Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2023, *20*(2): 138-158; DOI 10.22211/cejem/168579

Research paper

Effect of Natural Ageing on the Safety Parameters and Performance of TNT-based Melt Cast RDX/TNT Compositions

Tirupati Chander Sharma1,2), **Arjun Singh**1,*), **Pramod Kumar Soni**1), **Vasundhara Singh**2), **Prateek Kishore**1,3)
1) *Terminal Ballistics Research Laboratory, DRDO, Sector 30, 160030 Chandigarh, India*
2) *Department of Applied Sciences, Punjab Engineering College, (Deemed to be University), Sector 12, 160012 Chandigarh, India*
3) *Department of Nanoscience and Technology, Amity University, Gurugram, Haryana, India*
**E-mail:* arjunsngh@yahoo.com

Abstract: 2,4,6-Trinitrotoluene (TNT) based melt cast RDX/TNT compositions stockpiled for a period of time were exposed under natural environmental conditions, with humidity and temperature for storage in the range of 40-95% RH and 4-47 °C, respectively. The composition, chemical, thermal and mechanical properties of the RDX/TNT compositions before and after ageing were studied by high performance liquid chromatography, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry and a universal test machine, respectively. In addition, the safety, mechanical sensitivities, detonation velocity and blast parameters were also investigated through vacuum stability tests (VST), a BAM fall hammer apparatus, a BAM friction tester and a piezo-electric accelerator, respectively. The results showed that after ageing, the colour of the composition had become dark but there was no variation in the RDX and TNT content by high performance liquid chromatography (HPLC). The VST results showed that the volume of evolved gas was almost the same and less than 2 mL/g, indicating chemical stability. The results obtained from different analytical techniques demonstrated that there was no significant variation in the chemical, thermal and mechanical properties for the aged samples as compared to the fresh composition. The change in mechanical sensitivity is related to the components and the ageing mode. The detonation velocity and detonation pressure were found to be similar to those of the freshly prepared composition and consistent with the data obtained from overall natural ageing. The results of blast studies revealed that there was either a similar or slight variation in the blast peak over pressure and impulse for RDX/TNT compositions at different locations before and after ageing under natural environmental conditions.

Keywords: TNT/RDX explosive, melt cast composition, ageing, explosive properties

1 Introduction

Conventional melt cast explosives consist of 2,4,6-trinitrotoluene (TNT) and other high explosive compounds, mainly 1,3,5-trinitro-1,3,5-triazinane (RDX) or 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), in which the explosive crystals are dispersed in the TNT matrix. TNT based melt cast compositions, including RDX/TNT, HMX/TNT compositions etc. are mainly developed as the main charge for the manufacture of shells, artillery shells, bombs and other warheads in missiles systems [1-5].

TNT has a low melting point for casting, acceptable chemical and thermal stability in addition to compatibility with most energetic compounds with fairly high explosive power. These compositions and other TNT based compositions are mixed in melt-cast systems. They are usually melted and cast into rockets, bombs, shells etc. where they are allowed to cool and solidify. Of the TNT-based melt cast explosive compositions, RDX/TNT compositions are the best known and widely used in military applications because of their high energy content, relatively high detonation velocity, ease of processing for any shape [6, 7]. However, this composition has the drawback of its high sensitivity to mechanical stimuli [8-11]. It has been extensively studied for its safety parameters, in terms of thermal sensitivity, mechanical sensitivity and by theoretical studies [12-15].

TNT is in principle a reactive organic compound and is kinetically and thermodynamically capable of reacting with other components of many environmental systems. The TNT-based melt cast explosive compositions filled in warheads/munitions and stockpiled for many years always have the tendency for slow decomposition during storage under different environmental conditions. The decomposition process may accelerate due to direct contact with the casing, elevated temperature or direct exposure to the environment, thereby resulting in degradation of the physical, chemical and thermal properties. It may also enhance the sensitivity, and reduced the performance and service life [15]. The gases evolved due to decomposition may increase the pressure, which may lead to rupture/leakage of the casing. It is well established that changes in the physical, chemical, thermal, mechanical and explosive properties are of utmost importance for calculating the storage life [16]. The chemical stability and thermal properties are investigated by conducting several tests, including the vacuum stability test, gravimetric analysis (TGA) and differential scanning calorimetry (DSC) [17-27]. Therefore, it is important to predict and determine the shelf-life/storage life for safe storage and use of energetic materials and munitions.

Many researchers have predicted the shelf-life of solid propellants by the Arrhenius and Berthelot equations. Furthermore, the accelerated ageing method has also been reported for estimating the storage life of energetic compounds, munitions/energetic formulations and propellants [28-30]. The effects of thermally accelerated ageing of the explosive formulations and propellants composed of nitrocellulose and nitroglycerin have been extensively investigated to simulate ageing on performance and safety after undergoing accelerated ageing [31-34].

TNT based explosives degrade very differently to solid propellants based on ammonium perchlorate-loaded polymer binders. The Arrhenius relation suggests that storing samples of explosives or propellants at elevated temperatures for a short time is equivalent to natural ageing for prolonged periods. Actually, the relationship between the accelerated ageing time and the natural age of energetic materials is problematic due to shortcomings in the Arrhenius relation and several types of temperature-dependent processes. Therefore, we proposed to study the effect of naturally aged RDX/TNT compositions on their thermal stability, safety and performance. The outcomes from these studies were able to determine if this RDX/TNT material may be further used for military applications or should be discarded for safety reasons.

In our previous work, we have studied the effects of natural ageing on the properties of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB). The kinetic parameters of aged Composition B and Octol samples stockpiled for prolonged periods have been studied by isoconventional kinetic methods using TGA and DSC. In this context, the activation energies of aged TATB, Composition B and Octol have been studied by different kinetic methods using the DSC method [35-38].

In the present work, the effects of natural ageing on the composition, chemical, thermal, mechanical and safety properties were studied with RDX/TNT material and compared with fresh RDX/TNT material of the same composition. In addition, the effects of ageing on the performance and blast parameters were also investigated for both aged and fresh compositions.

2 Experimental

2.1 Materials

The most popular melt-cast RDX/TNT composition is the so-called Composition B. This consists of 60 wt.% of RDX and 40 wt.% of TNT, and was procured from the M/s Ordinance Factory, Bhandara, India. This material was in direct contact with the casing and was exposed for 32 years under natural environmental ageing conditions. The temperature and humidity of storage were in the range 4-47 °C and 40-95% RH, respectively. A fresh lot of RDX/TNT composition, having the same composition, was also recently procured from the M/s Ordinance Factory (Bhandara, India). The naturally aged and fresh samples were used for investigating the composition, chemical information, sensitivity and thermal properties.

In order to study the compressive strength, blast and detonation parameters, these materials were further cast by the melt cast technique in a vacuum cast facility into an explosive charge. The materials were kept in the vessel under continuous stirring in a steam jacketed anchor blade mixer at a temperature of 86 ±2 °C. These materials were stirred at 100 to 125 rpm for 40 min and then transferred to a suitable mould. After controlled cooling and solidification to ambient conditions, the explosive charges were removed from the mould and machined to obtain the required dimensions for compressive strength, detonation and blast parameter studies.

2.2 Test methods

HPLC was performed with the Agilent Series 1100 equipped with an in-line degasser, an auto sampler, a column thermostat and pump. Acetonitrile solvent was used to analyse the composition of the RDX/TNT sample.

FTIR spectra were obtained by using the KBr pellet technique (FTIR Nicolet Avtar 360 model) to study structural changes in the material. The powder sample was ground with KBr and then pressed into pellet form. The spectra were recorded from 4000 to 400 cm^{-1}.

A vacuum stability tester STABIL 21 (OZM Research, Czech Republic) was used for the Vacuum Stability Test (VST), to assess the chemical stability of the aged and freshly prepared material. In the VST method, 6.0 ±0.5 g of sample was placed in the heating tube followed by evacuation. VST measurements for all kinds of samples were performed at an isothermal temperature of 100 °C for 40 h. The amount of gas evolved was recorded.

The impact sensitivity was determined by a BAM Fall Hammer apparatus using the Bruceton staircase method. Approximately 39.0 ±1.0 mg of the dried sample was placed in between two cylinders which are covered by a guide ring. Then, a 2 kg standard weight was dropped from pre-determined heights. A sound was noted due to decomposition for a recorded event. The impact energy (*E*) was calculated using the following Equation 1.

$$E = m \cdot g \cdot h \tag{1}$$

where *m* is the mass of the drop weight, *g* is acceleration due to gravity and *h* is the height from which the weight was dropped.

A BAM friction apparatus (OZM Research s.r.o., Czech Republic) was used for the determination of the friction sensitivity of the fresh and aged samples. In the friction sensitivity test, approximately 20 ±5.0 mg of sample was uniformly placed on the porcelain plate and the frictional force was provided by standard BAM weights. The results were reported in terms of the mean frictional force at which 50% initiation of the samples occurred, and was obtained by conducting more than 25 trials using the Bruceton staircase method.

The thermal decomposition behaviour was studied by using a simultaneous Thermogravimetric/Differential Scanning Calorimetry analyser, TGA/DSC 1, manufactured by Mettler Toledo. The analyses were conducted in open alumina crucibles (standard volume 70 μL capacity) under a nitrogen atmosphere. Approximately 4-5 mg samples were subjected to heat in the TGA/DSC furnace from room temperature to 400 °C at a heating rate of 2 $°\mathrm{C}\cdot\mathrm{min}^{-1}$. The flow rate of nitrogen was kept constant at 30 $\mathrm{mL}\cdot\mathrm{min}^{-1}$ for all TGA/DSC measurements.

The compressive strength of aged and fresh compositions was measured by employing a Universal Testing Machine (UTM) supplied by Ashian Engineers Company (India). Pellets of standard size were prepared from the energetic composite. The pellets were machined to obtain charges having dimensions of 20×20 mm (diameter×length). The load cell was adjusted to compress the pellets at a speed of 10 $\mathrm{mm}\cdot\mathrm{min}^{-1}$. The pellets were compressed to their breaking point. The instrument recorded the data of the stress versus strain, from which the compressive strength was calculated.

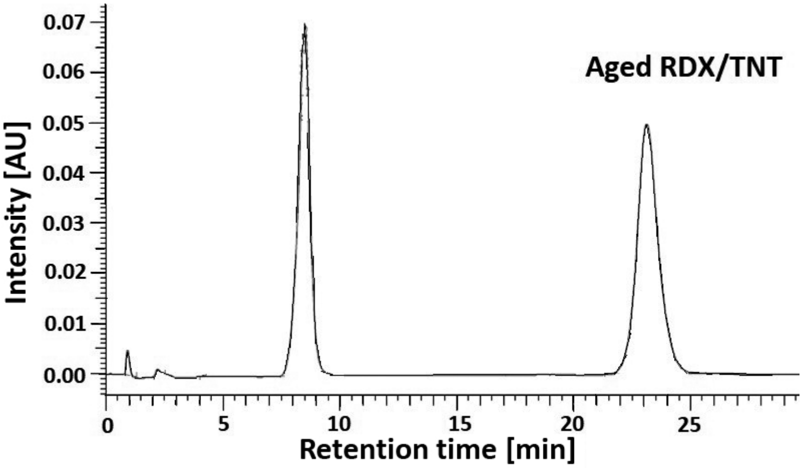
The detonation velocity of the aged composition was measured by pin ionization probes and streak photographic methods. The composition was prepared in the form of a cylindrical charge with dimensions of 50×150 mm (diameter×length). Three optical sensors were placed in each charge, with the sensor being placed at a distance of 50 mm from the surface equipped with the detonator. The shock wave passed through the cylindrical charge having pins attached at pre-determined distances and the arrival time of the shock wave was detected. The detonation velocity was calculated from the distance-time relationship.

The blast parameters were measured by piezoelectric transducers at different distances from the centre of initiation point. Main charges of fresh and aged RDX/TNT charges were equipped with plastic explosive Kirkee (Khadki, Pune, India), as a booster, and electric detonator 33. Detonator 33 is an instantaneous detonator with medium resistance to the effects of external sources of electricity. The RDX/TNT charge was detonated at standoff distances of 5.0, 7.0 and 9.0 m. The impulse was calculated by integrating the peak overpressure over the positive duration of the pulse using a MATLAB® program.

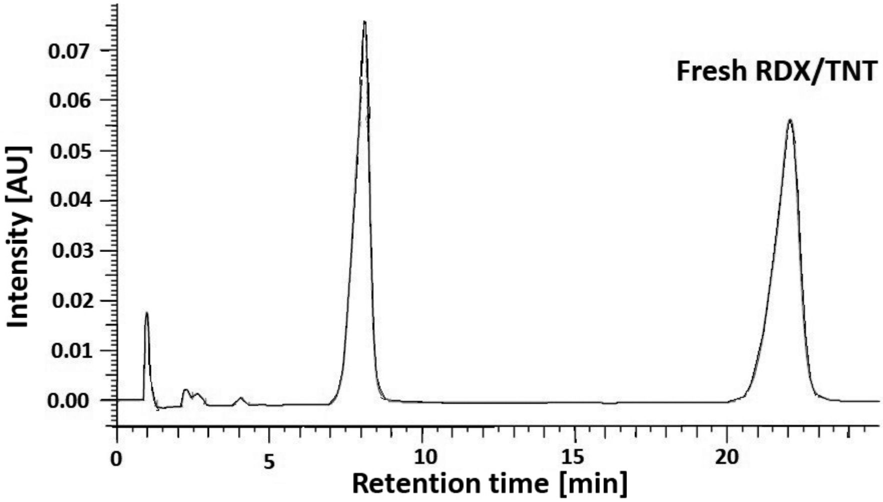
3 Results and Discussion

3.1 Composition analysis

For HPLC analysis, a mixture of water and methanol (60:40) was used as the mobile phase, while the sample was dissolved in acetonitrile. Figure 1 shows the chromatographs of the aged and fresh tested RDX/TNT compositions. For qualitative and quantitative analysis of the RDX/TNT, HPLC chromatography provides the retention time and the area under the peak.



(a)



(b)

Figure 1. HPLC chromatographs of aged (a) and fresh (b) RDX/TNT compositions

It was observed that the contents of RDX and TNT in naturally aged RDX/TNT material was found to be 60.5% and 39.3% respectively, while a freshly prepared sample was 60.8% RDX and 39.2% TNT. The results indicate that there was no effect due to the natural ageing environmental conditions for a prolonged period of time.

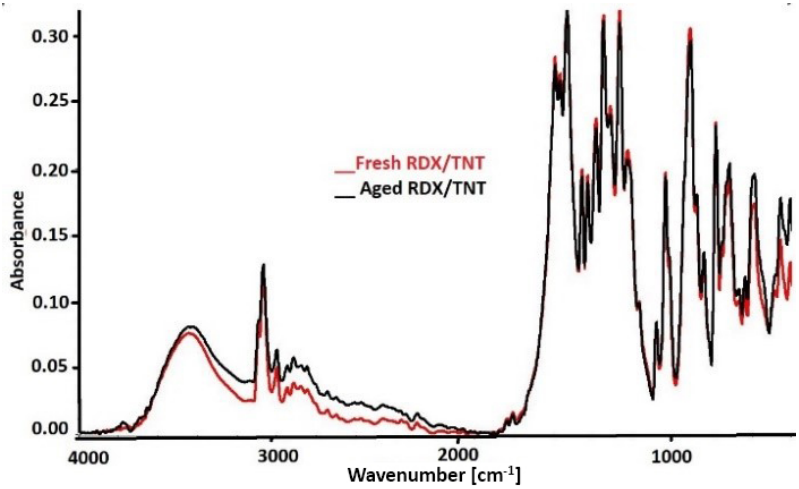
3.2 Chemical structural analysis

The chemical structure and functional groups of the aged RDX/TNT material were investigated by FTIR spectroscopy. The FTIR spectrum of the aged sample was recorded in the range 4000-400 cm^{-1} as shown in Figure 2. It can be seen that the absorption peaks appearing in the region 1359-1328 cm^{-1} correspond to the symmetric stretch of *p*-nitro group (4-NO_2), while absorption peaks appearing in the region 1562-1535 cm^{-1} are assigned to the asymmetric stretch of the *o*- nitro group (NO_2). The absorption peaks appeared at:

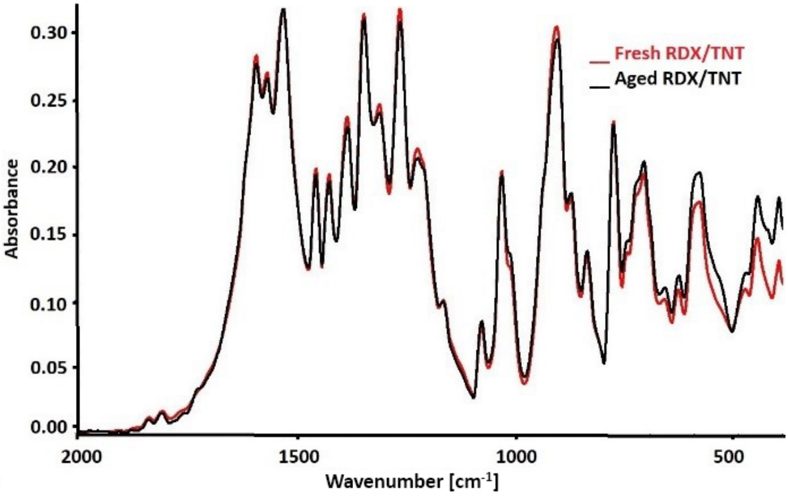
– 1592 cm^{-1} (antisymmetric stretching of –NO_2 group),
– 1269 cm^{-1} (symmetric stretching vibration of –NO_2),
– 1038 and 911 cm^{-1} (ring stretching),
– 784 cm^{-1} (δ and γ NO_2),
– 636 cm^{-1} ($\tau + \gamma$ NO_2) were observed due to the presence of RDX.

Similar absorption peaks were observed for a fresh RDX/TNT composition. The

FTIR characteristics of fresh and aged RDX/TNT material are listed in Table 1. The results of the FTIR study indicate there is no change in intensity or shift in the peaks for the aged composition as compared to the fresh composition, indicating that there is no degradation of the chemical structure after ageing under natural environmental conditions.



(a)



(b)

Figure 2. FTIR spectra of aged and fresh RDX/TNT compositions at 4000-400 (a) and 2000-400 (b) cm^{-1}

Table 1. FTIR characteristics of fresh and aged RDX/TNT material

Absorption peaks for the tested RDX/TNT compositions in [cm^{-1}]		Functional group
fresh	aged	
3070	3070	CH_2 stretching
1595	1596	Antisymmetric stretching vibration of $-NO_2$
1535	1534	2,6-NO_2
1351	1351	4-NO_2
1269	1269	Symmetric stretching vibration of $-NO_2$
1036	1038	Ring stretching
913	911	Ring stretching
784	784	δ and γ NO_2
636	636	$\tau + \gamma$ NO_2
589	589	NO_2

3.3 Vacuum stability test (VST)

It was observed that the amount of gas evolved increased on increasing the test time. The amount of gas evolved for the aged sample was 0.94 $mL \cdot g^{-1}$, while the amount for a fresh sample was 0.905 $mL \cdot g^{-1}$ after 40 h. These results indicate that there is no change in the amount of gas evolved for samples before and after ageing for a prolonged period of time. Furthermore, the amount of gas evolved was found to be less than 2.0 $mL \cdot g^{-1}$. This indicates that the aged composition possesses good chemical stability.

3.4 Impact and friction sensitivity

The impact and friction sensitivity were determined for aged and fresh compositions and the results are listed in Table 2. The value of the impact energy of the aged samples was found to be 6.32 J, while the value for a fresh sample was 5.56 J. The values of the friction sensitivity for aged and fresh compositions were found to be 360 and 294 N, respectively. This indicates that the aged composition exhibits comparatively less sensitivity towards impact and friction than a freshly prepared RDX/TNT composition.

Table 2. The results of mechanical sensitivities obtained from the BAM impact and friction test methods

RDX/TNT sample	Impact sensitivity for 2 kg falling weight		Friction sensitivity [N]
	H_{50} [cm]	Impact energy [J]	
Aged	31.62	6.32	360
Fresh	29.29	5.56	294

3.5 Thermal decomposition

Figure 3 shows the TGA thermograms and the corresponding differential curves. The DTG curves of the aged and fresh RDX/TNT compositions obtained for the temperature range 25-400 °C under a nitrogen atmosphere. The TG curves showed that the mass loss started gradually at 190 to 205 °C, and thereafter faster thermal decomposition of RDX and TNT. The DTG curve showed a single peak due to the thermal decomposition of RDX and TNT.

The thermal data, in terms of the onset temperature (T_{onset}), peak temperature (T_{p}) and endset temperature (T_{endset}), obtained from the TG/DTG curves are tabulated in Table 3. The values of the T_{onset} and T_{p} of the aged sample were 187.5 and 216.1 °C, respectively. The corresponding values for the fresh sample were 186.9 and 215.3 °C, respectively. As far as the thermal stability is concerned, the mass loss for all kinds of compositions before and after ageing was observed at a temperature above 170 °C. This indicates that the thermal stability of an aged composition is similar to that of a fresh composition. These results also demonstrate that thermal stability does not change for an RDX/TNT composition after ageing for a prolonged period of time.

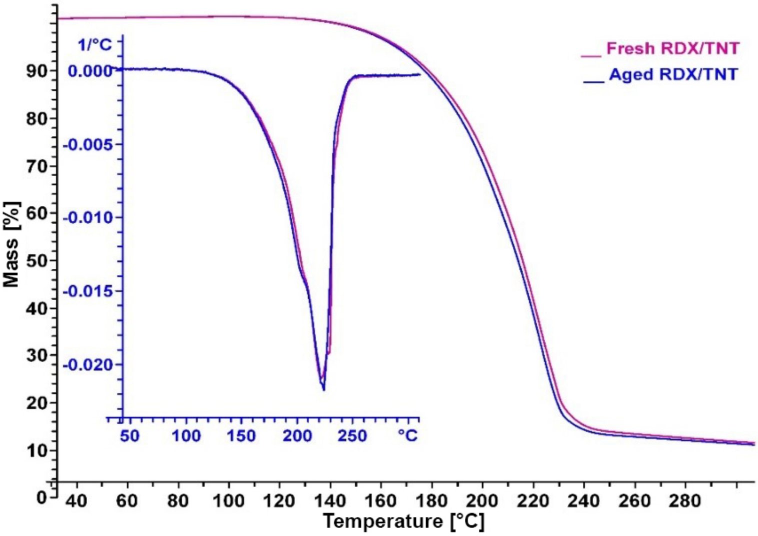
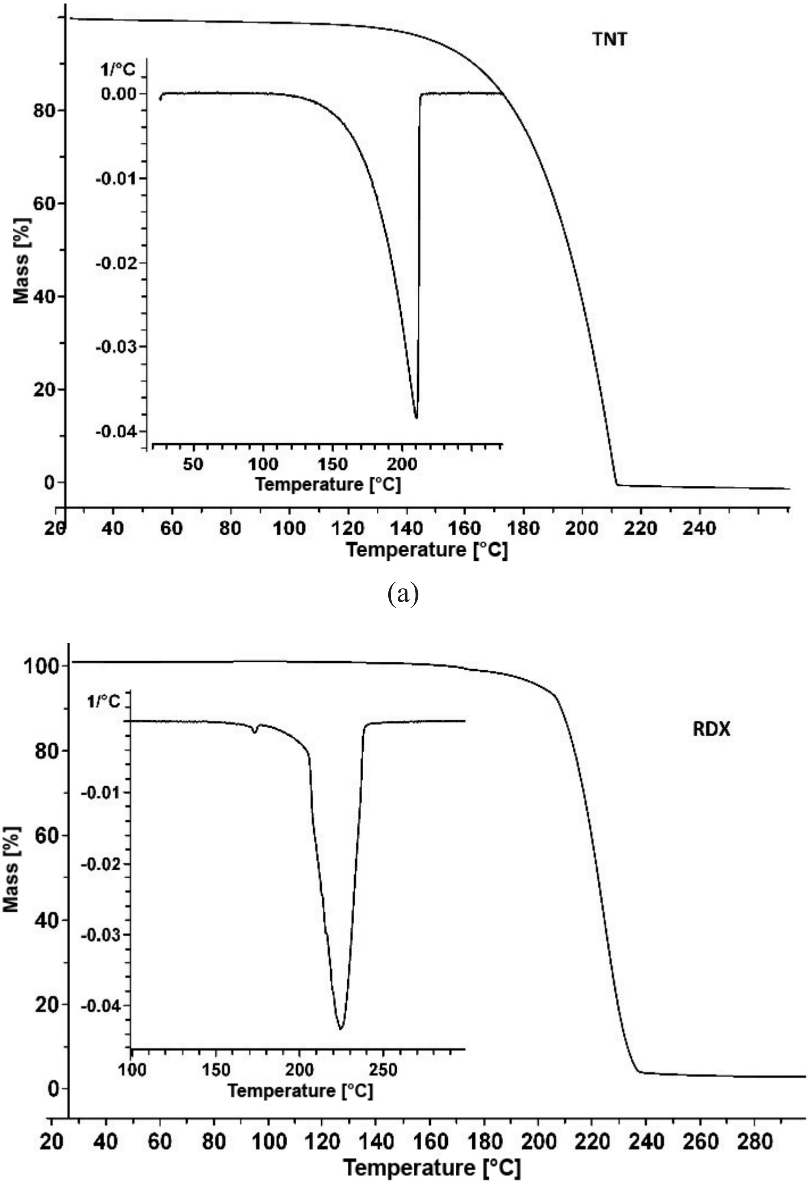


Figure 3. TG/DTG curves of aged and fresh compositions obtained at 25-400 °C and under a nitrogen atmosphere

The thermal decomposition of pure TNT and RDX was also studied by TGA at 25-400 °C under a nitrogen atmosphere. Figure 4 shows the TGA thermograms and their corresponding DTG curves for TNT and RDX. The TG curves showed that the mass loss started gradually at 175 to 200 °C, and thereafter faster thermal decomposition of TNT and RDX. The DTG curve showed a single peak due to the thermal decomposition of RDX and TNT. The thermal characteristic values of the T_{onset}, T_{endset}, and T_{p} are listed in Table 3. These results demonstrate that the thermal stability of pure TNT and RDX is comparable to those of aged and fresh RDX/TNT samples.



(a)

(b)

Figure 4. TG/DTG curves of TNT (a) and RDX (b) obtained at 25-400 °C and under a nitrogen atmosphere

Table 3. Thermal data, T_{onset}, T_{endset}, and T_p, along with the decomposition percentage obtained at 25-400 °C, heating rate of 2 $°C \cdot min^{-1}$ and under a nitrogen atmosphere

Sample	Decomposition temperature [°C]			Decomposition [%]
	T_{onset}	T_{endset}	T_p	
TNT	183.9	209.2	207.5	99.9
RDX	203.6	230.9	222.4	97.0
Aged RDX/TNT	187.5	225.7	216.1	90.8
Fresh RDX/TNT	186.9	337.1	215.3	90.5

The thermal decomposition behaviour was also studied by the DSC method in the temperature range 25-400 °C under a nitrogen atmosphere. Figure 5 shows the DSC curves of aged and fresh compositions at a heating rate of 2 $°C \cdot min^{-1}$ and under a nitrogen atmosphere. The DSC curves exhibit sharp endothermic and exothermic peaks corresponding to melting point and thermal decomposition, respectively. The first endothermic peak appeared around 80 °C which is corresponds to the melting point of TNT, followed by an exothermic peak due to the thermal decomposition of RDX.

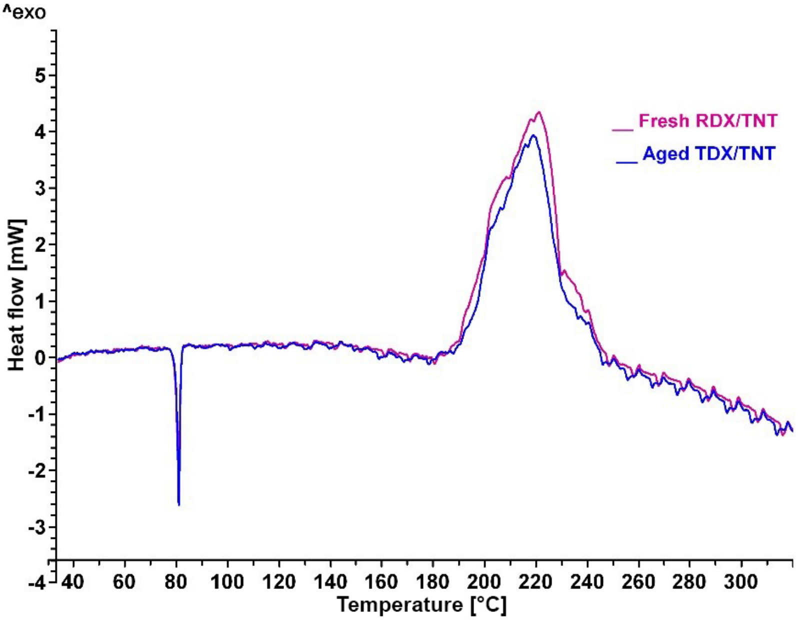


Figure 5. DSC curves of aged and fresh RDX/TNT compositions at 25-400 °C, heating rate of 2 $°C \cdot min^{-1}$ and under a nitrogen atmosphere

The DSC thermal data, T_{onset}, T_{p} and T_{endset}, along with the enthalpy for RDX/TNT before and after ageing are listed in Table 4. The values of the T_{onset} and T_{p} of the aged samples were 194.2 and 215.2 °C, respectively, while the corresponding values for the fresh composition were 193.2 and 213.5 °C, respectively. These studies further confirmed that these compositions possess high thermal stability. The results further confirm that there is no change in the thermal decomposition behaviour of RDX/TNT composition after ageing for a prolonged period of time.

Table 4. DSC data of aged and fresh RDX/TNT samples at 25-400 °C, at heating rate 2 °C/min and under a nitrogen atmosphere

RDX/TNT	Melting temperature [°C]	Decomposition temperature [°C]			ΔH [J·g^{-1}]
		T_{onset}	T_{endset}	T_{p}	
Aged	80.2	194.2	225.2	215.2	693.3
Fresh	80.1	193.2	225.3	213.5	645.4

3.6 Compressive strength

Pellets of the RDX/TNT with dimensions of 20 mm in diameter and 30 mm in length were machined to evaluate their compressive strength. The pellets were compressed to breaking point using a UTM, and the software recorded the data in terms of stress versus strain. It was observed that the stress initially increased linearly with the increasing strain from zero. After certain values, the stress was tremendously increased with further increasing strain and the stress curves passed through a maximum. This point of maximum stress was used for determining the compressive strength. The point at the maximum stress value is related to the failure strain. The results of compressive strength for both aged and fresh compositions are listed in Table 5.

Table 5. The compressive strength of RDX/TNT compositions obtained by the UTM technique

RDX/TNT sample	Strain	Compressive strength [MPa]	Average compressive strength [MPa]
Aged	0.04	10.31	9.19
	0.06	8.79	
	0.04	9.71	
Fresh	0.043	9.07	9.60
	0.037	8.79	
	0.040	9.71	

The compressive strength of the aged sample was 9.6 MPa, while the corresponding value for the fresh composition was 9.19 MPa. It can be seen that there is no variation in the compressive strength before and after ageing for a prolonged period of time.

3.7 Performance parameters

A detonation wave was obtained with the help of a donor charge, which passed through the cylindrical charge fitted with pin sensors (Figure 6). In this method, pins are inserted at different distance along the cylindrical charges. These pin sensors were placed at predetermined points for detecting the arrival time of the detonation wave. The charges were initiated by an electrically initiated detonator. The charge (loading) density of the pellets was measured gravimetrically after machining.

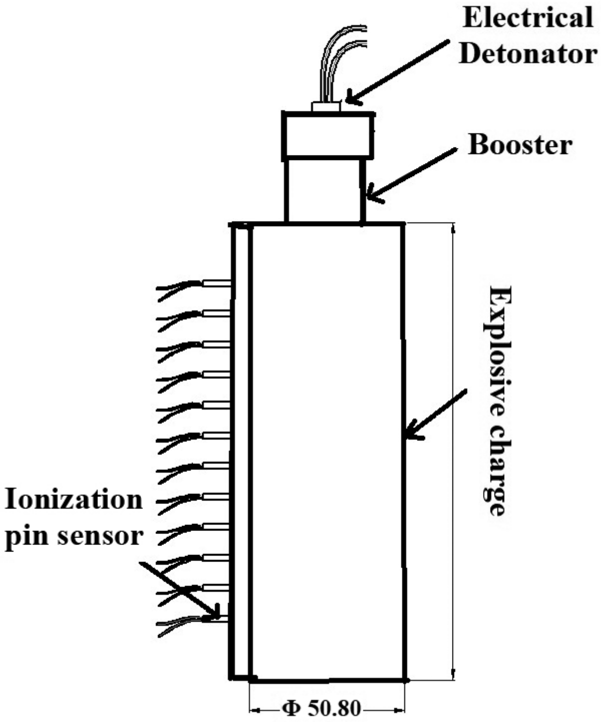


Figure 6. Schematic diagram for the experimental setup with the positioning of the sensors

The data acquisition was performed with an oscilloscope. Pin ionization oscilloscope graphs were recorded for the arrival of the shock wave through the energetic charges. In addition, streak photography was also used to measure the detonation velocity. The results of the detonation velocity measured from the pin ionization probes and the streak method along with the detonation pressure are listed in Table 6. The values of the detonation velocity of the aged and fresh compositions based on two measurements were found to be 7.79 and 7.81 km·s^{-1}, respectively. The results of the detonation velocity and detonation pressure were found to be almost same. This indicates that the performance of RDX/TNT does not change after ageing for 32 years under natural conditions.

Table 6. Detonation parameters of aged and fresh RDX/TNT samples obtained from high speed (streak) photography and pin ionization techniques

RDX/TNT sample	Detonation velocity [km·s^{-1}]		Detonation pressure [kbar]
	Streak camera	Pin ionization	
Aged	7.81	7.83	267
Fresh	7.79		262

3.8 Blast parameters

The blast parameters were determined by a configuration technical test trial set up and firing using a piezoelectric accelerometer. The overpressure parameter was measured using piezo-electric pressure transducers, *i.e.* gauges. The relationship of overpressure-time (p-t diagram) was obtained by software processing of the recorded signals. The piezoelectric transducers were placed at distances of 5.0, 7.0 and 9.0 m from the centre of the initiation point to obtain the time dependence of the shock wave overpressure in air. Both the aged and fresh charges were placed at a height of 1.5 m above the ground to avoid reflected wave from the ground. The set of probes was placed perpendicular to the direction of propagation of the shock wave front. Figure 7 shows the plots of peak overpressure of the blast shock arrival versus time for aged and fresh compositions. The results of peak overpressure, impulse and duration are listed in Table 7.

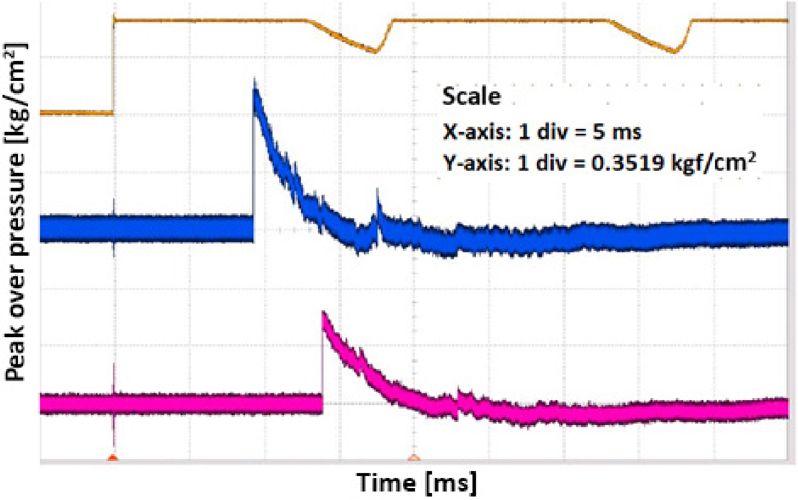


Figure 7. Plots of peak over pressure versus time for aged (blue) and fresh RDX/TNT (pink) compositions

Table 7. The results of peak overpressure, duration and impulse of before and after ageing RDX/TNT compositions

RDX/TNT sample	Standoff [m]	Peak overpressure [kgf·cm^{-2}] ([MPa])	Duration [ms]	Impulse [kgf·cm^{-2}·ms^{-1}]
Aged	5.0	1.126 (0.1104)	2.4	–
	7.0	0.901 (0.0884)	4.4	1.52
	9.0	0.528 (0.0518)	7.2	1.21
Fresh	5.0	1.055 (0.1035)	2.4	–
	7.0	0.844 (0.0828)	4.4	1.43
	9.0	0.528 (0.0518)	6.8	1.27

Impulse is important for design purposes because it refers to the total force (per unit area) applied on a structure due to the blast load [38]. The peak overpressure of the aged sample at distances of 5.0, 7.0 and 9.0 m was 1.126, 0.901 and 0.528 kgf·cm^{-2}, respectively, while the corresponding values for the fresh composition was 1.055, 0.844 and 0.528 kgf·cm^{-2}, respectively. The values of the impulse at a distance of 7.0 m were found to be 1.52 and 1.43 kgf·cm^{-2}·ms^{-1} for aged and fresh compositions, respectively. The impulse value at 5.0 m could not be calculated because the decay profile of the blast wave was disturbed and fluctuated. The results indicate that there is a similar peak overpressure and impulse data, with only slight variations at different distances, for aged and fresh compositions.

4 Conclusions

- In the present study RDX/TNT high explosive materials were stored under natural environmental conditions for a long period of time (32 years).
- The effects of the natural ageing process on composition, chemical, thermal and mechanical properties have been studied by different analytical techniques. Furthermore, the sensitivity, detonation and blast parameters have been investigated to see the effect of ageing. The composition of all the samples clearly indicated that the RDX, TNT contents are almost the same and no other peaks were detected by HPLC. The VST results indicated that the volume of gas evolved is the same and less than 2.0 $mL \cdot g^{-1}$ for RDX/TNT samples before and after ageing, which indicates high chemical stability. The thermal decomposition behaviour of the aged composition has been studied *via* the TGA and DSC methods. The results indicated that the aged samples are thermally stable and there is no significant change in thermal decomposition behaviour compared to the fresh material, as shown by TGA and DSC.
- The sensitivity study indicated that the impact sensitivity and friction sensitivity of the aged RDX/TNT material are comparable or better than those obtained from fresh RDX/TNT material.
- It was also observed that the compressive strength of the aged RDX/TNT material is comparable to that of fresh material.
- The detonation study revealed that the detonation velocity and detonation pressure are very similar to that of the freshly prepared material, consistent with overall natural ageing. The variations in the blast peak overpressure and impulse are not significant for RDX/TNT composition before and after ageing.
- It is concluded that this RDX/TNT material does not change in its performance and safety parameters and is considered to be safe to use up to 32 years on storage under typical natural ageing conditions.

Acknowledgement

The authors express their sincere thanks to Mr. Niladri Mukherjee, Technology Director for their constant motivation, guidance and fruitful discussion. The authors also express their sincere thanks and gratitude towards the Technology Directors and team of S&D and BDS Division for carrying out performance evaluation trials.

References

[1] Fouche, F.; Van, S. TNT-based Insensitive Munitions. *Proc. 27th Int. Annu. Conf. ICT*, Karlsruhe, Germany, **1996**.

[2] Huang, H.J.; Dong, H.S.; Zhang, M. Problems and Developments in Composition B Modification Research. *Chin. J. Energ. Mater.* **2001**, *9*: 183-186.

[3] Castorina, T.C.; McCahill, J.W.; Forsyth, A.C. Compatibility of Flocculating Agents with RDX/TNT/Comp. B. *J. Hazard. Mater.* **1977-1978**, *2*(2): 137-142; DOI: 10.1016/0304-3894(77)80014-9.

[4] Stepanov, V.; Anglade, V.; Balas Hummers, W.A.; Bezmelnitsyn, A.V.; Krasnoperov, L.N. Production and Sensitivity Evaluation of Nanocrystalline RDX-based Explosive Compositions. *Propellants Explos. Pyrotech.* **2011**, *36*(3): 240-246; DOI: 10.1002/prep.201000114.

[5] Trzciński, W.; Cudziło, S.; Dyjak, S.; Nita, M. A Comparison of the Sensitivity and Performance Characteristics of Melt-Pour Explosives with TNT and DNAN Binder. *Cent. Eur. J. Energ. Mater.* **2014**, *11*: 443-455.

[6] An, C.; Wang, J.; Xu, W.; Li, F. Preparation and Properties of HMX Coated with a Composite of TNT/Energetic Material. *Propellants Explos. Pyrotech.* **2010**, *35*(4): 365-372; DOI: 10.1002/prep.200900060.

[7] Vijayalakshmi, R.; Radhakrishnan, S.; Shitole, P.; Pawar, S.J.; Mishra, V.S.; Garg, R.K.; Talawar, M.B.; Sikder, A.K. Spherical 3-Nitro-1,2,4-triazol-5-one (NTO) based Melt-cast Compositions: -Heralding a New Era of Shock Insensitive Energetic Materials. *RSC Adv.* **2015**, *5*: 101647-101655; DOI: 10.1039/C5RA19010J.

[8] Singh, A.; Sharma, T.C.; Kumar, M.; Narang, J.K.; Kishore, P.; Srivastava, A. Thermal Decomposition and Kinetics of Plastic Bonded Explosives Based on Mixture of HMX and TATB with Polymer Matrices. *Def. Technol.* **2017**, *13*: 22-32; DOI: 10.1016/j.dt.2016.11.005.

[9] An, C.-W.; Li, F.-S.; Song, X.-L.; Wang, Y.; Guo, X.-D. Surface Coating of RDX with a Composite of TNT and an Energetic-polymer and Its Safety Investigation. *Propellants Explos. Pyrotech.* **2009**, *34*(5): 400-405; DOI: 10.1002/prep.200700286.

[10] Urbanski, T. *Chemistry and Technology of Explosives.* Vol. 1, Pergamon Press, Oxford, **1964**, pp. 290-300; ISBN 978-0080102382.

[11] Wiegand, D.A.; Pinto, J. The Mechanical Response of TNT and a Composite, Composition B, of TNT and RDX to Compressive Stress: III Dependence on Processing and Composition. *J. Energ. Mater.* **1991**, *9*(5): 349-413; DOI: 10.1080/07370659108019381.

[12] Qiu, H.; Stepanov, V.; Di, S.A.; Chou, T.; Lee, W.Y. RDX-based Nanocomposite Microparticles for Significantly Reduced Shock Sensitivity. *J. Hazard. Mater.* **2011**, *185*(1): 489-493; DOI: 10.1016/j.jhazmat.2010.09.058.

[13] Pinto, J.; Wiegand, D.A. The Mechanical Response of TNT and a Composite, Composition B, of TNT and RDX to Compressive Stress: II Triaxial Stress and Yield. *J. Energ. Mater.* **1991**, *9*(3): 205-263; DOI: 10.1080/07370659108019865.

[14] Nassim, B.; Zhang, Q. Thermal Stability of Explosive Mixture with Additives at Different Ambient Temperatures. *Propellants Explos. Pyrotech.* **2018**, *43*(2):

177-187; DOI: 10.1002/prep.201700204.

[15] Zhang, J.G.; Wang, K.; Niu, X.Q.; Zhang, T.L.; Zhou, Z.N. Theoretical Study of the Decomposition Mechanisms and Kinetics of the Ingredients RDX in Composition B. *J. Mol. Model.* **2012***, 18*(8): 3915-3926; DOI: 10.1007/s00894-012-1396-1.

[16] Long, G.T.; Brems, B.A.; Wight, C.A. Autocatalytic Thermal Decomposition Kinetics of TNT. *Thermochim. Acta* **2002**, *388*(1-2): 175-181; DOI: 10.1016/S0040-6031(02)00031-X.

[17] Adnan, H. *Investigation of the Service Life of Binders Used in Rocket Propellants and High Explosives.* MSc. dissertation, Military Technical College, Cairo, **1999**.

[18] Luo, L.; Guo, P.; Jin, B.; Xiao, Y.; Zhang, Q.; Chu, S.; Peng, R. An Isothermal Decomposition Dynamics Research Instrument and Its Application in HMX/TNT/Al Composite Explosive. *J. Therm. Anal. Calorim.* **2020**, *139*: 2265-2272; DOI: 10.1007/s10973-019-08554-5.

[19] Kumar, R.; Singh, A.; Kumar, M.; Soni, P.K.; Singh, V. Investigations of Effect of Hydroxyl-terminated Polybutadiene-based Polyurethane Binders Containing Various Curatives on Thermal Decomposition Behaviour and Kinetics of Energetic Composites. *J. Therm. Anal. Calorim.* **2021**, *145*: 2417-2430; DOI: 10.1007/s10973-020-09773-x.

[20] Singh, A.; Sharma, T.C.; Kishore, P. Thermal Degradation Kinetics and Reaction Models of 1,3,5-Triamino-2,4,6-trinitrobenzene-based Plastic-Bonded Explosives Containing Fluoropolymer Matrices. *J. Therm. Anal. Calorim.* **2017**, *129*: 1403-1414; DOI: 10.1007/s10973-017-6335-z.

[21] Singh, A.; Singh, S.; Sharma, T.C.; Kishore, P. Physicochemical Properties and Kinetic Analysis for Some Fluoropolymers by Differential Scanning Calorimetry. *Polym. Bull.* **2018**, *75*: 2315-2338; DOI: 10.1007/s00289-017-2153-5.

[22] Singh, A.; Soni, P.K.; Sarkar, C.; Mukherjee, N. Thermal Reactivity of Aluminized Polymer-bonded Explosives Based on non-Isothermal Thermogravimetry and Calorimetry Measurements. *J. Therm. Anal. Calorim.* **2018**, *136*: 1021-1035; DOI: 10.1007/s10973-018-7730-9.

[23] Singh, A.; Kumar, R.; Soni, P.K.; Singh, V. Compatibility and Thermokinetics Studies of Octahydro- 1,3,5,7-tetranitro-1,3,5,7-tetrazocine with Polyether-based Polyurethane Containing Different Curatives. *J. Energ. Mater.* **2019**, *37*(2): 141-153; DOI: 10.1080/07370652.2018.1552337.

[24] Singh, A.; Kumar, R.; Soni, P.K.; Singh, V. Compatibility and Thermal Decomposition Kinetics Between HMX and Some Polyester-based Polyurethanes. *J. Therm. Anal. Calorim.* **2021**, *143*: 3969-3981; DOI: 10.1007/s10973-020-09377-5.

[25] Malik, S.; Singh, A.; Kumar, R.; Soni, P.K.; Kaur, A. Compatibility and Thermokinetics Studies of 4-Amino Triazolium Picrate with Various Polymers. *J. Therm. Anal. Calorim.* **2023**, *148*: 6371-6387; DOI: 10.1007/s10973-023-12161-w.

[26] Singh, A.; Kumar, R.; Soni, P.K.; Singh, V. Investigation of the Effect of Diisocyanate on the Thermal Degradation Behavior and Degradation Kinetics of Polyether-based Polyurethanes. *J. Macromol. Sci., Part B: Phys.* **2020**, *59*(12): 775-795; DOI: 10.1080/00222348.2020.1802850.

[27] Singh, A.; Soni, P.K.; Singh, M.; Srivastava, A. Thermal Degradation, Kinetic

and Correlation Models of poly(Vinylidene Fluoride-chlorotrifluoroethylene) Copolymers. *Thermochim. Acta* **2012**, *548*: 88-92; DOI: 10.1016/j.tca.2012.08.031.

[28] Wei, R.; Huang, S.; Wang, Z.; Wang, X.; Ding, C.; Yuen, R.; Wang, J. Thermal Behavior of Nitrocellulose with Different Aging Periods. *J. Therm. Anal. Calorim.* **2019**, *136*: 651-660; DOI: 10.1007/s10973-018-7653-5.

[29] Sorensen, D.N.; Quebral, A.P.; Baroody, E.E.; Sanborn, W.B. Investigation of the Thermal Degradation of the Aged Pyrotechnic Titanium Hydride/Potassium Perchlorate. *J. Therm. Anal. Calorim.* **2006**, *85*: 151-156; DOI: 10.1007/s10973-005-7365-5.

[30] Kim, Y.; Ambekar, A.; Yoh, J.J. Toward Understanding the Aging Effect of Energetic Materials via Advanced Isoconversional Decomposition Kinetics. *J. Therm. Anal. Calorim.* **2018**, *133*: 737-744; DOI: 10.1007/s10973-017-6778-2.

[31] Itkis, D.G.; Bohn, M.A. Simulation of Heat Flow Curves of NC-based Propellants – Part 1: Determination of Reaction Enthalpies and Other Characteristics of the Reactions of NC and Stabilizer DPA Using Quantum Mechanical Methods. *Propellants Explos. Pyrotech.* **2021**, *46*(8): 1188-1203; DOI: 10.1002/prep.202000314.

[32] Wei, R.; Huang, S.; Wang, Z.; Wang, C.; Zhou, T.; He, J.; Yuen, R.; Wang, J. Effect of Plasticizer Dibutyl Phthalate on the Thermal Decomposition of Nitrocellulose. *J. Therm. Anal. Calorim.* **2018**, *134*: 953-969; DOI: 10.1007/s10973-018-7521-3.

[33] Volk, F.; Bohn, M.A.; Wunsch, G. Determination of Chemical and Mechanical Properties of Double Base Propellants during Ageing. *Propellants Explos. Pyrotech.* **1987**, *12*(3): 81-87; DOI: 10.1002/prep.19870120305.

[34] Itkis, D.G.; Bohn, M.A. Simulation of Heat Flow Curves of NC-based Propellants – Part 2: Application to DPA Stabilized Propellants. *Propellants Explos. Pyrotech.* **2021**, *46*(8): 1204-1215; DOI: 10.1002/prep.202000313.

[35] Singh, A.; Kaur, G.; Sarkar, C.; Mukherjee, N. Investigations on Chemical, Thermal Decomposition Behavior, Kinetics, Reaction Mechanism and Thermodynamic Properties of Aged TATB. *Cent. Eur. J. Energ. Mater.* **2018**, *15*(2): 258-282; DOI: 10.22211/cejem/84993.

[36] Singh, A.; Sharma, T.C.; Singh, V.; Mukherjee, N. Thermal Degradation Behaviour and Kinetics of Aged TNT-based Melt Cast Composition B. *Cent. Eur. J. Energ. Mater.* **2019**, *16*(3): 360-379; DOI: 10.22211/cejem/112234.

[37] Singh, A.; Sharma, T.C.; Singh, V.; Mukherjee, N. Studies on the Thermal Stability and Kinetic Parameters of Naturally Aged Octol Formulation. *J. Therm. Anal. Calorim.* **2021**, *145*: 411-421; DOI: 10.1007/s10973-020-09750-4.

[38] Karlos, V.; Solomos, G. *Calculation of Blast Loads for Application to Structural Components. Administrative Arrangement No JRC 32253-2011 with DG-HOME Activity A5 – Blast Simulation Technology Development.* Publications Office of the European Union, Luxembourg, European Union, JRC87200, Report EUR 26456, **2013**; DOI: 10.2788/61866.

Received: May 17, 2022
Revised: June 26, 2023