12th INTERNATIONAL SCIENTIFIC CONFERENCE ON DEFENSIVE TECHNOLOGIES
OTEH 2026
Serbia, Tara, 21 - 24 October 2026

STABILITY EVALUATION OF MULTI-COMPONENT PBX UNDER VARYING CLIMATIC CONDITIONS

MIRJANA KRSTOVIĆ
Military technical institute, Belgrade, mirjana.krstovic@mod.gov.rs

TEODORA STANČIĆ
Military technical institute, Belgrade, teodorastancic@gmail.com

VESNA PETROVIĆ
Technical Overhaul Facility Kragujevac, lab@trzk.co.rs

KATARINA NESTOROVIĆ
Military technical institute, Belgrade, katarina.nestorovic@gmail.com

JELENA ŠULTANS
Technical Overhaul Facility Kragujevac, lab@trzk.co.rs

DANICA BAJIĆ
Military technical institute, Belgrade, danica.bajic@mod.gov.rs

Abstract: *Polymer-bonded explosives (PBX) are widely recognized as reduced-sensitivity energetic materials with improved safety characteristics and satisfactory stability during prolonged adequate storage. However, despite their favorable stability characteristics, the influence of different climatic conditions on their long-term behavior has not been sufficiently investigated, especially when it comes to complex multi-component formulations, like thermobaric (TBX). Systematic studies investigating the combined effects of temperature, humidity, and/or corrosive marine atmospheres on stability of these formulations remain limited. In this paper, multi-component PBX based on hydroxyl-terminated polybutadiene-based binder, containing octogen as the energetic filler, ammonium perchlorate as oxidizer and aluminum and magnesium metal powders were examined. The samples were subjected to controlled environmental conditioning designed to simulate three distinct climatic regimes: continental climate conditions, elevated temperature and humidity conditions, and Mediterranean climate conditions involving exposure to salt-mist to reproduce a marine corrosive atmosphere. The treated samples were evaluated using the vacuum stability test STANAG 4556 procedure and by heat flow calorimetry. The combined application of standardized stability testing and sensitive thermal analysis enabled a comprehensive assessment of climate-induced changes in PBX behavior. The results provide insight into the stability-related responses of PBX under diverse environmental stresses and contribute to a better understanding of their performance and reliability in different climatic deployment scenarios.*

Keywords: *PBX, Vacuum Stability Test, Heat flow calorimetry, environmental conditioning*

1. INTRODUCTION

Cast-cured polymer bonded explosives (PBX) have attracted significant interest due to their reduced sensitivity compared to conventional TNT-based formulations and due to their broad range of detonation characteristics [1]. The main benefits of PBX include significant mechanical strength, increased filling density, reduced sensitivity during handling and storage, good thermal stability and the capability to modulate detonation velocity according to requirements [2]. The potential to integrate metal powders into compositions to produce a thermobaric effect, specifically generating a fireball by the combustion of metal powders post-detonation [3-5], highlights the increase application of these compositions in the weapons industry. Such compositions provide significantly enhanced efficiency in both enclosed spaces, such as tunnels and caves, and in open, cleared areas.

Although many PBX formulations have been developed and generally show low sensitivity to external influences, the effect of environmental factors on their long-term behavior is still not widely studied. There are several reasons for that: the explosives are stored under controlled conditions and sealed in hermetically closed warheads, which limits their exposure to the environment. The extensive variety of munitions that can incorporate these formulations, coupled with their diminished sensitivity, allows for the development of new munitions that, under storage conditions, would not necessitate complete hermetization (for instance, an opening in the liner for the insertion of explosives and placing fuze) until the time of usage. Due to these potential designs, it is essential to

Corresponding author: M. Krstović;
E-mail: mirjana.krstovic@mod.gov.rs
DOI: 10.5937/OTEH26041K

gather information concerning the behavior of these compositions under various climatic conditions, corresponding to different types of temporary storage and exploitation.

This paper examines three samples of multi-component thermobaric PBX explosives that were manufactured five years ago and stored in continental climate conditions during that time. To replicate various climatic events, the samples were subjected to a regime of elevated temperature and air humidity in the climate chamber, along with a regime of high temperature and salt mist to imitate extreme climatic conditions. The explosives were further evaluated using vacuum stability tests and heat flow calorimetry to determine their chemical stability and to acquire a broader understanding of their behavior under extreme environmental conditions.

2. EXPERIMENTAL

Samples of PBX were selected, that represent promising thermobaric compositions with small differences in mass ratio of the ingredients. Formulations with aluminum are very widespread because its characteristics (high heat of combustion, cost and availability [3]), while the Al-Mg combination is used because Mg lowers the ignition temperature and improves reactivity [6].

2.1. Materials

TBX samples were prepared based on:

- Cyclotetramethylenetetranitramine (HMX) from "Prva Iskra Namenska", Barič, Serbia
- ammonium perchlorate (AP), from "Poliex", Berane, Montenegro
- aluminium powder (Al), from "SRCT", China
- magnesium powder (Mg), from "Jengo Spa", China
- binder: hydroxyl-terminated polybutadiene, HTPB ("Polyvest HT Evonik") cured with isophorone diisocyanate, IPDI ("Sigma Aldrich"), and plasticized with dioctyl adipate, DOA.

The appearance of the individual components that are part of TBX formulation can be seen in Figure 1.

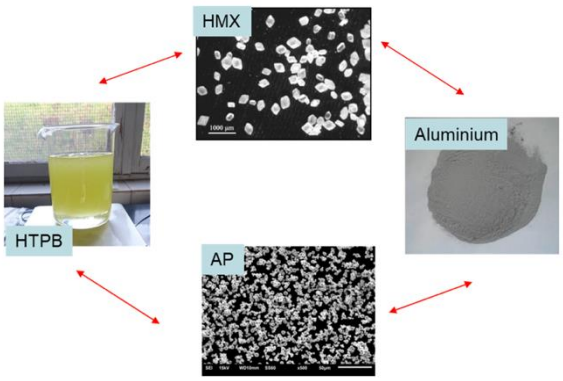


Figure 1. Samle ingridients: HTPB, HMX, Al and AP

2.2. Sample preparation

All the samples have been produced in a vertical homogenizer at 60°C under vacuum according to the process specified by the Military technical institute. Three sample types have been manufactured from three distinct batches, two have the same formulation, while the third has two types of metal powders. All the samples were cast and cured in heating chamber at 70°C during 5 days. The analyzed samples compositions were as follows:

TBX 1: HMX/Al/AP/HTPB;
TBX 2: HMX/Al/AP/HTPB;
TBX 3: HMX/Al/Mg/AP/HTPB.

After the production process, samples from each batch were poured into a vessel with an opening, cured and stored, to provide complete exposure to environmental conditions in storage on one side.

The samples are divided (cut) into three parts: one represents a sample exposed to natural aging, one to be additionally exposed to accelerated aging in continental conditions, and last one to accelerated aging in Mediterranean conditions. The first part, without any additional treatment, was subjected to stability tests and is a reference sample naturally aged in a warehouse for five years in continental climate conditions. The second part was exposed to the process of accelerated aging in the conditions of a continental climate, which was simulated in a climate chamber with an elevated temperature of 60°C and air humidity of 65%, which can be seen in Figure 2.

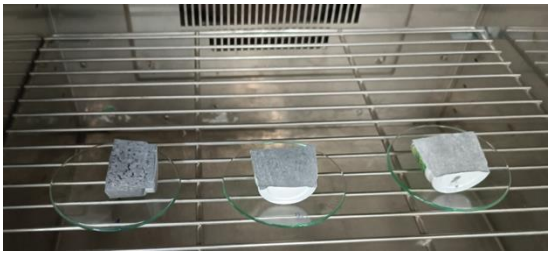


Figure 2. TBX in climate chamber (from left: TBX 3, TBX 2, TBE 1)

The third part of the samples was exposed to extreme conditions - a temperature of 30°C and air humidity of 90% in conditions of marine atmosphere imitated by a salt-mist camber. The sample that was in the salt-mist chamber for 48 hours, after the experiment, due to extremely high humidity, was covered with salt water that condensed on the lid of the chamber during the operation of the chamber and dripped on the samples.

After treatment, all samples were mechanically powdered to particles of approximately 2×2 mm (Figure 3) in order to prepare them for further analysis.

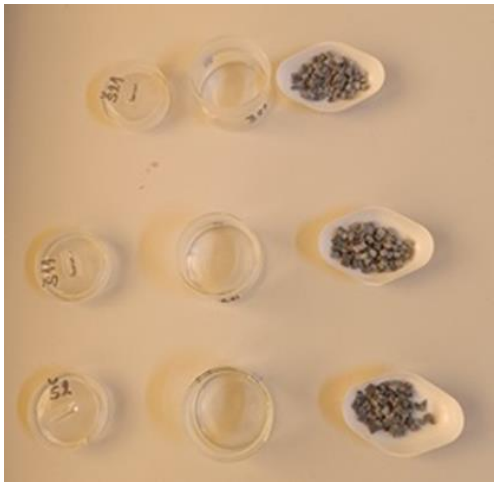


Figure 3. Chopped samples of naturally aged TBX

The moisture content of each sample had been previously determined using the drying method at 10

0 °C for 2 h, in order to evaluate the influence of moisture on the treated samples.

2.3. Methods

Chemical and thermal stability of the investigated materials was evaluated using the STABIL system (modernized vacuum stability tester) apparatus manufactured by OZM Research, Czech Republic. Method was performed by STANAG 4556 [7,8] procedures, by using 2.5 g of sample. The chopped samples are placed in a test tube (Fig. 4a) and heated at 100 °C for a duration of 40 h.



Figure 4. a) Prepared sample of TBX in test tube for VST and b) prepared sample of TBX in vial for HFC

Heat flow calorimetry was method of choice because it can also yield information about the stability of energetic materials measuring the decomposition rate. Experiment was carried out by at 85°C and using Heat Flow Calorimeter, TAM IV TA Instruments with 24 channel for 7 days. Approximately 3g of the chopped sample was placed in the vial for microcalorimetry (Fig. 4b).

3. RESULTS AND DISCUSSION

All samples undergo the same type of tests, with the same conditions to obtain the comparable results in stability.

3.1. Vacuum stability results

The moisture level of the surface and middle layers was initially assessed, and the results of moisture content are given in Table 1. Vacuum stability test at first was carried out for both layers for naturally aged samples to detect the slight differences in moisture content and the gas evolved in the vacuum stability test tube for the two layers are shown in Table 2.

Table 1. Moisture content for naturally aged samples

Sample	naturally aged		clime chamber		salt-mist chamber	
	surface layer (mass%)	middle layer (mass%)	surface layer (mass%)	middle layer (mass%)	surface layer (mass%)	middle layer (mass%)
TBX 1	0.02	0.04	0.04	0.05	0.04	0.04
TBX 2	0.00	0.04	0.04	0.04	0.04	0.04
TBX 3	0.28	0.41	0.14	0.08	0.06	0.12

Table 2. Vacuum stability test result for naturally aged samples by layers

Sample name		Gas evolved [cm3/g]		
		test tube 1	test tube 2	average
surface layer	TBX 1	0.115	0.118	0.117
	TBX 2	0.116	0.117	0.117
	TBX 3	0.398	0.404	0.401
middle layer	TBX 1	0.100	0.101	0.101
	TBX 2	0.106	0.108	0.107
	TBX 3	0.364	0.364	0.364

Table 2. demonstrates that all samples exhibit almost full resistance to moisture. The elevated value primarily reflects the formulation including a bi-component mixture of fuel, i.e. aluminum and magnesium. According to the fact that the samples were not hermetically sealed during storage, and had an opening on one side, it was necessary to consider the influence of moisture. Considering that the trend remains the same across all compositions and that similar values are observed in different layers and within the same samples for both moisture and released gases (Table 3) during the stability test, the remaining samples will be evaluated only in one middle layer and compared to that layer of naturally aged samples.

Samples exposed to the climate chamber under conditions of elevated humidity and temperature had their moisture content assessed, whereas undried samples were submitted to the vacuum stability test. The obtained results are given in Table 3.

Table 3. Vacuum stability test result for climate chamber samples

Sample name	Gas evolved [cm^3/g]		
	test tube 1	test tube 2	average
TBX 1	0.156	0.147	0.151
TBX 2	0.144	0.134	0.139
TBX 3	0.348	0.346	0.347

Extreme conditions, even in a relatively short time interval, lead to changes in the amount of gas released. The compositions containing only Al show an increase of as much as 30 to 50%, while the composition containing the combination of Al and Mg after exposure to the climate chamber gives a lower value by about 5%. However, it is important to note that even those, at first glance extremely high values, are not even close to critical values, which range from 1.2 to 2 cm^3/g according to test criteria [10].

Table 4 summarizes the results acquired from compositions subjected to salt mist. Despite being completely submerged in salt water, the sample's minimal moisture content indicates that the cross-linking of the HTPB with IPDI produced a sufficiently resilient rubbery binder structure that exhibits remarkable resistance to moisture and water.

Table 4. Vacuum stability test result for salt-mist chamber samples

Sample name	Gas evolved [cm^3/g]		
	test tube 1	test tube 2	average
TBX 1	0.195	0.198	0.172
TBX 2	0.198	0.199	0.199
TBX 3	0.331	0.321	0.326

Considering the composition of TBX 1, in each of the mentioned atmospheres, there is a clearly noticeable trend of change in the amount of evolved gases in rapidly ging samples in clime and salt-mist chambers. In Figure 4 we may observe the differences between atmospheres.

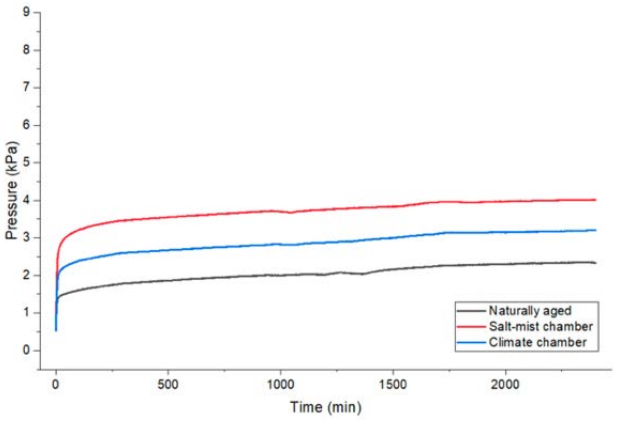


Figure 5. Sample of TBX 1 in different atmospheres

Figure 5 presents shows that all samples exhibit a rapid initial pressure increase during the early stage of the test, followed by a gradual stabilization phase. The sample exposed to the salt-mist chamber shows the highest-pressure values throughout the entire testing period, reaching approximately 4.0 kPa while climate chamber sample stabilizing around 3.1–3.2 kPa. Naturally aged samples exhibit the lowest pressure development over time, reaching approximately 2.3 kPa.

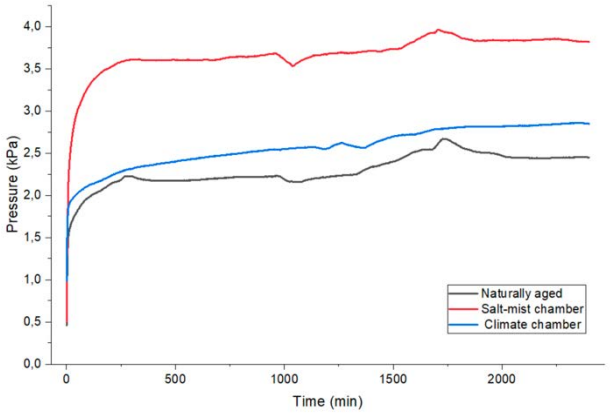


Figure 6. Sample of TBX 2 in different atmosphere

The differences between the samples are obtained almost immediately, the curves reach maximum values in first minutes of the test. The curve shapes indicate stabile behavior during test period, without any sharp picks which could reveal instability. Although this finding proving chemical stability providing extremely low values of evolved gas compared to German test criteria, it emphasizes significantly environmental influence on samples [11,12]

A very similar trend was recorded in sample TBX 2, which is identical in composition to TBX 1. The values of the naturally aged sample and the sample from the air conditioning chamber are somewhat closer, while there is a big noticeable difference in the sample exposed to the simulation of the Mediterranean climate.

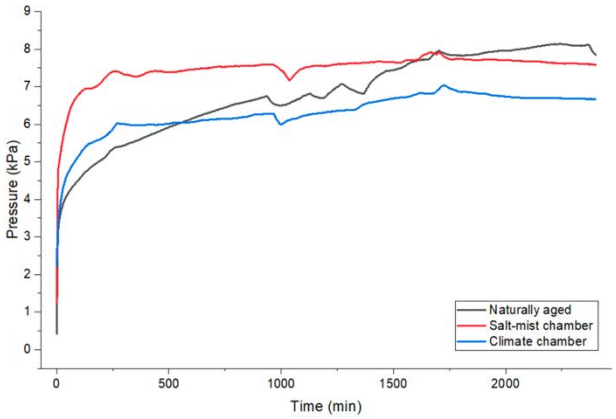


Figure 7. Sample of TBX 3 in different atmosphere

The sample TBX 3, shown in Figure 7 clearly indicate that the behavior of composites that contain a combination of two metal powders, Al and Mg, does not follow the trend observed in samples TBX 1 and TBX 2. Samples of TBX 3 from all three atmospheres show a higher sensitivity to the stability test, which in some

segments is even three times higher compared to equally treated samples that do not contain magnesium. However, a greater resistance to the influence of the atmosphere is also clearly noticeable, that is, all three samples show very similar behavior and reach close values.

Also, it can be detected that the pressure of naturally aged sample changes linearly with time, while the samples exposed to the climate chamber and salt-mist chamber after the initial pressure change, keep their values stable. The values obtained for the magnesium-containing compositions indicate a certain variation in stability over time. Although all measured parameters remain well below the prescribed limit values, it is evident that their thermal stability behavior differs compared to TBX 1 and TBX 2. This deviation does not necessarily imply instability; however, it suggests that the presence of magnesium influences the thermal response of the system. Therefore, these compositions require continued monitoring and additional investigation to fully understand their long-term stability and performance characteristics.

3.2. Heat flow capacity

Considering that the examined PBXs have different components, the behavior of each individual sample exposed to different treatment was monitored using the HFC method. Table 5 provides an overview of the measured maximum heat flow for all samples.

Table 5. Maximum heat flow for TBX 1-3

Samp.	treatment	Max heat flow (μW/g)		
		sample 1	sample 2	Average
TBX1	naturally aged	4.26	4.27	4.26
	climate chamber	3.66	4.02	3.84
	salt-mist chamber	4.09	4.09	4.09
TBX2	naturally aged	3.42	3.52	3.47
	climate chamber	3.67	3.65	3.66
	salt-mist chamber	5.07	4.35	4.71
TBX3	naturally aged	218.3	214.9	216.6
	climate chamber	183.3	194.5	188.9
	salt-mist chamber	257.0	280.8	268.9

The table reveals that samples TBX 1 and TBX 2 have comparable results that are significantly below the thresholds established by STANAG 4582 (for 85°C for 5,98 days heat flow limit is 201μW/g). It is important to note that the document addresses gunpowder and rocket fuels [8,9], which are susceptible to thermal breakdown and self-ignition under critical conditions, but in absence of adequate standard method for PBX, this criteria was chosen for the examined explosives as well. However, the thermal activity shows significantly different results when the TBX 3 sample is taken into consideration. Its values slightly exceed the allowed limit, which indicates that should conduct additional analyzes and introduce other methods that would give additional insight into the thermal stability of the mentioned compositions.

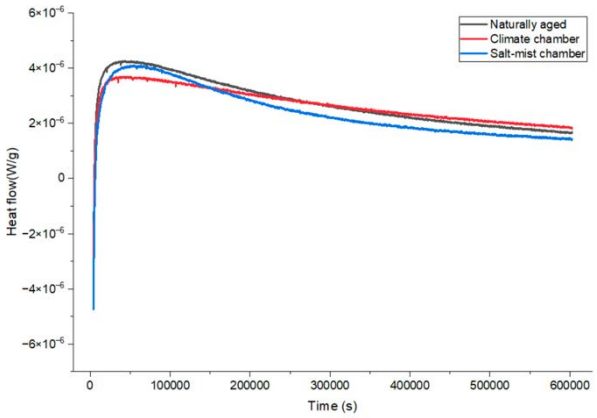


Figure 8. HFC diagram for sample TBX 1

As it can be seen in figure 8, all treated samples of PBX 1 exhibited an initial exothermic peak followed by a gradual decline in heat flow over time. The maximum heat flow values followed the order: naturally aged, salt-mist chamber and climate chamber. The naturally aged sample showed the highest peak intensity, indicating the greatest initial reactivity. The salt-mist exposed sample displayed a slightly lower maximum, while the climate chamber sample exhibited the lowest heat flow. The initial exothermic peak could be potentially influenced by residual moisture since the samples were not pre-dried. Following the maximum, all samples exhibited a similar decay trend, without pronounced and low endothermic or exothermic peaks with a tendency to decrease thermal activity over time.

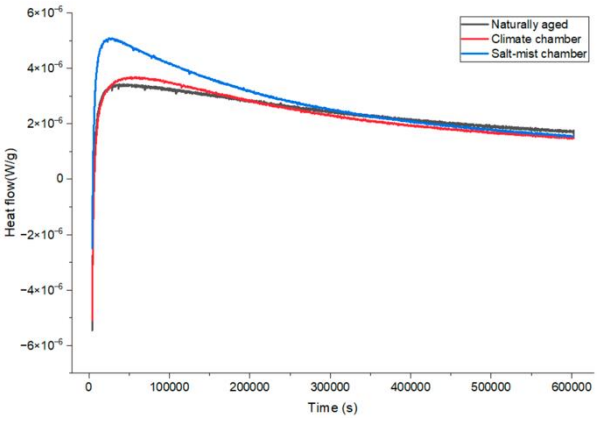


Figure 9. HFC diagram for sample TBX 2

At Figure 9, for TBX 2 the heat flow curves also showed a pronounced initial exothermic peak followed by a gradual decay for all three conditioning treatments. In contrast to the PBX 1 sample, the maximum heat flow has a different trend of thermal response with highest values for salt-mist treated sample, the climate chamber sample shows intermediate reactivity, while the naturally aged specimen presents the lowest maximum heat flow. The sharper and higher peak observed for the salt-mist sample suggests enhanced initial reactivity which can be caused both by oxidation and moisture-related processes.
After the maximum, all curves exhibit a similar long-term decay trend, indicating progressively and limited reactions.

Compared to Figure 8, a different trend can be noticed and clear reversal in maximum heat flow. The unexpected variations in thermal response among samples of identical composition can be attributed to their derivation from distinct batches, wherein the raw materials can possess difference pretreatment processes, particularly at elevated temperatures, such as those employed during the HFC test. Overall, the comparison indicates that environmental conditioning significantly alters the initial kinetics, while long-term behavior remains governed by similar diffusion-controlled mechanisms.

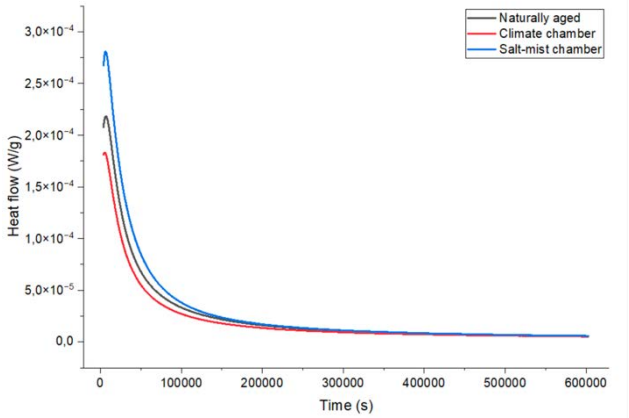


Figure 10. HFC diagram for sample TBX 3 in different atmospheres

However, regarding the PBX 3 sample, it is an entirely different sample. Specifically, the maximum heat flow is up to 50 times higher than in the formulation that comprises only Al as the fuel component.

All tree samples show very intense initial exothermic response followed by a rapid decay toward near-zero heat flow. The peak occurs very early and is sharp, indicating a highly reactive initial process. After 28 hours all curves converge and approach very low heat flow values, suggesting depletion of reactive processes. The salt-mist sample exhibits the highest peak, while the climate chamber sample consistently shows the lowest reactivity. In all three cases the rapid decay suggests that the process is primarily surface-controlled rather than diffusion-controlled over long times, according to the fact that the tested samples were not previously dried, so the initial reactions may be the result of a small residual amount of moisture in the samples

Analyzing all three samples, it is clearly observed that there are differences in the thermal response of samples exposed to certain conditions of high temperature, humidity or salt mist, which indicate that environmental conditioning significantly affects thermal stability of the examined PBX.

Salt-mist exposure tends to enhance initial reactivity, which can be seen particularly evident in the second and third diagram, while climate chamber exposure generally reduces maximum heat flow.

Despite differences in peak magnitude, all datasets eventually converge to low heat flow values, indicating exhaustion of reactive ingredients and transition to kinetically limited process. This behavior indicates pronounced short-term temperature sensitivity. It is important to note that PBX compounds are not exposed to excessively high temperatures during production, as mixing and crosslinking processes do not exceed 70 °C. Furthermore, the operational temperature range of ammunition is relatively moderate, typically between −30 °C and +50 °C. The HFC diagrams, together with the maximum heat flow values, demonstrate that all detectable processes, whether associated with the release of residual moisture, reactions with oxygen present in the vial, or relaxation of the polymer matrix, occur within a limited time interval no longer than 24 hours. After this initial period, the heat flow rapidly decreases, indicating that the system reaches a relatively stable state with no sustained long-term exothermic activity.

4. CONCLUSION

This study evaluated the environmental and thermal stability of three PBX formulations subjected to natural aging, elevated temperature and humidity, and salt-mist exposure to simulate Mediterranean climate. Vacuum stability testing demonstrated that all compositions released gas amounts significantly below the critical limits defined by 1.2 cm^3/g, confirming their overall chemical stability. Nevertheless, environmental conditioning influenced early gas evolution kinetics. Salt-mist exposure produced the highest-pressure development, while naturally aged samples consistently exhibited the lowest values. It is also noticed that compositions containing only aluminum (TBX 1 and TBX 2) showed comparable and stable behavior for all conditioning treatments. In contrast, TBX 3, which incorporates a combination of aluminum and magnesium powders, revealed increased sensitivity in both vacuum stability and heat flow measurements. Although it exhibited acceptable safety in vacuum stability testing, TBX 3 exhibited substantially higher thermal activity. Heat flow capacity results confirmed that TBX 1 and TBX 2 remained far below the STANAG 4582 heat flow limit, whereas TBX 3 exceeded the prescribed threshold, indicating the need for further thermal characterization.
Environmental exposure primarily affected early-stage reaction kinetics, particularly enhancing reactivity after salt-mist conditioning, while long-term behavior converged toward low heat flow values for all formulations. The results confirm that the cross-linked polymer matrix provides effective resistance to moisture and atmospheric influence. However, the presence of magnesium significantly alters thermal response, emphasizing the importance of continued monitoring and additional long-term stability investigations for Mg-containing formulations. Also, the findings encourage further research in establishing criteria and finding appropriate methodology of testing the long-term stability of multi-component PBX.

Acknowledgement

This work was supported by the Ministry of science, technological development and innovations (Serbia), Contract No. 451-03-34/2026-03/200325, and University of Defense, Military Academy, Proj. No. VA-TT/1/22-24.

References

[1] SIMIC D: *Liveni termobarični PBX eksplozivi*, Vojnotehnički institut Beograd, Naučnotehničke informacije, Vol53, No. 2, ISSN 1820-3418, 2016.

[2] ORBOVIC N. B.: *Uvod u energetske materijale, hemijski aspekti razlaganja energetskih materija*, KIZ CENTAR, Beograd, 2020.

[3] TÜRKER L.: *Thermobaric and enhanced blast explosives (TBX and EBX),* Defense Technology 12 (2016), pp. 423–445

[4] TRZCINSKI W. A., MAIZ L.: *Thermobaric and enhanced blast explosives – properties and testing methods,* Propellants, Explosives, Pyrotechnics, 2015, Vol.40, No.5, pp.632-644.

[5] KRSTOVIC M., BAJIC D., TIMOTIJEVIC M., NESIC J., FIDANOVSKI B.: *The influence of nano-scale aluminum on the energetic materials – theoretical and experimental observations*, Scientific Technical Review, Vol. 74, No. 1, 2024. pp. 36-42

[6] S. CUDZIŁO, W. A. TRZCIŃSKI, J. PASZULA, M. SZALA, Z. CHYŁEK: *Performance of Magnesium, Mg-Al Alloy and Silicon in Thermobaric Explosives – A Comparison to Aluminum*, Prop., Explos., Pyrotech. 2020, 45, 1691.

[7] STANAG 4556, *Explosives: Vacuum Stability Test, (Edition 1)* 22 November 1999; MAS/1436-PPS/4556; North Atlantic Treaty Organization.

[8] KRSTOVIĆ M., STANČIĆ T., NESTOROVIĆ K., BAJIĆ Z., BOGDANOV J., BAJIĆ B.: *Vacuum stability evaluation of pyrotechnic mixture - double-base propellant compatibility*, New Trends in Research of Energetic Materials, University of Pardubice, Pardubice, 22-24 April 2026, pp. 426-435.

[9] Ek S., Sjöblom M., Brantlind M., and Johansson J.: *Synthesis and characterization of the energetic plasticizer Bu-AENA,* New Trends in Research of Energetic Materials, University of Pardubice, Pardubice, 2-4 April 2025, pp. 109-117.

[10] Bohn, A. M: *NC-based energetic materials – stability, decomposition, and ageing, Presentation on the Meeting Nitrocellulose – Supply*, Ageing and Characterization, April 24 to 25, 2007, AWE, Aldermaston, England

[11] SANZHEN W., MINGKUN F., XINGLIANG W., GUANGFEI G., JUNHONG W., SEN X.: *Effects of temperature, particle size, and air humidity on sensibility of typical high-energetic explosives*, Journal of Measurement Science and Instrumentation, 2024, 15（3）：pp. 408-416.

[12] HAOYING L., LI H., YANCHUAN J. AIFENG J., DONGMING S.: *The influence of temperature and humidity on the decomposition of HMX-HTPB polymer-bonded explosives*, Thermochimica Acta, Volume 749, 2025,