11TH INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
OTEH 2024
Serbia, Tara, 9-11 October 2024

MONITORING PLASTICIZER`S MIGRATION IN THE HMX/DOA MIXTURE UNDER ELEVATED TEMPERATURES

MIRJANA KRSTOVIĆ
Military Technical Institute, Belgrade, mirjana.krstovic@mod.gov.rs

DANICA BAJIĆ
Military Technical Institute, Belgrade, danica.bajic@mod.gov.rs

TEODORA STANČIĆ
Military Technical Institute, Belgrade, teodorastancic@gmail.com

MLADEN TIMOTIJEVIĆ
Military Technical Institute, Belgrade, mladen.timotijevic@gmail.com

BOJANA FIDANOVSKI
Military Technical Institute, Belgrade, bojana.fidanovski@mod.gov.rs

Abstract: *Polymer-bonded explosives and plasticizer-coated nitramine based explosives represent a group of energetic materials that have been extensively manufactured in recent years in order to satisfy requirements ranging from boosters to the main charges of warheads. From the aspect of their production technology, physical-mechanical properties, and further detonation properties, it is important to properly select and incorporate specific functional additives into the explosive-polymer matrix. Dioctyl adipate (DOA) is the predominant plasticizer utilized in PBX formulations to enhance their processability. To enhance the safety of transporting HMX from the factory to the manufacturing facilities, it is not uncommon for HMX to be blended with DOA instead of using wetting explosives to make the highly reactive explosive less sensitive. This semi-product may be further incorporated in multi-component PBX formulations or pressed into booster charges. Occasionally, the HMX/DOA mixture is held for an extended period prior to utilization, which may be a problem, knowing the migration ability of DOA molecules. The aim of this paper is to monitor and measure the migration of DOA from the HMX/DOA mixture. The samples were exposed to slightly elevated temperatures for a certain period of time and compared with samples exposed to ambient temperatures. The content of DOA in the HMX/DOA system was monitored and determined using both classical and instrumental methods. The results indicate the migration of DOA is influenced by temperature, i.e. that the migration is more pronounced at a higher temperature, as well as the differences in the presence of DOA in the layers becomes more noticeable over time.*

Keywords: *HMX, dioctyl adipate, migration, plasticizer, polymer-bonded explosives.*

1. INTRODUCTION

In recent decades, significant advance has been achieved in the synthesis and formulation of novel explosive compositions with the objective of enhancing fragmentation, penetration, and brisance. A particular field of focus for development has been, and continues to be, the formulation of polymer bound explosives (PBX's). PBX is an acronym that refers to an extensive variety of explosive materials that contain polymer binders. It encompasses not only plastic compositions that can be shaped by hand, but also formulations designed by pressing and solid compositions that are chemically cross-linked and can be produced using casting techniques [1].

This type of energetic materials has attracted a lot of attention due to the fact that they enable a very wide range of characteristics of the final product, depending on the choice of additives and their mass fractions in the explosive composition. The initial PBX formulations were created in the 1950s, with the aim of developing formulations that had decreased sensitivity and increased safety during production and handling. Furthermore, PBX's have enhanced processability and mechanical characteristics [2-3]. The fundamental structure of PBX is comprised of high-explosive particles, polymers, with the inclusion of additives such as metal powder as a fuel component or the addition of oxidants to generate the desired effects, and the processing additives to the binder which make production easier.

Secondary explosives, such as PETN (pentaerythritol tetranitrate), RDX (hexogen), and HMX (octogen), are frequently integrated into PBX. Their distinctive attributes allow the final products to have a desirable impact on the target. Namely, PETN has detonation velocity of 8310 m/s at a density of ρ=1.77 g/cm^3 [4], while RDX has detonation velocity of 8750 m/s at a density of ρ=1.76 g/cm^3 [4]. Among the most common

Corresponding author: M. Krstović;
E-mail: mirjana.krstovic@mod.gov.rs
DOI: 10.5937/OTEH24039K

secondary explosives HMX has highest possible efficiency due to detonation velocity of 9110 m/s at a density of ρ=1.89 g/cm^3 [4].

The selection of a binder has a substantial impact on the performance of the final product and the available production options. In general, polymer binders in energetic materials serve as matrices, binding all solid particles together into a cohesive structure. This allows the energetic material to possess the desired properties, and ensures that the resulting final product has the necessary geometric shape. While a multitude of polymers have been artificially created so far, only a limited number satisfy the stringent requirements to be considered a suitable matrix for energetic materials. More precisely, the chosen polymer must be compatible with other components, possess the desired mechanical properties, maintain its integrity within the operational temperature range, withstand various stresses during flight, and be suitable for the production process and technique. The extensive range of requirements imposed on polymers used in energetic materials significantly limits the selection of potential candidates for polymer matrices in ordnance.

Nowadays, the polymers utilized in energetic materials can be categorized as either inert or energetic, depending on whether they actively contribute their energy during the detonation process or not. In the context of inert polymers, the most commonly employed systems are those involving inert thermal cross-linking resin. These systems are primarily composed of polyurethane, specifically hydroxyl-terminated polyols that are crosslinked with isocyanates [5,6]. Hydroxyl-terminated polyols can be categorized into polyesters, polyethers, and polybutadienes based on their structural composition. Polyethers and polybutadienes are widely used compounds due to their extensive availability in the market, suitable viscosity, and rapid cross-linking speed. Furthermore, elastomers derived from these materials exhibit remarkable resistance to abrasion and favorable characteristics at low temperatures. The most commonly utilized polyurethanes are those derived from hydroxyl-terminated polyethers (HTPE), carboxyl-terminated (CTPB), and hydroxyl-terminated polybutadiene (HTPB). Each additive in energetic materials serves a distinct purpose. Metal powders enhance energy output; polymers enhance mechanical properties and bind all ingredients together into a dense structure. Curing agents initiate solidification of polymers providing the solid form of the charges, while plasticizers aid in the processing of the materials [7].

The utilization of plasticizers in energy materials offers several advantages: it enhances mechanical properties at low temperatures, softness, and has a direct influence on processability [8]. Incorporating this particular additive yields advantageous attributes in the final products (ammunition) in terms of preservation, application, and transporting [9]. Considering that plasticizers are responsible for achieving various desirable properties, they typically consist of low-viscosity liquid organic compounds that enhance viscosity control during mixing and prolong the *pot life* during casting. Plasticizers, in general, are a frequent ingredient of all energetic materials. For example, powders and rocket fuels have had plasticizers for decades. Some of them, like nitroglycerin, can energetically participate in the combustion process, while certain are non-energetic. Some of them, including phthalates, have been utilized in gunpowder and rocket propellants for decades, while novel plasticizers are continually being developed.
Nevertheless, there might be a significant time lapse between the synthesis and implementation of novel plasticizers in complex structures like ammunition. Due of the relatively low mass percentage of plasticizer in energetic material formulations, the research on these additives is typically overlooked. The main reason for the preference of already tested plasticizers in new compositions is that they have been proven to be effective. In research, however, greater focus is given to modifying the other components that can result in a substantial boost in energy output.

A frequently employed composition for PBX, is consists of RDX or HMX as the secondary explosive, HTPB as the prepolymer, isophorone diisocyanate (IPDI) as the curing agent, and dioctyl adipate (DOA) as the plasticizer, along with the inclusion of different size of metal powder. The mentioned explosive compositions, with varying mass ratios have been widely recognized for a few years, with the possibility of modeling characteristics by varying the size and type of metal powder. However, the utilization of DOA as a plasticizer in energetic materials requires additional attention given its tendency for exudation i.e. migration. The issue of migration is not solely limited to DOA, but rather is a widespread problem that arises with the majority of plasticizers now in use. On the positive side, the addition of a small amount of this additive can improve the flow-ability of the energetic composition slurry by elongating the polymer chain structure. On the other hand, over time, it can lead to the infringe of the homogeneous structure due to migration [10].

The secondary explosives can only be stored or transported with a significant presence of moisture. This type of treatment of explosives requires its drying before their use in production facilities. One of the potential options that could enable the avoidance of wetting and thus drying of the explosive, involves coating the crystal particles with some phlegmatizing substance such as plasticizers, which itself is one of the ingredients of the PBX formulation. Applying a layer of DOA on explosive particles in production facilities and transporting them to factories for PBX production is an effective solution that significantly decreases the time required to prepare raw materials for mixing the mass used in casting PBX. However, considering the fact that specific plasticizers have a tendency to migrate, the question arises regarding the long-term behavior of this two-component composition under storage conditions, if it is not immediately used for the manufacturing of final products. The aim of this paper is to simulate the aging conditions of the HMX/DOA mixture and monitoring the plasticizer content in certain parts of its volume in order to determine

the behavior of DOA over time.

HMX - high melting point explosive (Fig.1) is known for its increased potency while remaining relatively resistant to various stimuli such as heat, impact, friction, and spark. These properties make them suitable for use as explosive fillings in bombs, shells, and other munitions [4,7].

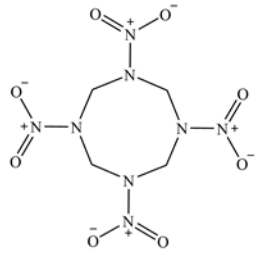

Figure 1. Octogen (HMX)

As it can be seen in Figure 1. HMX has a molecular structure that consists of an eight-membered ring made up of alternating carbon and nitrogen atoms. Each nitrogen atom in the ring is attached to a nitro group. HMX possesses a higher level of complexity in its manufacturing process compared to the majority of explosives, which limits its usage to specialized applications [10].

Table 1. HMX characteristics [3]

Characteristic	Value
Enthalpy of formation (kJ/kg)	252.8
Oxygen balance (%)	-13.51
Specific volume of gases (cm^3/g)	927
Heat of the explosion (kJ/kg)	5679
Density (g/cm^3)	1.91
Melting point (°C)	275
Auto-ignition temperature (°C)	240
Detonation velocity (m/s)	9120
Sensitivity to impact (Nm)	120
Sensitivity to friction (N)	7.4
Critical diameter (mm)	8

DOA ($C_{22}H_{42}O_4$) is colorless, very faint, slightly greasy odor of its own, light resistance, transparent oily liquid known as a cold plasticizer commonly used in the production of polyvinyl chloride, polyethylene copolymers, polystyrene, nitrocellulose, ethyl cellulose, and synthetic rubber [11]. The extensive applicability of DOA (Figure 2.) as a plasticizer is attributed to its organic nature, which allows it to be compatible with all the aforementioned materials.

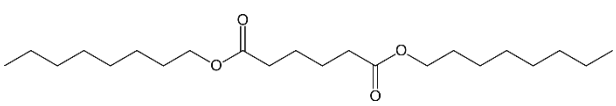

Figure 2. Dioctyl adipate DOA

Dioctyl adipate is a diester compound formed by the combination of adipic acid and octanol, as indicated by its alternative name, adipic acid dioctyl ester. The core of the chemical consists of the remaining adipic acid, where the end carboxylic acid groups have been converted into esters by reacting with the hydroxyl groups of two molecules of 1-octanol. The symmetrical dioctyl adipate consists of two ester groups, each of which is sequentially connected to a regular and unbranched octyl radical [12].

Dioctyl adipate, with two functional groups, is capable of undergoing the standard reactions associated with an ester. These methods involve acid-catalyzed hydrolysis and saponification with a base, which reverts the octanol back to its original form and produces a salt of adipic acid. The solubility of the material is dictated by the extended, hydrophobic octyl chains. Due to the presence of polar ester groups, dioctyl adipate exhibits low solubility in polar solvents like water. It is common to combine DOA with other plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) in various applications such as cold-resistant agricultural plastic film, frozen food packaging film, cables, electric wires, and more [13]. The utilization of DOA as a plasticizer in any industry, including the military, requires the acquisition of an already prepared commercial product available in the market. In Table 2. are shown some characteristics of commercial DOA.

Table 2. DOA characteristics [11]

Characteristic	Value
Molecular weight	370.57
Relative density	0.922
Boiling point	374.4 ° C at 760 mmHg
Flash point	168.9 °C

DOA is a type of synthetic ester oil that is produced through the process of esterification, which involves combining adipic acid and 2-ethyl hexanol [14]. Because of its high thermal-oxidation stability, low carbon residue formation, outstanding viscosity index, strong thermal conductivity, and significant specific heat capacity, it is extensively used in different industry sectors [15-17].

2. MATERIALS AND METHODS

2.1. Materials

In this study, a blend of HMX/DOA was employed consisting of the following fundamental components:

- HMX Prva Iskra Namenska Barič and
- DOA provided by Trayal corporation.

The HMX/DOA mixture, as per the manufacturer's standard, consists of approximately 3wt.% commercial DOA, and 97wt.% HMX explosive.

Samples from the same batch of octogen coated with DOA were examined. All of the samples were evenly distributed among identical test tubes as it is shown in Figure 3.

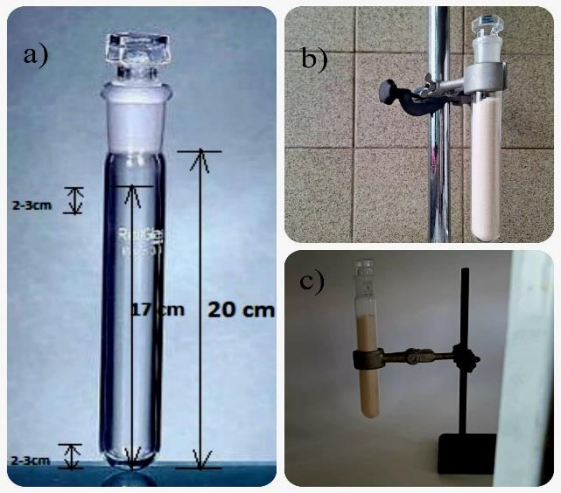

Figure 3. a) Test tube for samples with its dimensions, b) sample exposed to light and ambient temperature, c) sample stored in a dark on ambient temperature

Two reference samples were kept at ambient temperature for 30 days, one sample stored in a dark and the other one exposed to natural light. The remaining ten test tubes were placed in a thermal blocks.

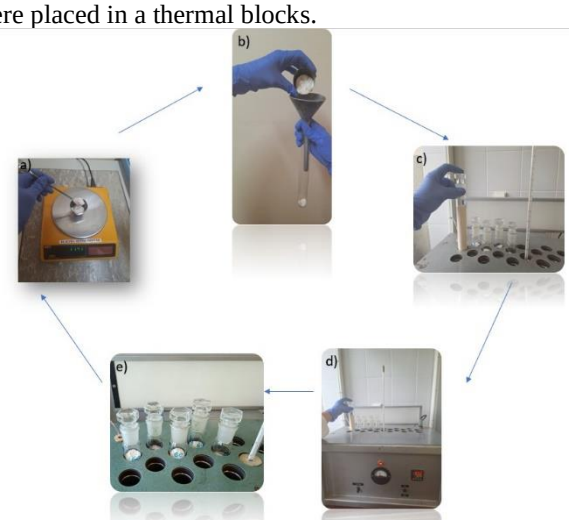

Figure 4. a) sample measurement, b) pouring the sample into the test tube, c) placing the test tube in the thermal block, d) thermal block with digital temperature gauge and control thermometer, e) five test tubes placed at a same temperature

Five of them were set at a temperature of 60°C and the other five were set at 80°C. At intervals of 5 to 10 days, a test tube was removed from the thermal blocks and the levels of DOA in three layers were analyzed.

2.2. Instrumental methods

The Fourier-transform infrared spectroscopy (FTIR) method was employed to analyze the raw ingredients used in the HMX/DOA mixture, as well as the filtrate produced after the rinsing process with organic solvents, while Differential scanning calorimetry (DSC) was used to investigate the melting behavior of crystalline explosives in order to experimentally verify the complete removal of DOA from the HMX particles.

2.3. Classical method

A classical method was employed to determine the DOA content in the HMX/DOA mixture relying on the solubility of these chemicals in specific solvents. Regarding DOA, it has excellent solubility in carbon tetrachloride, dichloromethane, alcohols and n-heptane. In this study, two appropriate solvents, dichloromethane, and n-heptane, were selected for separating the two-component mixture.

1 gram of the HMX/DOA mixture sample as well as 1 g of pure HMX was measured with a precision of 0.0001 g. The control sample, consisting of pure HMX, serves to quantify the amount of HMX wasted during the dissolution process in solvent and subsequent filtration. Every individual sample was placed inside graduated beakers and a volume of 20 cm^3 of dichloromethane was introduced to each sample. The samples were left during 30 minutes with intermittent agitation, after which they were subjected to filtration using a glass filter crucible, with a porosity level of 4. The beakers containing samples were thoroughly rinsed multiple times, using a total of 50 cm of liquid, to ensure the complete transfer of all insoluble material to the glass filter crucibles. Subsequently, the crucibles were placed in the oven and maintained at a temperature of 80°C until they attained a constant mass. After the drying process, the glass filter crucibles were measured, and the content of DOA was determined using the subsequent formula (1):

$$\%DOA = \left[1 - \frac{m_3(m_2 - m_1)}{m_0(m_5 - m_4)}\right] \cdot 100 \qquad (1)$$

where:

m_0 – HMX/DOA mixture sample weight,

m_1 – weight of empty glass filter crucible for HMX/DOA mixture sample,

m_2 – weight of glass filter crucible with HMX/DOA mixture sample after the drying process,

m_3 – pure HMX sample weight,

m_4 – weight of empty glass filter crucible for pure HMX sample and

m_5 - weight of glass filter crucible with pure HMX sample after the drying process.

3. RESULTS AND DISCUSSION

The conventional gravimetric method is applied for all samples. The analysis was conducted in triplicate, and the results given encompassed the complete range of values obtained. Table 3. presents the measured mass loss of pure HMX in both solvents, taking into consideration even the slightest margin of error. The average value has been reduced to two decimal places.

Table 3. Pure HMX mass loss

Solvent	*Mass loss [%]*	*Average [%]*
Dichloromethane (CH_2Cl_2)	0.161	0.16
	0.153	
	0.172	
n-heptane	0.084	

($CH_3(CH_2)_5CH_3$)	0.089	0.09
	0.093	

The gravimetric measurement of pure HMX clearly demonstrated that the selection of solvents was appropriate, with a minor quantitative advantage observed for n-heptane. But, in terms of safeguarding human health, n-heptane poses a higher risk due to its toxicity.
Table 4. presents the results obtained from analyzing the HMX/DOA mixture sample. The examination was conducted before the samples were exposed to elevated temperatures and involved using formula (1) to calculate the loss of pure explosive during the filtering procedure using the chosen solvent.

Table 4. Quantification of DOA in the initial sample

Solvent	*DOA [%]*
Dichloromethane (CH_2Cl_2)	2.84±0.14
n-heptane ($CH_3(CH_2)_5CH_3$)	2.62±0.11

Using either solvent produces consistent measurements of the DOA content in the sample, with the findings deviating by 0.2% of the DOA content. When rinsing with n-heptane, the values obtained are 7.1% lower than those obtained when using dichloromethane.
Samples that were exposed to elevated temperatures, in order to simulate accelerated aging with the aim of observe and quantify DOA migration, were analyzed successively, with the dynamics that followed the removal test tubes with samples from the thermal blocks. Table 5. showed the results for both solvents by days and temperatures they were exposed to.

Table 5. Results of monitoring the DOA migration due to exposure of samples to elevated temperatures

day	Temp. [°C]	*layer*	*Dichloromethane* (CH_2Cl_2)	*n-heptane* ($CH_3(CH_2)_5CH_3$)
10	60	upper	2.82	2.42
		middle	2.84	2.45
		lower	2.98	2.49
	80	upper	2.83	2.32
		middle	2.93	2.42
		lower	3.09	2.53
15	60	upper	2.81	2.30
		middle	2.97	2.33
		lower	2.98	2.58
	80	upper	2.69	2.23
		middle	2.81	2.52
		lower	3.10	2.58
		upper	2.70	2.17
20	60	middle	2.85	2.40
		lower	2.97	2.60
	80	upper	2.70	2.12
		middle	2.78	2.17
		lower	2.88	2.31
25	60	upper	2.44	1.99
		middle	2.65	2.17
		lower	2.82	2.48
	80	upper	2.31	1.61
		middle	2.44	1.63
		lower	2.85	2.64
30	60	upper	2.41	1.94
		middle	2.51	2.23
		lower	3.06	2.68
	80	upper	2.15	1.51
		middle	2.34	1.54
		lower	3.19	2.81

Table 5. clearly demonstrates that DOA migration is detected within just 10 days of exposing the samples to increased temperatures. A temperature of 60°C resulted in a 0.16% disparity between the upper and bottom layers in samples treated with dichloromethane, but this disparity is half less (0.07%) in samples treated with n-heptane. After being subjected to a temperature of 80°C for a period of 10 days, the samples showed a larger migration of DOA, likely caused by the elevated temperature. Consequently, the dichloromethane-treated samples exhibited a disparity of 0.26% in the concentration between the upper and bottom layers of the HMX/DOA mixture, whilst the n-heptane-washed samples displayed a difference of 0.20%. Upon initial examination of the first samples, it is evident that there is a discernible alteration in the DOA content across different levels. Specifically, the plasticizer in question demonstrates a tendency to migrate towards the lower layers.
After a duration of 15 days, the samples that underwent tempering at 60°C and were treated with dichloromethane exhibit nearly equivalent outcomes to those subjected to the same temperature for 10 days. Notably, in this instance, the DOA value in the intermediate layer closely resembles that of the bottom layer. In the samples subjected to a temperature of 60°C during 10 days, the value of the middle layer closely approximated the values of the upper layer. These findings suggest that accelerated aging leads to a slow migration of DOA towards the lower layers. The values obtained after treatment with n-heptane result in a larger disparity between the layers, measuring 0.28%. Upon analyzing the obtained values of the sample that was exposed to a temperature of 80°C for 15 days, a significant difference between the upper and lower layers is observed. For samples treated with

dichloromethane, that difference is 0.41%, while for samples treated with n-heptane, that difference is 0.35%. It is an extremely high percentage, bearing in mind that DOA in the HMX/DOA mixture is present in a very small percentage (2.62-2.98%, Table 3). It means that about 1/8 of the total DOA migrated from the upper layers to the bottom of the test tube in first 15 days on higher temperature.

After subjecting the samples to heating at 60°C for a period of 20 days, the samples rinsed in dichloromethane showed a difference of 0.28% between the layers. On the other hand, the samples rinsed with n-heptane exhibited a higher difference between the layers, around 0.40%. However, samples that had been heated to a temperature of 80°C during 20 days yield data that suggest the absence of DOA in the sample. Simultaneously, while conducting the sampling process, two occurrences are noted. Firstly, a highly potent odor of DOA is detected, which is absent in the samples treated at 60°C. Secondly, the glass test tube retains a significant amount of grease, suggesting that a certain amount of the DOA adheres to the inner walls of the test tube.

After 25 days of being heated to high temperatures, the odor of DOA becomes detectable even in samples that have been exposed to the temperature of 60°C. Compared to the 20th day, there was a modest increase in the difference between the layers for samples in dichloromethane (0.38%) and in n-heptane (0.49%). There is a discernible decrease in the amount of DOA in the sample, indicating that some of the plasticizer adhered to the inner walls of the test tube.

After 25 days, two selected solvents yield significantly different values at a temperature of 80 degrees. Specifically, the analysis of the samples treated with dichloromethane reveals a discrepancy of 0.51% between the upper and bottom layers, whereas the samples treated with n-heptane exhibit a twofold difference of 1.03%. Both examples demonstrate a noticeable decrease in the overall concentration of DOA in the sample.

As anticipated, results were obtained after a period of 30 days, showing the highest migration of DOA. The samples subjected to a temperature of 60°C exhibited a disparity of 0.65% in the stratification between the upper and bottom layers for the samples treated with dichloromethane, whereas this discrepancy was 0.74% for the samples treated with n-heptane.

After being exposed to accelerated aging at 80°C for 30 days, the samples showed that over one-third of the initial amount of DOA had moved to the bottom of the test tube. The samples treated with dichloromethane exhibit a disparity of 1.04% between the upper and lower layers, whereas the samples subjected to n-heptane rinsing showed a disparity of 1.3% between the top and lower layers. Furthermore, it is apparent that the intermediate layer values closely resemble those of the upper layer for both solvents, indicating that DOA predominantly moved towards the bottom of the test tube.

Table 6. Results of monitoring the DOA migration for samples exposed to ambient temperature for 30 days

day	*ambient temp.*	*layer*	*Dichloromethane* (CH_2Cl_2)	*n-heptane* ($CH_3(CH_2)_5CH_3$)
30	Exposed to light	upper	2.92	2.59
		middle	2.95	2.64
		lower	2.98	2.67
	Kept in dark place	upper	2.89	2.58
		middle	2.93	2.66
		lower	2.96	2.69

In order to evaluate the impact of temperature on the migration of DOA in the HMX/DOA composition, control samples were included. These samples were not subjected to accelerated aging due to high temperatures, but were instead kept in the test tubes at the same ambient temperature. Table 6 indicates a 30-day duration resulted in barely disparities between the upper and bottom layers. The results closely resemble those obtained after subjecting the samples to a temperature of 60°C during 10 days. Furthermore, it is noted that there are no substantial differences in the results regarding light exposure, aligning with the manufacturer's information about light resistance [11].

Considering that classical methods are less reliable than instrumental methods, the efficacy of separating two components - HMX and DOA was controlled using FTIR and DSC. Specifically, following each rinsing utilizing the DSC method, the residual content in the glass filter crucible was analyzed to confirm the absence of any residual DOA in the sample. In Figure 5 the respective DSC diagram is given, which corresponds to HMX without the presence of DOA.

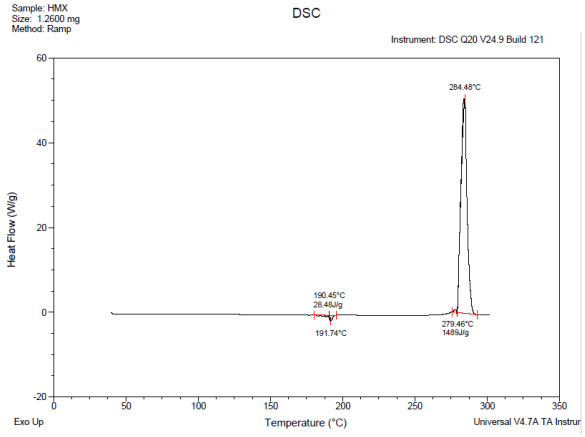

Figure 5. DSC diagram of HMX remaining in the glass filter crucible after solvent rinsing

Figure 6. shows the FTIR spectra for the HMX/DOA mixture, as well as the spectrum from the database for pure HMX and pure DOA.

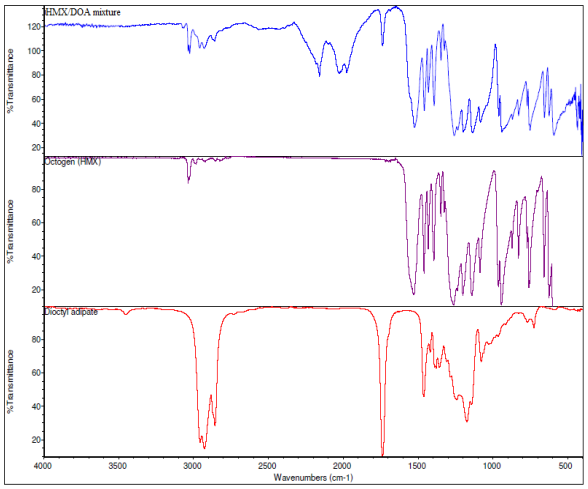

Figure 6. FTIR spectrum for HMX/DOA mixture, HMX and DOA

After the process of rinsing, the solvent was completely evaporated, leaving just the DOA that had been removed from the samples in the bottles. Figure 7 shows the FTIR spectrum of the remaining DOA after evaporation of dichloromethane. On the spectrum, peaks corresponding to DOA can be observed, attributed to the following groups: -COOR, $-CH_2$, $-CH_3$ and C–C. predominantly at 3000 cm^{-1}, then the stretching vibration ν(C=O) peak in ester group -COOR forming a strong absorption band in 1750~1735 cm^{-1}. The stretching vibration produced by -C-O-C- bond forms a wide range of absorption peak in the range of 1300~900 cm^{-1}.

Further, there are peaks due to HMX in the region of 900 to 770 cm^{-1}, as well as from 1500 to 1200 cm^{-1}. and

1560 cm^{-1}($-NO_2$), 1145 cm^{-1}($-NO_2$, N-ring), 965 and 945 cm-1(ring stretching bands), 830 and 760 cm^{-1}($-NO_2$), and 625 and 600 cm^{-1}($-NO_2$).

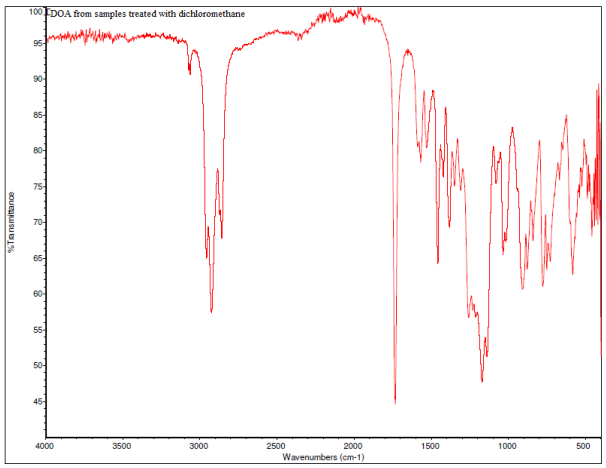

Figure 7. DOA spectrum from the samples treated with dichloromethane

This establishes the fact that when DOA is dissolved in dichloromethane and subsequently rinsed under vacuum, a portion of HMX is removed as well from the HMX/DOA mixture. In order to take into consideration for the loss of a minor quantity of HMX in the final calculation, it is essential to utilize formula (1) when determining the content of DOA in the sample (Table 3).

While analyzing the spectrum produced from the evaporation of n-heptane to identify DOA, distinct DOA peaks are readily recognized primarily at 3000 cm^{-1}, exhibiting minimal overlap with HMX, which corresponds to the fact that a very small amount of pure HMX is removed by n-heptane, which can be seen in Figure 8.

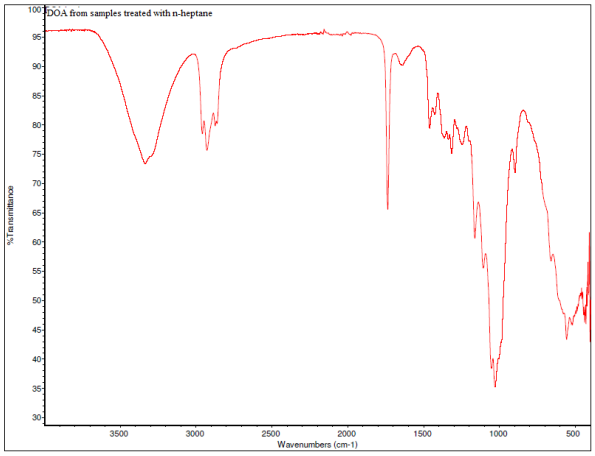

Figure 8. DOA spectrum from the samples treated with n-heptane

The peaks observed at 3300 cm^{-1} are a result of the presence of the OH group, indicating an inadequately matched sample. However, these peaks are not significant for the identification of DOA and HMX.

5. CONCLUSION

The monitoring of the migration of the plasticizer from the HMX/DOA mixture was analyzed. The samples were subjected to accelerated aging at two temperatures of 60°C and 80°C and were analyzed successively at intervals of 10, 15, 20, 25 and 30 days by the classic gravimetric method. The control of this approach was conducted using the instrumental methods of FTIR and DSC. Control samples were subjected to a 30-day period at room temperature, with one sample being exposed to natural sunlight and the other being kept in darkness.
Following conclusions can be made:

- regardless of the selection of solvents, it is important to consider the reduction in mass of pure HMX using formula 1,
- Within 10 days of being subjected to increased temperatures, the migration of DOA to the bottom layer commences gradually. This process becomes more pronounced at higher temperatures (80°C),
- After examining the data from the sample that was subjected to a temperature of 80°C for 15 days, a noticeable disparity between the top and bottom layers is detected. The discrepancy between samples treated with dichloromethane is 0.41%, but for those treated with n-heptane, the discrepancy is 0.35%. The percentage is remarkably high, considering that the presence of DOA in the HMX/DOA mixture is just a modest proportion (2.62-2.98%, Table 3). Approximately 12.5% of the total (DOA) moved

from the upper layers to the bottom of the test tube within the first 15 days at a higher temperature,

- The samples, which were subjected to a temperature of 80°C for a period of 20 days, produced results indicating the lack of DOA in the sample, followed by powerful smell of DOA, which is not present in the samples that were subjected to a temperature of 60°C and accumulation of DOA on the glass test tube,
- After being subjected to high temperatures for a period of 25 days, the scent of DOA becomes noticeable even in samples that have been exposed to a temperature of 60°C. After a period of 25 days, two specifically chosen solvents produce noticeably distinct values when exposed to a temperature of 80 degrees. Both cases exhibit a significant reduction in the total concentration of DOA in the sample,
- After a 30-day period, the statistics indicate the greatest migration of DOA in each sample. The samples exposed to a temperature of 60°C displayed a difference of 0.65% in the separation between the top and bottom layers for the samples treated with dichloromethane, while this difference was 0.74% for the samples treated with n-heptane, while the samples exposure to accelerated aging at a temperature of 80°C for a duration of 30 days, it was seen that more than one-third of the initial quantity of DOA had migrated to the lower portion of the test tube. The samples treated with dichloromethane display a difference of 1.04% between the upper and lower layers, whereas the samples submitted to n-heptane washing demonstrate a difference of 1.3% between the top and bottom layers,
- Control samples, stored in test tubes at the ambient temperature for 30 days, showed minimal differences between the top and bottom layers. The results closely reflect those obtained by exposing the samples to a temperature of 60°C for a period of 10 days. Moreover, it is seen that there are no significant disparities in the outcomes concerning light exposure, which is consistent with the manufacturer's claims on light durability.

The gravimetric method is highly efficient, as it is characterized by its rapidity and does not necessitate the use of costly equipment or the consumption of expensive chemicals. Within a brief timeframe, using only basic laboratory equipment, it yields quantitative data regarding the composition of the constituents. However, instrumental technique FTIR may provide some qualitative insight in this research, regarding the dissolving of HMX along with DOA in the selected selective solvents, and may help identify the presence of the remaining DOA on HMA after rinsing. The method used to determine the remaining pure explosive involves coloring the plasticizer, rather than directly detecting the plasticizer level.

Further work should encompass the influence of the total quantity of the sample (volume of the test tubes), the influence of total DOA content on its migration, as well as effects of different temperatures and longer periods of time.

ACKNOWLEDGEMENT

This work was supported by the Ministry of science, technological development and innovations (Serbia), Contract No. 451-03-66/2024-03/200325, and University of Defense, Military Academy, Proj. No. VA-TT/1/22-24.

References

[1] SZALA, M.: *Polymer-bonded secondary explosives*, High Energy Materials, 2021

[2] KLAPÖTKE, M.T.: *Chemistry of high-energy materials*, 3rd edition, De Gruyter Graduate, Berlin, 2015.

[3] SIMIĆ, D.: *Liveni termobarični PBX eksplozivi*, Kumulativna naučnotehnička informacija Vojnotehnički institut, Beograd, LIII (2) (2016.)

[4] BAJIĆ, Z.: *Inicijalni i brizantni eksplozivi*, AGM knjiga, Beograd, 2015.

[5] JEREMIĆ R., *Praktikum za raketna goriva*, Vojna akademija , Beograd, 2008.

[6] ANTIĆ G.: *Livene eksplozivne smeše za podvodnu primenu*, Kumulativna naučnotehnička informacija, Vojnotehnički institut, Beograd, XXXIX (1) (2005.)

[7] AGRAWAL, J.P.: *High energy materials, propellant, explosives and pyrotechnics*, Wiley-VCH, 2010.

[8] Pinalia A., Prianto B., Setyaningsih H.: *Preliminary results of DOA plasticizer effect on AP/HTPB composite propellant characteristics*, AIP Conference Proceedings 2366, 040009 (2021); https://doi.org/10.1063/5.0061303, Published Online: 13 September 2021

[9] Libardi J., Ravagnani S.P., Morais A.M.F., Cardoso A.R., Diffusion of Plasticizer in a Solid Propellant Based on Hydroxyl-Terminated Polybutadiene Polimeros 20, 241 (2010).

[10] Yaacob I.N., Asli A.F., Norkhairunnisa M., Ahmad K.A., Ismail O., Salleh N.A., Shahedi: *A review on viscoelastic behaviour of plasticizers in ap/al/htpb based composite solid propellant*, Materials Today: Proceedings

[11] https://www.go-plasticizer.com/dioctyl-adipate-doa.html?google-network=g-campaignid=1768789814-adgroupid=70416065193-target=kwd-317041811721-creative=517586296988-device=c-placement=-keyword=dioctyl%20adipate&gad_source=1&gclid=Cj0KCQjw_-GxBhC1ARIsADGgDjsh6sqGzu3DCVlISCojz_iZZpD0Y958eTvyEmCLXgm8bnJfQhQlQmoaAunvEALw_wcB

[12] https://www.penpet.com/products/coatings-and-paints-printing-inks/dioctyl-adipate-doa

[13] https://chemceed.com/products/dioctyl-adipate-doa/

[14] Stanisław G. Enzyme catalysed synthesis of some

adipic esters. J Mol Catal B-Enzym 15: 9–13 (2001)

[15] Kolwzan B, Gryglewicz S. Synthesis and biodegradability of some adipic and sebacic esters. J Synthetic Lubric 20:99–107 (2003)

[16] He Y F, Zolper T J, Liu P Z, Zhao Y Z, He X L, Shen X J, Sun H W, Duan Q H, Wang Q. Elastohydrodynamic lubrication properties and friction behaviors of several ester base stocks. Friction 3(3): 243–255 (2015)

[17] Sander J. The aspects of designing lubricants using an environmental product assessment. NLGI Spokesman 61(11): 18–27 (1998)

[18] Sparkman DO, Penton Z, Kitson FG *Gas Chromatography and Mass Spectrometry: A Practical Guide*. Academic Press. (17 May 2011), ISBN 978-0-08-092015-3.