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# Friction Sensitivity of Nitramines. Part Ⅰ: Comparison with Impact Sensitivity and Heat of Fusion

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**Abstract**: Fractions of β-HMX (β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane) have been used to demonstrate the mutual relationship between friction and impact sensitivities. Inclusion of an additional twelve nitramines into this scenario resulted in a series of partial relationships, which were determined from the molecular structure of these substances. It was also found that there is a relation between increasing heats of fusion of the nitramines studied and their decreasing friction sensitivities. Comparison of friction sensitivity with heats of fusion, $\Delta H_{m,tr}$ of the studied nitramines shows that the increase in $\Delta H_{m,tr}$ values is more or less connected with a decrease in friction sensitivity.

**Key words**: explosives; friction; heat of fusion; impact; nitramines

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## 1 Introduction

Sensitivity of high energy materials (HEMs) represents a very important characteristic from the standpoint of safety during their manufacture and handling. This sensitivity is primarily due to the chemical character of these materials, which enables using the term "initiation reactivity of HEMs" in this situation [1]. Over the last 20 years, the main interest in HEMs has been focused on studies of shock and impact sensitivities. However, no such attention has been focused on the characteristics of friction sensitivity (*FS*) of energetic materials. Our experience shows that the results of *FS* determination can be heavily influenced by "human variability". Nevertheless, careful measurements by a single researcher provide results showing mutual relationships which are also correlated with the output of other stability and physico-chemical tests; our intention is to document this correlation in this series of papers. The current paper represents a study of *FS* of the technically attractive explosive β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (β-HMX) and a set of interesting nitramines comparing their impact sensitivity and heats of fusion.

## 2 Substances and Data Sources

The relationship between granule size and friction sensitivity was studied using HMX of Russian origin (its quality was close to Class 3 according to the standard [2]), which was separated into fractions by means of sifting; the individual fractions (oversize fractions) are denoted in Table 1 by the respective mesh sizes. Each of these fractions was characterized by determination of its granule size distribution performed by laser radiation scattering with a Horiba Partica LA-950® apparatus; the nitramine suspension for the measurement was prepared by dispersing particles of the sample in demineralized water with the addition of the non-ionogenic surfactant Sologela W®. From this measurement an estimate of the specific surface area of the given fraction was also obtained. The results are summarized in Table 1.

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**Table 1** A summary of the HMX fraction characteristics and their friction and impact sensitivities

| The HMX fraction retained using mesh size of (μm) | Median /μm | Specific surface /$cm^2 cm^{-3}$ | Friction sensitivity/N | Impact sensitivity/J |
|---|---|---|---|---|
| 20 | 56.94 | 1206 | 152.26 | 6.35 |
| 50 | 87.45 | 920 | 141.99 | 6.55 |
| 100 | 127.15 | 759 | 141.70 | 6.65 |
| 200 | 223.14 | 335 | 142.46 | 6.88 |
| 315 | 406.03 | 147 | 126.88 | 9.17 |
| 400 | 575.37 | 105 | 114.12 | 10.72 |

Table 2 presents a set of cyclic nitramines and their impact sensitivity data. Purity of the nitramines tested in this study was checked by means of HPLC. The sensitivity was determined by means of a standard impact tester with an exchangeable anvil (Julius Peters [3,4]), the amount of tested substance being 40 $mm^3$ [3]. The detection was based on the sound effect [4,5,6]. The drop hammers of 1 and 2 kg weight were used [3,4]. A probit analysis [7] 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 cases of 50 % probability of initiation are used in this article and reported in Tables 1 and 2. A part of the $E_{dr}$ values was taken from the literature [5,6,8,9-11]. All the $E_{dr}$ values are presented in Table 2 and for the HMX fractions in Table 1. Table 2 also presents the heats of fusion, $\Delta H_{m,tr}$, taken from References [12,13]; for a given substance these values represent the sum of heats of all polymorphic transitions and the heat of melting [14].

The friction sensitivity of all the nitramines studied was determined by means of a BAM friction test apparatus; this was used to determine the sensitivity to friction by applying the standard test conditions [4]. The sensitivity to friction was determined by spreading about 0.01 g of the dry 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

**Table 2** A survey of the nitramines studied, their impact and friction sensitivities and their heats of fusion, $\Delta H_{m,tr}$ (see in papers [11-13] and references therein)

| Data No. | Chemical name of nitramine | Code designation | Impact sensitivity | | Friction sensitivity/N | Heat of fusion [12,13] $\Delta H_{m,tr}$/kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | $E_{dr}$/J | Ref. | | |
| 1 | 2-Nitro-2-azapropane | DMNA | | | 82.4 | 17.26 |
| 2 | 1,4-Dinitro-1,4-diazabutane | EDNA | 8.33 | 6 | 47.4 | 23.24 |
| 3 | 2,4-Dinitro-2,4-diazapentane | OCPX | 65.60 | a | 74.9 | 16.35 |
| 4 | 2,4,6-Trinitro-2,4,6-triazaheptane | ORDX | 29.50 | a | 147.7 | 34.10 |
| 5 | 2,5-Dinitro-2,5-diazahexane | DMEDNA | 21.04 | a | 57.9 | 29.41 |
| 6 | 1,3-Dinitroimidazolidine | CPX | 17.96 | 11 | 57.7 | 22.57 |
| 7 | 1,4-Dinitropiperazine | DNDC | 42.7 | a | 122.3 | 33.82 |
| 8 | 1,3,5-Trinitro-1,3,5-triazinane | RDX | 5.58 | 6 | 148.5 | 33.01 |
| 9 | 1,3,5-Trinitro-1,3,5-triazepane | HOMO | 4.55 | 11 | 119.96 | 27.73 |
| 10 | 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane | HMX | 6.37 | 6 | 154.4 | 32.10 |
| 11 | *cis*-1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]-imidazole | BCHMX | 2.98 | 9 | 66.12 | 31.89 |
| 12 | 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane | HNIW | 11.90 | 10 | 69.0 | 43.03 |
| 13 | 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane | TEX | 23.00 | 8 | 161.3 | 36.10 |

Note: a) the value was measured during this study.

the porcelain pistil and the plate. Initiation of the sample was observed using sound, smoke appearance, or from the characteristic smell of the decomposition products. Using the probit analysis [7] (35 measurements per sample), only the normal force at which 50 % of initiations occur is reported as the friction sensitivity in Tables 1 and 2.

## 3 Results and Discussion

In our earlier work concerning plastic bonded explosives based on nitramines [15] we found a semi-logarithmic relationship between their impact and friction sensitivities. The same relationship follows from a similar comparison of these sensitivities for the HMX fractions studied, as can be seen in Fig. 1; in this diagram, decreasing granule size is related to decreasing friction sensitivity and increasing impact sensitivity. The value of impact sensitivity (drop energy) published for HMX [6] corresponds well in Table 2 with the value for the 20 – 50 μm fraction of this nitramine from Table 1. It has to be emphasized that the published drop energies of this kind (e. g., see Refs [6,10]) correlate well with the characteristics of the molecular structure of polynitro compounds in general [1,5,13]. Thus, the using the relationship in Fig. 1, an *FS* value of 152.6 N would be assigned to the corresponding HMX fraction; from Table 2 it can be seen that pure HMX (crystallized in the laboratory) exhibits a value of 154.4 N, which is in good agreement and this value should be applicable to molecular-structural and other correlations with *FS*.

The difference between initiation by impact (uniaxial compression) and initiation by friction (shear slide with a fixed volume) is described in the theoretical paper by Zhang [16] concerning the influence of the desensitizing mechanism of olefins; the friction force during shearing is proportional to the contact area. This contact area is proportional to the radius of the spheres [17]. In our case it should be the smallest for the fine HMX fractions in Fig. 1, which are characterized by the lowest *FS* values. An approximate relationship between the specific surface of particles of the HMX fractions studied and the corresponding *FS* values is given in Fig. 2; for the 50 – 200 μm fractions (median 87.45 – 223.14 μm) the *FS* values are practically identical, which is also reflected by small differences between the impact sensitivity values of the fractions mentioned. Interpretating the figures in Fig. 2 can be carried out as follows: decreasing HMX granule size corresponds to an increase in the number of the hot spots on their surface (it may be documented by trend in the specific surface) which leads to increasing sensitivity during the uniaxial compression, while in the case of shear slide, with a fixed volume, the same trend leads to a loss of a shear modulus (the resultant dust behaves as a liquid) -here for a specific surface greater than 1200 $cm^2 cm^{-3}$. The problem of a roughly constant *FS* (and also corresponding impact sensitivity) in a certain range of specific surface sizes (granule sizes) needs further study.

The theoretical analysis of friction sensitivity (*FS*) [18] considers the change of friction force acting on a high-energy explosive due to melting of the explosive. One of the characteristics of melting is the heat of fusion, $\Delta H_{m,tr}$. The relationships of impact sensitivity of polynitro compounds with the corresponding $\Delta H_{m,tr}$ values, which have been reported, show the dependence of this sensitivity upon intermolecular interactions in the crystal (i. e. the stabilizing influence of the crystal lattice) [1,5]. No analogous relationship for the friction sensitivity has been studied so far; in this paper, Fig. 3 shows this, representing a linear relationship between *FS* and $\Delta H_{m,tr}$ values; this is different from analogous relationships for the impact sensitivity [1,5] (semi-logarithmic relationship in the case of detection as "the first reaction" and a logarithmic one for detection by sound). Therefore, the mechanism of transfer of the friction impulse to the reaction centre of the HEM molecule should be different too. In Fig. 3 the nitramines studied are divided into three groups on the basis of molecular-structural kinship and, hence, similarity of the initiation reactivity. In all the three groups, the increase in the $\Delta H_{m,tr}$ values is connected with a decrease in the friction sensitivity. This trend is reversed in the case of the impact sensitivity detected by sound [1,5]. and as already mentioned it is described by logarithmic relationships [1,5].

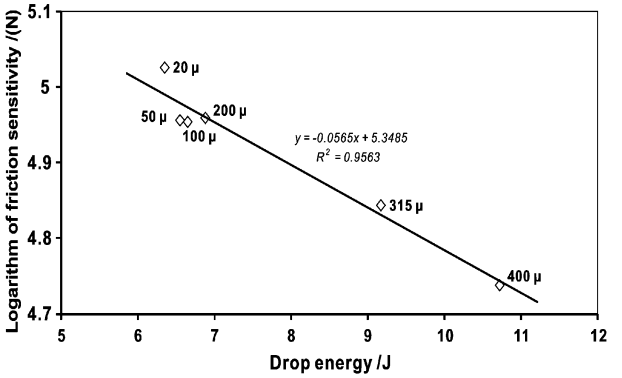


**Fig. 1** Comparison of impact sensitivity (expressed as drop energy) with friction sensitivity of the HMX fractions studied (The numbering of the points in Fig. 1 corresponds to the fraction designation according to Table 1)

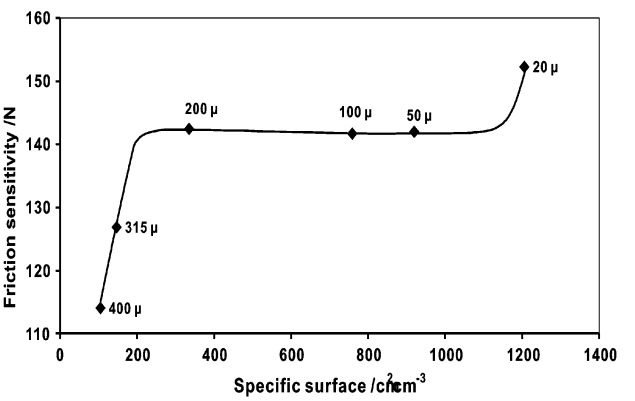


**Fig. 2** Comparison of friction sensitivity with specific surface of the th – e HMX fractions studied (The numbering of the points corresponds to the fraction designation according to Table 1)

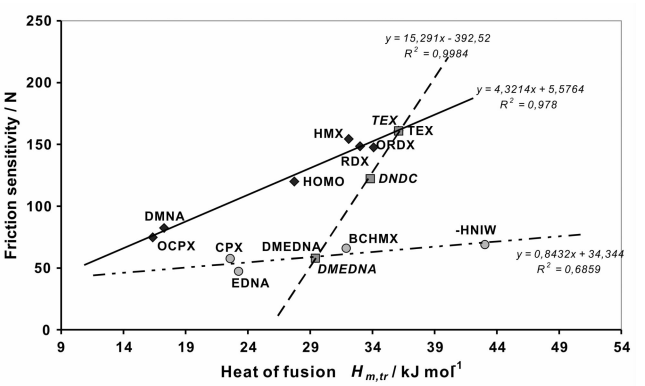


**Fig. 3** Comparison of friction sensitivity with heat of fusion of the nitramines studied as listed in Table 2

The relationship between the friction and impact sensitivities of nitramines from Table 2 is shown in Fig. 4. The nitramines studied here are divided into four groups on the basis of their molecular-structural kinship. Group A contains cyclic compounds with a methylenenitramine arrangement, differing from one another by the flexibility of their molecules: $\beta$-HMX has four polymorphic modifications, RDX has two, HOMO has not yet been described from this point of view, and BCHMX has a rigid skeleton and a sensitivity to mechanical stimuli at the level of that of pentaerythritol tetranitrate (PETN)[9]. Straight line B in Fig. 4 seems as if it should describe an imaginary composition of the skeleton of globular HNIW molecule, viz. as composed of two molecular skeletons of HOMO and two skeletons of CPX. Straight line C includes compounds with an ethylenedinitramine skeleton in the molecule, a skeleton to which "desensitizing" substituents are attached (in the order from EDNA to DNDC). One can imagine Group D compounds to be generated from a dimethylnitramine fragment; in the sense of Fig. 3 the respective $\Delta H_{m,tr}$ values decrease in the series from TEX to OCPX. Hence the molecular-structural and intermolecular interaction factors are the justification for the division of the nitramines studied in the sense of Fig. 4.

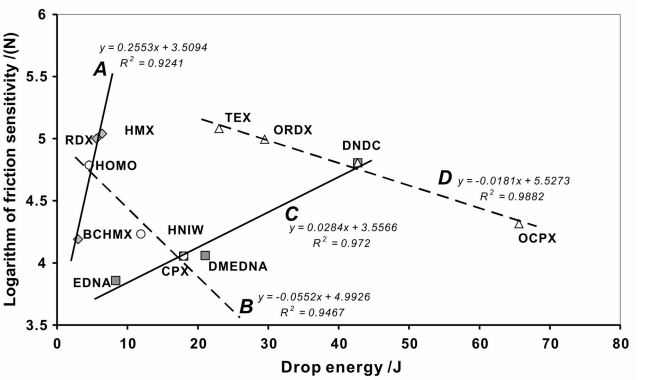


**Fig. 4** Semi-logarithmic relationship between the friction sensitivity and impact sensitivity, expressed as drop energy, of the nitramines studied as listed in Table 2

## 4 Conclusion

The relationship between friction sensitivity (*FS*, shear slide with fixed volume) and impact sensitivity (IS, uniaxial compression) can be described by a semi-logarithmic equation. The investigation of HMX fractions with different granulometric distributions showed that the lowest IS is connected with the highest *FS* and vice versa; there exists a relatively wide range of HMX granule sizes in which the *FS* is practically the same. Inclusion of a wider assortment of nitramines into the above-mentioned study results in their splitting into a number of partial groups, which are relatively closely connected with the molecular-structural characteristics of the nitramines studied. Comparison of *FS* with heats of fusion, $\Delta H_{m,tr}$ shows that the increase in $\Delta H_{m,tr}$ values is more or less connected with a decrease in friction sensitivity.

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