Effect of Polar Plasticizers on the Characteristics of Selected Cyclic Nitramines

Ahmed ELBEIH[1*], Svatopluk ZEMAN[2] and Jiri PACHMAN[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: Dioctyl sebacate (DOS) is a plasticizer used with oily material for the softening of polyisobutylene binder (PIB) to form a polymeric matrix. This matrix was used for the preparation of various plastic explosives. The following energetic cyclic nitramines were used as explosive fillers: BCHMX (*cis*-1,3,4,6-tetranitrooctahydroimidazo [4,5 d]imidazole), ε-HNIW (ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane). For comparison, Fluorel binder was used for the preparation of several plastic bonded explosives (PBXs) based on the same selected explosives. Impact and friction sensitivities of the prepared samples and the pure explosive fillers were measured. The thermal stability was studied using differential thermal analysis (DTA). High performance liquid chromatography (HPLC) was used to detect the presence of BCHMX dissolved in dioctyl sebacate (DOS). The heat of combustion of the prepared samples and of the pure explosive fillers was measured using a bomb calorimetry. The results show that PIB softened by plasticizer (DOS) has a greater positive effect on decreasing the impact sensitivity of the studied pure explosives than Fluorel binder. On the other hand, the plasticizer acts as a solvent for the energetic materials and decreases the decomposition temperature of these plastic explosives.

Keywords: energetic materials, polymers, sensitivity, combustion, thermal stability

Introduction

Polymeric matrices are used with energetic materials to increase safety during transportation, loading and handling of these materials, and to enhance their mechanical properties [1-2]. BCHMX (*cis*-1,3,4,6-tetranitro-octahydroimidazo-[4,5 d]imidazole; bicycloHMX) is a new attractive nitramine which has been prepared at the Institute of Energetic Materials (IEM) by a two-stage synthetic method [3]. The sensitivity and detonation characteristics of BCHMX bonded by polymeric matrices were studied [4-9]. The thermal stability of BCHMX as a pure and as a plastic explosive was studied in publications [10-11]. The decomposition of a pure substance is always accelerated by heat (during production, storage or usage) and sometimes by the presence of other substances which are not compatible with the energetic material itself. Decomposition leads to the degradation of both the chemical and mechanical properties and is generally accompanied by heat generation and evolution of gases. In extreme cases self-heating may initiate burning and lead to an explosive accident [12]. This paper therefore presents a brief study of the effects on the thermal stability of the new energetic material BCHMX, of the additional ingredients which are incorporated in a plastic matrix. Two different binder systems (PIB plasticized by the polar plasticizer, DOS, and Fluorel binder) were used. For comparison, ε-HNIW (ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) were also evaluated when bonded by the same matrices. The effects of the polymeric matrices on the sensitivity and thermal stability of BCHMX and of the selected nitramines are presented. The heats of combustion of all of the prepared samples, as well as of the pure explosive fillers, were measured.

Experimental

Nitramines

RDX was a product of Dyno Nobel (mixture of Classes 2 and 5 according to the standard [13]), β-HMX was imported from Russia and its particle size was close to Class 3 according to the standard [14]), technical-grade ε-HNIW was a product of Explosia pilot plant, and BCHMX was prepared by a two-step continuous laboratory synthesis at the IEM.

Preparation of Plastic Explosives and PBXs

Two different polymeric matrices were used in the study. The first polymeric matrix (composition C-4 polymeric matrix) consisted of 25 wt% of polyisobutylene plasticized by 59 wt% of dioctyl sebacate (DOS) and 16 wt% of oil HM46. The preparative procedure for the plastic explosives is presented in reference [4]. The prepared samples are designated as RDX-C4, HMX-C4, BCHMX-C4 and HNIW-C4. The second polymeric matrix is based on Fluorel FT2481 binder (terpolymer of vinylidene fluoride, hexafluoropropylene and tetra-fluoroethene). The preparation of PBXs based on Fluorel using the slurry technique is presented in reference [5]. The prepared samples are designated as RDX-FL, HMX-FL, BCHMX-FL and HNIW-FL. All of the prepared samples contain 91 wt% of explosive and 9 wt% polymeric matrix.

Impact Sensitivity Measurements

A standard impact tester with exchangeable anvil (Julius Peters [15]) was used; the amount of tested substance being 50 mm^3; drop weights of 2 and 5 kg weight were used. The probit analysis [16] was used to determine the probability levels of initiation. The sensitivity obtained was expressed as the drop energy, E_{dr}, versus percentage of initiation. Only the 50% probability of initiation is used in this article and is reported in Table 1.

Friction Sensitivity Measurements

A BAM friction test apparatus was used to determine the sensitivity to friction by applying the standard test conditions [15]. The sensitivity to friction was determined by spreading about 0.01 g of the plastic 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 [16], only the normal force at which 50% of initiations occur is reported in Table 1 as the friction sensitivity.

Heat of Combustion measurements

An automatic isoperibolic combustion calorimeter MS10A, Laget, was used for determining the internal energy of combustion of all of the prepared samples as well as of the pure explosives fillers used. A weighed sample was placed in contact with platinum wire inside the bomb containing 5 mL of water (saturating the internal space with water vapor), and then filled with an excess of oxygen (20 atm). The high pressure of oxygen is necessary to ensure complete

combustion. The measurements are based on recording the temperature increase in the calorimetric vessel after the combustion process [17]. The results obtained from the measurements are reported in Table 1 as heats of combustion.

Thermal Stability Studies

A DTA 550 Ex apparatus was used for thermal analysis of the explosives [18]. The measurements were carried out at atmospheric pressure, with the tested sample in direct contact with the air. The tested sample (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminum oxide. A linear heating rate of 5 °C min^{-1} was used. The results are typical DTA thermograms with upwards oriented peaks for exotherms and downwards oriented peaks for endotherms. The temperatures of the maxima of the decomposition peaks at a linear heating rate of 5 °C·min^{-1} are listed for all samples in Table 1.

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

No.	Code designation*	Impact sensitivity [J]	Friction sensitivity [N]	DTA Peaks at 5 °C·min^{-1}	Heat of combustion [J g^{-1}]
1	RDX cryst.	5.6	120	214.6	9522
2	HMX cryst.	6.4	95	273.2	9485
3	BCHMX cryst.	3.2	88	225.3	9124
4	ε-HNIW cryst.	4.1	64	222.4	8311
5	RDX-C4	21.1	213	212.9	12356
6	HMX-C4	20.2	193	261.5	12382
7	BCHMX-C4	11.6	181	215.9	12163
8	HNIW-C4	12.4	148	212.3	11452
9	RDX-FL	10.8	352	221.2	9662
10	HMX-FL	10	312	275.3	9647
11	BCHMX-FL	5.4	299	225.5	9379
12	HNIW-FL	7.2	255	223.8	8634

*Each code designation is described in the experimental part under the sub-title "Preparation of plastic explosives and PBXs".

Analysis Method

High performance liquid chromatography (HPLC) was used to determine the solubility of the tested nitramine explosives in the plasticizer used in the studied matrix. The liquid chromatography system consisted of the following components (all from Agilent 1200 series): degasser G1322A, pump G1311A,

autosampler G1329, column thermostat G1316A, and diode array detector G1315D operated by software HP Chem Station B03.01. The column material was BDS Hypersil C-18, particle size 5 μm, pore size 12 nm and column dimensions 250 mm × 4.6 mm.

Pure BCHMX (0.1 g) was placed in a beaker containing 10 mL of dioctyl sebacate and magnetically stirred for 15 min at normal temperature and pressure. The contents of the beaker were then filtered to remove the solid BCHMX from the dioctyl sebacate. The same procedure was repeated with another sample at 70 °C under vacuum. The solutions obtained were diluted with mobile phase (water/methanol 50:50) and then injected into the HPLC. The flow rate of the mobile phase was 1 mL·min^{-1}. The peak assignment was based on retention times acquired from pure standards measured under the same conditions.

Results and Discussion

In order to study the effects of the selected matrices on the characteristics of the explosives, a comparison between the results is presented. Figure 1 shows a comparison between the results of the heat of combustion measurements and the impact energy needed for 50% probability of initiation of all of the samples studied.
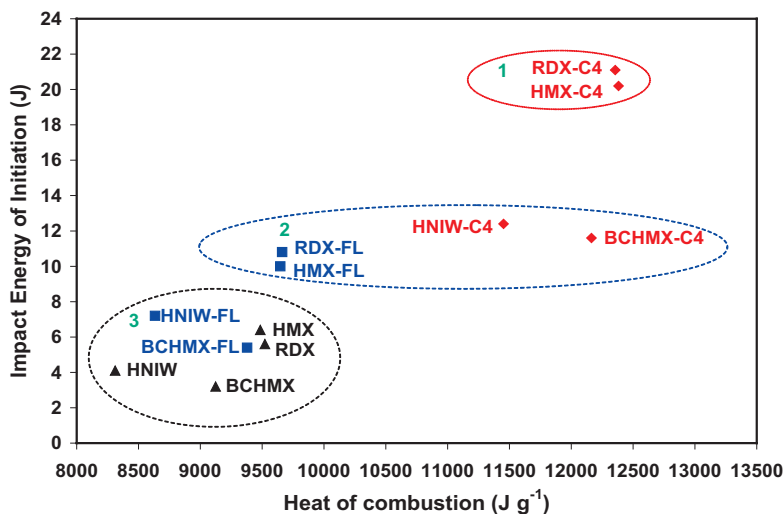

Figure 1.   Results of heat of combustion measurements compared with the impact energy of initiation for all the samples studied.

Regarding the impact sensitivity, three groups of explosives are presented in Figure 1. The first group includes RDX-C4 and HMX-C4 which have low sensitivity to impact (more than 20 J) and have the highest heats of combustion of all of the samples studied. The second group includes HNIW-C4, BCHMX-C4, RDX-FL and HMX-FL. This group has impact sensitivities between 10-13 J, whilst a significant difference appeared between them regarding the heats of combustion. The third group represents sensitive samples (impact sensitivity less than 8 J) and low heats of combustion. The figure shows that elastic samples (plasticized by DOS and oily material) have lower impact sensitivities and higher heats of combustion than samples based on Fluorel binder for each individual explosive.

Furthermore the heats of combustion of samples based on RDX and HMX have nearly the same values for each individual polymeric matrix. Samples based on BCHMX have heats of combustion lower than samples based on RDX and higher than samples based on HNIW for each individual polymeric matrix.

On the other hand, Figure 2 shows a comparison between the frictional force needed for 50% probability of initiation and the decomposition temperatures of all of the samples studied.
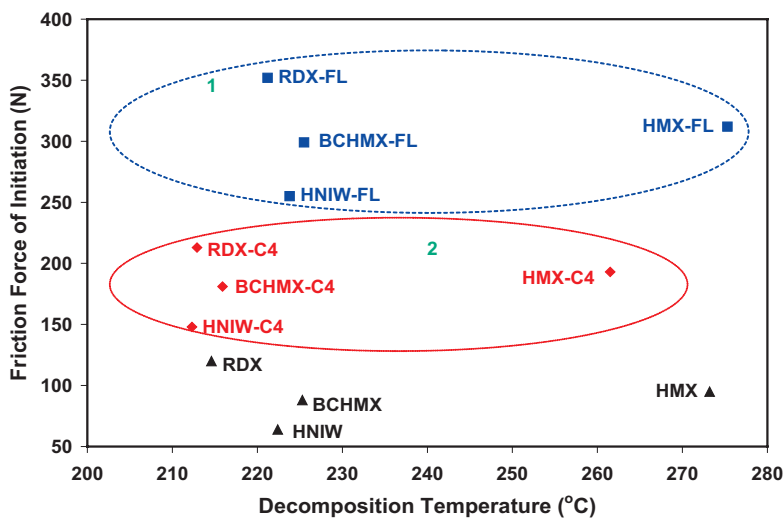
Figure 2. Comparison between the decomposition temperature by DTA and the frictional force of initiation for all of the samples studied.

It is clear from Figure 2 that Fluorel binder has a great effect on decreasing the friction sensitivity of each individual explosive, where all of the samples based on Fluorel have lower friction sensitivities than all of the other samples

studied. This means that a softened polymeric matrix (containing DOS) has a lower desensitizing effect than a binder with high mechanical properties in the case of friction sensitivity. For each individual polymeric matrix, samples containing RDX have the lowest friction sensitivity while samples containing HNIW have the highest. Sensitivity to friction of samples based on HMX and BCHMX are close to each other. At the same time, samples based on the C4 matrix have a lower decomposition temperature than the individual pure explosives. To understand the reasons for these results, typical DTA measured peaks are presented in Figure 3.
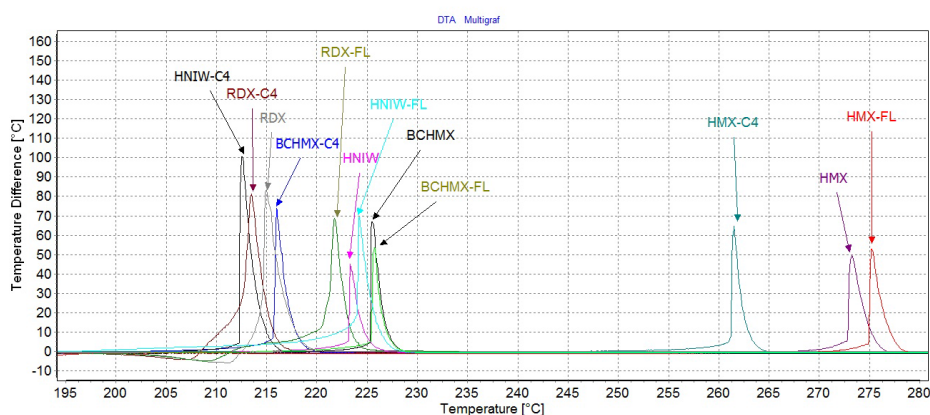
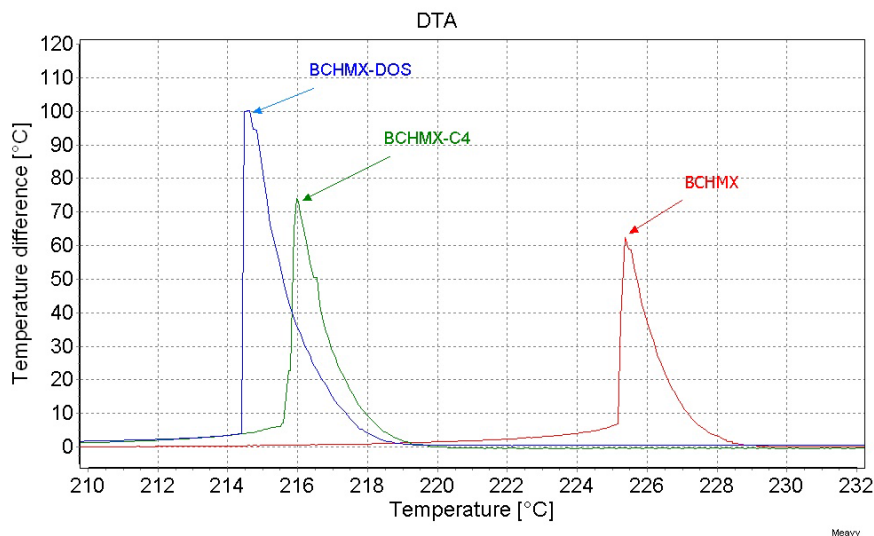**Figure 3.**   Typical DTA measured peaks for all of the samples studied.

In Figure 3, the thermal behavior of the pure explosives studied is compared with the samples prepared based on the C4 matrix and on Fluorel binder. The DTA measurements of samples based on the C4 matrix showed that the peak temperatures of decomposition of these mixtures are lower than those of the corresponding explosives in their pure state. These results might be due to the presence of the polar plasticizer (DOS) in the polymeric matrix acting as a solvent for the explosives and leading to a decrease in the decomposition temperatures of the explosives.

At the same time the peak temperatures for all of the samples prepared based on Fluorel binder are higher than those of the pure explosives. The slight increase in the decomposition temperatures proves that Fluorel binder increases the thermal stability of the explosives. BCHMX-FL has a higher decomposition temperature than all of the samples based on RDX and HNIW.

Also it is clear that the decomposition temperature of BCHMX-C4 is lower than that of pure BCHMX by nearly 10 °C. To understand the reason for this

result, a new sample was prepared by mixing pure BCHMX with 5.3 wt% of DOS plasticizer (the same wt% used in the C4 polymeric matrix) without the addition of any binder and was designated as BCHMX-DOS.

The thermal behavior of this new sample was studied by the DTA technique using the same conditions as in the case of the previous samples. The DTA peaks of the new sample BCHMX-DOS, pure BCHMX and BCHMX-C4 are presented in Figure 4.


Figure 4.   Typical DTA measured peaks for BCHMX-DOS compared with those for BCHMX-C4 and pure BCHMX at 5 °C·min^{-1}.

Figure 4 clearly shows that BCHMX-DOS has a lower decomposition temperature than either pure BCHMX or BCHMX-C4. This fact agrees with the suggestion that DOS decreases the decomposition temperature of the pure explosive. Furthermore the higher decomposition temperature of BCHMX-C4 compared with BCHMX-DOS proves that the polyisobutylene binder (PIB) acts as an inhibitor and decreases the negative effect of DOS on the thermal stability of the explosive.

In order to check the assumption that the polar plasticizer may act as solvent for the pure explosives, pure BCHMX was placed in beaker containing DOS and stirred as discussed in the analysis method. The results of the liquid chromatography measurements are presented in Figure 5.
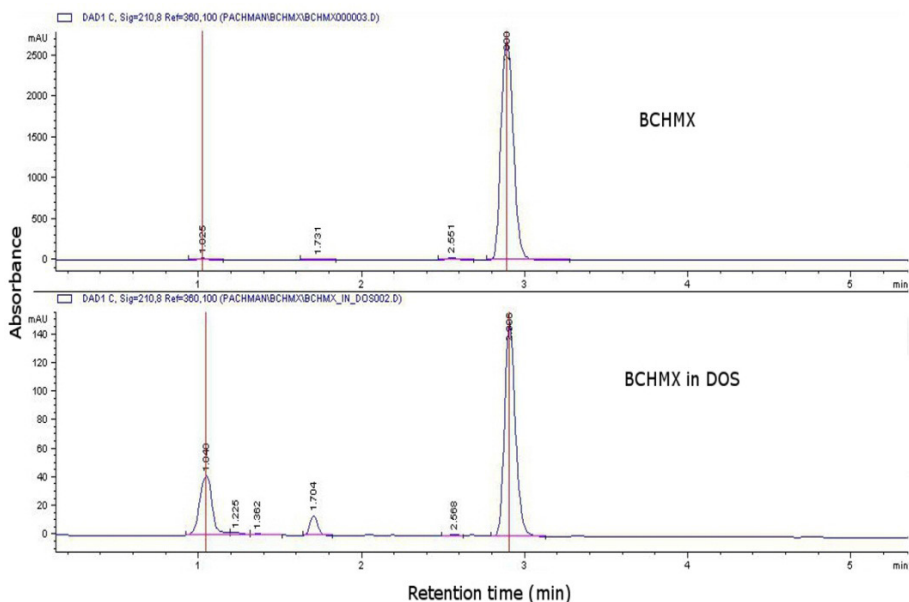
Figure 5.   HPLC chromatogram of standard BCHMX and BCHMX in DOS.

In the chromatogram, standard BCHMX appears as a peak at retention time 2.88 min. It also shows the relatively high purity of the sample. In the case of the DOS sample, a peak appeared at 2.89 min retention time, representing BCHMX, which means that the tested sample of DOS contains BCHMX. It was therefore proven that the plasticizer dissolves part of the energetic filler in the plastic explosive, and explains why the decomposition temperatures of samples based on DOS are lower than those of the pure explosives.

Conclusions

Addition of the selected polymeric matrices to the nitramines studied increased their heat of combustion. Samples based on the C4 matrix have higher heats of combustion and lower sensitivities to impact than those based on Fluorel binder for each individual explosive. Samples based on Fluorel binder have lower friction sensitivities than samples based on the C4 matrix for each individual explosive. The Fluorel binder showed a positive effect on the decomposition temperatures of the explosives whilst the C4 matrix decreased the decomposition temperatures of these explosives. The suggestion that DOS

(polar plasticizer) acts as a solvent for BCHMX (explosives) was confirmed by the HPLC study. Furthermore the idea that the decreased decomposition temperatures of the explosives when DOS was used, was due to DOS dissolving the explosives, was confirmed.

References

[1] Park C., Jeong S., Huh H., Park J., Mechanical Characteristics of PBX Simulant Considering Strain Rate Effect, *31st Int. Pyrotechnics Semin.*, Colorado, USA, **2004**, 679.

[2] Jemmett P., Davies N., Mechanical and Chemical Characterization of a Polymer Bonded Explosive During Aging, *42nd Int. Annu. Conf. of ICT*, Karlsruhe, Germany, **2011**, 82/1-82/11.

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

[4] 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.

[5] Elbeih A., Pachman J., Zeman S., Trzcinski 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.

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

[7] 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.

[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] Zeman S., Elbeih A., Akštein Z., Preliminary Study of Several Plastic Bonded Explosives Based on Cyclic Nitramines, *HanNeng CaiLiao* (*Chinese Journal of Energetic Materials*), **2011**, *19*(1), 8.

[10] 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.

[11] Zeman S., Elbeih A, Yan Q., 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*(2), 1503.

[12] Perry W., Zucker J., Dickson P., Parker G., Asay B., Interplay of Explosive Thermal Reaction Dynamics and Structural Confinement, *J. Appl. Phys.*, **2007**, *101*, 074901.

[13] *Detail Specification RDX*, Military Standard MIL-DTL-398D, US Dept. of Defence, April 17, **1999**.

[14] *Detail Specification HMX*, Military Standard MIL-DTL-45444C, US Dept. of Defence, Nov. 26, **1996**.

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

[16] Finney D.J., *Probit Analysis*, Cambridge University, 3rd ed., **1971**.

[17] *Solid fuels – Determination of Heat of Combustion by Calorimetric Method in the Pressure Vessel and Calculation of Calorific Value*, Czech Tech. Standard ČSN ISO 1928, Czech Inst. of Standards, June **1999**.

[18] Krupka M., Devices and Equipment for Testing of Energetic Materials, *New Trends Res. Energ. Mater.*, *Proc. Semin., 4th*, Univ. Pardubice, **2001,** 222.