Preliminary Research of Composite Rocket Propellants Including Octogene

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Composite solid propellants based on ammonium perchlorate/hydroxyterminated polybutadiene/isophorone dyisocyanate including different contents of octogene (HMX) have been represented in this paper. The mass of HMX increased in relation to oxidant, with constant bimodal fraction ratio. Combustion of the propellants has been improved by adding of titanium (IV) oxide powder as stabilizer. Parameters of burning rate laws were determined and compared for the propellants of the same total solid phase. Also, the apparent viscosity, uniaxial mechanical characteristic, density and energetic values were determined for the same formulations.

Key words: composite rocket propellant, ammonium perchlorate, hydroxyterminated polybutadien, octogen, titanium (IV) oxide, ballistic properties, burning rate, mechanical characteristics.

Introduction

INCREASING the solid motor performance can be managed by use of compounds with high energy, such as pure explosives. These materials application into cast composite propellants gives improved specific impulse and greater range for a rocket system.

The problems, especially related to combustion stability, and the prediction of the main characteristics corresponding to basic composite propellant, occur when the explosive level in the propellant is increased. Combustion designing can be used to tailor propellants as to achieve desired, optimum, steady and non-steady burning characteristics.

This research is planned to inquire a combustion of composite solid propellants consisting of bimodal ammonium perchlorate mixture and high energy cyclotetramethylene-tetranitramine (octogene) crystals in a polybutadiene binder. These formulations will be used to predict the parameters of burning rate law, for a variety of propellants consisting of various combinations of oxidizers crystals, together with other important properties significant for use.

Theoretical part

The performances of composite solid propellants (CSP) (physical, mechanical and combustion properties) depend on characteristics, followed by type of ingredients and their concentrations.

The oxygen is needed for the explosive reaction to take place. It can be introduced by chemical reactions or by mechanical incorporation of the materials containing bound oxygen. The most important solid-state oxidizers are ammonium perchlorate [1].

The amount of oxygen, expressed in weight percent, liberated as a result of complete conversion of the explosive material to CO_2, H_2O, SO_2, Al_2O_3, etc. is "positive" oxygen balance. If the amount of oxygen bound in the explosive is insuffient for the complete oxidation reaction ("negative" oxygen balance), the deficient amount of the oxygen needed to complete the reaction is reported with a negative sign.

Examples for oxygen balance of explosives and explosive components:

trinitrotoluene TNT ($C_7H_5N_3O_6$)	−74.0 %
octogene ($C_4H_8N_8O_8$)	−21.6 %
nitroglycerine ($C_3H_5N_3O_9$)	+ 3.5 %
ammonium nitrate (NH_4NO_3)	+20.0 %
ammonium perchlorate (NH_4ClO_4)	+ 34.0 %
barium nitrate ($Ba(NO_3)_2$)	+ 30.6 %
dinitrotoluene (DNT)	−114.4 %
nitroguanidine (NGV)	− 30.8 %

Commercial explosives must have an oxygen balance close to zero to minimize the amount of toxic gases, CO, and nitrous gases, which are evolved in the fumes.

Ammonium perchlorate (AP), Fig.1, is the most widely used crystalline oxidizer to formulate composite propellants for rockets. Unlike alkali metal perchlorates, it has the advantage of being completely convertible to gaseous reaction products.

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Nitramines (such as HMX) are high-energy-density materials that produce high-temperature gaseous products. When some portion of the AP particles in propellant is replaced with nitramine particles, an AP-nitramine propellant is formulated [2].

Figure 1. Ammonium perchlorate powder

The white AP orthorombic crystalline particles are stable at room temperature. At 520 K (247°C) a phase transformation places to cubic crystalline structure, liberated the energy of 85 kJ/kg. Autocatalized decompose of AP begins at 250°C according to the following chemical reaction:

$$4NH_4ClO_4 \rightarrow 2Cl_2 + 3O_2 + 8H_2O + 2NO_2$$
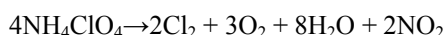
In the composite propellants, the AP decomposes first in the sub-surface region to form perchloric acid ($HClO_4$), and the polybutadiene binder decomposes to produce fuel in the form of hydrocarbon fragments and hydrogen. $HClO_4$ decomposes further to form smaller oxidizing species [3]. These decomposed gases consisting of fuel and oxidizer components mix together to form a diffusion flame above the propellant-burning surface.

Nitramine, like cyclotetramethylene tetranitramine (HMX), is a powerful and relatively insensitive nitroamine high explosive, and important ingredient in propellants used in solid rocket propulsion. HMX in its pure form is an explosive and can be very hazardous due its sensitivity to shock. It is a colorless solid with a melting point of 276 to 286°C. The molecular structure of HMX, Fig.2, consists of an eight-membered ring of alternating carbon and nitrogen atoms, with a nitro group attached to each nitrogen atom.
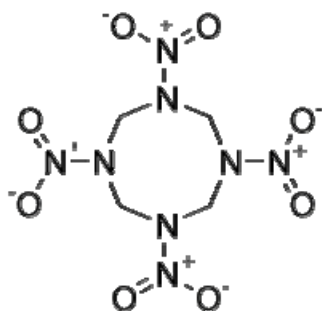

Figure 2. Octogene (HMX)

Because of its high molecular weight, it is one of the most potent chemical explosives manufactured. The average molecular weight of the combustion products of composite nitramine propellants is lower than that of more conventional AP based composite propellants.

The decomposition reactions of HMX are stoichiometrically balanced when it is assumed that CO, rather than CO_2, is formed as a combustion product [4]:

$$HMX: C_4H_8O_8N_8 \rightarrow 4CO + 4H_2O + 4N_2$$
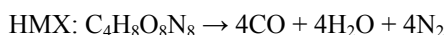
Consequently, the propellant performance is greater than AP propellants at equivalent flame temperatures since propellant performance is inversely proportional to the molecular weight of the exhaust products. Besides, propellants with HMX crystals, shown in Fig.3, tend to have higher densities than AP propellants and, thus, their density impulse is greater. Other advantages gained by using nitramines in propellant formulations include excellent thermal stability, low propellant flame temperature and non-toxic, non-corrosive combustion products. HMX explodes violently at high temperatures (552 K (279°C) and above). Because of this property, HMX is used exclusively for military purposes. The use of HMX as a propellant and in maximum-performance explosives is increasing [2].
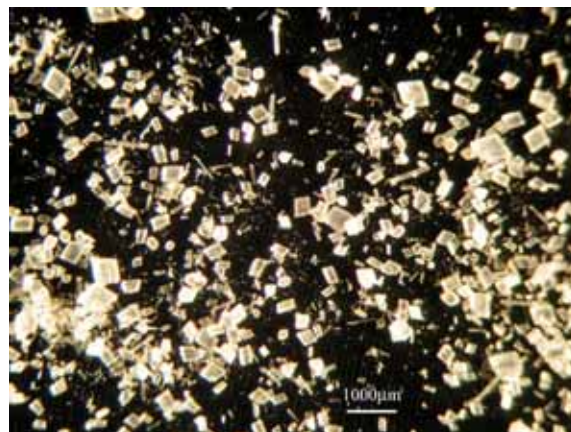

Figure 3. The particles of HMX

As HMX is slowly heated to between 185°C and 190°C, it undergoes an endothermic crystallographic phase change process from beta to delta HMX. Further heating leads to slightly exothermic decomposition, beginning at about 271 °C. This process is interrupted by a sharp endotherm at the melting point, which is then quickly followed by exothermic deflagration at about 280°C. Concerning the relatively narrow temperature range over which the principal events occur, crystallographic phase changes at around 190°C, solid phase decomposition at 271°C, melting at 284°C and, finally, deflagrating between 285°C and 500°C [2].

However, numerous problems have been encountered by the substitution of HMX for AP in propellant formulations. These include high burn rate exponents, exponent shifts, low burning rate, and difficulty in tailoring these low burning rates and high pressure exponents. In addition, nitramine composite propellants are much more difficult to ignite when compared to AP-based composite propellants [5].

In contrast to propellants based on AP, nitramine propellants do not produce hydrochloric acid (HCl) unless, AP is incorporated into the propellant to serve as a ballistic modifier. Besides being corrosive, HCl in the exhaust provides nucleation sites for moisture droplets to condense upon, thereby producing a visible contrail or secondary smoke [2].

The burning rates of HMX propellants are usually much lower than comparable propellants containing AP. HMX inert binder propellants have burning rates of 1.3 to 5.1 mm·s^{-1} at 70 bar versus rates of 7.6 to 38 mm·s^{-1} for similar inert binder propellants containing AP, because fine AP particles will give higher burning rates. However, for HMX propellants, variations in particle size have minimal effect on changing the burning rate as can be seen by comparing

the burning rate range above with that of AP propellants. In order to increase the burning rate, propellant formulators have turned to additives such as metal catalysts, but the pressure exponent was high and these rates are still below that of AP based propellants. For a minimum variation in the thrust or chamber pressure, the pressure exponent and the temperature coefficient should be small [5].

The tailorability of HMX, or other nitramine, - active binder propellants is therefore more limited than for AP propellants [5].

In order to produce a usable propellant formulation, it is necessary to control the propellant burn rate, to prevent unacceptable performance (too high or too low pressure) for the intended purpose of the device.

The burning rate of an energetic material is represented by the Vieille's law (Saint Robert's law) according to the equation linking the burning rate parameters (1).

$$v = B \times p^n \qquad (1)$$

where:
- v—burning rate,
- p—pressure in the motor chamber,
- B—const. depending on grain temperature and
- n—pressure exponent.

In general, the burning rate of an energetic material is seen to increase linearly with increasing pressure in an ln p versus ln v plot represented by Eq. (1) at constant initial temperature. Thus, the pressure sensitivity of burning rate at a constant initial temperature, n, is defined by [6]

$$n = (\partial \ln v / \partial \ln p)T \qquad (2)$$

The instability during the combustion has to be avoided because of many undesirable processes and can be prevented by adding of specific additives. These compounds may have an influence on parameters of all characteristics, especially the ballistic performance and achieving the necessary requirements for the propellant [7]. One of the refractory oxides, such as TiO_2 are used in this research because of their ability to effect on combustion process, even forming plateau in the compositions of wide distribution of AP particle sizes. TiO_2 reputes as very effective in almost all solid rocket propellants and has sustained the plateau from 50 bar to 100 bar, especially in HTPB systems where it enables stable burning in the wide range of pressures [8, 9].

The burning behavior and flame structure of an AP/HTPB propellant system are influenced by the chamber pressure, local velocity, AP particle size and mass fraction. The appearance of irregular combustion may occur at a specific particle size distribution of oxidizer or explosive powder (the packing density and unfilled space between) and AP/binder ratio. In order to achieve certain requirements and provide good properties, it is necessary to define different combinations of AP particle size distribution of various fractions, total AP and total solid phases content. When the particle size ratio (coarse/fine) is increased up to a level of significant interspace, the burning of fine AP particles will be inhibited by the melting layer of the binder. For the particle size of 20 μm, it may be assumed that the AP and HTPB are thermally isolated in the condensed phase. If an energy transfer between the two segments is allowed, the surface temperature of the AP will be reduced, leading to a decrease in the overall burning rate [8]. If there are some compounds taking over the energy transfer to themselves, because of the higher melting points, it is possible to change the combustion process during the

form of laminar flow [9].

TiO_2 (melting temperature: 1870ºC), added to a CSP based upon HTPB, acts to increase the binder melt layer viscosity restoring normal burning at low and high pressures, leaving abnormal burning of a solid propellant, thereby preventing stirring with fine oxidizer particles and enables the plateau effects at intermediate pressures. It has been concluded that TiO_2 is a positive catalyst for decomposition but at pressures well below those where the burning plateau has been observed (50 - 100 bar). It has been speculated that, if the same observations area is valid at higher pressures, then TiO_2 may dampen the amount of heat released and contribute to a reduction of the burning rate, so it can also be used for the pressure exponent equalization. It has been suggested that the amount of TiO_2 in the CSP should be from 1 - 2 mas.%. The addition of 2% provides the most distinctive plateau, but it depends on the formulation of CSP. In pyrolysis experiments of AP/HTPB mixtures, an accelerated rate of evolution of gaseous products was reported when quantity of 5 mas.% was added [10].

The normal burning of CSP produces a burn rate/pressure curve including relatively constant positive slope over the range of expected operating pressures.
The regime thrust, ideally, should be met in all operating conditions, especially in the application temperature range. However, the ballistic properties of propellants show a significant dependence on the external temperature, which affects the operation in a given range.

The combustion of CSP consists of the series of processes. The energetic characteristics and performing rate of these processes determine the burning rate, surface temperature, flame height and burning surface appearance.

Experimental part

The three main groups of compositions based on:
- constant bimodal ratio of ammonium perchlorate and
- constant polybutadiene/dyisocyanate NCO/OH ratio
have been prepared for this research:
I   the »empty« one, i.e. referent formulation,
II the »unstabilized« nitramine and
III the »stabilized« nitramine formulations.

The content of HMX varied at four levels in stabilized and two in unstabilized batches, shown in Table 1.

Table 1. The preparing compositions of propellant

No	AP-200 [mas.%]	AP-7 [mas.%]	HMX [mas.%]	TiO2 [mas.%]
17	52	28	-	-
36	45.50	24.50	10	1.5
44	42.25	22.75	15	2
51	39.00	21.00	20	2
52	35.75	19.25	25	2.5
69	42.25	22.75	15	-
70	35.75	19.25	25	-

The propellant binder matrix was based on hydroxyl-terminated polybutadiene (HTPB) as prepolymer and isophorone-diisocyanate (IPDI) as curing agent, with addition of other standard components such as dioctyl adipate as plasticizer, triethylene tetramine as bonding agent and antioxidant – phenyl -2- naphtylamine.
In all cases:
- bimodal mixture ratio of AP was 65:35 (including the average particle sizes of 200 μm and 7 μm);
- parts of AP are exchanged with HMX;
- used HMX was class 5 (< 125 μm) [11];

- total (energetic) solid phase (AP+HMX) was 80 mas.%;

From the previous chapter it is obvious that the particle size control is very important part of the research. This especially applies to AP powder, because of a great influence of particle size distribution on burning rate law.

The fine AP particles have been prepared by grinding of entering powder, i.e. coarse 200 μm fraction in Hammer mill ACM-10, whose housing is shown in Fig.4, into very small, nonspherical particles of AP.

Figure 4. Hammer mill ACM-10 - input housing

The average particle diameter value of grinded (so called »fine«) fraction of AP is measured by the Fischer subsieve sizer (FPA), and the measuring results of two samples could be seen in Fig.5. From the diagram it was obvious from examining powder that the average size of those small fractions is about 7 μm.

All ingredients have been homogenized at 60ºC in the laboratory vertical planetary mixer upon vacuum condition, according to the applied mixing sheet related to adding order (consists of premix, consecutive adding of dried bimodal AP and HMX and curing agent in the end of the process).
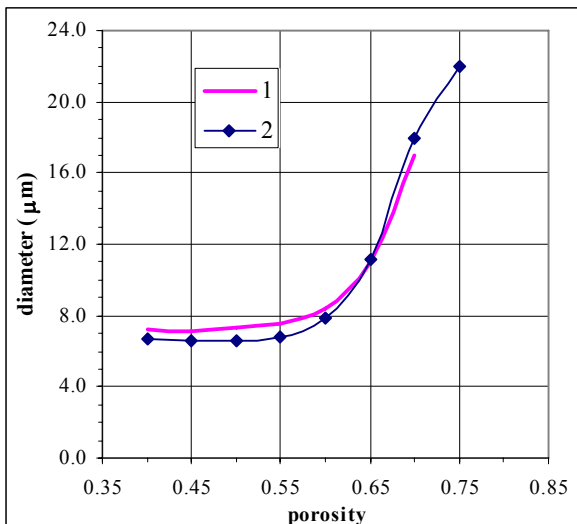

Figure 5. Particle size values of two fine AP samples delivered from FPA

The view at mixer blades covered with uncured AP/HMX propellant after finishing the homogenization process is given in Fig.6.

Figure 6. Uncured AP/HMX propellant on the blades

Afterwards, the propellant is cast in PVC chambers of 2 inch experimental motors, shown in Fig.7, that is used for the static tests at fire station for solid rocket propellants.

Figure 7. PVC chambers of 2 inch experimental motors (ready for propellant casting)

Alongside the specimens casting for static tests, a block of the propellant and a small part of uncured propellant were separated from the bowl for measuring mechanical and energetic characteristics and apparent viscosity values. From the very beginning of cure time, every 15 minutes, the values are read out from the Brookfield HBT viscosymeter dial, at (60±2ºC), shown in Fig.8.

Figure 8. Brookfield HBT viscosymeter dial

Energetic values were examined at calorimeter shown in Fig.9, uniaxial mechanical characteristics at universal tester

and measurements of density at Mohr balance in toluene as referent fluid at 20ºC.

Figure 9. Isoperibolic calorimeter C 2000

Propellant grains for static tests and block of propellant for other determinations were cured at (70±2 ºC) for 5 days and after cooling at ambient environment, the grains were dearranged from cure tools. After laboration at testing motors including appropriated nozzles and cutting the specimen slabs for the rest examinations, Fig.10, specimens are ready for tempering at the test condition in the temperature chamber and the use for measuring.

Figure 10. Propellant slab for test specimens

After uniaxial mechanical testing, the specimens are used by cutting for density and heat of combustion determining.

Results of examinations

All measured and calculated results of examination are shown in the following tables.

The results of viscosity measurements of uncured nitramine propellants during prolonged period of time at 60ºC are shown in Table 2.

Table 2. Viscosity values of the propellants during time

No	Viscosity (Pa·s) vs. time (min)					
	15	30	45	60	75	90
17	97.6	102.4	129.6	147.2	184	216
36	160	188.8	220.8	251.2	288	
44	176	236	280	312	352	384.2
51	182.4	238.4	276.8	318.4	360	
52	264	368	419.2	494.4	541.4	
69	104	128	160	184	202.2	
70	134.4	164.8	195.2	228.8	248.4	

The uniaxial mechanical characteristics by tensile test were determined for some formulations at room temperature and the results are shown in Table 3: tensile strength (σ_m), strain at maximum load (ε_m) and Young modulus of elasticity (E).

Table 3. The values of mechanical characteristics at 20 ºC

No	σ_m [daN·cm^{-2}]	ε_m [%]	E [daN·cm^{-2}]
17	7.90	32.90	40.34
36	9.10	29.40	46.56
44	9.55	27.80	53.29
51	13.36	12.16	174.91
52	11.18	12.76	139.17

The burning rate law parameters were examined from diagrams p=f(t) by performing the static tests at 20 ºC and the results are presented in Table 4: burning rate values at 70 bar (v_{70}), pressure exponents (n) and constant (B).

Table 4. Burning rate law parameters at 20 ºC

No	v_{70} (mm·s^{-1})	n	B
17	6.62	0.2138	2.6676
36	6.95	0.2399	2.5083
44	6.97	0.2510	2.3992
51	6.52	0.2735	2.0384
52	6.37	0.2840	1.9062
69	6.24	0.2490	2.1667
70	5.62	0.2865	1.6648

The test results of density (ρ) and heat of combustion (Q) determinations are represented in Table 5.

Table 5. Density and heat of combustion values

No	ρ [g·cm^{-3}]	Q [kJ·kg^{-1}]
17	1.595	4294.1
36	1.624	4275.4
44	1.633	4207.4
51	1.623	4069.2
52	1.642	4016.9
69	1.606	3999.0
70	1.575	3868.7

Discussion

These propellants represent the preliminary examinations of exchange possibilities AP and explosives, such as HMX in this case. The change of viscosity values at mixing temperature, uniaxial mechanical properties, determined energetic and density values and burning rate laws at an ambient temperature will be graphically presented for the sake of a more convenient consideration and comparison of the nitramine compositions.

The "pot life" of those propellants is very important to emphasize for the preparation process quality and it is very clear from Fig.11, based on Table 2.
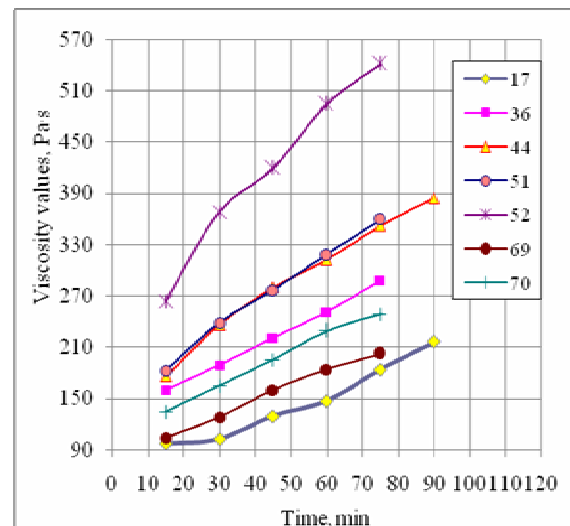

Figure 11. Viscosity changes at 60 °C

It is obvious that entering the HMX instead AP has a relatively small negative effect in relation to viscosity values. The huge molecule of HMX affects the more prominent steric hindrances than a smaller compound of AP. Moreover, adding of some other solid ingredient leads to significantly larger differences between those with TiO_2 and others. It is, obviously, the consequence of increasing of total solid phase, and probably of some kind of complex compound presence. It is more visible in case of propellants with HMX molecules.

The effects of HMX molecule and presence of stabilizer`s small molecule of titania dioxide on uniaxial mechanical characteristics were grafically presented in Figures 12 – 14, respectively.
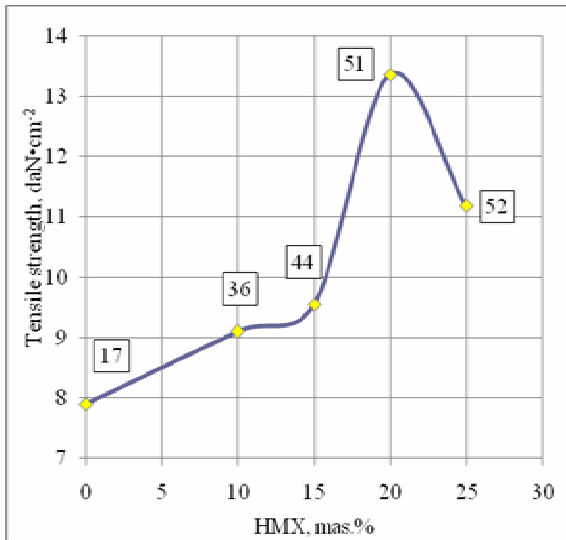

Figure 12. Propellant`s tensile strength values at 20 ºC

In all formulations the same AP coarse/fine particles ratio was used and remained after. Adding of HMX has never changed 65/35 ratio between 200 μm and 7 μm particles of AP. So the effect of contact surface could be eliminated in this way.
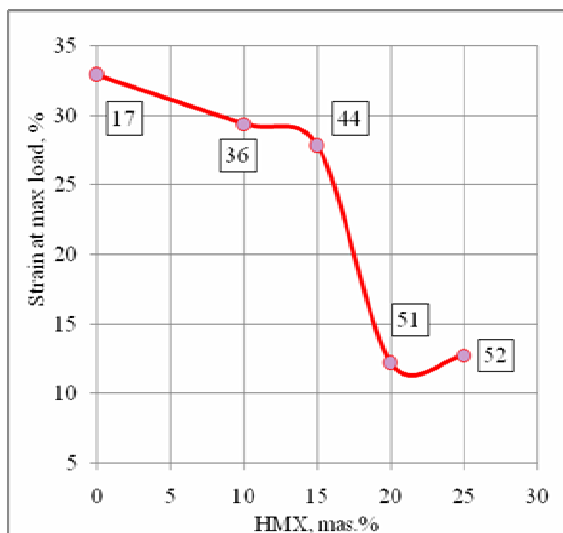

Figure 13. Propellant values of strain at maximum load at 20 ºC

The values of strain at maximum load (Fig.13) and modulus of elasticity (Fig.14) correspond to those that we have just discussed in the area of uniaxial mechanic characteristics. The increase of fillers in solid phase has a converse effect on changing tensile strength and modulus values at one side and strain from the other.
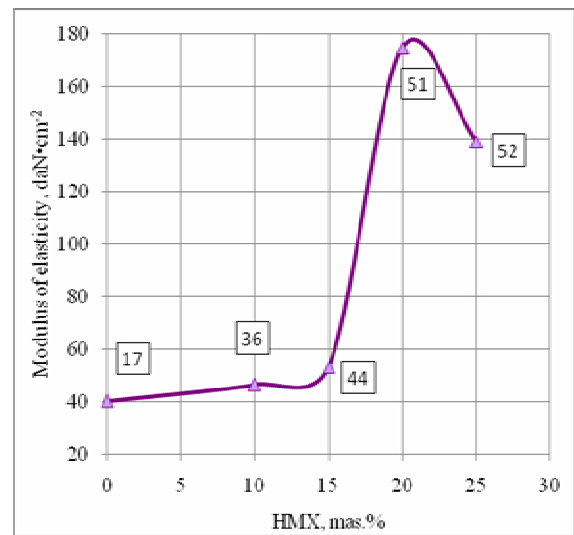

Figure 14. Propellant values of modulus of elasticity at 20 ºC

The higher content of huge molecul of HMX with great polarity (Fig.2) provides the higher values of tensile strength than referent propellant including 80 mas.% AP (No 17), that is evident in Fig.12. However, it should be mentioned that all nitramine propellants are stabilized with TiO_2, so the solid phase is larger than in the referent one. The most interesting moment in Fig.12 is the increase of tensile strength values from 9,55 daN·cm^{-2} (No 44) to 13.36 daN·cm^{-2} (No 51) when the content of HMX is changed for 5 mas.% and stabilizer is at the same level. The same as for the density levels, the packaging of different types and sizes of molecules could not be neglected and it is obvious by further adding of HMX.

Density of used components TiO_2, AP, HMX decreases in a row $4,23 > 1,95 > 1,91$ g·cm^{-3}, so it is expected to achieve propellant density values accordingly.
The measured values are shown in Fig.15.

Since the titania compound was added only as a combustion stabilizer, the higher density values of "stabilized nitramine compositions" (labeled as HMX-s), including HMX and TiO_2 are the consequence of the higher total solid phase. The mode of packing in the course of exchanging AP and HMX, due to dimensionality of these two molecules, dictates the level of densities.
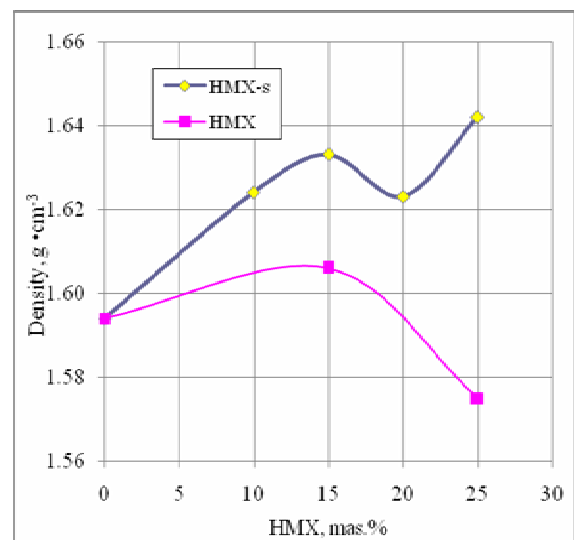

Figure 15. Density values of propellants

The energies of nitramine propellants released as heat during the combustion process are given in Fig.16.
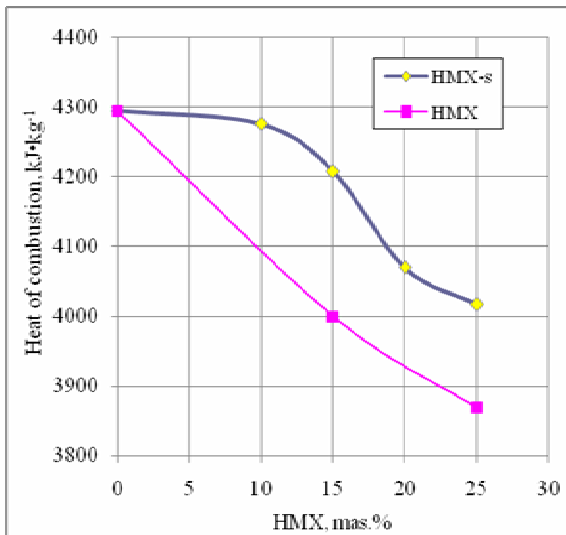
Figure 16. Propellant values of heat of combustion

Adding of nitramine components in composite propellants decreases heat of combustion value corresponding to propellants based on AP. However, the range of missile depends on molecule sizes of combustion products [12].

For better conclusions, the parameters of burning rate law are presented in a few next graphics. First of all, there is a diagram with "rupture" in burning rate law curve. This means that slope of the line is changed at some point of working pressure; the phenomenon is very important to predict the burning behaviour of propellants. In this case it is noticed for composition 36 containing 10 mas.% HMX and 1.5 mas.% of stabilizer (Table 1) in Fig.17.
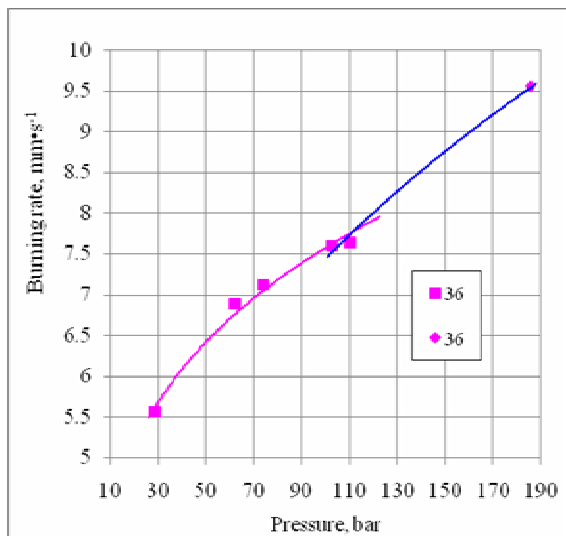

Figure 17. Burning rate law with "rupture" for propellants No 36

The values of exponent of pressure (and segment at ordinate axe) for both part of curve is shown in Table 6.

Table 6. Burning rate law parameters for No 36

No	n	B	R^2
36[1]	**0.2399**	**2.5083**	**0.9876**
36[2]	0.4033	1.1602	0.9914

[1] including 5 points up to 110 bar;
[2] including 3 points from 110 – 185 bar.

The correlation coefficients for both parts are sufficiently high so it is clear that at some region upward 100 bar the mode of combustion is changed. That is obvious due to pressure exponent values for two region of combustion.

The same appearance is occured during combustion referent composition No 17 and batch No 44 (Table 1) that is shown in Figures 18 and 19, respectively.
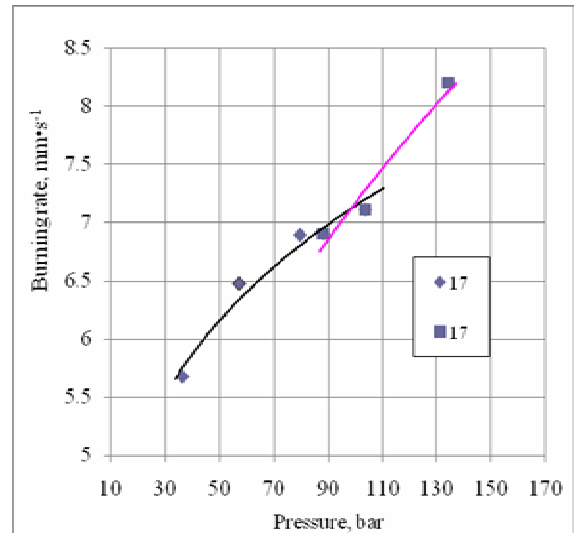

Figure 18. Burning rate law with "rupture" for propellants No 17

The values of exponent of pressure, segment at ordinate axe and correlation coefficient for both part of curve for these two formulations, No 17 and No 44, are shown in Table 7 and Table 8.

Table 7. Burning rate law parameters for No 17

No	n	B	R^2
17[1]	**0.2138**	**2.6676**	**0.9686**
17[2]	0.4239	1.0176	0.9496

[1] including 5 points up to 100 bar;
[2] including 3 points from 100 – 135 bar.
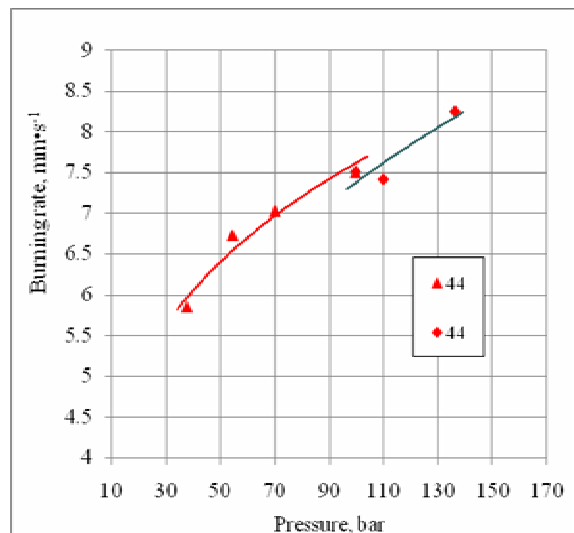
Figure 19. Burning rate law with "rupture" for propellants No 44

Table 8. Burning rate law parameters for No 44

No	n	B	R^2
44[1]	**0.2510**	**2.3992**	**0.9580**
44[2]	0.3317	1.6008	0.8279

[1] including 4 points up to 100 bar;
[2] including 3 points from 100 – 135 bar.

It looks like the rupture phenomenon is a consequence of referent propellants, because the change of slopes is largest

for No 17, and decrease in the following order: No 17, No 36, No 44, corresponding to content of HMX in the mixture.

The values of burning rate parameters laws given in Table 4 correspond to a part of curves without rupture, i.e. up to 100 bar.

The next Fig.20 shows burning rate laws of four stabilized propellants and for the referent one at 20ºC.

No 51 and No 52 have a very high coefficients of correlation: R^2 (51)=0.9989 and R^2 (52)=0.9998 and it could not be seen any rupture point on these two dependencies.

It is noticed from Fig.20 that by increasing the content of HMX the burning rate is slow down along with rather low increasing of pressure exponent. Comparing the values of referent one (No 17) it can be seen that it is in the middle of stabilized (dashed line).
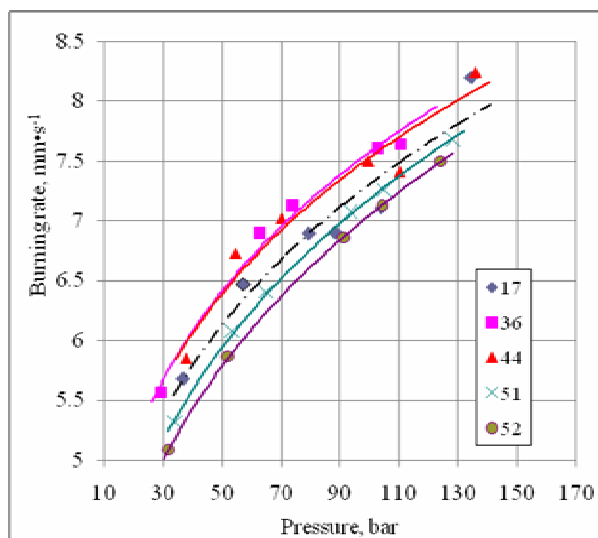

Figure 20. Burning rate laws for stabilized propellants

The next dependencies shown in Fig.21 two burning rate laws for unstabilized compositions against the referent one, without nitramine components.
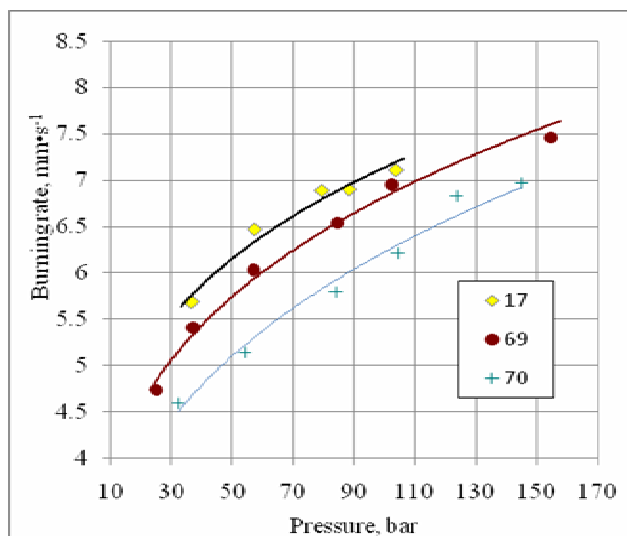

Figure 21. Burning rate laws for unstabilized propellants

The same appearance is noticed in Fig.21: content of HMX has the opposite effect on burning rate with low increasing of pressure exponent. Comparing to the values of No 17 it is remarkable that both nitramine batches have lower burning rates. Except that the correlation coefficients

are high enough: R^2 (69)=0.9902 and R^2 (70)=0.9815, so the slope of the curve could be unchangeable for the wide region up to 150 bar.

In Fig.22 the effect of TiO$_2$ as well as the difference between stabilized and unstabilized propellants at two levels of HMX content were observed: 15 mas.% and 25 mas.%.

Very important fact from Fig.22 is that the burning rates of unstabilized propellants (No 69 and No 70) are lower than those including TiO$_2$ for the same content of HMX (No 44 and No 52). It means that the effect of HMX on decrease of burning rate values could be reduced with TiO$_2$. The other positive influence of the same component is even better: the decrease of pressure exponent especially for higher HMX content.
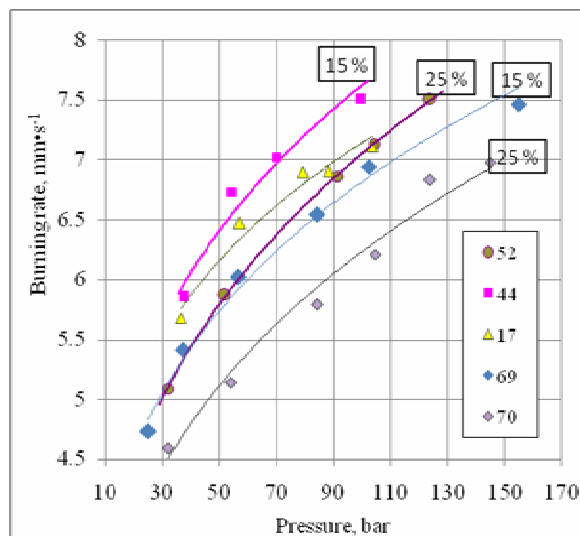

Figure 22. Effect of TiO$_2$ on burning rate laws

At first sight it is not expected, because in stabilized AP composite solid propellant systems, there comes a decrease of burning rate as the consequence of pressure exponent fall due to TiO$_2$ (in case of the same bimodal AP fraction) [8]. So, it has to be the result of different chemical structure influence between AP and HMX.

On the other hand, exchange of AP with HMX, shown in Fig.22, proceeds to overturn the burning rate in both cases incorporated 25 mas.% HMX and presence of stabilizer. From literature it is well known that the burning rates of HMX propellants are usually much lower than comparable propellants containing AP [7]. An explanation for the small variation in burning rate at pressures less than 200 bar is that HMX composite propellants, although heterogeneous in physical structure, burn more as a homogeneous propellant. During burning, the crystalline HMX, shown in Fig.3, melts (276 °C to 286 °C) together with the polymeric binder on the propellant burning surface and forms a chemically energetic liquid mixture. Because of this melting, the combustion waves in the gas phase are homogeneous.

An interesting literature data from observing the combustion of HMX are the discontinuities in the burning rate dependence on pressure, an abrupt change in the burning rate at around 50 bar where the pressure exponent becomes very large over a narrow pressure range and elevates the burning rate by several orders of magnitude. One explanation for this burning rate behavior states that the added heat transfer to the larger crystals causes the crystals to crack due the added thermal stresses. The thermal cracking increases the exposed crystal surface area.

The greater surface area increases the burning rate by allowing even greater heat transfer into the solid. The above explanation indicates that the slope breaks result from structural changes in the HMX crystals, and not changes in the actual burning rate pressure dependence of pure HMX. In the follow up the authors of that work said that small HMX particles do not show this behavior and have a much smoother burning rate versus pressure curve [5], which is exactly clear opened in our work.

Indeed, in this research the particle size of HMX was smaller than 125 μm which is the finest particles of HMX for use. So the appearance of crystal cracking is not really expressed. Except that, after replacement with HMX the remaining AP had the same ratio of course and fine particles, which is the most favorable mixture ration for those particle sizes in the point of combustion stability view [13]. So, adding of HMX shows more than acceptable values of pressure exponent (Table 4), especially in titanium (IV) oxide, even its effect was not extremely significant. There are other suplements with the same role and consequence, for example cupro (II) phtalocyanine, which is intented for stabilization of nitramine propellants.

Conclusion

Examination from this paper represents the preliminary research of exchange possibilities oxidizers and explosives, through development of composite solid propellants based on ammonium-perchlorate (AP) and formulations with four levels of cyclotetramethylene-tetranitramine i.e octogene (HMX). The binder was based on hydroxyl-terminated polybutadiene prepolymer and isophorone-diisocyanate as a curing agent. The seven compositions were prepared and in four of them TiO_2 was added as a combustion stabilizer. 80 mas.% of bimodal AP mixture (200 μm and 7 μm in ratio 65/35) was the basic solid phase: the exchange with HMX has been done at four levels 10 mas.%, 15 mas.%, 20 mas.% and 25 mas.% whereby the rest of AP remains at the same ratio. Particles of HMX was class 5 (< 125 μm), and considered as fine size. Two propellants were repeated at 15 mas.% and 25 mas.% of HMX without stabilizer. The seventh of the composition was the referent one including only AP.

The change of viscosity values at mixing temperature, uniaxial tensile mechanical characteristics, density, heat of combustion values and burning rate law parameters at 20 ℃ were determined and discussed in this work.

Entering the HMX instead AP has a relatively small negative effect in relation to viscosity values. The huge molecule of HMX affects the more prominent steric hindrances than a smaller compound of AP. Moreover, adding of some other solid ingredient leads to significantly larger differences among these compositions. It is the consequence of total solid phase increasing, and the presence of some complex compounds, due to huge HMX molecules.

The higher content of molecul of HMX with great polarity provides the higher values of tensile strength than referent propellant. Because of the presence of TiO_2, the solid phase is larger than in the referent one. The most interesting fact is the increase of tensile strength values by increasing the content of HMX for 5 mas.% with stabilizer at the same level. In that manner, the packaging of different types and sizes of molecules is important and it is obvious after further adding of solid components.

The increase of fillers in solid phase has a converse effect on changing tensile strength and modulus values at one side and strain from the other, as expected.

The mode of packing in the course of exchanging AP and HMX, due to dimensionality of these two molecules, and each density of components and their presence, dictates the level of densities.

Adding of nitramine components in composite rocket propellants decreases the heat of combustion value corresponding to propellants based on AP. However, the range of missile depends on molecule sizes of combustion products.

The combustion properties of propellants with HMX in relation to the "the empty (referent) one" shows that burning rate is decreasing by adding of HMX. But, the burning rates of unstabilized ones, especially with higher parts of HMX, show even lower rates. The influence on AP composite solid propellant systems is known as a decrease of burning rate as the consequence of pressure exponent fall due to TiO_2. Hence, this unpredictable appearance has to be the result of different chemical structure influence between AP and HMX.

The fine particles of HMX were smaller than 125 μm, so the appearance of crystal cracking is not really expressed. After replacement with HMX the remaining AP had the same ratio of bimodal mixture, which is the most favorable mixture ratio for those combination of particle sizes in the point of combustion stability. Adding of HMX shows more than acceptable values of pressure exponent, lower than 0.3. However, referent composition and two of them with smaller parts of HMX show the rupture in the burning rate laws, although it is not visible for nitramine propellants over 15 mas.% HMX.

There are several advantages in using HMX as a propellant ingredient. Due to the high energy content of HMX, its high density and low molecular weight of gas produced during combustion, high values of specific impulse for rocket propellants and impetus for gun propellants can be achieved [14].

These formulations are the beginning of development of these types of propellants with long range and at last smokeless composite solid propellants. The principal benefit of these types of propellants is their lack of visible signature. This enables the firing position to remain concealed and thus less vulnerable to hostile action.

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Preliminarna istraživanja kompozitnih raketnih goriva sa oktogenom

U radu su prikazana istraživanja kompozitnih raketnih goriva na bazi amonijum perhlorata, hidroksiterminiranog polibutadiena i izoforon diizocijanata sa različitim udelima oktogena (HMX). Masa HMX je povećavana na račun oksidatora, konstantnog bimodalnog sastava. Sagorevanje goriva je stabilizovano dodatkom titanijum (IV) oksida. Određivani su parametri zakona brzine sagorevanja i poređeni sa vrednostima za goriva istih sastava čvrstih faza. Takođe su određivane vrednosti prividnog viskoziteta, jednoosnih mehaničkih karakteristika, gustina i energetskih vrednosti istih sastava.

Ključne reči: kompozitno raketno gorivo, amonijum perhlorat, hidroksiterminirani polibutadien, oktogen, titan oksid, balističke karakteristike, brzina sagorevanja, mehaničke karakteristike.

Предварительные исследования композитных ракетных топлив с октогеном

В этой статье представлены исследования композитных ракетных топлив на основе перхлората аммония, гидроксилированного полибутадиена и изофорондиизоцианата, содержащих различные пропорции октогена (HMX). Маса HMX была увеличена на счёт окислителей с постоянным бимодальным составом. Сжигание топлива стабилизировалось с добавлением оксида титана (IV). Определены параметры закона скорости горения и сравниваны с величинами для топлив одинаковых составов твёрдых фаз. Также определены измеренные значения кажущейся вязкости, одноосных механических характеристик, плотности и значений энергии адекватных составов.

Ключевые слова: композитное ракетное топливо, перхлорат аммония, гидроксилированный полибутадиен, октоген, оксид титана (IV), баллистические характеристики, скорость горения, механические характеристики.

Recherches préliminaires sur les propergols composites à octogène

Dans ce papier on a présenté les recherches sur les propergols composites à la base de l'ammonium perchlorate, polybutadiène hydroxiterminé et l'isophorone diisocyanate aux différentes parts d'octogène (HMX).La masse de HMX a été augmentée sur le compte d'oxydant de composition bimodale constante. La combustion de propergol a été stabilisée par l'addition de titane (IV) oxyde. On a déterminé les paramètres des lois de la vitesse de combustion et on les a comparés avec les valeurs des propergols ayant les mêmes compositions des phases solides. On a déterminé aussi les valeurs pour les viscosités apparentes des caractéristiques mécaniques uniaxes, la densité et les valeurs énergétiques des mêmes compositions.

Mots clés: propergol composite, ammonium perchlorate, polybutadiène hydroxiterminé, octogène, titane (IV) oxyde, caractéristiques balistiques, vitesse de combustion, caractéristiques mécaniques.