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Basic Characteristics for Estimation Polynitrogen Compounds Efficiency

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Abstract: Basing on analysis of experimental data for physicochemical parameters of 300 energetic compounds from different chemical classes, a set of basic characteristics (enthalpies of formation, molecular crystals densities, detonation parameters, as well as sensitivity to different kinds of impact) has been considered and some calculations schemes have been elaborated to estimate these characteristics for polynitrogen compounds. The limits of physicochemical values for energetic materials (EMs) parameters have been estimated. A large set of compounds has been investigated and some of them seem to be rather effective as explosives or monopropellants. There are about ten powerful compounds (e.g. octanitrocubane, hexanitrohexaazaisowurtzitane, azanitrofurazan, etc.), explosives-oxidizers (such as ammonium dinitroamide and bis(difluroamine-dini troethil) nitroamine) and several hypothetic substances (not synthesized yet), such as octaazacubane, octaazatetraen, tetranitrotetraazacubane etc. Energetic properties were estimated as for individual compounds, as well as for energetic compositions containing these substances together with other ones in the aim to estimate the effectiveness of their use as components of solid composite propellants.

Keywords: polynitrogen compounds, oxidizers, hypothetic nitrogen allotropes, enthalpy of formation, density, detonation parameters, sensitivity

Introduction

During a few last decades intensive investigations allowed to synthesize a huge amount of new energetic compounds, having rather diversified chemical structures, a wide range of energetic, explosive and physicochemical properties. The level of the heat of explosion achieved 7530 kJ/kg, pressure of detonation ~40-44 GPa, metal acceleration performance ~108-110% in velocity of accelerated plate, or ~112-120% in energy (in comparison with 1,3,5,7-tetranitro-1,3,5,7-tatraazacyclooctane (HMX)). The shock waves sensitivity level of most high-power explosives is rather high and even impermissible (critical pressure of the detonation initiation is about ~0.3-1.0 GPa), which corresponds to the best sensitivity level of pentaerythritol tetranitrate (PETN).

In recent years, new studies have appeared considering hypothetic polynitrogen compounds and nitrogen allotropes. Investigations included a large set of theoretical estimations on the possibility of their real obtaining, forecasts of possible levels of energetic and detonation parameters and calculations of the main physicochemical properties (molecular crystal density and enthalpy of formation) [1-5]. Prediction of structure for the compounds with extremely high energetic parameters has been accomplished basing on the same methods that had been applied for calculation of the similar parameters for real compounds and therefore it was not correct every time since it is not clear yet whether their energetic values are really maximal. In this paper we have tried to solve this problem and to estimate the energetic level which may be achieved.

Method for Explosives Properties Forecast

To develop the system of explosion and other parameters estimation we have studied experimental data for about 300 individual explosives considering the following characteristics: heat of explosion (for 55 compounds), detonation velocity (138 ones), C-J-detonation pressure (90 ones), shock sensitivity by large scale gap test (25 ones), metal acceleration performance (74 ones) [6], as well as some others.

Experimental explosives set under consideration had the following range in element content (gram-atoms/kg): $C \in [0; 44.1]$, $H \in [0; 49.1]$, $N \in [7.0; 39.3]$,

$O \in [0; 40.8]$. To estimate the correlations between explosion parameters, on one hand, and the element content and the molecular structure, on the other hand, we have developed new methods for the main explosive parameters estimation. The regression analysis procedure has been used. Average (%) and root-mean-square errors were the following: for detonation velocity: 0.077 and 1.256, for C-J-pressure: 0.59 and 6.84; for the metal acceleration performance: 0.11 and 1.88; and for the heat of explosion: 0.28 and 3.45, respectively. The value of the relative deviation of the calculations was almost constant for all the area of variations.

As a result, the complex system for estimation of the main parameters of energetic compounds includes 25 equations and the main ones are represented below.

It is known that the determination of the metal acceleration performance is one of the main ways to estimate the effectiveness of individual explosives, as well as of compositions containing them. The most common, the metal acceleration, is evaluated with the measurement of the velocity for the expansion of cylindrical shell, accelerated by the products of sliding detonation or with the measurement of the velocity of a plate throwing. These methods together with the relative impulse determination allow to estimate the velocity of the throwing body too. The data on the dynamics of cylindrical shells expansion may be used for derivation of the equation for the state of detonation products. Some of the most widely used methods are considered rather in detail [6].

In our study the metal acceleration performance in comparison with HMX (η) has been estimated from the velocity of butt end bar thrown by explosion products (eq. 1):

$$\eta = 1.23 \cdot \rho^{0.871} \cdot Q_{cal}^{0.432} \cdot N_g^{0.230} \quad (1)$$

The critical pressure of detonation initiation (P_{cr}) is also quite valuable parameter for explosives effectiveness evaluation. The method of its measurement is widely known as Gap-test [7, 8] (the transfer of an initiating variable impulse through an inert barrier). This parameter is the most acceptable among all diversity parameters describing explosives safety for preliminary choice of explosives components. P_{cr} value correlates with characteristics describing the material stability to shock and to penetrative actions, as well as with parameters of combustion to explosion transfer.

We calculate P_{cr} as shock sensitivity of a compound in large scale gap test (eq. 2):

$$P_{cr} = (\rho \cdot B)^{2.732} Q_{max}^{-1.534} \cdot \alpha^{-1.105} - 5 \quad (2)$$

For many decades detonation parameters and, first of all, the detonation velocity (D), have been the most often evaluated and under discussion. Generally, the interest in these parameters is due to the fact that for a long time the effectiveness of explosives in many applications has been associated with the detonation velocity itself. However, a lot of data persuade us to use the calorimetric heat of explosion as more preferable characteristic for preliminary estimation of explosion effectiveness [9, 10]. Anyway, the detonation velocity still remains in literature the main parameter of explosives, maybe traditionally. Undoubtedly, D is a rather important parameter and the relatively simple method of its measurement in comparison with other parameters (as well as accuracy and repeatability factor) allows to use it sufficiently when considering some aspects of the explosion processes. In our investigation the detonation velocity (D) has been estimated by eq. 3:

$$D = 0.481 \cdot \rho^{0.607} \cdot c^{0.089} \cdot \alpha^{0.066} \cdot Q_{cal}{}^{0.221} \cdot N_g{}^{0.19} \quad (3)$$

C-J-detonation pressure ($P_{C\text{-}J}$) is also considered for explosives effectiveness evaluation. However, in our opinion, this value determines just a shattering effect of the explosion. We suggested estimation of the C-J-detonation pressure ($P_{C\text{-}J}$) by eq. 4:

$$P_{C\text{-}J} = 2.139 \cdot 10^{-2} \cdot \rho^{2.100} \cdot c^{0.102} \cdot \alpha^{0.147} \cdot Q_{max}{}^{0.519} \cdot N_m{}^{0.554} \quad (4)$$

Calorimetric heat of explosion (Q_{cal}) is the main energetic parameter of explosion and widely used for preliminary evaluation of energetic abilities of explosives, as well as for the calculation of different kinds of explosion and detonation parameters. The Q_{cal} numerical value is equal to the maximal efficiency work of explosion. The method of this parameter estimation [11-13] is based on measurement of the temperature growth (due to heat release at explosion) of calorimetric liquid where a calorimetric chamber with an explosive sample was put.

Calorimetric heat of explosion for compounds containing C,H,N,O-elements has been estimated by eq. 5:

$$Q_{cal} = Q_{pvm} \cdot 4.261 \cdot \rho^{0.291} \cdot c^{0.049} \cdot d^{0.072} \cdot (\Delta H_f{}^0 + 1000)^{-0.261} \cdot a^{-0.107} \cdot b^{-0.012} + \Delta H_f{}^0 \quad (5)$$

Calorimetric heat of explosion for compounds containing C,H,N,O,F-elements has been estimated by eq. 6:

$$Q_{cal} = Q_{pvm} \cdot 0.59 \cdot \rho^{0.075} \cdot (\Delta H_f{}^0 + 1000)^{0.018} \cdot a^{-0.063} \cdot c^{0.132} \cdot e^{0.027} + \Delta H_f{}^0 \quad (6)$$

The amount of moles of gaseous products (N_g) is determined in the same experiment as the heat of explosion by gases pressure measurement after the sample explosion [11-13]. Together with the heat of explosion, the value N_g is used for calculations of detonation parameters and explosion action. The amount of moles (N_g) of gaseous combustion products has been calculated according to eq. 7:

$$N_g = 0.777 \cdot \rho^{-0.153} \cdot B^{0.715} \cdot (\Delta H_f^0 + 1000)^{0.1} \cdot Q_{max}^{0.238}, \quad (7)$$

where: ρ – density of the explosive; ρ_{max} – maximal theoretic density of the explosive; $\rho_{rel.} = \rho/\rho_{max}$; Q_{max} – maximal heat of explosion; B – gross-sum of gram-atoms of all chemical elements containing in 1 kg of the explosive under consideration,·α – coefficient of the oxidizer excess; Q_{cal} – calorimetric heat of explosion; N_m – amount of moles of gaseous combustion (explosion) products corresponding to Q_{max}; a, b, c, d, e – amount of gram-atoms of chemical elements in 1 kg of the explosive $C_aH_bN_cO_dF_e$; Q_{pvm} – maximal energy of combustion products; ΔH_f^0 – enthalpy of formation.

We compared the accuracies of the main physical and chemical parameters calculations in our method with some others [12, 14-16]. Using the dispersive analysis we showed that our technique (equations 1-7) has higher accuracy in comparison with the above-mentioned methods.

The estimation of about 1100 individual explosives or potential compounds of propellants has been carried out using the complex system for explosives properties forecast. In the substances set under consideration there were represented different classes of organic compounds with the following range in elements content (gram-atoms/kg): $C \in [0; 45.8]$, $H \in [0; 60.0]$, $N \in [7.0; 49.9]$, $O \in [0; 43.0]$ (for full-nitrogen compounds (N_x), naturally, N = 71.4 gram-atoms/kg). Such a wide range in elements content considers, practically, all the region of existence for any covalent explosive substance. Thus, basing on such a wide set of base substances and using our computing methods, we may affirm that the developed complex system for explosives properties forecast is quite reliable.

Below we present some results of the forecast estimation in the context of known substances, and the results for hypothetic substances with the following requirements to the «new powerful» explosives:

- density of molecular crystals $\rho \geq 1.90$ g/cm^3,
- heat of explosion ≥ 5800 kJ/kg,
- coefficient of the oxidizer excess $\alpha = O/(2C+0.5(H-Cl))$ should be close to 1.

Results and Discussion

Powerful explosives

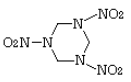
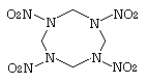
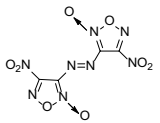
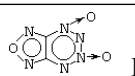
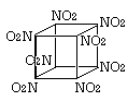
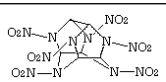
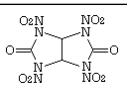
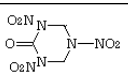
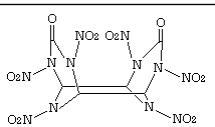
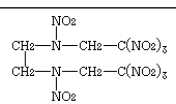
In seventies and eighties of the 20th century investigators had been expecting that explosive characteristics, providing use and technology safety of compounds, must be close to 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) parameters. However later, after starting investigations and finally wide applying of such perspective powerful explosives as hexanitrohexaazaisowurtzitane (CL-20) and 1,3,3-trinitroazetidine (TNAZ), the level of the safety performances appreciably decreased (up to PETN level). The increase of performance may be accomplished either with the balancing of oxidizer and combustible fragments in the substance under consideration or with the introduction of high-enthalpy structures. Table 1 presents the main parameters, determining the increase of the explosive energy. If in column D there are two values, the first one is the *experimental* detonation velocity D and the second one is the real density of the charge (i.e. 8600_{1730}); if in column D there is only one value, it means the *calculated* detonation velocity for monocrystal density.

Let us consider the main ways to energy increase for some nitramines (see, for example, K-6 (keto-RDX) [19] and 1,1,1,3,6,8,8,8,-octanitro-3,6-diaza-octane (ZOX) [20]). In a molecule of HHTDD-1 (2,4,6,8,10,12-hexanitrazatricyclo(7.3.0.0) dodecan-5,11-dione, #9, Table 1) the hydrogen content is lower than in RDX. Besides, the number of cycles is higher and that is a potential reason for increasing the density (up to 2.07 g/cm^3). Correspondingly, even in the case of lightly increasing explosion, heat value in the metal acceleration performance for HHTDD-1 is already 105.7% relatively to HMX. Parameters of CL-20 (for example, [21, 22]) also illustrate the influence of the number of strained cycles and the decrease of hydrogen content upon the performance.

In the seventies and eighties furazans and furoxans derivatives had been considered as perspective explosives. ANF (4,4'-dinitro-azofuroxan) [8, 23] contains furoxan and diazene groups and that is the main reason for the high energetic capacity and for the high value in metal acceleration performance. But at the same time, that is a reason for unacceptable low safety properties of ANF (see, for example, the value of shock sensitivity (P_{cr})).

The compound furazanotetrazinedioxide (FTDO) [24] has extremely high enthalpy of formation (among all synthesized explosives), as well as the worse safety properties (e.g. shock sensitivity values). Resuming the analysis of considered parameters of furoxan derivatives we have to notice that structural peculiarities of these substances, as usual, are the reason of relatively low mechanical strength of the crystals.

Table 1. The main parameters of some powerful explosives

№	Compound	α	$\rho_{0,}$ g/cm^3	ΔH_f^0 kJ/kg	Q_{cal} kJ/kg	D, m/s	P_{CJ}, GPa	η, %	P_{cr}, GPa
1	 RDX	0.67	1.816	276.1	5564	8600_{1730}	32.7	96.7	2.05
2	 HMX	0.67	1.907	251.0	5523	9100_{1900}	36.1	100	2.4
3	 ANF	1.00	2.000	2320	7280[2)]	9700[2)]	40.6[2)]	110.3[2)]	0.2[2)]
4	 FTDO	0.75	1.852	4184	7530[1)]	9600[1)]	40.3[2)]	106[1)]	0.3[1)]
5	 ONC	1.00	1.982	937	7271[1)]	9350[1)]	39.0[1)]	108.2[1)]	0.9[1)]
6	 CL-20	0.80	2.040	837	5857[1)]	9460_{1930}	42.8[1)]	105.9[1)]	1.6[1)]
7	 Sorguyl	1.03	2.030	75.3	5440	9260_{2030}	39.7[1)]	102	1.3[1)]
8	 K-6	0.88	1.930	-182	5543	9170[1)]	36.0	99[1)]	2.0
9	 HHTDD-1	1.00	2.071	-33.5	5774[1)]	9800[1)]	42.5[1)]	105.7[1)]	1.2[1)]
10	 ZOX	1.00	1.875	14	6426	9100_{1870}	35.9	102[1)]	1.5

1) calculated value (the calculation of the detonation velocity and the metal acceleration performance in comparison with HMX (η) has been carried out for the density value indicated in the column ρ_0);
2) calculation accordingly the data [17, 18].

Long-term search for ways to synthesize octanitrocubane (ONC) had rather ambitious perspectives. However, the really synthesized (finally) compound had the monocrystal density in 0.2 g/cm^3 lower than the expected

value. So, this temporary slight beam of hope disappeared. Anyway, it is evident that CL-20 is a compound of a new generation with rather unique set of properties, but its comparison with other representatives of nitramines shows that CL-20 has not the highest parameters even in this class of compounds. Investigations for improving of manufacturing methods for CL-20, as well as investigations of neat CL-20 and formulations basing on it, have been carried out as the result of wide international cooperation. These investigations are still developed even despite a bit higher level to mechanic and shock wave impact influence than the value that was expected earlier. In [25] it was shown (using «Drop height» and «Friction test») that the sensitivity level of CL-20 is close to the level of PETN. All attempts to improve the quality of CL-20 crystals and to decrease its sensitivity (as it was done with I-RDX, so-called insensitive-RDX) failed.

Oxidizers

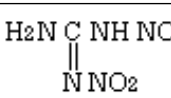
Separation of explosive oxidizers in a separate group is connected with their peculiarities for estimation of their future prospects. The α value increase in over 1 is not advisable for the power rise of an individual explosive. Actually, the emphasizing of some structures to one or other listings of oxidizers is rather conditional because the only criterion is the requirement $\alpha \geq 1$. The advantage of explosives with «excess» oxygen evinces in mixtures only and appoints the ways for the search of perspective compounds in this class of explosives.

Table 2 illustrates the calculated parameters of some explosives that are of the highest interest because of the set of their properties. Ammonium perchlorate (AP), that is a widely used compound in solid composite propellants and explosive compositions, is presented in the table for comparison.

The α value of ammonium salt of dinitramide (ADN) [26-28] is equal to 2 and is lower than for AP (2.67). But the main advantage of ADN in comparison with AP is its higher value of formation enthalpy and that is why ADN became a better component in many formulations of solid composite propellants. But the density of ADN is not high enough for successful use in explosive compositions, where the «price» of density is rather higher than in rocket propellants.

The compound furazanotetrazinedioxide (FTDO) [24] has extremely high enthalpy of formation (among all synthesized explosives), as well as the worse safety properties (e.g. shock sensitivity values). Resuming the analysis of considered parameters of furoxan derivatives we have to notice that structural peculiarities of these substances, as usually, are the reason of relatively low mechanical strength of the crystals.

Table 2. The main parameters of some oxidizers

Oxidizer	α	$\rho_{0,}$ g/cm^3	ΔH_f^0 kJ/kg	Q_{cal} kJ/kg	D, m/s	P_{cr}, GPa
NH_4ClO_4 AP	2.67	1.950	-2125	2008	4390	3.4
$O_2NN[CH_2C(NO_2)_2NF_2]_2$ B(DFADNE)NA	1.25	2.045	-100	6234	9100	0.3
$(NO_2)_2\bar{N}\ NH_4^+$ ADN	2.00	1.840	-1209	3096	6480	2.5
 DNQ	1.14	1.906	0	4979	9200	1.2[1)]
$H_2N—NH_2\cdot CH(NO_2)_3$ GNF	1.33	1.910	-393	5146	9200	1.2[1)]
$O_2NN[CH_2C(NO_2)_3]_2$ BTNENA (HOX)	1.4	1.960	-63	5397	8750	6

1) see Table 1

The compound furazanotetrazinedioxide (FTDO) [24] has extremely high enthalpy of formation (among all synthesized explosives), as well as the worse safety properties (e.g. shock sensitivity values). Resuming the analysis of considered parameters of furoxan derivatives we have to notice that structural peculiarities of these substances, as usually, are the reason of relatively low mechanical strength of the crystals.

The data on the level of detonation parameters for B(DFADNE)NA (bis(2-difluoramino-2,2-dinitroethyl)nitramine) have been published in [17]. Table 2 shows that a high content of oxidizing fragments in a molecule of B(DFADNE)NA provides reasonable density and power of this compound.

Hypothetical structures

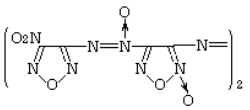
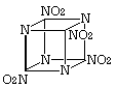
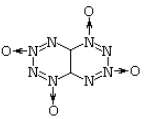
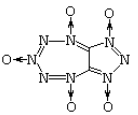
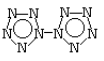
Table 3 illustrates our calculated data of parameters of some hypothetic structures.

Sometimes our calculations give lower values of properties than other researchers do, but anyway our results confirm very high energetic properties of these compounds. However, these substances are extremely dangerous in use if they exist.

Besides, the enthalpy of formation and molecular crystal density increase (that is the main way to improve the performance) for substances being at the upper board of real explosives existence area is an additional proof that the thermal stability of these substances falls drastically. We have to notice that

rather high deviations in the estimation data of performance are often due to disparagement to their explosion heat worth in the throwing process, as well as to refusal of this factor while metal acceleration performance use.

Table 3. Calculation data for hypothetic structures of power explosives

№	Compound	α	ρ_0, g/cm^3	ΔH_f^0 kJ/kg	Q_{cal} kJ/kg	D, m/s	P_{CJ}, GPa	η, %	P_{cr}, GPa
1	 BNAFFO	0.75	1.990	3260	7320	9700	43	110 (122)	0.9
2	 TNTAC	1.00	2.040	1810	7030	9860	45	110 (121)	0.6
3	 OAC	-	2.280	5615	5615	10970	59.7	112.9 (127.5)	0.1
4	 OANT	1.00	2.220	3350	7030	10700	55	120 (144)	0.5
5	 OAPO	1.25	2.260	3170	6700	10800	53	119 (141)	0.4
6	 OATE	-	1.810	6200	6200	9950	42	99 (98)	0.4
7	 TATE	-	1.513	6800	6800	9060	26.9	89.8	0.1
8	 PP	-	1.940	6443	6443	10290	43.3	105.4	0.4
9	 PA	-	1.770	6109	6109	9640	34.8	95.7	0.2
10	 BP	-	1.930	5569	5569	9920	39.7	98.5	0.6

* in column «η» in brackets there is relative deviation of the square for the velocity of butt end bar throwing; this parameter is used by several researchers.

The analysis of many experimental data on the explosion heat and the metal

acceleration performance test [32-34] showed that the missile velocity correlates intensely with the calorimetric heat of explosion and it allows the estimation of performance with an accuracy close to the experimental one.

Estimation of energetic parameters for the forecast of promising compounds as components of solid composite propellants

We have accomplished a range of thermodynamic calculations to estimate the potential level of compounds represented in Tables 1-3 if they are used as components (oxidizers) in solid composite propellants. Estimating energetic abilities of the compounds under consideration we did not study any concrete composite powders or propellants, because each of these materials has its own requirements to its performances. We have compared the oxidizers under consideration accordingly the value of specific impulse (I_{sp}) of the optimal binary mixtures with hydrazine. Here we have to notice that it is useless to compare oxidizers power basing on I_{sp} of individual oxidizers, without other components – in this case the most rich in oxygen oxidizers would be the least powerful because of hydrogen deficit or even absence. Thus, the most powerful solid oxidizer nitronium perchlorate (NO_2ClO_4) would become the least favorable.

Twenty-eight oxidizers have been studied (Figure1) and among them, there are very powerful inorganic oxidizers (hydroxylammonium perchlorate and nitronium perchlorate) together with some other compounds (Tables 1-3).

The results represented in Figure 1 allow us to rank the oxidizers according their energetic potential. Many oxidizers (e.g. OAPO (octoazopentooxide), ANF (4,4'-dinitro-azofuroxan), FTDO (furazano-tetrazine-dioxide)) are considerably more powerful than HMX. Actually, I_{sp} of the optimal mixture (OAPO + hydrazine) is 277 sec, while HMX (it does not need neither additional combustible nor additional oxidizer) shows I_{sp} equal only to 253 s.

The most powerful among real compounds is FTDO (I_{sp} = 281 s) with rather high enthalpy of formation (4184 kJ/kg). It shows the same I_{sp} value as the optimal binary mixture NO_2ClO_4 with hydrazine does (in this mixture the content of hydrazine is the highest (higher than 20%), because NO_2ClO_4 is the oxidizer with the highest oxygen content among all compounds under consideration in this paper). Anyway, practical use of NO_2ClO_4 is impossible – it is so reactive that it cannot stay compatible with any other component.

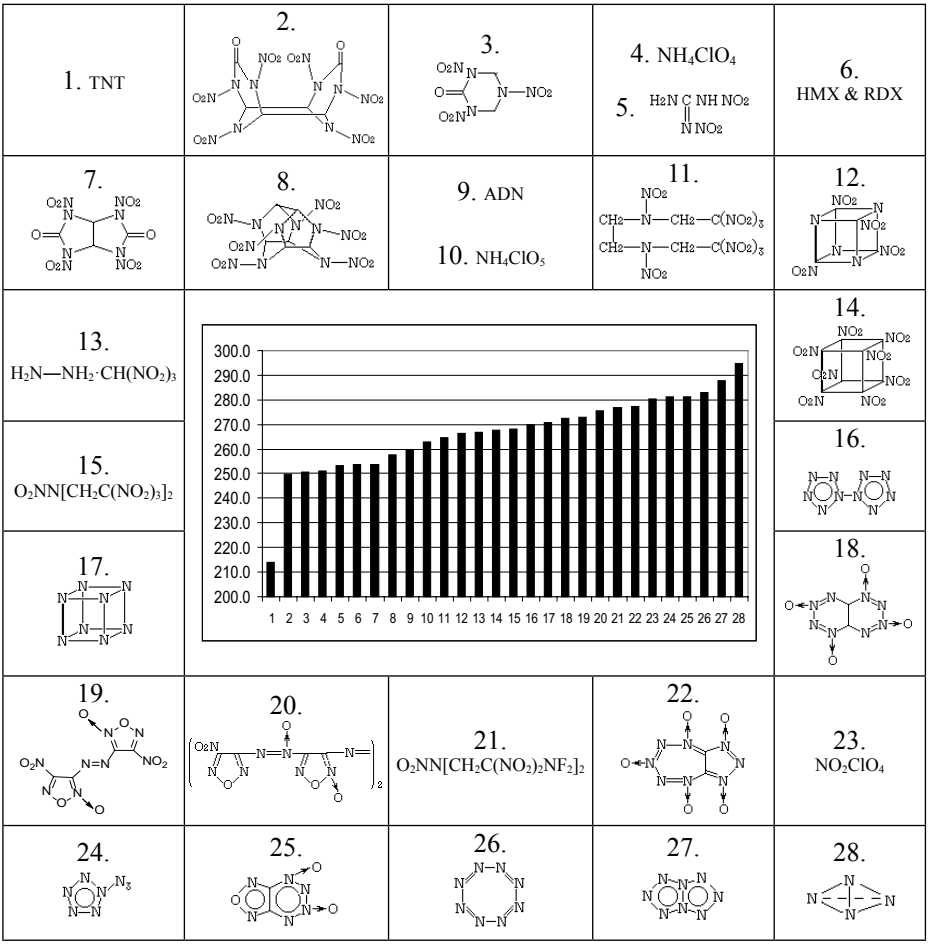


Figure 1. I_{sp} values (at pressure in the combustion chamber and in the exit nozzle section being 40 and 1 atm, respectively) for optimal mixture of the oxidizer with hydrazine.

High-enthalpy compounds composed of N-atoms only have very high energetic parameters (I_{sp} up to 295 s). These compounds (N_x) do not need any fuel (even hydrazine). Having so high enthalpy of formation there is no reason (if we consider I_{sp} only) to decrease the total formation enthalpy of a mixture with hydrazine, though hydrazine elements content is more favorable because of a lot of hydrogen. It means that, in this case, the compromise between enthalpy of formation and hydrogen portion [34] is won by the enthalpy of formation. For compounds composed of N-atoms only the increase of the enthalpy of formation value in each 100 kJ/kg does increase I_{sp} in 2 s.

Summary

The analysis of the dependence of explosives performances upon their chemical content and molecular structure allows to affirm that it is possible to obtain explosives with energetic parameters higher than the achieved ones (that the most powerful real explosives show).

For the considered explosives it is possible to achieve monocrystal density close to 2.3 g/cm^3 and the enthalpy of formation equal to 6000 kJ/kg or so. It allows to achieve heat of explosion ~7800 kJ/kg, detonation pressure 50-60 GPa, metal acceleration performance ~115-125% (in comparison with HMX). However all these compounds would have unacceptable safety properties: shock sensitivity (1.5-5 kbar). Presently, we do not see any real ways to decrease their dangerous character to an acceptable level.

The estimation of performances for nitrogen allotropes (N_x) of very different structures shows that the most probable properties that may be got one day are the following: density ~2.0 g/cm^3, enthalpy of formation ~6800 kJ/kg (this time it is equal to the explosion heat), detonation pressure ~50 GPa, metal acceleration performance ~100-115%, but sensitivity of the compounds under consideration must be very high.

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