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INFLUENCE OF DIFFERENT HMX/RDX CONTENTS IN COMPOSITE ROCKET PROPELLANTS ON THE VACUUM STABILITY TEST RESULTS

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Abstract: *The stability control system for energetic materials during storage involves testing, which need to ensure their reliable performance and stability over time. Any change in these materials, due to compatibility or stability issues, can cause serious consequences. Therefore, rigorous testing using specific methods is essential during the development and initial testing phases to conform all required criteria. Composite solid propellants based on ammonium perchlorate (AP)/hydroxyterminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI), including various contents of octogen (HMX) and hexogen (RDX), have been thoroughly investigated for their chemical stability. To achieve this, a highly effective modern method for testing the stability of pure explosives, explosive mixtures, solid rocket propellants and pyrotechnic mixtures the Vacuum Stability Test was employed. This test based on monitoring changes during gas diffusion, where vacuum conditions provide the highest sensitivity for the quantification of evolved gas, is another requirement for choosing this method within this research.*

Keywords: *Composite Rocket Propellants, RDX, HMX, Chemical Stability, Test Vacuum Stability Method.*

1. INTRODUCTION

Under normal storage conditions, energetic materials (EMs) are placed in warehouses positioned at different locations with varying microclimatic conditions until their use. The storage period for EMs is often long, sometimes exceeding 20 years. Typically, storage facilities for explosive materials decreased in automatic heating and/or cooling systems, leading to temperature variations based on the microclimatic conditions of the location. This raises several questions and issues regarding the stability of the energetic materials, which require specific research and testing.

The concept of stability of energetic materials can be defined based on two aspects: safety (safe storage) and reliability (probability of functioning and retaining designed properties after storage). From a safety and reliability perspective, it is important that the stored energetic material remains unchanged (or partially changed within defined limits) for a certain period during storage and does not undergo chemical decomposition [1]. In general, safety refers to chemical stability, while reliability refers to mechanical and ballistic stability [2]. The stability of an energetic material implies a state in which the material retains its chemical, ballistic, and mechanical characteristics at a level that allows its use and storage under storage conditions without any risk.

Regarding composite rocket propellants (CRPs), mechanical stability involves maintaining shape, dimensions, homogeneity of composition and structure, while mechanical properties are crucial for ensure reliability and safety during use. Preserving the values of specific heat and burning rate parameters within specified limits represents the basis of ballistic stability. Chemical stability involves the ability to keep the chemical characteristics of the material during storage under varying temperature conditions, which includes monitoring the chemical decomposition of the energetic material that affects both ballistic and mechanical characteristics.

Composite rocket fuels are heterogeneous mixtures of organic fuel-binding components (binders), oxidizers, and additives (metal fuel components, inhibitors or combustion rate catalysts, stabilizers, etc.) [3]. To ensure stable operation during combustion, they need to release large quantities of low-molecular-weight gases at high temperatures, by directing the combustion products

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through a nozzle opening, kinetic energy is provided for rocket propulsion.

The combustion of CRPs based on the oxidizer ammonium perchlorate (AP) and butadiene or polyol polyurethane prepolymers in a rocket engine yields the main combustion products: HCl, CO_2, H_2O, and N_2. Considering HCl molecules, as a product of AP combustion, along with atmospheric moisture, formed undesirable visible white fog [4]. On the other hand, the use of rocket propellants based on ammonium perchlorate represented a great advancement in the field of energetic materials, but at the same time, these materials contribute to environmental pollution due to combustion products rich in chloride compounds. The dominance characteristic of ammonium perchlorate is its complete conversion into gaseous reaction products during combustion. One attempt to obtain compositions with lower chloride content, for less smokiness, pollution, and/or improvement of the characteristics of new composite rocket fuels, is the use of nitramine compounds as energetic components and oxidizers. Besides the aspect of environmental protection, there is also the possibility of achieving better energy performance (e.g., improving the specific impulse value to increase the range of rocket means). The elimination of chloride compounds also leads to smokeless (improved concealment of personnel and equipment) and non-corrosive combustion products (longer service life of launch tubes) [5].

Nitramines, such as cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX), are used as an alternative to ammonium perchlorate, with the potential for obtaining better fuel energy performance. Due to the high concentration of hydrogen atoms, their combustion yields low-molecular-weight gases, resulting in an increase in the specific impulse value [5]. During the combustion of RDX, known as hexogen, a visible, defined liquid layer is formed, and it is assumed that the number of significant reactions contributing to the combustion process below the melting temperature is very small. The temperature of the melted layer is not determined, except according to literature data [6]. The higher burning rate of rocket fuel with RDX is a result of the larger amount of heat released from the combustion surface [7]. The increased amount of gases and the return heat flux from RDX are explained by the large temperature gradient near the combustion surface [8].
HMX, known as octogen, has a molar mass of 296.16 $g \cdot mol^{-1}$, a density of 1.91 $g \cdot cm^{-3}$, and a melting temperature between 276-286 °C [7]. It is a white powder, slightly soluble in water. Only a small amount of HMX evaporates into the surrounding environment. It develops a strong explosion at high temperatures. Due to its characteristics, it is in use in various types of explosives, rocket fuels, and booster charges.

Research in the field of CRPs containing certain amounts of RDX and HMX aims to determine the degree of influence of individual composition factors that can affect the aging process or decrease the stability of the fuel. To assess chemical stability, it is necessary to determine a parameter that best describes the aging process, as well as an appropriate method for reliably determining the value and monitoring the change of that parameter over time. There are several methods for testing chemical stability. The most suitable one for examination the CRPs/explosives is instrumental method the Vacuum Stability Test. The instrumental method Vacuum Stability Test was develop in the USA and accepted in several countries, and that was modification of the W. Taliani Test, where the gaseous reaction products are determined volumetrically rather than using a manometer [9]. This test, conducted at 100°C, lasts for 40 hours, unlike the Taliani Test, which was terminated upon reaching a certain pressure or released gas volume. The Vacuum Stability Test is based on monitoring changes caused by gas diffusion into the surrounding environment during heating [10].

In addition, very important examination, before starting the Vacuum Stability Test, is analyzing the chemical structure of CRP with RDX and HMX by using the Fourier Transform Infrared Spectroscopy (FTIR). This instrument was applied to examine the chemical interaction between CRP and RDX, as well as between CRP and HMX compound.

2. EXPERIMENTAL SECTION

2.1. Composite rocket propellants with HMX and RDX

Samples of composite rocket propellants used for this research consist of oxidizer, which is a bimodal mixture of AP particles, pre-polymer hydroxyl-terminated polybutadiene, HTPB (manufacturer Arco), cross-linked isophorone diisocyanate (IPDI), plasticizer dioctyl adipate (DOA) and bonding agent triethylene-tetramine, TET. Titanium(IV) oxide, which in earlier research periods of similar compositions proved to be a favorable combustion stabilizer, affecting the reduction of the pressure exponent value in the combustion rate law, was also included in this CRP. [11, 12]. Compositions of CRP with different concentration of octogen and hexogen, which were the main subject of study in this paper, are presented in Table 1.

Table 1. Mixed composition formula of the CRP with HMX and RDX

No	Sample	HMX, %	RDX, %	TiO2, %
1.	CRP-H25	25	-	2.5
2.	CRP-H30	30	-	2.5
3.	CRP-R15	-	15	2.0
4.	CRP-R20	-	20	2.0

2.2. Vacuum Stability Test

Description of the apparatus and equipment

The tests were performed on a Vacuum Stability Test device, STABIL 20, OZM Research, used for testing the chemical stability of all type of energetic materials.
The Vacuum Stability Test method is based on determining the volume of released gases that develop in

a closed controlled system, under vacuum, above the test samples [13]. All values of relisted gases were recorded during the measurement of chemical stability every minute, tabulated and graphically, as dependencies of pressure change of the gas over time.

Sample preparation

Sample preparation involves so-called "coarse" and "fine" mechanical preparation. Coarse preparation involves reducing the samples to smaller dimensions, while fine preparation involves cutting with scalpels to the prescribed sample size of 2 mm. CRP samples, except for mechanical preparation, do not undergo additional preparation.

Criterion of chemical stability

In the Vacuum Stability Test, the criterion of chemical stability is based on values of the volume of released gas, which is calculated using equation (1)

$$V = \left(V_c + V_t - \frac{m}{\rho} \right) \cdot \left(\frac{p_2 \cdot 273}{273 + t_2} - \frac{p_1 \cdot 273}{273 + t_1} \right) \cdot \frac{1}{1{,}013} \quad (1)$$

Where are:
- V - volume of gas released from the sample, cm^3
- V_c - volume of the piezoelectric transducer, cm^3
- V_t - volume of the glass test tubes, cm^3
- m - mass of the sample, g
- ρ - density of the test sample, $g \cdot cm^{-3}$
- p_1 - calculated pressure measured at the beginning of the experiment, bar
- p_2 - calculated pressure measured at the end of the experiment, bar
- t_1 - room temperature at the beginning of the experiment, °C
- t_2 - room temperature at the end of the experiment, °C

The volume of released gas from the tested sample (expressed in cm^3), calculated based on equation (5), is recalculated to a unit mass ($cm^3 \cdot g^{-1}$) [13]. Based on the known criteria, Table 2., it can be determined whether the observed sample is chemically stable or not.

Table 2. Criteria for chemical stability for CRP samples

Sample	T, [°C]	m, [g]	Time of experiment, [h]	Criteria of stability, [$cm^3 \cdot g^{-1}$], SPT*
CRP	100	2.5	40	≤ 1.2

*SPT - Standard Pressure and Temperature

2.3. FTIR-ATR analysis

Fourier transform infrared spectroscopy method (FTIR) was employed to investigate and/or confirmed the chemical structure, according to characteristics peaks, of CRP samples with different proportions of two types of pure explosives. FTIR spectrometer, Thermo Nicolet iS10, with the Attenuated Total Reflectance (ATR) measurement mode was used with the sample mounted on a diamond crystal. Absorption spectra were recorded in the range of 4000 to 500 cm^{-1}, with a resolution of 4 cm^{-1}.

3. RESULT AND DICUSION

The first steps after sample preparation, according to given percentage of ingredients Table 1., was to analyzed the characteristic FTIR spectra. Figure 1. and 2., shows the specific peaks for each of used organic compounds HMX and RDX.

The observed FTIR spectra for two CRP-HMX samples, Fig.1., showed presence of characteristic peaks corresponding to HMX [14], which is the main component of examined composite rocket propellants. The major bands can be assigned as follows: peaks corresponding to absorptions of the nitro group: 1564 cm^{-1} are from stretching vibrations of the nitro group; 1145 cm^{-1} are stretching vibrations of the nitro group and the ring; peaks 830-761 cm^{-1} are from bending vibrations of the nitro group; and the praks at 630 cm^{-1} and 600 cm^{-1} are from vibrations of the nitro group, along with peaks characteristic for ring vibrations at: 2996 cm^{-1}, 1145 cm^{-1}, 964 cm^{-1} and 946 cm^{-1}. It can be concluded that characteristics peaks unmistakably indicates presents of HMX in examined samples, as well as the chemical interaction between CRP and HMX.

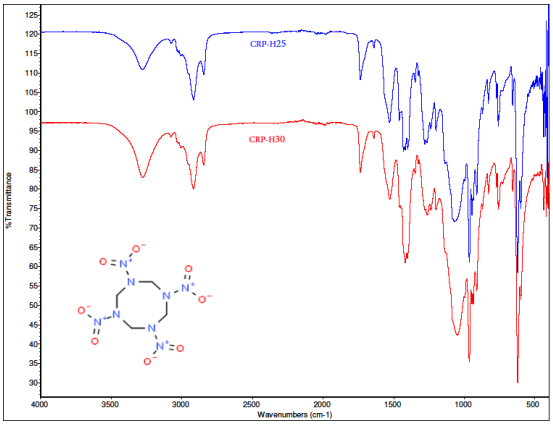

Figure 1., FTIR spectra of the samples CRP with HMX

FTIR spectra for the samples with RDX compound, Fig.2., also indicated existence of peaks corresponding to the absorptions of the nitro group [15]. More precisely: peaks at 1590 cm^{-1} and 1308 cm^{-1} correspond to stretching vibrations of the nitro group; 1039 cm^{-1} and 910 cm^{-1} are from in-plane bending vibrations of the nitro group, and the peak at 1039 cm^{-1} is characteristic for out-of-plane bending vibrations of the nitro group. In addition, ring vibration peaks were also registered at the following wavenumbers: 3074 cm^{-1}, 3065 cm^{-1} (CH vibration stretching (doublet) in the chain); 3003 cm^{-1} (CH vibration stretching); 1570 cm^{-1} (CH_2 out-of-plane stretching vibrations); 1418 cm^{-1} (CH_2 in-plane stretching vibrations); 1265 cm^{-1} and 1231 cm^{-1} (CH_2 group, deformation vibrations); and 945 cm^{-1} (CH vibration

stretching in the plane). All the examined peaks clearly indicate the presence of hexogen, and the chemical interaction between CRP and RDX.

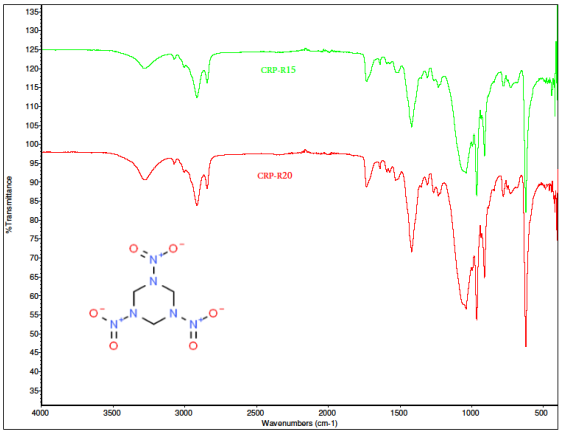

Figure 2., FTIR spectra of the samples CRP with RDX

The results of measurement and average value of the evolved gases, i.e. volume/volume per gram of the samples with HMX and RDX, as well as the density are given in Table 3. and Table 4. All measurements were performed on the Vacuum Stability Test instruments, and the mass of all examined samples was 2.5 ± 0.0001 g.

Table 3. Results of the TVS method for CRP samples with different percentage of HMX

No	Sample name	ρ [g·cm^{-3}]	V, [cm^3]	V, [cm^3·g^{-1}]
1.	CRP-H25	1.642	0.144	0.057
2.			0.145	0.058
3.			0.148	0.059
4.	**Average value**		**0.146**	**0.058**
5.	CRP-H30	1.626	0.098	0.039
6.			0.099	0.039
7.			0.100	0.040
8.	**Average value**		**0.099**	**0.039**

Table 4. Results of the TVS method for CRP samples with different percentage of RDX

No	Sample name	ρ [g·cm^{-3}]	V, [cm^3]	V, [cm^3·g^{-1}]
1.	CRP-R15	1.620	0.246	0.098
2.			0.164	0.065
3.			0.207	0.083
4.	**Average value**		**0.205**	**0.082**
5.	CRP-R20	1.614	0.273	0.109
6.			0.302	0.121
7.			0.202	0.089
8.	**Average value**		**0.264**	**0.106**

The theoretical values of enthalpy of formation of HMX and RDX are positive (74.88 kJ·mol^{-1} vs. 70.63 kJ·mol^{-1}), which indicated that the resultant volume of released gases can be correlated with the existing bond energies and the enthalpies of formation of all input components. In addition, based on the united graphical time-pressure diagram of the separated gases, Figure 3., the character of all the curves is specific and shows the same trend during the test time, regardless of the type of explosive or its share in the composition. Furthermore, throughout the entire testing period, there is a contribution to the increase in pressure, the curve shows a gradient of rise, and there is no difference in the levels of the curves, for either samples with RDX or samples with HMX.

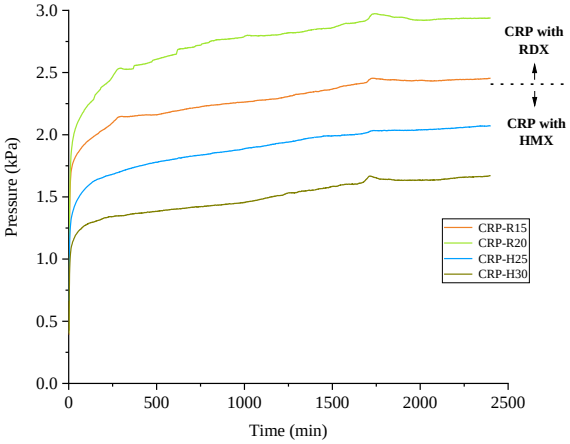

Figure 3., United time-pressure diagram for CRP samples with HMX and RDX

The values of released gases per gram for samples with RDX, Table 4. are similar 0.082 and 0.106 cm^3·g^{-1}. The obtained values of released gases per gram for samples with HMX, Table 3. are also mutually similar 0.058 and 0.039 cm^3·g^{-1}, and are much lower than the values for samples with RDX. Knowing the fact that, RDX has three nitramine bonds (-C-N-NO_2) while HMX has four same molecule, it was expected that less energy is required for their dissociation. Therefore, the CRP with RDX compositions release more gaseous fragments, i.e. have increased in the value of evolved gases than CRP with HMX. Some data for the examination of pure substances for the quantities of gases record values for nitramine compounds ranging from 0.1 to 0.4 cm^3·g^{-1} [16].

In terms of chemical stability and based on the requirements where the value who indicate chemical stability should be ≤ 1.2 cm^3·g^{-1}, Table 2., and according to results, Tables 3. and 4., it can be seen that the corresponding values of the volumes of released gases for both examined compositions are below the set criteria. The evidence from given results implies that both compositions CRP are chemically stable.

The titanium(IV) oxide was added in amount range from 2.0 to 2.5 wt.% in all examined compositions. Based on previously published results, the volume of released gases decreases slowly but consistently, in both compositions, i.e. CRP with RDX and in those with HMX [11, 18, 19]. Thermochemical calculations indicate that the contribution of burn rate inhibitors (such as titanium(IV) oxide or lithium fluoride) is negative, meaning they reduce the energetic potential of the propellants [12]. These compounds indicated decreases in the combustion temperature of the fuel by consuming the energy generated during combustion. The enthalpies of formation of these compounds are always positive; the reactions are

endothermic and consume the heat needed for decomposition. If the same role of the inhibitor is analogously applied here, it appears that its presence reduces gas emissions, leading to the conclusion that it also serves as a stabilizer. The enthalpies of formation of these compounds are always positive; the reactions are endothermic and consume the heat needed for decomposition. If the same role of the inhibitor is analogously applied here, it appears that its presence reduces gas emissions, leading to the conclusion that it also serves as a stabilizer.

4. CONCLUSION

The paper presents the results of tests conducted using the Vacuum Stability Test method on the composite rocket propellants (CRP) based on AP/HTPB/IPDI using the STABIL 20 instrument, while the chemical structure of the samples was examined using the "Thermo Nicolet iS10" FTIR spectrometer with ATR. The CRP compositions tested were made with nitramine explosives, hexogen, and octogen, added as energy components and oxidizers. The explosive was added at different mass content levels instead of oxidizer content, up to a total designed solid phase of 80 wt.%, and with titanium(IV) oxide as combustion stabilizer.

The chemical structure examination of the nitramine CRP compositions was performed by comparing characteristic peaks of the corresponding chemical groups of the tested samples, which indicated good matching of the characteristic peaks and thus confirmed the presence of the interaction between CRP and HMX/RDX.

The chemical stability test method for CRP is based on determining the volume of released gases during a standard prescribed heating period under vacuum. For various nitramine CRP compositions, and their contents, results as pressure-time diagram, as well as, values of gas-released volumes were obtained. The tested CRP HMX/RDX compositions exhibit high stability according to the chemical stability criterion applied to explosive charges and CRP, which is $V \leq 1.2$ $cm^3 \cdot g^{-1}$ [20]. However, analysis of the results indicated that in the increasing order of gas release volumes during the test (i.e., in the order of decreasing chemical stability of the composition), are nitramine CRP with RDX content compared to nitramine CRP with HMX.

In addition, regardless of the content of RDX in the composition, increase in the values of released gas volumes compared to compositions with HMX, indicated their significantly higher stability. The reason for the greater “instability” of CRP/RDX compositions compared to CRP/HMX is in the number of methylnitramine groups (three versus four, respectly) and the overall energy required for the breaking the chemical bonds. The strength of chemical bonds within different molecules of the CRP components determines the amount of released gases, which is higher for less stable compositions whose molecules have lower total bond energy.

Furthermore, it is necessary to emphasize that, the determined results of the amount of released gases do not take into account the gases produced by AP degradation. It is interesting that a higher amount of HMX gives a lower pressure and vice versa in the case of RDX. This phenomenon, in addition to the higher stability of HMX compared to RDX, can be also potentially attributed to AP (a bimodal mixture of AP particles present in the examined CRP), which will be our next steps in a further study of this topic.

The main conclusion of this work is that by altering part of the AP quantity with used nitramine explosives, compositions with favorable chemical stability can be obtained. Furthermore, since the current imperative is that the components that are in use, especially their decomposition products, are environmentally friendly, the obtained results supports the potential use of nitramine CRP in devices that are or will be in use in the Serbian Army.

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