., Akštein Y., Vávra P., Detonation Characteristics and Penetration Performance of Plastic Explosives, *Proc. 2011 International Autumn Seminar on Propellants, Explosives and Pyrotechnics*, (Li S., Niu P. Eds.), Nanjing, Sept. 20-23, **2011**; *Theory and Practice of Energetic Materials*, Vol. *IX*, Sci. Press, Beijing, **2011**, pp. 508-513.