Calculations and Analysis of Basic Characteristics for Polynitrogen Compounds

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Abstract

A large set of physical-chemical parameters for 900 chemical substances of different classes has been considered. Basing on analysis of parameters for the whole set of compounds the borders of existence for energetic materials (EM-s) and explosives have been found out. Calculating algorithms for the evaluation of the main characteristics of EM-s and explosives have been elaborated. The limits of physical-chemical values for EM-s parameters have been estimated. The basic evaluated performances of some individual energetic compounds, as well as the forecast of their effectiveness while being used as components of solid composite propellants are under consideration

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Introduction

It is known that recently there are many different ways for the evaluation of physical-chemical parameters of EMs for different goals. Among these ways there are additive schemas, methods of molecular dynamics and quantum chemistry, method of computer simulation, statistics models etc. A self-sufficient course for the basic characteristics estimation has been elaborated basing on so called Quantitative Structure-Property Relationship (QSPR) aproach. The main principles of all these methods have been presented in many papers and monographs [see, e.g. 1-20]. We should notice that all known approaches have their advantages and drawbacks.

As for polynitrogen compounds (they are considered recently as the most perspective substitutes for traditional nitrocompounds), in literature there are many data with overcharged performances and basic physical-chemical parameters. Thus, the effectiveness of these compounds in propellants may be overcharged too. For example, basing on some calculated performances the authors of [21-25] propose to synthesize tetraazatetranitrocubane, hexaazadinitrocubane and some other polynitrogen compounds that seem to be very perspective. However the represented performances are strongly overvalued and they are not harmonized with known tendencies received from all previous investigations of physical-chemical parameters of energetic materials.

Thus, the goal of the present paper is the development of the main principles for the obtaining reliable, scientifically established forecasts in the EMs performances evaluation. By resolving this task on one hand we tried to find out the borders of extreme values of physical-chemical parameters of EMs, on the other hand – to elaborate statistic models for their evaluation and forecasting.

Basic points of the suggested methodology

One of our main principles for the forecasting of performances for EMs is the validation that **energetic compounds do not represent any isolated class of chemical substances**, but they are related with all aggregate of chemical substances with a lot of regularities. Therefore the nature of energetic compounds is not restricted by itself only and is positioned on the regularities of the whole set of compounds from all others chemical classes. That is why amount of samplings for creation of calculation schemes should be, on one hand, as large as possible, but on the other hand - soundly minimal

The necessary requirement at statistic models composition (we are considering namely these models for forecasting of physical-chemical performances for EMs) is supplying with the randomisation, the orthogonality and the saturation of the initial data set.

We have to notice that it is impossible to provide any preset step in chemical content variation, because the change of the content of one element requires the adequate change of the content of other elements. The process of elements content change is related with the rules, determining the possibility of functional groups rearrangement at the basis molecule frame, as well as the structure of the frame itself.

Sine the whole region of existence for chemical substances is built accordingly well-defined rules, the performances change inside this region can not be casual. Therefore, a regressive equation, describing any performance, is reliable only for the region, limited with the parameters of explored values. The possibility to extrapolate the inside regularities outside the borders of this region has to be controlled with a special procedure, that determines the regularities outside of the initial region basing on the inside bonds. The requirement to use larger set of experimental data at simultaneous providing of their variation proceeds from the urge towards high calculation accuracy.

The procedure of «the method for regularities detection» is rather traditional and requires the regression analysis applying. The selection of valuables factors has been carried out using procedures of cross-validation («inclusion/exclusion») and step-by-step regression till the successive obtaining the interpolate regularities accordingly a few iterations, and after each of them the burned-out data have been eliminated. Along with these procedures the task data that were not belonged to the given statistic have been eliminated too. As a rule, the last procedure was carried out by a few iterations with output the new regularities and with the evaluation of accuracy by statistic methods after each step. The amount of deselected results usually was not higher than 10-20% of the initial massive

As an example of the noted basic principles we are considering the molecular crystal density ρ. This performance has a very important role the estimation of EM-s effectiveness. Fig.1 illustrates the interconnection of the density with the specific summary content of gram-atoms (**B**) in the structure of compounds. The value **B** (so called «gross-sum») is the sum of all atoms in gross-formula, referred to the molecule mass.

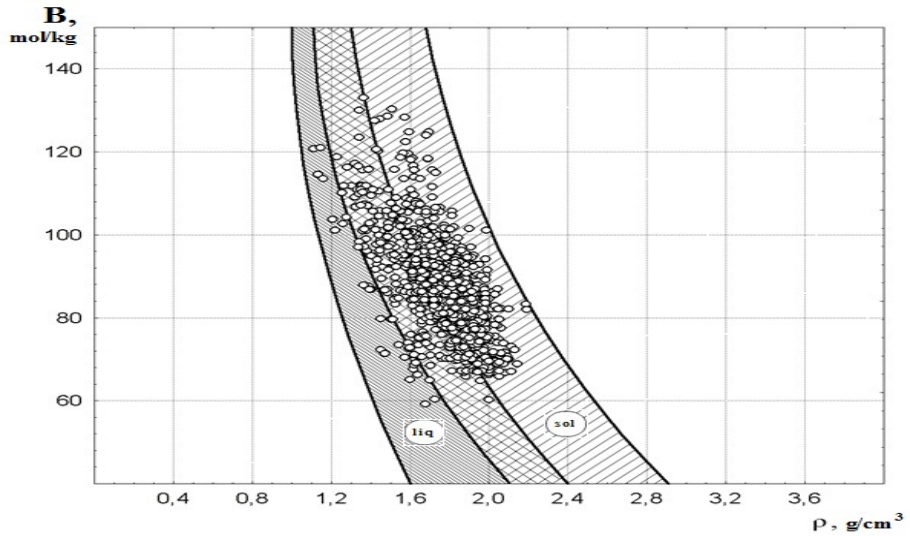


Fig.1. Dependence of **ρ** upon **B** for 900 ($C_xH_yN_zO_q$) chemical substances (region of energetic compounds existence corresponds to points «◦»).

In Fig.1 the area of solid compounds existence is shaded with positive angle, while the area shadded with negative angle corresponds to liquids. The intersection of these two shaded areas is the area of existence both solid and liquids. Outside these regions energetic compounds can not exist in these two aggregative states. The limits of physical-chemical values for EM-s parameters will be presented below.

Calculational tools for the prediction of parameters of EM-s parameters

Basing on the pointed principles, we have elaborated statistical models for evaluation of the basic physical-chemical characteristics for compounds from the different chemical classes that may be used as high energy materials.

We have studied experimental data for 250 individual energetic compounds considering the following characteristics: heat of explosion (55 compounds), detonation velocity (138 ones), C-J pressure (90 ones), shock sensitivity by large scale gap rest (25 ones), metal acceleration performance (74 ones) [22], as well as some other parameters.

Experimental compounds set under consideration had the following range in the element content (in gram-atoms/kg):

$C \in [0; 44,1]$; $H \in [0; 49,1]$; $N \in [7,0; 39,3]$; $O \in [0; 40,8]$.

For estimation the correlations between EM-s parameters we have considered the relationships between the element content and molecular structure. The regression analysis procedure has been used. As the result, average (%) and

root-mean-square errors are as the following: 0,077 and 1,256, respectively, for detonation velocity; 0,59 and 6,84 for C-J-pressure; 0.11 and 1.88 for the metal acceleration performance; and 0,28 and 3,45 for the heat of explosion. The value of relative deviation for the calculations is almost constant for all the area of variations.

As the result, the main parameters of energetic compounds were calculated basing on 25 equations that were formulated and some of them are represented lower.

The Metal Acceleration Performance in comparison with HMX (η) has been estimated from the velocity of butt end bar throwing by the explosion products:

$$\eta = 1.23\cdot\rho^{0,871}\cdot Q_{cal}^{0,432}\cdot N_g^{0,230} \quad (1)$$

Shock Sensitivity by Large Scale Gap Test:

$$P_{cr=} (\rho\cdot B)^{2,732}\, Q_{max}^{-1,534}\cdot\alpha^{-1,105}\text{--}5 \quad (2)$$

C-J Detonation Pressure:

$$P_{C\text{-}J} = 2,139\cdot 10^{-2}\cdot\rho^{2,100}\cdot c^{0,102}\cdot\alpha^{0,147}\cdot Q_{max}^{0,519}\cdot N_m^{0,554} \quad (3)$$

Detonation velocity:

$$D = 0,481\cdot\rho^{0,607}\cdot c^{0,089}\cdot\alpha^{0,066}\cdot Q_{cal}^{0,221}\cdot N_g^{0,19} \quad (4)$$

Calorimetric heat of explosion for EM-s containing C,H,N,O - atoms:

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

Amount of moles of gaseous combustion products:

$$N_g = 0.777\cdot\rho^{-0.153}\cdot B^{0.715}\cdot(\Delta H_f^0+1000)^{0.1}\cdot Q_{max}^{0.238} \quad (6),$$

where ρ - the density of explosive; ρmax – maximal theoretic density of explosive; $\rho rel. = \rho/\rho max$; Qmax – maximal heat of explosion; B – gross-sum (the gram-atoms of the chemical elements in 1 kg of explosive under consideration);$\cdot\alpha$ - the coefficient of oxidizer excess; Qcal – calorimetric heat of explosion; Ng – quantities of moles under gaseous combustion (explosion) products; Nm - amount of moles in gaseous combustion (explosion) products corresponding to Qmax; a, b, c, d – amount of gram-atoms of chemical elements in 1 kg of the explosive with CaHbNcOdFe; Qpvm – maximal energy of combustion products; $\Delta Hf0$ – the enthalpy of formation.

The estimation of 250 individual energetic compounds has been carried out using the suggested methods [26-27] for calculations of explosives properties forecast. In the substances set under consideration there were represents the different classes of organic compounds with the following range of 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 the full-nitrogen compounds (Nx), naturally, N is equal to 71,4 gram-atoms/kg). Such a wide range of element content considers practically the whole region of existence for any covalent EM-s substances. Thus, basing on such a wide set of basic substances and using rather precise calculation methods we may affirm that the developed complex system for explosives properties forecast is quite authoritative.

Results and discussion

For confirmation the quality and effectiveness of the obtained equations system for the evaluation of the basic performances of EM, and to define the borders of EM-s existence let us consider the isolines of the Metal Acceleration Performance (η) (Fig.2). This parameter (η) can determine the effectiveness of the EM-s using. In fact, as it follows from Fig.2 the increase of energetic capacity of compound is accompanied with increasing of sensitivity to impact. The interdependence of sensitivity and energetic capacity determines the borders of the region for existence of a lot of EM-s. Decrease of the energetic capacity lower than the critical value makes the compound under consideration incapable for detonation. In Fig.2 such compounds are limited with the bisector of the coordinate angle (left higher corner). If the compound accumulates extra-energy it becomes extra-sensible and extra-unstable as a chemical substance. The region of EM-s existence is limited with the Y-axis, crossing the null value of the critical pressure for initiation. .

As it follows from the analysis of the results (basing on above presented equations to evaluate the main parameters of EM-s & explosives), a relative increase of sensitivity (eq.2) because of energy capacity (Qmax) increase outruns considerably the relative increase of detonation parameters (eq.4,5) and the detonation effectiveness (eq.1).

Summary, basing on analysis of EM-s area existing it is possible to determine the limits for Energetic Materials (with the formulas of C2÷5N52÷68O2÷10 (hydrogen-free)) parameters existence:

- ✓ monocrystal density ≤ 2.2 g/cm^3,

- ✓ enthalpy of formation ≤ 6000 kJ/kg or so,
- ✓ heat of explosion ≤ 7800 kJ/kg,
- ✓ detonation pressure ≤ 50÷60 GPa,
- ✓ acceleration ability (m-40) ≤ 120% (in comparison with HMX).
- ✓ However all these explosives would have unacceptable safety properties:
- ✓ shock sensitivity (1.5÷5 kbar),

To illustrate the results of our suggested methodology, below we represent the results of our calculations for based performances of some real and hypothetic compounds

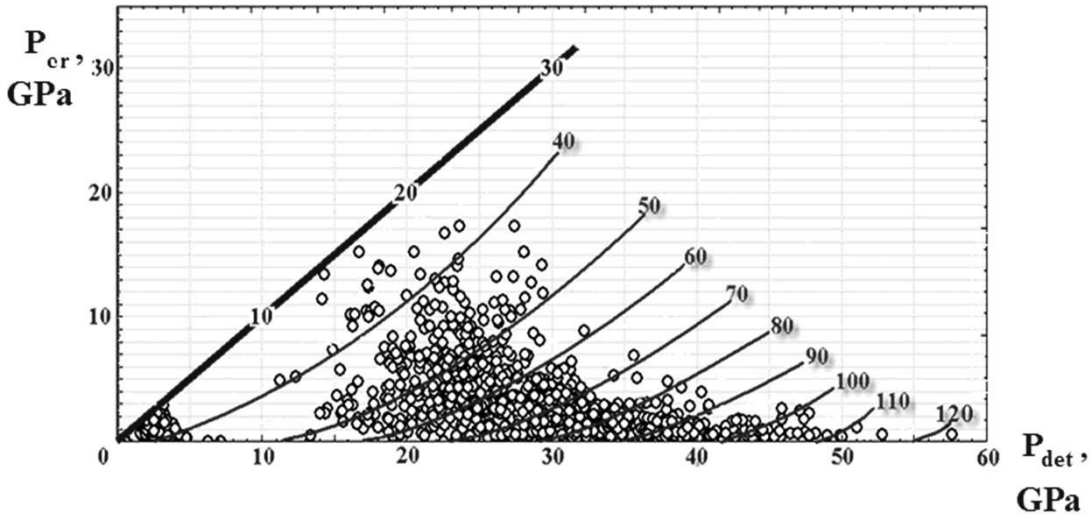
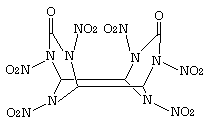
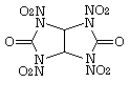
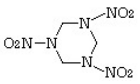
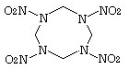
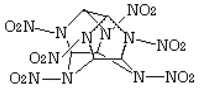
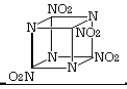
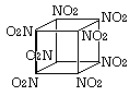
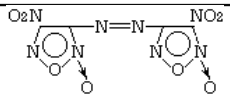
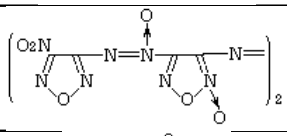
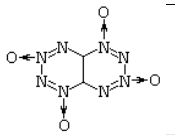
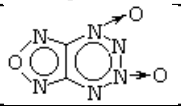
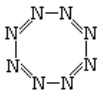


Fig.2. Metal Acceleration Performance isolines in axes: detonation pressure - P_{det} (X-coordinate) and shock sensitivity - P_{cr} (Y-coordinate

Below we are representing results of our calculations for several performances of some real and hypothetic compounds.

Table 1. Some basic parameters of energetic compounds.

№	Energetic compound	α	$\rho_{0,}$ g/cm^3	$\Delta H_f^{0,}$ kJ/kg	Q_{cal} kJ/kg	P_{CJ}, GPa	P_{cr}, GPa	η, %	Isp^{opt}, s	%*	Isp**,s
1	NH_4ClO_4	2.67	1.95	-2500	2008	9,75 (1500)	3.4	-	240.6	10	236.9
2	NO_2ClO_4	-	-	250	-	-	-	-	263.4	22	-
3	$(NO_2)_2\bar{N}\ NH_4^+$	2.00	1.84	-1209	3096	-	2.5	-	252.0	8	243.9
4	$O_2NN\left[CH_2C(NO_2)_2NF_2\right]_2$	1.25	2.04	-100	6234	-	0.3	-	271.4	6	261.5
5		1.00	2.07	-33.5	5774[1]	42.5[1]	1.2[1]	105.7	244.2	4	223.1
6		1.03	2.03	75.3	5440	39.7[1]	1.3[1]	102.0	246.8	4	231.5

7		0.67	1.81	276.1	5564	32.7	2.05	96.7	253.4	0	217.3
8		0.67	1.90	251	5523	36.1	2.4	100	252.9	0	216.8
9		0.80	2.04	837	5857[1]	42.8[1]	1.6[1]	105.9[1]	256.2	0	228.4
10		1.00	2.04	1810	7030	45	0.6	110 (121)	260.9	6	248.4
11		1.00	1.98	937	7271[1]	39.0[1]	0.9[1]	108.2[1]	259.3	8	249.4
12		1.00	2.00	2320	7280[2]	40.6[2]	0.2[2]	110.3[1]	262.9	6	249.3
13		0.75	1.99	3260	7320	43	0.9	110 (122)	273.4	2	254.4
14		1.00	2.22	3350	7030	55	0.5	120 (144)	271.6	4	252.8
15		0.75	1.85	4184	7530[1]	40.3[2)]	0.3[1)]	106[1]	279.3	4	260.1
16		-	1.81	6200	6200	42	0.4	99 (98)	282.8	0	248.0

I_{sp}^{opt} – specific impulse of the optimized binary mixture for the compound under investigation with polyethylene (combustion pressure is 40 atm, exit nozzle section pressure is equal to 1 atm);

%* - polyethylene content in the optimal mixture, %;

I_{sp}^{**} - maximal specific impulse for the binary mixture of the compound under investigation with polyethylene if the content of polyethylene is not lower than 12% (combustion pressure is 40 atm, exit nozzle section pressure is equal to 1 atm);

[1)] - settlement size (calculation of detonation speed and the relative impulse for the density specified in column ρ_0);

[2)] – calculations of [28,29];

In column «η» in brackets there is relative standard deviation for velocity of butt end bar throwing (this parameter is used by several researchers).

As it follows from Table 1, the calculated parameters of some compounds are of the highest interest because the set of their properties. Ammonium perchlorate (NH_4ClO_4, # 1) is widely used compound for solid composite propellants and for explosive compositions and is present in Table 1 just for comparison. Ammonium salt of dinitramide (ADN, # 3) [31,32] has the α value equal 2, that is lower than the value α of NH_4ClO_4 (1)**,** but the main advantage of ADN in comparison with AP is its higher value of the enthalpy of formation and that is why ADN became better oxidizer in many formulations of solid composite propellants. At high content of oxidizing fragments in # 4 compound provides high density and power of this explosive.

In compound HHTDD-1 (# 5) the hydrogen content is lower than in RDX (# 7), 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 of explosion heat value the Metal Acceleration for HHTDD-1 is already 105.7% relatively

HMX. Parameters of CL-20 (# 9) also illustrate the influence of the number of strained cycles and the decrease of hydrogen content upon the performance.

The compound FDTO (# 15) 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, is the reason of relatively low mechanical strength of the crystals.

In [30] we have evaluated the energetic abilities of some compounds from Table 1 as components of composite propellants in mixture with hydrazine. In the present paper we are considering their energetic abilities with polyethylene (PE). First, because it is a solid, second - PE is rather close to different kinds of hydrocarbon binders and that is necessary for solid composite propellants. Besides the value I_{sp}^{opt} (specific impulse of the optimized binary mixture with polyethylene) here we demonstrate another value - I_{sp}^{**} - the maximal specific impulse of the binary mixture for the compound under investigation with PE if the content of polyethylene is not lower than 12%. This parameter (I_{sp}^{**}) evaluates the real ability of the compound under consideration as a component of solid composite propellants because the volume percentage of the binder has to be not lower than 20 vol.% and that is about 12 mass. % or so far.

Fig.3 and 4 illustrate the relative rosters of the compounds. Oxidizers with rather low oxygen balance require low content of PE, somewhere even null. Ammonium perchlorate (AP) seems to be one of the least powerful oxidizers if we compare oxidizers accordingly their optimal mixtures with PE. The reason is rather clear – AP has a high oxygen balance, so it requires many PE (10%) while all other compounds in Table 1 (except NO_2ClO_4) require lower amount of PE. That is why the rosters of oxidizers (Fig.3 & 4) depend on the element content of the second compound, of its enthalpy of formation, of additional requirements (e.g. the portion of the second compound has to be not lower than the given value), etc. Many compounds are more powerful in binary mixtures with hydrazine [30] than with PE or another kind of binder (e.g. so called active binders, containing such functional groups as NO_2- , NNO_2, ONO_2 etc and it a goal of our following researches) **and the sequence of different systems is different (Fig. 3 & 4).**

However, one can see that many compounds in Table 1 are rather more powerful oxidizers for solid composite propellants than traditional oxidizers, such as ammonium perchlorate, ammonium dinitramine (ADN), HMX, etc

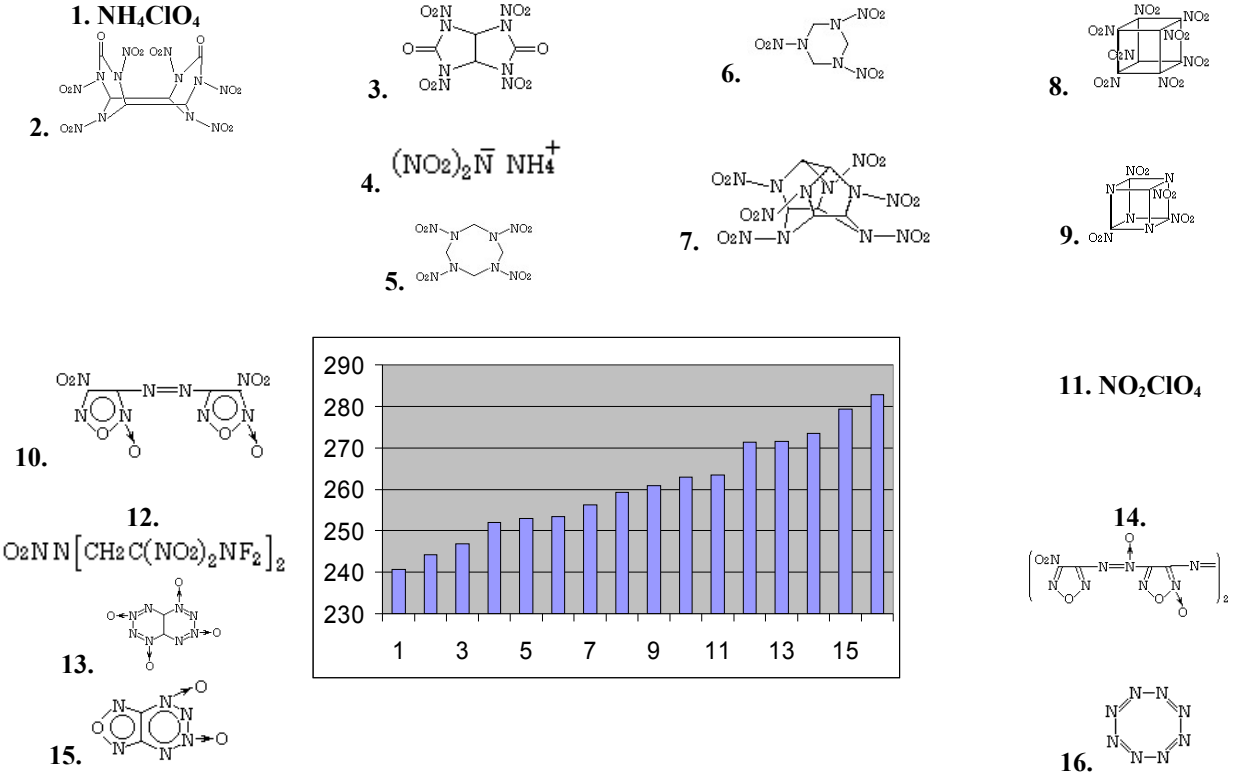


Fig.3. I_{sp}^{opt} for the optimal binary mixture oxidizer with PE.

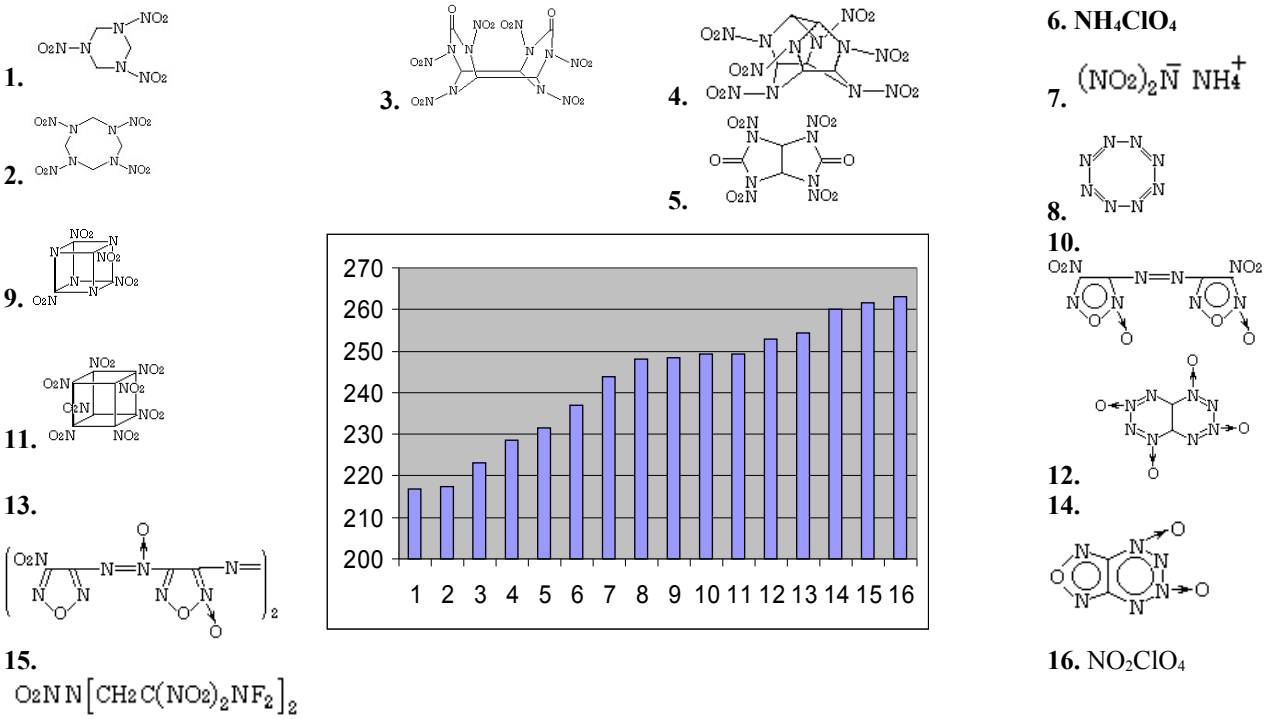


Fig.4. I_{sp}^{**} for the binary mixture oxidizer with PE (content is not lower than 12%).

However, one can see that many compounds in Table 1 are rather more powerful oxidizers for solid composite propellants than traditional oxidizers, such as ammonium perchlorate, ammonium dinitramine (ADN), HMX, etc.

Summary

Analysis of the dependence of energetic compounds 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 shows).

However all these explosives would have unacceptable safety properties. Presently we do not see any real ways to decrease their danger to the acceptable level.

Acknowledgment

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