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Combustion of non-catalyzed cyclotrimethylenetrinitramine-composite modified double-base propellants (Part II)

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The burning rate and the burning rate law of non-catalyzed reference double-base (DB) and cyclotrimethylenetrinitramine-composite modified double-base (RDX-CMDB) propellants were studied in order to elucidate the effect of the RDX addition on burning rate characteristics of these propellants. The burning rate characteristics were measured using a particular small-scale ballistic evaluation motor. It was found that the burning rates of RDX-CMDB propellants decrease with the increase of the RDX concentration, with the burning rate relatively independent of the RDX particle size. Also, it was established that the pressure exponent in the burning rate law increases, while the combustion index decreases linearly with the increase of the RDX concentration. The burning rate activity decreases slowly as the pressure increases. The temperature sensitivity of burning rate at a constant pressure of RDX-CMDB propellants is slightly lower than that of the conventional nitrocellulose and nitroglycerin based double-base propellant and for both propellants it decreases slowly and exponentially as the pressure increases. Since the mole fraction of NO_2 produced by the initial decomposition of RDX is lower than that of NO_2 produced by the initial decomposition of DB propellant, and because the ratio of NO_2/aldehydes of a DB propellant as an initial decomposition product is decreased by the addition of RDX, the addition of RDX shifts the equivalence ratio of NO_2/aldehydes towards fuel rich. As a result, the reaction rate in the fizz zone decreases and the heat feedback from the gas phase to the burning surface decreases when RDX is mixed within double-base propellants. Consequently, the burning rate of RDX-CMDB propellants decreases comparing to the double-base propellants, used as the base matrix of RDX-CMDB propellants.

Key words: **cyclotrimethylenetrinitramine-composite modified double-base propellant, burning rate, temperature sensitivity, flame structure, the surface and gas phase reactions, burning rate characteristics.**

Introduction

THERE have been numerous experimental and theoretical studies of the nitramine propellants combustion [1-10]. Double-base propellants which contain RDX (cyclo-trimethylenetrinitramine) or HMX (cyclotetramethylene-tetranitramine) have been developed as high-energy smokeless propellants. These types of propellants are commonly called nitramine-composite modified double-base (CMDB) propellants.

In general, the burning rate of solid propellants increases with the increase of the energy contained in the unit mass of propellants. This was observed for ammonium-perchlorate composite propellants and for double base propellants [1-10]. However, it has been reported that the burning rate of RDX-CMDB or HMX-CMDB propellants decreases by increasing the concentration of these nitramines [1-10]. In other words, the burning rate of nitramine-CMDB propellants decreases with the increase of the energy contained in the unit mass of the propellants. Such results concerning the burning rate have been obtained for different nitramine-propellant formulations using a chimney-type strand burner, pressurized by nitrogen and strand-shaped propellant samples (usually 7mm x 7mm in cross-section and 70mm in length) [1-10].

In this study, the burning rates of RDX-CMDB propellants were measured using a particular small-scale ballistic evaluation motor. The aim of this work was to determine the burning rate laws and the burning rate temperature sensitivity of the propellants considered under the most frequent operating conditions of real rocket motors. Moreover, this research was conducted in order to acquire better understanding of chemical and physical processes of the RDX-CMDB propellants combustion.

RDX-CMDB propellant formulations

In order to elucidate the effect of the RDX addition on combustion characteristics of RDX-CMDB propellants, five types of propellants were prepared. A propellant consisting of 61mass% nitrocellulose with 12.30 mass% of nitrogen, NC1230, as a polymeric matrix, 33 mass% of nitroglycerin, NG, being an energetic gelatinizer of nitrocellulose, 3 mass% of ethylcentralite, CI, as a stabilizer, and 3 mass% of dibutylphthalate, DBP as a plasticizer of nitrocellulose, was made as a reference DB propellant throughout this study. Four types of RDX-CMDB propellants which contained 10, 20 and 30 mass% RDX, respectively, were prepared, as well. The sizes of used RDX particles were approximately 50 and 200 μm. Detailed chemical compositions of these propellants are shown in Table 1.

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Table 1. Chemical composition and densities of DB and RDX-CMDB propellants

	$P0_{00}$	$P0_{10}$	$P0_{20}$	$P0_{30}$	$P0^*_{20}$
NC1230, mass%	61.0	54.5	48.3	42.0	48.3
NG, mass%	33.0	29.5	25.7	22.0	25.7
RDX, mass%		10	20	30	
RDX*, mass%					20
CI, mass%	3	3	3	3	3
DBP, mass%	3	3	3	3	3
Density, g/cm^3	1.59	1.61	1.63	1.64	1.76

RDX – average value of particles in diameter is 200 μm
RDX* - average value of particles in diameter is 50 μm

DB and RDX-CMDB propellant samples were prepared by a modified technological process [11] for the production of extruded double base rocket propellants using semi-industrial equipment, and the technological parameters were optimized as a function of quantity and RDX features [11]. The extrusion of the homogenized and gelatinized propellant mass (carpet rolls) was performed on the vertical press through the tool (die which inner diameter was 32 mm with a thorn which outer diameter was 16 mm).

Theoretical combustion performances

The basic theoretical combustion performances of DB and RDX-CMDB propellants and RDX respectively, calculated using the computer program [12] for the assigned chamber pressure (p_c=70 bar), are presented in Table 2. It is possible to notice from this Table the superiority of RDX compared to the reference DB propellant with respect to the heat of explosion, namely with respect to the energy per unit mass of energetic material, and with respect to the oxygen balance, as well. Moreover, as seen from this Table, the addition of RDX to a DB propellant gives an energetic material for obtaining high propulsive forces for rockets, in view of the fact that this material has higher density and produces higher T_c and lower M_c, i.e. it has higher thermodynamic potential compared to a DB propellant.

Table 2. Theoretical combustion performances of DB and RDX-CMDB propellants and RDX

	$P0_{00}$	$P0_{10}$	$P0_{20}$	$P0_{30}$	RDX
Enthalpy of formation, $\Delta_f H$, J/g	-2272.9	-2010.2	-1747.6	-1484.9	318.0
Heat of explosion, $\Delta_{ex} H$, J/g	4215.8	4282.0	4348.1	4414.3	5742.4
Oxygen balance, %	-35.4	-35.4	-35.3	-35.2	-21.6
Flame temperature, T_c, K	2604	2639	2674	2709	3299
Molecular mass of the combustion products, M_c, g/mole	24.229	24.043	23.858	23.676	24.238
Thermodynamic potential, E, (g/cm^3) (mol K/g)$^{1/2}$	16.50	16.86	17.21	17.57	20.65

Burning rate measurements

The propellant grains with a circular central port with flat, uninhibited end surfaces, and dimensions: outer diameter/inner diameter/length 32/16/125 mm, mass about 120 g (depending on the propellant formulation), were made by lathe machining on the inside of extruded experimental models and by cutting to the required length. The burning area versus burnt web is constant for these samples, with no combustion tail-off; the pressure decrease at burnout is controlled only by the venting of the combustion chamber. The burning rate of these materials was measured using a small-scale ballistic evaluation motor (Fig.1) in which the samples burnt across the outside and inside surfaces and from both fronts, thus a steady-state neutral combustion was realized. The ignition of samples was conducted using an electrically heated squib EU-25 set on 2.5 g of the black powder No.7 in the igniter carrier of each ballistic evaluation motor.

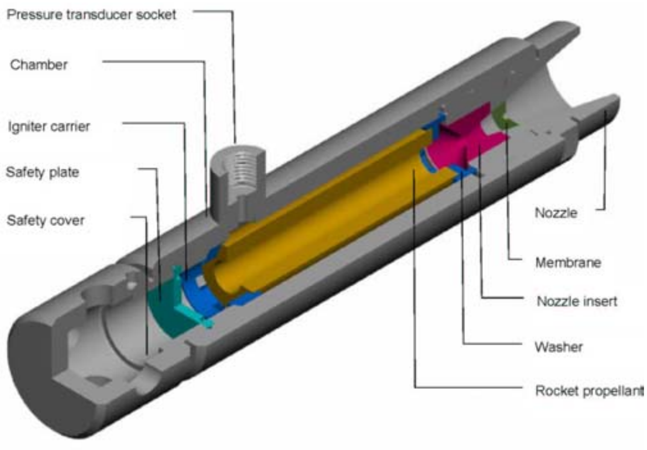

Figure 1. Small-scale ballistic evaluation motor

Based on the curve pressure-combustion time, p-t curve, the effective combustion time t_{ef} and the effective pressure p_{ef} were calculated through a series of iteration, Fig.2.

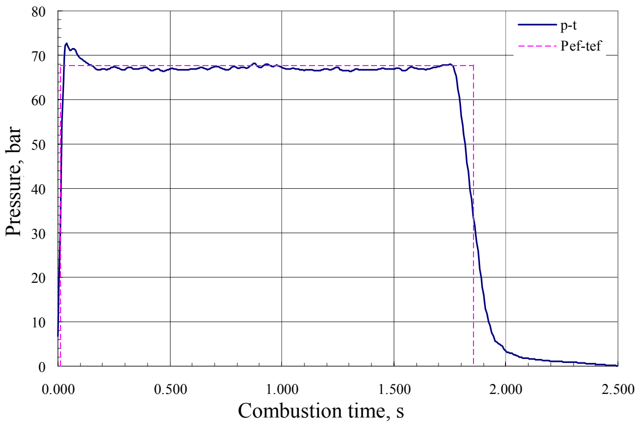

Figure 2. Pressure versus the combustion time curve for the RDX-CMDB sample – Determination of effective combustion time and effective pressure

The burning rate was computed as a ratio of the average half-wall grain thickness (Web) and the effective combustion time and it is related to the corresponding effective pressure.

The ratios of RDX-CMDB samples burning surfaces and the areas of used nozzle throats, K_N were in the range from 300 to 600 (in this interval the real rocket motors operate most frequently).

All combustion tests were performed at 20^{o}C, while for the reference propellant $P0_{00}$ and for the propellant sample with the maximum content of RDX, $P0_{30}$, these tests were performed at extreme temperatures –30^{o}C and +50^{o}C, as well.

Results and discussion

The results of the burning rate measurements of propellant experimental models are shown in Fig.3 and 4 as a function of pressure *(p).* As seen from these figures, the burning rates *(r)* of RDX-CMDB propellants decrease with the increase of the RDX concentration (Fig.3), with the burning rate relatively independent of the RDX particle size (Fig.4). Moreover, by the regression analysis of the results it was found that the pressure exponent *n* in the burning rate law, $r=ap^n$, increases, while the combustion index *a* decreases linearly with the increase of the RDX concentration (Fig.5), according to the following equations

$$n = 0.6554 + 0.0048 \cdot C_{RDX}\,, \quad R^2 = 0.998 \tag{1}$$

$$a\left[\text{mm/s}\right] = 0.5153 - 0.011 \cdot C_{RDX}\,, \quad R^2 = 0.9512 \tag{2}$$

where C_{RDX} is the RDX concentration in mass percentages and R^2 are the corresponding coefficients of determination.

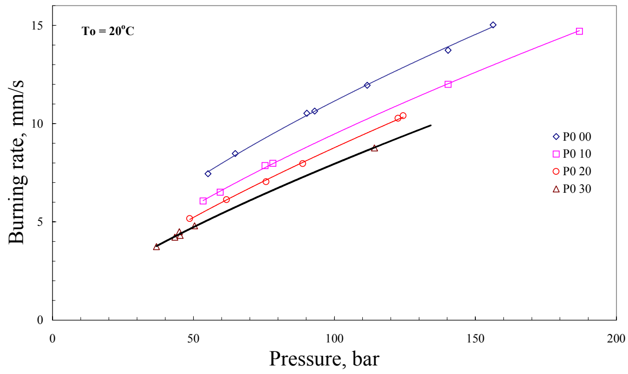

Figure 3. Burning rates of non-catalyzed DB and RDX-CMDB propellants at 20°C as a function of pressure

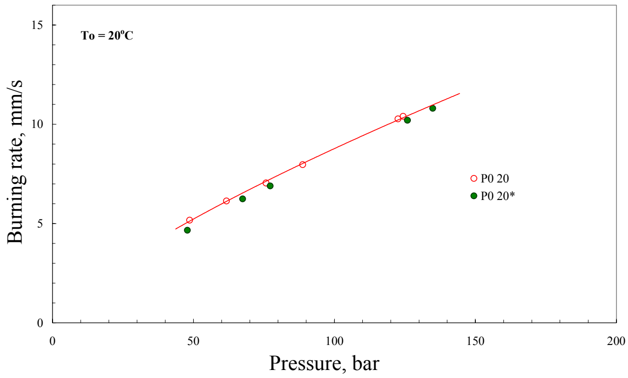

Figure 4. Burning rates of non-catalyzed RDX-CMDB propellants at 20°C as a function of pressure

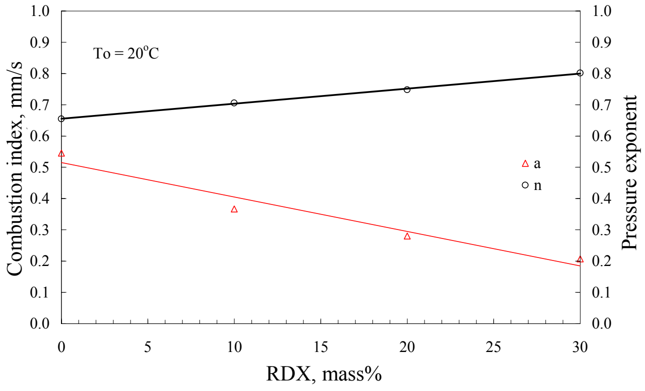

Figure 5. Pressure exponent *n* and the combustion index *a* of DB and RDX-CMDB propellants as a function of RDX concentration

The effect of the RDX addition is shown as a function of the burning rate activity (η), defined by

$$\eta = \frac{r_{DB} - r_{RDX-CMDB}}{r_{DB}} \tag{3}$$

where r_{DB} is the burning rate of the reference DB propellant and $r_{RDX\text{-}CMDB}$ is the burning rate of RDX-CMDB propellants at a constant pressure and initial temperature. As shown in Fig.6, the burning rate activity decreases slowly as the pressure increases at the initial temperature of 20°C. Having in mind the eqs.(1) and (2), the previous equation becomes

$$\eta = 0.0213 \cdot C_{RDX} \quad p^{-0.0048 \cdot C_{RDX}} \tag{4}$$

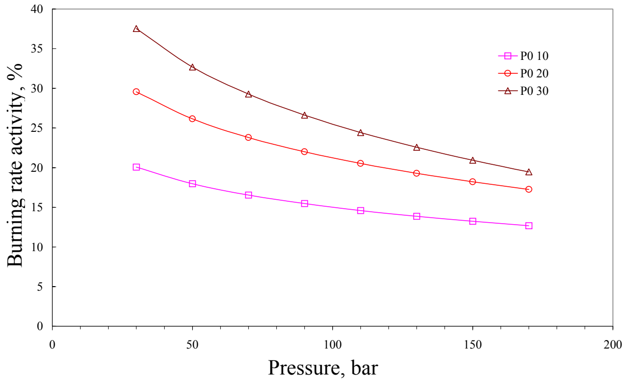

Figure 6. Burning rate activity of non-catalyzed RDX-CMDB propellants at 20°C as a function of pressure

Furthermore, as in the case of the reference DB propellant (Fig.7), the burning rates of RDX-CMDB propellants increase with the increase of the initial temperature of propellants, Fig.8.

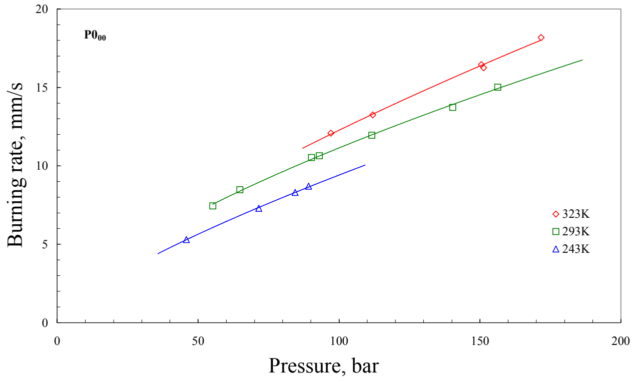

Figure 7. Burning rates of the reference DB propellant at three temperatures as a function of pressure

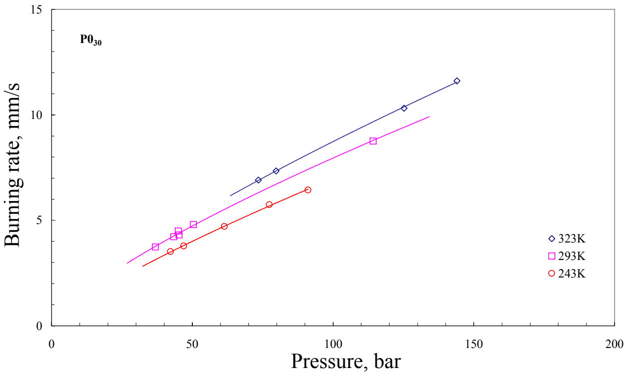

Figure 8. Burning rates of the RDX-CMDB propellant at three temperatures as a function of pressure

The temperature sensitivity of burning rate (σ_p) at a constant pressure defined as

$$\sigma_p = \left(\frac{\partial \ln r}{\partial T_o} \right)_p \tag{5}$$

was determined as a function of pressure for both propellants, $P0_{00}$ and $P0_{30}$. The results are shown in Fig.9. Since σ_p of a conventional nitrocellulose and nitroglycerin based double-base propellant is approximately 0.003/K, the results from Fig.9 confirm this fact for the reference DB propellant, and σ_p of the RDX-CMDB propellant $P0_{30}$ was found to be slightly lower than that of the conventional nitrocellulose and nitroglycerin based double-base propellant. As shown in Fig.9, σ_p of both propellants considered decreases slowly as the pressure increases according to the following equations

$$\sigma_p\left(P0_{00}\right) = 0.0053 \cdot p^{-0.1015}, \ R^2 = 0.999 \tag{6}$$

$$\sigma_p\left(P0_{30}\right) = 0.0056 \cdot p^{-0.1491}, \ R^2 = 0.999 \tag{7}$$

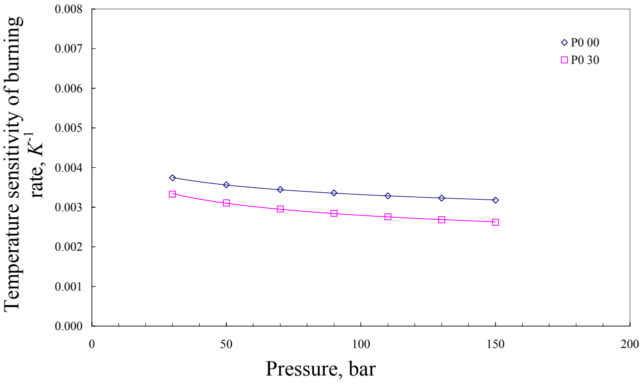

Figure 9. The temperature sensitivity of the burning rate of non-catalyzed DB and RDX-CMDB propellants

Burning rate analysis

The burning process is largely dependent on the combustion wave structure. This wave structure is a function of the propellant composition, pressure, and other various operating conditions. Propellants produce heat and high-temperature gas by the phenomena of combustion. The heat feedback from the high-temperature gas to the unburnt portion of the propellant raises this propellant portion to the decomposition temperature. As a result, the unburnt portion gasifies and produces heat by an exothermic chemical reaction. This successive heat feedback process makes the propellant burning occur continuously in order to sustain a steady-state burning.

The gas phase structure of conventional DB propellants, similarly to the gas phase structure of RDX-CMDB propellants, consists of a two-stage flame: the first stage is the fizz zone just above the burning surface, and the second stage is the dark zone, which produces the luminous flame zone.

The temperature in the propellant combustion wave increases rapidly from the initial temperature to the burning surface temperature. On the burning surface, a decomposition reaction occurs and generates reactive gaseous species. These species react exothermically, and the temperature in the fizz zone increases. The heat feedback from the gas phase to the burning surface, such as the burning rate of propellants, predominantly depends on the burning rate in the fizz zone.

As in the case of the cyclotetramethylenetetramine combustion, HMX [5,6], the overall initiation decomposition reaction of RDX can be stated as

$$2\left(CH_2NNO_2\right)_3 \rightarrow 2NO_2 + 2N_2O + 3N_2 + 6HCHO \tag{8}$$

and produces oxidizer and fuel fragments. Since nitrogen dioxide reacts quite rapidly with formaldehyde, the gas phase reaction [1,2,5,6]

$$7NO_2 + 5HCHO \rightarrow 7NO + 3CO + 2CO_2 + 5H_2O \tag{9}$$

is probably the dominating reaction followed immedia-tely by the decomposition reaction. The reaction product of NO oxidizes the remaining fuel fragment such as H_2 and CO. However, the oxidation reaction by NO is reported to be slow in producing final combustion products. The dominating gas-phase reaction on the RDX burning rate is the reaction by NO_2. When RDX is mixed with a DB propellant, RDX acts as an energy addition on the combustion products because no excess oxidizer components are available.

On the other hand, the overall initiation decomposition reaction of DB propellants, because they contain less quantity of the nitrogen and more amount of the carbon than that of RDX, can be stated as [12]

$$\begin{aligned} C_cH_hO_oN_n \rightarrow & \frac{1}{2}\left(o-c\right)NO_2 + \frac{1}{4}\left(2n-o+c\right)N_2 + \\ & + \frac{h}{2}HCHO + \left(c - \frac{h}{2}\right)CO \end{aligned} \tag{10}$$

where *c,h,o* and *n* are the coefficients in the molecular formula of the propellant.

As in the case of RDX, the gas phase reaction (9) is probably the dominating reaction followed immediately by the decomposition reaction, as well.

Using the overall initiation decomposition reactions (8) and (10) and the data from Table 2, the concentrations of reaction products were calculated for all propellants considered in this study. The results are represented in Table 3.

Table 3: Concentration of the reaction products on the surfaces of DB, RDX-CMDB propellants and RDX

	$P0_{00}$	$P0_{10}$	$P0_{20}$	$P0_{30}$	RDX
	Mole fractions				
NO_2	0.234	0.225	0.216	0.207	0.15
N_2O					0.15
N_2	0.05	0.08	0.11	0.14	0.23
CO	0.23	0.21	0.19	0.17	
HCHO	0.486	0.485	0.484	0.482	0.462
NO2/HCHO	0.48	0.46	0.45	0.43	0.33

As seen from this Table, the mole fraction of NO_2 produced by the initial decomposition of RDX is less than that of NO_2 produced by the initial decomposition of DB propellant. Also, based on the results from this Table, it can be concluded that the ratio of NO_2/aldehydes of a DB propellant as an initial decomposition product is decreased by the RDX addition. This indicates that the RDX addition shifts the equivalence ratio of NO_2/aldehydes towards fuel rich. As a result, the reaction rate in the fizz zone decreases and the heat feedback from the gas phase to the burning surface decreases when RDX is mixed within double-base propellants. Consequently, the burning rate of RDX-CMDB propellants decreases comparing to the double base propellants, used as the base matrix of RDX-CMDB propellants.

Conclusion

The burning rates of RDX-CMDB propellants decrease with the increase of the RDX concentration, with the burning rate relatively independent of the RDX particle size.

The pressure exponent in the burning rate law increases, while the combustion index decreases linearly with the increase of the RDX concentration.

The burning rate activity decreases slowly as the pressure increases in an exponential way.

The temperature sensitivity of burning rate at a constant pressure of RDX-CMDB propellants is slightly lower than that of the conventional nitrocellulose and nitroglycerin based double-base propellant and for both propellants it decreases slowly and exponentially as the pressure increases.

Since the mole fraction of NO_2 produced by the initial decomposition of RDX is lower than that of NO_2 produced by the initial decomposition of DB propellant, and because the ratio of NO_2/aldehydes of DB propellant as an initial decomposition product is decreased by the addition of RDX, the addition of RDX shifts the equivalence ratio of NO_2/aldehydes towards fuel rich. As a result, the reaction rate in the fizz zone decreases and the heat feedback from the gas phase to the burning surface decreases when RDX is mixed with double-base propellants. Consequently, the burning rate of RDX-CMDB propellants decreases comparing to the double-base propellants, used as the base matrix of RDX-CMDB propellants.

References

[1] YANO,Y., KUBOTA,N. Combustion of HMX-CMDB Propellants (I). *Propellants, Explosives, Pyrotechnics*, 1985, no.10, pp.192-196.

[2] YANO,Y., KUBOTA,N. Combustion of HMX-CMDB Propellants (II). *Propellants, Explosives, Pyrotechnics*, 1986, no.11, pp.1-5.

[3] KLOHN,W., EISELER,S. Nitramine Solide Rocket Propellants with Reduced Signature. *Propellants, Explosives, Pyrotechnics*, 1987, no.12, pp.71-77.

[4] RAMAN,K.V., SINGH,H. Ballistic Modification of RDX-Based CMDB Propellants. *Propellants, Explosives, Pyrotechnics*, 1988, no.13, pp.149-151.

[5] KUBOTA,N., KUWAHARA,T. Combustion of GAP/HMX and GAP/TAGN Energetic Composite Materials. *Propellants, Explosives, Pyrotechnics,* 1997, no.25, pp.86-91.

[6] KUBOTA,N., AOKI,I. Burning Rate Characterization of GAP/HMX Energetic Composite Materials. *Propellants, Explosives, Pyrotechnics,* 2000, no.25, pp.168-171.

[7] KUBOTA,N. Survey of Rocket Propellants and Their Combustion Characteristics, in KUO, K. K., Summerffield, M. (eds), *Fundamentals of Solid Propellant Combustion*, *Progress in Astronautics and Aeronautics*, 1984, vol.90, AIAA, New York.

[8] DAVENAS,A. *Technologie des propelgols solids*. Masson, Paris, 1989.

[9] SUTTON,G.P. *Rocket Propulsion Elements*. John Wiley & Sons, Inc., New York, 1992.

[10] DAVENAS,A. *Solid Rocket Propulsion Technology*. Pergamon Press, New York, Oxford, 1993.

[11] STOJANOVIĆ,R., *Kompozitna modifikovana dvobazna raketna goriva na bazi heksogena*, Int. doc., VTI-004-01-00160, Beograd, 1997.

[12] FILIPOVIĆ,M., STOJANOVIĆ,R., Combustion of non-catalyzed cyclotrimethylenetrinitramine-composite modified double-base propellants (Part I). *Scientific Technical Review*, 2003, vol.LIII, no.2, pp.19-26.

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Sagorevanje nekatalizovanih ciklotrimetilentrinitramin-kompozitnih modifikovanih dvobaznih goriva (Drugi deo)

Merena je brzina gorenja i određivan zakon brzine gorenja referentnog DB goriva i nekatalizovanih RDX-CMDB goriva u cilju utvrđivanja uticaja sadržaja RDX na karakteristike gorenja CMDB goriva. Brzine gorenja su merene u eksperimentalnom raketnom motoru. Zaključeno je da se brzina gorenja RDX-CMDB goriva smanjuje sa povećanjem sadržaja RDX u gorivu i da je praktično nezavisna od veličine čestica RDX. Takođe je utvrđeno da se eksponent pritiska u zakonu brzine gorenja linearno povećava, a da se indeks sagorevanja linearno smanjuje sa povećanjem sadržaja RDX u gorivu. Aktivnost brzine gorenja smanjuje se eksponencijalno sa povećanjem pritiska sagorevanja. Temperaturna osetljivost brzine gorenja pri konstantnom pritisku RDX-CMDB goriva smanjuje se eksponencijalno sa povećanjem pritiska sagorevanja i nešto je manja od temperaturne osetljivosti konvencionalnih DB goriva na bazi nitroceluloze i nitroglicerina. S obzirom da je molski udeo NO_2 koji je dobijen početnim razlaganjem RDX manji od molskog udela NO_2 koji je dobijen početnim razlaganjem DB goriva, kao i da se odnos NO_2/aldehidi smanjuje sa povećanjem sadržaja RDX u CMDB gorivu, brzina gorenja u fizz zoni, kao i odgovarajući toplotni fluks iz gasne faze ka površini sagorevanja smanjuje se sa dodatkom RDX, zbog čega se smanjuje i brzina gorenja ovih goriva u poređenju sa konvencionalnim DB gorivima.

Ključne reči: **ciklotrimetilentrinitramin-kompozitno modifikovano dvobazno (RDX-CMDB) raketno gorivo, brzina gorenja, temperaturna osetljivost, struktura plamena, reakcije na površini sagorevanje i u gasnoj fazi, karakteristike brzine gorenja.**

Combustion des propergols à double base non-catalysés et modifiés par le cyclotriméthylènetrinitramine (Partie II)

La vitesse de combustion et la loi de vitesse de combustion étaient étudiées pour les propergols RDX-CMDB non-catalysés et le propergol DB servant comme la référence afin de déteriminer l'effet de la teneur en RDX sur les caractéristiques de la combustion du propergol CMDB, mesurées dans le moteur-fusée expérimental. On a trouvé que la vitesse de combustion du propergol RDX-CMDB diminue avec l'accroissement de la teneur en RDX et quelle est presque indépendante de la grandeur de particules de RDX. On a aussi demontré que l'exposant de pression dans la

loi de vitesse de combustion augmente linéairement et que l'indice de combustion diminue linéairement avec l'accroissement de la teneur en RDX. L'activité de la vitesse de combustion diminue exponentiellement avec l'augmentation de la pression de combustion. La sensibilité à la chaleur de la vitesse de combustion pour la pression constante du RDX-CMDB diminue exponentiellement avec l'augmentation de la pression de combustion et elle est un peu inférieur à la sensibilité à la chaleur des propergols DB classiques à base de nitrocellulose et nitroglycérine. Comme la fraction molaire du NO_2 obtenue par la décomposition initiale du propergol DB, et comme la relation NO_2/aldéhydes diminue avec l'augmentation de la teneur en RDX dans le propergol CMDB, la vitesse de combustion dans la zone dite 'fizz' aussi bien que le flux de chaleur de la phase gazeuse vers la surface de combustion diminuent en ajoutant RDX. Par consequence, la vitesse de combustion de ce type des propergols diminue par rapport la vitesse de combustion des propergols DB classiques.

Mots-clés: **propergol à double base modifié par le cyclotriméthylènetrinitramine, vitesse de combustion, sensitivité à la chaleur, structure de la flamme, réactions sur la surface et dans la phase gazeuse, caractéristiques de la vitesse de combustion.**