Analysis of the Aging Process of Double-Base Propellants Without an Organic Stabilizer

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This paper describes studying the chemistry of the double-base propellant aging process of the grains from the START motor of the Soviet ground-to-air missile system, S-125 "Neva. This system was introduced in the armament of the Army of Serbia, in the early seventies of the last century and it is still in use. In order to determine the extent of degradation of propellants and then assess their chemical stability, ten methods were used. Modern analytical methods confirmed that typical organic propellant stabilizers are not present in the tested propellants. Therefore, the chemical stability of this propellant had to be additionally tested by the methods which are not based on measuring the consumption of stabilizers such as: microcalorimetry method of heat flux measuring, vacuum stability test, heat storage test at 100°C, methyl violet test at 120°C and mass loss test.

Key words: double-based rocket propellant, chemical stability, aging process, microcalorimetry, liquid chromatography, heat flux, stabilizer, ground-to-air missile.

Used symbols

AOP – Allied Ordnance Publication;
DNT – Dinitrotoluene
DB RP – Double base rocket propellant
EF – Extended flow
GC-MS – Gas Chromatography-Mass Spectroscopy
HFC – Heat Flow Microcalorimetry
HPLC – High Performance Liquid Chromatography
ICP-OES – Inductively coupled plasma optical emission spectrometry
ML – Mass loss
NC – Nitrocellulose
NATO – North Atlantic Treaty Organization
PDA – Photodiode array detector
SORS – Standard Defense of the Republic Serbia;
STANAG – Standardisation Agreement of NATO/PfP.

Introduction

UNDER tekstthe influence of different physical and chemical processes during storage, nitrocellulose (NC) propellants change their properties. This is so-called aging of propellants. The nitric ester constituents of NC propellants undergo slow thermal decomposition even at ambient temperature. The products of degradation can cause a reduction of chemical stability which can lead to self-ignition due to the exothermic nature of reactions involved. To remove the products of degradation and reduce the risk of the mentioned effect, stabilizers are added to propellant formulations [1-3]. In order to determine the extent of the degradation of propellants and then assess their stability, different analytical methods are used.

This paper studies the chemistry of double based rocket propellant (DB RP) aging using the results of the chemical stability assessment of nitrocellulose DB RP grains of the start motor of the Neva missile system. The S-125 "Neva" ground-to-air missile system was produced in the USSR in the 1960s. It is still in use in many countries, including Serbia. It is a missile defense system for anti-aircraft defense. In the armament of the Army of Serbia, the S-125M-Neva missile system was introduced in the early seventies of the last century.

The monitoring of the aging of the "Neva" DB RP was performed by a periodic control and technical inspection of the mentioned propellant samples. The following components in the "Neva" DB RP were identified: nitroglycerin, trinitrotoluene, dinitrotoluene and dibutylphtalate, but it is important to emphasize that the presence of any of the commonly used stabilizers such as ethyl centralite, methyl centralite, 2-nitrodiphenylamine, akardite and diphenylamine, was not confirmed [4-6].

The issue of the assessment of the chemical stability of the "Neva" DB RP (in the following text this propellant will be called only DB RP) is very specific because of the impossibility to use the methods for assessing the chemical

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stability by determining the content of stabilizers prescribed by Serbian standard SORS 8069/91 [7], and NATO standard AOP-48 Ed.2 [3].

Hence, the chemistry of aging and the chemical stability of these propellants have to be checked by other techniques not based on stabilizer consumption, such as Heat Flow Calorimetry according to standard SORS 9372/13 [8], Vacuum Stability test according to standard SORS 9374/13 [9], traditional high-temperature methods of chemical stability control according to standard SORS 9373/13 [10] and mass loss (ML) test [11,12].

The optimal work conditions of the semi-preparative high performance liquid chromatography (HPLC) for the separation and isolation of the organic components of DB RP will be defined. Isolated fractions will be identified by gas chromatography and mass spectrometry (GC-MS) [13,14]. The method of inductively coupled plasma - optical emission spectrometry (ICP-OES) will be used for determining the content of the metal component in the examined samples of DB RP [13,15]. A possible presence of an unknown component which plays a role of a stabilizer will be checked.

Experiment

Semi-preparative HPLC experiments

In order to develop the semi-preparative HPLC method for the separation and isolation of the organic components of DB RP, the samples were prepared according to the following procedure. The samples of propellants were cut to the dimension of 2 mm x 2 mm x 2 mm. About 2 g of a DB RP sample was weighed with an accuracy of ±0.1 mg and put in a 50 mL volumetric flask. The sample was extracted for 48 hours with 40 mL of dichloromethane. Then, the content of the volumetric flask was diluted to 50 mL with dichloromethane. By pipetting, 1 mL of the solution was transferred into a normal flask of 10 mL. Methylene chloride was evaporated in a water bath and finally, the content of the volumetric flask was diluted to 10 mL with methanol. The HPLC injection sample solution size was 200 μL [13].

The semi-preparative HPLC operational conditions were developed in accordance with the conditions of the analytical HPLC method. For the analytical and semi-preparative HPLC analysis, aWaters 1525 EF (extended flow) Binary HPLC Pump instrument with a photodiode array detector (PDA) was used. The HPLC system has the possibility of application in the analytical mode (with a flow rate of the mobile phase in the range between 0 mL/min and 10 mL/min) and the semi-preparative mode (with an extended flow rate of the mobile phase up to 22.50 mL/min). The manual injector, photo cells for the PDA detector and the loops for the injection of samples can be used in the analytical mode or the semi-preparative mode.

Identification of the isolated fractions of the DB RP sample by the GC-MS method

The semi-preparative HPLC method was used for the separation and isolation of the organic components of the DB RP samples. Then, the separated components of DB RP 66/88/24 were collected as fractions in volumetric flasks of 25 mL volume. The isolated fractions of DB RP were identified using the capillary GC with the Mass Detector by comparing the obtained mass spectra of each unknown component to a library of mass spectra of known components [13,15].

Qualitative analysis of the methylene chloride extract of DB RP by GC-MS

In order to identify a potential stabilizer presence in DB RP 66/88/24, the qualitative analysis of the methylene chloride extract of sample 66/88/24 was additionally carried out by the GC-MS, [13].

Quantitative analysis of DB RP samples

The quantitative analysis of the methylene chloride extract of DB RP samples was carried out by the methods of gas chromatography using a flame ionization detector (FID) and high performance liquid chromatography (HPLC) using a photo diode array detector (PDA) [13,15]. The content of the metal components in the DB RP samples was determined by the method of inductively coupled plasma optical emission spectrometry (ICP-OES) [13,15].

Heat Flow Calorimetry experiments

The heat flow measurements of the same tested DB RP propellants were performed in accordance with standard SORS 9372/13 on the HFC microcalorimeter TAM III [8]. The measurement was carried out at $90^{\circ}C$ and the duration of the test was 3.43 days from the time when the released heat became greater than the limit value, 5 J/g. To satisfy the requirements for propellant stability, the value of the measured heat flux should be lower than the criterion prescribed for the limits of heat flux, 350.0 μW/g at 90°C [8,12,13,15,16].

Vacuum stability test

The DB RP samples were cut into small pieces with the dimensions of 2 mm x 2 mm x 3 mm. Approximately 2,500 ± 0.0001 g of samples were put in glass heating tubes (140 ± 5 mm long and 18 mm in diameter) [18]. Since moisture plays a significant role in gas evolution, drying of samples is necessary. All samples were dried for 4 hours at 55°C, then cooled to room temperature in a desiccator. A modernized STABIL 20 apparatus was used for these measurements (manufactured by OZM Research). The temperature for the isothermal measurements was 90°C, according to standard SORS 9374/13 [9]. The samples in evacuated glass test tubes were placed into the heating block for 40 hours and heated to the desired temperature. Pressure transducers continuously estimated the pressure increase in the glass tubes. The results were in the form of the time dependence of the gas volume evolved from 1 g sample per second [9,18].

Heat Storage Test at $100^{\circ}C$

This is a qualitative method for the assessment of the chemical stability of propellants. The DB RP samples were heated at $(100 ± 1)$ $^{\circ}C$. The time from the start of heating to the appearance of brown gases of nitrogen oxides was measured. All measurements were performed according to standard SORS 9373/13 [10].

Methyl violet test at $120^{\circ}C$

The methyl violet (MV) test is a qualitative method for the assessment of the chemical stability of propellants. It is based on the change of MV paper color, due to the decomposition of propellants at elevated temperature. The time in minutes from the start of DB RP heating at $120^{\circ}C$ to a complete change of the MV paper violet color into the color of salmon, was measured. All measurements were performed according to standard SORS 9373/13 [10].

Mass loss test

The measuring of mass loss was performed in the DB RP artificially aged for 23 days at 90°C in Pyrex tubes with loosely inserted ground stoppers [11,12]. The initial ML is mass loss after heating for 1 hour at 100°C in an open tube. The Final ML = mass loss after 18 days at 90°C reduced by the initial ML. Criteria: ML ≤ 3% and no red-brown fumes up to 18 days at 90°C. This period of heating corresponds to 50 years at 25°C isothermal storage aging [11,12].

Results and Discussion

Separation of DB RP components by the semi-preparative HPLC

The semi-preparative HPLC operational conditions were developed in accordance with the optimal conditions of the analytical HPLC method. Therefore, the optimal operational conditions of the *analytical* HPLC in the gradient mode, which provide a satisfactory separation of the components of DB RP Neva 66/88/24 and an optimal analysis time, were defined [13,15].

Then, the optimal operational conditions of the *semi-preparative* HPLC in the gradient mode, for the separation of the components of DB RP 66/88/24, were defined. The analytical and semi-preparative columns had the same stationary phases, lengths and particle sizes. The transition from the analytical HPLC into the semi-preparative HPLC is based on data related to diameters of the columns (4.6 mm-*analytical* and 9.4 mm- *semi-preparative*) and the flow of the mobile phase through the analytical column (1 ml/min). Using the Waters OBD Prep Calculator, the flow rate through the semi-preparative column (4.73 ml/min) was automatically calculated [13,15,17]. The operational conditions were: Agilent ZORBAX Eclipse XDB-C18 semi-preparative column with the internal diameter of 9.4 mm; length 250 mm; the particle size of package, 5 μm; PDA detector with a semi-preparative photo-cell, oven temperature 30°C, the mobile phase is solvent A: 10% methanol in deionization water and solvent B: 100% methanol; flow rate of the mobile phase 4.73 ml/min; 200 μl volume of the sample loop or sample injected [13,15].

The change in the mobile phase composition during the gradient mode of the semi-preparative HPLC analysis of DB RP 66/88/24 was shown in Table 1. The flow is in ml/min.

Table 1. Gradient mode of the semi-preparative HPLC--DB RP 66/88/24-

Programmed Flow

Pump Mode: Gradient

	Time	Flow	%A	%B	%C	Curve
1		4.73	50.0	50.0	0.0	
2	1.00	4.73	50.0	50.0	0.0	6
3	5.00	4.73	40.0	60.0	0.0	6
4	10.00	4.73	30.0	70.0	0.0	6
5	11.00	4.73	0.0	100.0	0.0	6
6	15.00	4.73	0.0	100.0	0.0	6
7	16.00	4.73	50.0	50.0	0.0	6
8	20.00	4.73	50.0	50.0	0.0	6

The results of the DB RP 66/88/24 analysis are presented on the chromatogram, Fig.1 [12,14]. The figure shows the simultaneous overlay chromatograms of the same sample DB RP 68/88/24 obtained by the semi-preparative HPLC using the PDA detector at the wavelengths of 220 nm (blue line) and 254 nm (red line) [13,15]. The peaks present the separated components of the sample, which were collected as fractions in the flasks at the detector outlet. The fractions are designated as samples 1 to 5, and then identified using the GC-MS method [13,15].
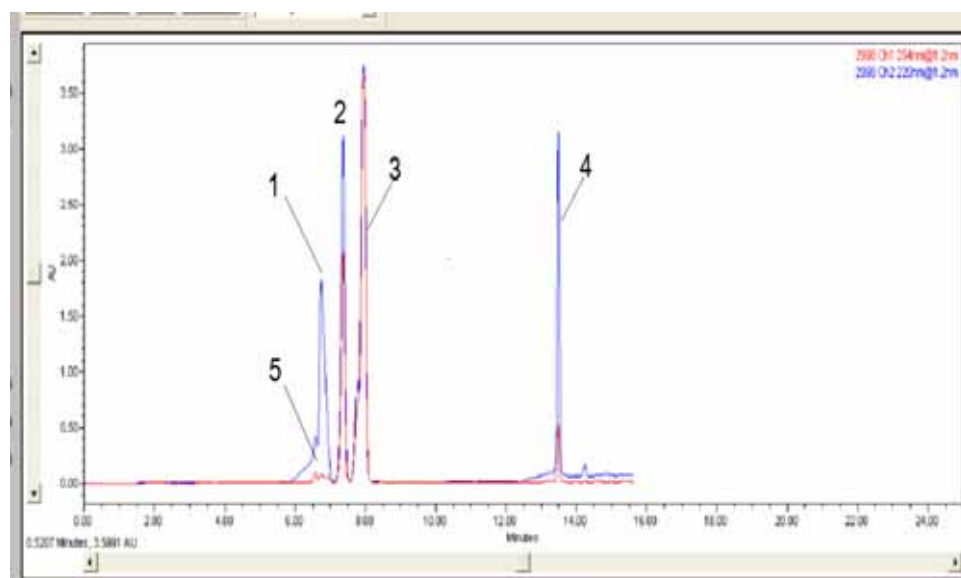

Figure 1. Semi-preparative HPLC chromatogram of DB RP 68/88/24

Identification of the isolated fraction of the DB RP sample by the GC-MS method

Isolated fractions of DB RP were identified using the capillary GC with the Mass Detector and by comparing the obtained mass spectra of each unknown component to a library of mass spectra of known components [13,15]. As an example, (a) chromatogram of fraction 4 and (b) mass spectra of the most abundant peak at the retention time RT=15.71 min is presented in Fig.2.

Figure 2. GC-MS identification of "fraction 4" isolated from DB RP 68/88/24

Figure 3. GC-MS analysis of DB RP 68/88/24
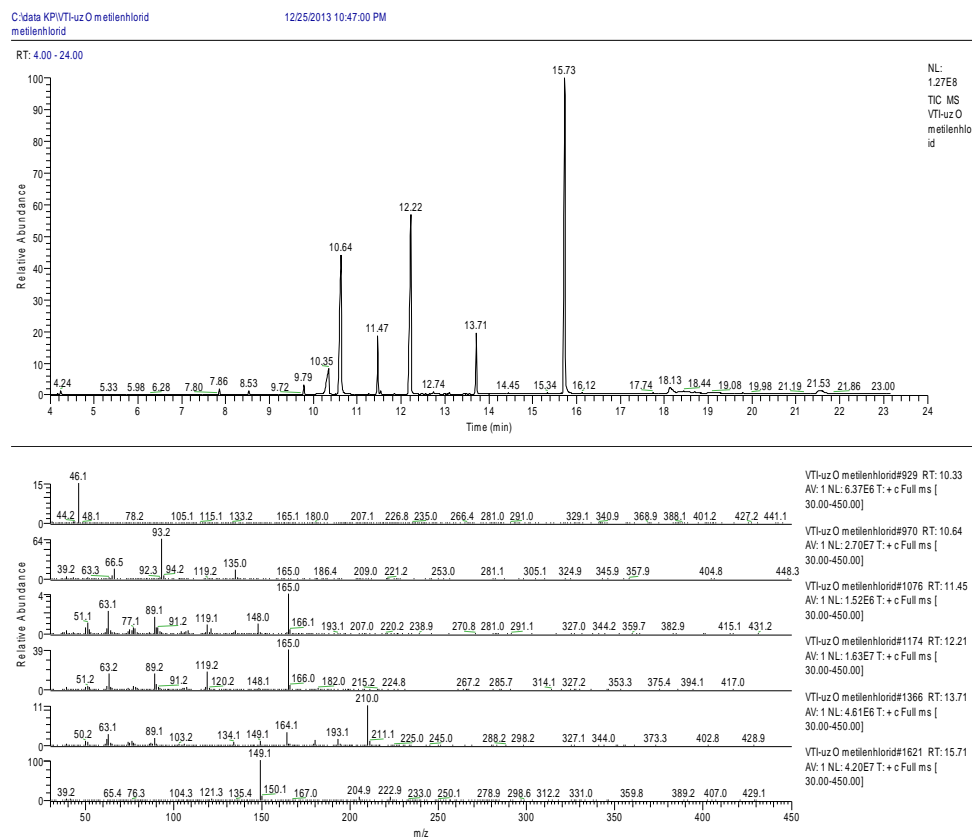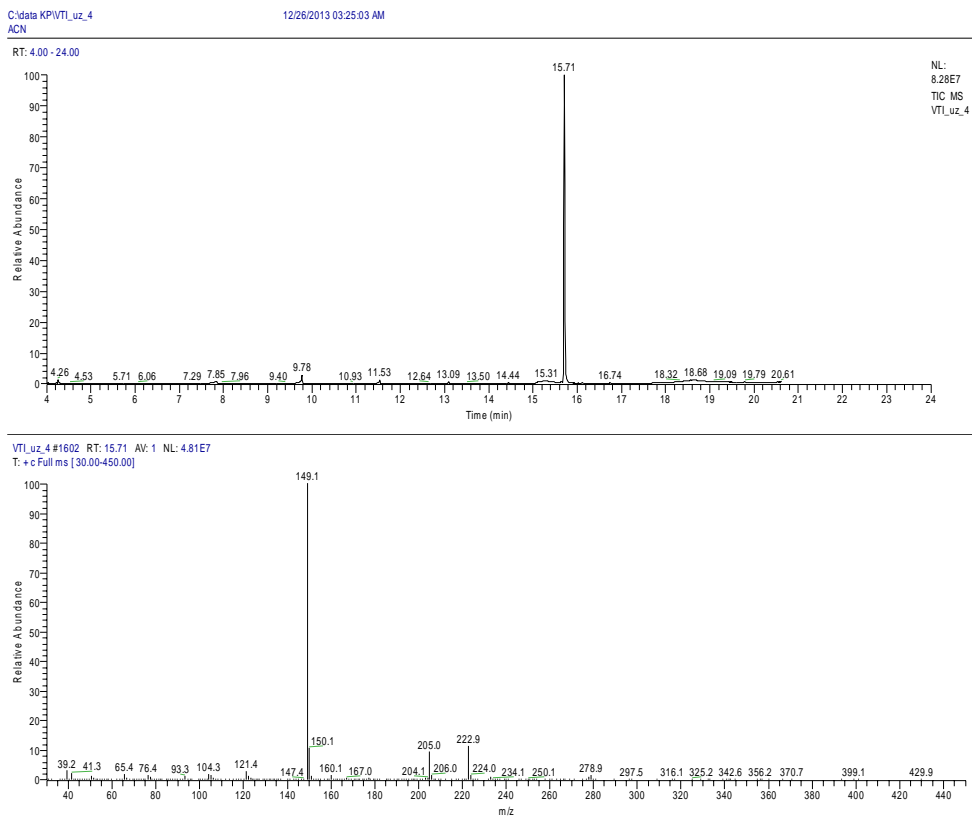
By the analysis of the figure, a component of the sample DB RP 68/88/24 isolated by the semi-preparative liquid HPLC was identified as dibutyl phthalate [13,15]. The results of the GC-MS analysis of other fractions (1, 2, 3 and 5) are given in the literature [13]. In the absence of an automated fractional collector, collection was performed manually, which reduced the possibility of obtaining pure fractions. So, fractions 1 and 5 represent a mixture in which, in addition to nitroglycerin, there are different isomers of dinitrotoluene (2,3-DNT and 2,6-DNT) [13,15]. The results of the identification of the separated and isolated fractions of DB RP 68/88/24 by the GC-MS method are given in Table 2.

Table 2. Isolated and identified components of DB RP 68/88/24 by the GC-MS

Fraction	Components
2	Trinitrotoluene
3	2,4-dinitrotoluene
4	Dibutylphtalate
1 and 5	Nitroglycerin, isomers of DNT: 2,3- DNT; 2,6- DNT

GC-MS analysis of the methylene chloride extract of DB RP

The GC-MS qualitative analysis of the methylene chloride extract of DB RP 68/88/24 was carried out. The GC hromatogram and the mass-spectral analysis of each peak of the GC chromatogram are presented in Fig.3.

By the GC-MS analysis of the methylene chloride extract of DB RP 68/88/24, the components shown in Table 3 were identified [13,15].

Table 3. Qualitative analysis of the methylene chloride extract of DB RP 68/88/24 by the GC-MS

RT, min	Component
10.35	Nitroglycerin
10.64	Acetanilide (internal standard)
11.45	2,6- dinitrotoluene
12.21	2,4- dinitrotoluene
13.71	Trinitrotoluene
15.71	Dibutylphtalate

In the tested sample, 2,3-dinitrotoluene and 3,4- dinitrotoluene were identified, as well [13,15].

Quantitative analysis of the DB RP samples

The results of the quantitative analysis of the tested DB RP by GC, HPLC and ICP-OES methods are presented in Table 4 [13,15].

Table 4. Quantitative analysis of the DB RP samples

Content, mas %	66-88-24	44- Я-137	713-X-70	44- Я-153
NG	22.50	22.17	23.60	22.90
2.4 -DNT	4.79	4.67	4.34	4.57
TNT	1.75	1.90	1.79	1.82
DBP	3.00	2.91	2.96	2.77
Mg	1.96	1.69	1.62	1.72
Ca	0.25	0.26	0.22	0.28

HFC chemical stability assessment of DB RP

The results of the HFC measurements of the examined DB RP according to standards [8] are presented in Table 5 [13,15].

Table 5. HFC measurements of the examined DB RP

DB RP	Heat flow, µW/g	Criterion [8]
66-88-24	111,957	≤ 390 µW/g $\Downarrow$ chemically stable ≥ 10 years at 25°C
44-Я-137	88.304	

The results of the examination predict and guarantee that DB RP will remain chemically stable for a minimum of 10 years of storage at ambient temperature (25°C), because after aging for 3.43 days at 90°C, the heat flow is ≤ 390 µW/g, so the criterion is met.

A satisfactory chemical stability of the examined DB RP can be explained by the fact that the role of the stabilizer is not performed by typical organic stabilizers, but inorganic stabilizers, such as magnesium oxide, MgO and calcium carbonate, $CaCO_3$ and aromatic compounds such as dinitrotoluene and trinitrotoluene [3,13,15,19,20].

Vacuum stability test

The results are presented in Table 6, in a form of the time dependence of the gas volume evolved from 1 g sample per second (i.e. V values in mL g^{-1} s^{-1}) and corrected to standard conditions [9,18].

Table 6. Results of the vacuum stability test

DB RP	mass, g	V, mL	V, mLg^{-1}s^{-1}	$V_{average}$ mLg^{-1}s^{-1}	Criterion of chemical stability, mL g^{-1} s^{-1}
66-88-24	2.5077	1.378	0.550	0.547	≤ 1.2
	2.5005	1.377	0.551		
	2.7051	1.352	0.540		
44- Я-137	2.5034	1.342	0.536	0.534	
	2.5074	1.335	0.532		
713-X-70	2.5001	1.261	0.504	0.500	
	2.5037	1.239	0.495		
44- Я-153	2.5015	1.206	0.482	0.484	
	2.5001	1.215	0.485		

In Table 6, all the results for the tested DB RP are ≤ 1.2 mL g^{-1} s^{-1}. So, the mentioned criterion is met and DB RP is chemically stable [9].

Heat Storage Test at 100°C *and Methyl violet test at* 120°C

The results of the assessment of the chemical stability of the examined DB RP according to the standard are presented in Table 7. All results are satisfactory, according to the criteria for the assessment of chemical stability [10]. Therefore, the tested samples of DB RP are chemically stable.

Table 7. Heat storage test at 100°C and Methyl violet test at 120°C

DB RP	Heat Storage test at 100°C, days	Criterion, days	Methyl violet test at 120°C, min	Criterion, min
66-88-24	> 7	6	62	60
44- Я-153	7		67	
44- Я-137	7		67	
713-X-70	7		73	

Mass loss test

The results of the ML test of the examined DB RP are presented in Table 8.

Table 8. Results of the mass loss test of DB RP

DB RP	100°C/ 1 h	90°C/ 18 days	final ML, mass %
	initial ML, mass %	overall ML, mass %	
66-88-24	0.68	3.06	2.38
44- Я-153	0.64	3.58	2.94
44- Я-137	0.57	3.16	2.59
713-X-70	0.61	3.52	2.91

The initial ML (1 hour of heating at 100°C) was subtracted from the overall ML (18 days heating at 90°C), and the final value of ML was calculated [12]. All DB RP satisfy the limit criterion of stability $\leq 3\%$ mass loss, during 18 days of isothermal heating at 90°C. Therefore, the mass loss test predicts and guarantees that the tested DB RP will remain chemically stable for a minimum of 50 years of storage at ambient temperature (25°C).

Conclusion

The chemistry of the aging of DB RP grains of the START motor of the missile system S-125 Neva was studied by different analitycal methods. First, the operational conditions of the semi-preparative HPLC method for the separation and isolation of the organic components of the DB RP grain

samples of the mentioned rocket system START engine were defined. Then, the isolated organic components were identified by the method of GC-MS as: nitroglycerin, trinitrotoluene, dinitrotoluene and dibutylphtalate. These experimental results confirmed the fact that the role of the stabilizer in the tested DB RP, some of which were 40 years old, is not performed by typical organic propellant stabilizers.

Hence, the extent of degradation as well as the chemical stability of these propellants were checked by the methods not based on stabilizer consumption. The results of the chemical stability assessment of the examined DB RP samples obtained by traditional methods (vacuum stability test, heating storage at 100^oC, metilviolet test at 120^oC and mass loss test) were satisfactory, in accordance with the criteria. Although the traditional mass loss test predicts and guarantees the chemical stability of DB RP for a minimum of 50 years of storage at ambient temperature (25^oC), the preference is given to the results of heat flow calorimetry as a leading modern method for DB RP stability assessment. Heat flow calorimetry predicts and guarantees that the tested DB RP will remain chemically stable for a minimum of 10 years of storage at 25^oC. The satisfactory chemical stability of the tested DB RP may be explained by the presence of inorganic stabilizers, such as magnesium oxide and calcium carbonate, and aromatic compounds such as dinitrotoluene and trinitrotoluene, as well. Because of the impossibility to use the method for assessing the chemical stability by determining the stabilizer content, for this DB RP type, the priority is given to the method of heat flow calorimetry and the vacuum stability test as well as to internationally recognized methods not based on monitoring the consumption of stabilizers.

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Analiza procesa starenja dvobaznih raketnih goriva bez organskih stabilizatora

U radu je opisano izučavanje hemije procesa starenja dvobaznih raketnih goriva punjenja start motora sovjetskog raketnog sistema zemlja-vazduh S-125 "Neva". Ovaj sistem je uveden u naoružanje Vojske Srbije sedamdesetih godina prošlog veka i još uvek je u upotrebi. U cilju određivanja stepena degradacije dvobaznih raketnih goriva, a zatim i ocene njihove hemijske stabilnosti, primenjeno je deset analitičkih metoda. Savremene analitičke metode, potvrdile su da tipični organski stabilizatori nisu prisutni u ispitanim raketnim gorivima. Stoga je njihova hemijska stabilnost morala biti dodatno ispitana metodama koje se ne zasnivaju na merenju potrošnje stabilizatora, kao što su: mikrokalorimetrijska metoda merenja toplotnog fluksa, test vakuum stabilnosti, test grejanja na 100^oC, metilviolet test na 120^oC i test merenja gubitka mase.

Ključne reči: **dvobazno raketno gorivo, hemijska stabilnost, starenje, mikrokalorimetrija, tečna hromatografija, toplotni fluks, stabilizator, raketa zemlja-vazduh.**

Пример анализа процесса старения двойных базовых ракетных топлив

Эта статья описывает исследование химии процесса старения двойных базовых ракетных топлив для зарядки и запуска двигателя советской ракетной системы земля-воздух S-125 "Нева". Эта система была введена во вооружение сербской армии в семидесятые годы XX века и до сих пор используется. Для того чтобы определить степень деградации двойных базовых ракетных топлив, и затем и рассмотреть их химическую стабильность, применяется десять аналитических методов. Современные методы анализа подтвердили, что в тестируемых ракетных топливах не присутствуют типичные органические стабилизаторы. Таким образом их химическая стабильность должна быть дополнительно проверенна методами, которые не основаны на измерении расхода стабилизаторов, таких как: микрокалориметрический метод измерения теплового потока, тест стабильности вакуума, тест нагрева при 100°C, метилвиолет - тест на 120°C и испытательные потери массы.

Ключевые слова: двойное базовое ракетное топливо, химическая стабильность, микрокалориметрия, жидкостная хроматография, тепловой поток, тест на стабильность вакуума, стабилизатор, ракета земля-воздух.

Un exemple d'analyse du processus de vieillissement chez les propergols bibasiques

Ce papier décrit l'étude de la chimie du processus de vieillissement chez les propergols bibasiques de la charge du moteur d'appoint chez le système de missile terre – air soviétique S-125 "Neva". Ce système a été introduit dans l'armement de l'Armée de Serbie pendant les années soixante-dix du siècle dernier et il est toujours en utilisation. Dans le but de la détermination du degré de dégradation des propergols bibasiques et puis pour estimer leur stabilité chimique on a utilisé dix méthodes analytiques. Les méthodes analytiques modernes ont confirmé que les stabilisateurs organiques typiques n'étaient pas présents dans les propergols étudiés. Pour cette raison leur stabilité chimique a dû être étudiée de plus par les méthodes qui ne sont pas basées sur le mesurage de la consommation des stabilisateurs tels que : méthode micro calorimétrique du mesurage de flux thermique, test de stabilité vacuum, test de chauffage à 100ºC, méthyle violet test à 120ºC et le test de mesurage de la perte de masse.

Mots clés: propergol bibasique, stabilité chimique, micro calorimétrie, chromatographie liquide, flux thermique, test de stabilité vacuum, stabilisateur, missile terre – air.