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Analysis of stability of naturally aged single base propellants

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In this work chemical changes in 42 years old single base propellant induced by natural aging were evaluated. The sample was stored for a long time under uncontrolled conditions. The chemical stability was tested using High performance liquid chromatography (HPLC), High-performance thin-layer chromatography (HPTLC), the vacuum stability test (VST), SEM/EDX and visual analysis by Stereo Microscope. Heat flow calorimetry (HFC) method was used for analysis of thermal behavior of the sample. Visual changes in appearance of the 42 years old propellant sample surface were apparent. HPLC analysis showed that the sample contains very low effective stabilizer content (<0.2%) and VST measured very high gas release (ΔVST gas >2 ml/g). Therefore, the propellant is classified as very unstable. Although the effective stabilizer is almost completely consumed, the sample demonstrated very good thermal properties measured using HFC where the heat flow limit of 114 μW/g was not exceeded. The presence of inorganic stabilizers which could contribute to stability was examined using SEM/EDX. The results showed only presence of C, O and N and traces of Si. It could be assumed that even though all the parent DPA is almost consumed, the remaining daughter stabilizer products continue to protect the propellant from possible self-ignition for a long period of time.

Key words: Propellants, natural aging, chemical stability.

INTRODUCTION

Conventional propellants contain nitrocellulose as the main energetic components. By nature, nitrocellulose as nitrate ester is very unstable. During the course of storage, propellants slowly and spontaneously degrade and release nitrogen oxides which undergo consecutive reactions with other decomposition products or with other propellant ingredients and cause degradation of physical and ballistic properties of propellant (Vogelsanger, 2004; De Klerk, 2015).

The decomposition reactions of nitrocellulose can cause accumulation of heat, which in certain critical conditions may lead to self-ignition of the material. The

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reaction is exothermic and may eventually lead to autocatalysis and self-ignition of the propellants. Stabilizers are added to the propellant at the time of manufacture to serve as scavenger for the nitrogen oxides and slow down the decomposition of nitrogen esters (Trache and Tarchoun, 2018). Without stabilizer, or if stabilizer content is low, these released nitrogen oxides can catalyze the decomposition of the nitrate esters (Lurie, 1995).

Diphenylamine (DPA) is one of the most common stabilizers used for single base propellants. Also, nitrated analog of DPA formed during process of stabilizing decomposing propellant such as N-nitroso diphenylamine (N-NO-DPA) is used as stabilizers themselves (Lussier et al., 2000). The stabilizers are added in the amount of 0.5–2% of the total amount of the formulation. The amount of the stabilizer is depleted with time. Propellants in storage should be periodically tested for the amount of stabilizer remaining. Stabilizer depletion is one indication of the ageing that has occurred within a propellant. Monitoring the content of the stabilizer is one of the most reliable and modern methods used for chemical stability control and shelf life prediction of propellants (Bohn and Volk, 1987; Lopez et al., 2013).

Often 0.2 % DPA is used as a minimum content. In most cases the propellant can be stored much longer after this limit has been reached without any risk for self-ignition. The degradation process is routinely monitored using High Performance Liquid Chromatography (HPLC) analysis to quantify the effective stabilizer content that is remained in the propellant (Curtis and Rogasch, 1987). The HPLC data are useful for the assessment of the current propellant stability; however, it does not predict the future storage life of the propellant. Also, despite measured high DPA values during a long period of time, sudden drops in DPA contents have been reported (Halilović et al., 2020). It is thus associated with a certain risk to predict shelf life only from HPLC-results. The method that can supplement monitoring of the stability is the heat flow calorimetric (HFC). Data on the thermal stability of energetic materials can be used to obtain safety information for handling, storage and use (Heil et al., 2019; Rat et al., 1997).

The fundamental principle of HFC is that all chemical and physical reactions that produce heat are recorded during the measurement. The amount of heat produced is proportional to the rate of degradation of the material. The propellant is subjected to elevated temperature and the heat evolved from the propellant is monitored over a certain period of time, simulating further storage. This is a forced ageing method used to predict how the propellant will behave during storage. For approved propellants, the heat flow from the propellant must not show any signs of accelerated degradation during the simulated storage time. Many studies have been performed addressing accelerated ageing of propellants at elevated temperatures, but there are few studies about long time ageing at ambient storage conditions (Sućeska et al., 2010). The aim of this work is to evaluate the stabilizer content in 42 years old naturally aged single base propellant. The initial composition and the storages history of the analyzed sample were unknown. The stabilizer diphenylamine content and its nitro and nitroso derivatives, produced in sample on long storage, were examined by HPTLC and HPLC. Additionally, chemical stability was tested by vacuum stability test (VST) and HFC. Visual test was performed using Stereo Microscope and chemical composition was analyzed by SEM/EDX.

MATERIALS AND METHODS

The tested single base propellant was obtained by dismantling of bullets 105 mm caliber, manufactured in 1978 in former Yugoslavia. The initial composition and the conditions where the sample was stored were unknown.

All initial stabilizers; diphenylamine (DPA) 1000 µg/ml in ethanol, N-nitrosodiphenylamine (N-NO-DPA) 1000 µg/ml in dichloromethane and 2-nitrodiphenylamine (2-NO2-DPA) 100 µg/ml in acetonitrile, purity >99%, were purchased from AccuStandard, USA. Acetonitrile and methanol for Chromasolv HPLC 99.9% were obtained from Honeywell International, Inc. DPA 99% and N-NO-DPA ≥ 97% for HPTLC were purchased form Sigma-Aldrich, Germany. Acetone, 99.8 % and toluene, 99.9% were purchased form Fisher scientific, U.K. and acetonitrile, 99.8 % from Carlo Erba, France.

Visual analysis was performed using Stereo Microscope NIKON SMZ18 with GX Capture-T-software. High performance liquid chromatography (HPLC) measurements were conducted using a Perkin Elmer apparatus, with a ZORBAX, Bonus RP column (3.5 µm, 4.6 x 100 mm) and UV/VIS detector operating at 254 and 214 nm. The mobile phase was acetonitrile/methanol/ water (15/35/50 vol.%), with a flow rate of 1.0 $cm^3 \cdot min^{-1}$. The sample injection volume was 10 µl and the separation temperature was 25°C. The propellant samples for the HPLC measurements were prepared according to STANAG 4620/1 and AOP-48/2 (STANAG 4620, 2007; AOP-48, 2008). 1 g of propellant sample was mixed with 20 cm^3 of acetonitrile and extracted for a minimum of 4 h at room temperature. Afterwards, 5 cm^3 of warm water (60-70°C) was added to precipitate the nitrocellulose and the precipitate was allowed to settle for at least 1 h.

High performance thin layer chromatography (HPTLC) was performed using CAMAG LINOMAT 5 automatic sample applicator, equipped with corresponding software and TLC scanner quantitative detector. HPTLC Silica gel 60 F254 (20 x 10 cm) was used. Analysis was performed according to AOP-48/2 standard. Detection was performed at 254 nm at room temperature. Standard solutions of DPA and N-NO-DPA in acetonitrile in the range of 0.2-0.8% and 0.8-1.4% were prepared. Vacuum stability test (VST) was performed in OZM Research apparatus. Approximately 5 g of sample was placed in 25 ml glass heating tubes (140 ± 5 mm long and 18 mm in diameter). The temperature for the isothermal measurements was 100°C for nitrocellulose single-base propellants, according to standard STANAG 4556 (STANAG 4556, 1999). The glass test tubes were placed into the heating block for 40 h. Pressure transducers continuously estimated the pressure increase in the glass tubes. The results were expressed as gas volume evolved from 1 g sample.

Heat flow calorimetry (HFC) experiments according to STANAG 4582/1 (STANAG 4582, 2004) were carried out in a TAM III microcalorimeter with 3x multicalorimeters. The temperature for the isothermal storage is 80°C for 10.6 days, which is equivalent to at

Figure 1. Yellow substance-pasta on the surface of the sample (up - 30x magnification).

Table 1. Propellant samples information and results of HPTLC and VST analysis.

Ammunition caliber	Year of manufacture	HPTLC			VST
		Scanned stabilizer	DPA [%]	N-NO-DPA [%]	ΔVST gas [ml/g]
105 mm	1978	DPA, N-NO-DPA	0.11	0.16	3.437

least a 10 years storage at 25°C. Approximately, 3 g of samples in parallel were placed in 3 ml glass vials. Loading density was 0.8-1.1 $g \cdot cm^{-3}$ and for the porous propellants of 0.4-0.6 $g \cdot cm^{-3}$. The net heat flow is recorded in μW/g. The results were processed with the TAM Assistant. Elemental analysis of samples (EDX) was performed by energy dispersive X-ray analysis with an INCA Energy system attached to a Zeiss SupraTM 3VP microscope. Scanning electron micrographs (SEM) were taken on electron microscope Zeiss SupraTM 3VP microscope. The sample was prepared by cutting lengthwise.

RESULTS AND DISCUSSION

Visual analysis showed visible changes in appearance of the single base propellant sample after long time natural ageing. The presence of an unknown yellow substance is visible on sample surfaces (Figure 1), which is visual sign of degradation of the sample. The Methyl Violet test (MVT) was performed at 134.5°C. In this test, a strip of paper impregnated with methyl violet changes its color to blue-green and then to salmon-pink. Certified strips should change the color after 50 min. The sample changed the color of the strip after 27 min, which indicated chemical instability of the propellant according to MIL-STD-286C/Method 404.1.2.

Table 1 shows information from tested single-based propellants sample and results from HPTLC and VST analysis. The 42 years old sample was used for manufacture of 105 mm bullet caliber ammunition. For propellants analysis, HPTLC quantitative method described in AOP 48 was used for detection of main stabilizers DPA and its first degradation product N-NO-DPA. Results showed that propellants contain less than 0.2% DPA, which is a sign of high rate of degradation. However, effective stabilizer content as the sum of DPA and 0.85x content of N-NO-DPA is 0.25% and is slightly above the recommended minimum of 0.2% of effective stabilizer. Therefore, this sample should be used in priority.

Vacuum stability test (VST) result is presented in Table 1. Results from VST are very important for stability categorization of propellants. According to STANAG 4556, samples with released gases more than 2 ml/g show advanced degradation and are classified as unstable. Tested sample showed very high gas release and is classified as highly unstable, despite the satisfactory effective stabilizer content which is greater than 0.2%.

In order to further analyze the stability of tested single base propellants, stabilizer content in the sample of propellants was determined by HPLC method according to STANAG 4620/1 and AOP-48/2. Results are presented in Table 2. Measured content of DPA, N-NO-DPA and the total effective stabilizers are much lower by HPLC in comparison to HPTLC analysis. These differences can be attributed to different sample preparation, sampling and solvents used for these methods (Halilović et al., 2019). However, the final stability assessments were identical.

In addition to DPA and N-NODPA detected in HPTLC, second degradation product 2-nitrodiphenylamine (2-NDPA) was detected. Very low amount of DPA (0.03%)

Table 2. HPLC and HFC results of tested single base propellant samples.

HPLC (STANAG 4620/1 and AOP-48/2)	DPA %	0.03
	N-NO-DPA %	0.09
	2-NO_2-DPA %	0.09
	Effective stabilizer %	0.11
	Loss of mass after ageing at 80°C, 10,6 days	0.47-1.11
HFC (STANAG 4582/1)	Total measurement duration (days)	10.6
	Heat release until time of evaluation [J/g]	51.1
	Max. heat flow (Pm) within time of evaluation [µW/g]	50.7
HFC (STANAG 4582/1)	Total measurement duration (days)	28
	Heat release until time of evaluation [J/g]	125
	Max. heat flow (Pm) within time of evaluation [µW/g]	70

and effective stabilizer content of 0.11% were measured, which is well below required minimum of 0.2% of effective stabilizer. It confirms VST results and classifies the sample as very unstable sample which should be destroyed.

In order to further study the ageing process of tested sample, the tested propellant sample was artificially aged at 80°C for 24 and 28 days. Calculated mass loss was 0.73-0.75% at 24 days and 2.75-2.92% at 28 days, which is less than required 3% mass loss. This relatively low rate of the sample mass loss corresponds to low molecular mass decomposition products of nitrocellulose with no autocatalysis. The mass loss test predicts that the tested sample will remain chemically stable for a minimum of 25 years of storage at ambient temperature (25°C) (Bohn, 2011). HPLC analysis of the sample after artificial ageing at 80°C for 24 days showed slightly reduced content of effective stabilizer (0.09%) in comparison to sample before aging (0.11%). Figure 2 shows chromatograms of the sample before and after artificial aging at 80°C.

Besides traces of DPA, peaks that correspond to first degradation products N-NO-DPA, 2-nitrodiphenilamine (2-NO2-DPA) and 4-nitrodiphenilamine (4-NO2-DPA) were visible on the chromatogram after artificial aging. Those degradation products still have stabilizing effect. Also, N-nitroso-2-nitrodiphenylamine (N-NO-2-NO2-DPA) and N-nitroso-4-nitrodiphenylamine (N-NO-4-NO2-DPA) as the second degradation products were registered in both samples, but the peak intensity is slightly large after artificial aging. Heat flow calorimetry (HFC) measurement was performed according to AOP-48/ED.2 where the decomposition rate is calculated from the recorded heat flow curve and yields information regarding the stability of propellants as well as the prediction of their lifespan. The fundamental principle of HFC is that all chemical and physical reactions that produce heat are recorded during the whole measuring time. Figure 3 shows the first 28 days of microcalorimeter heat flow data from the sample measured at 80°C. Surpassingly, the sample demonstrated very well thermal properties measured using HFC. The heat flow was almost constant for all four measurements at a value of 50-70 µW/g. The heat flow limit of ≤114 µW/g was not exceeded. As an endothermic peak appeared after 17 days at one measurement, the experiment was repeated as required by STANAG 4582/1. After repeated measurement, both curves in parallel were constant for up to 24 days. Therefore, the HFC result predicts that tested sample will remain chemically stable for a minimum of 10 years of storage at ambient temperature (25°C)

The HFC results were not in agreement with other results that indicate decomposition of the analyzed sample. HPLC results of the sample showed that very little effective stabilizer were remaining in the sample. Usually, once the stabilizer is depleted, the heat release immediately rises. In a correlated experiment stabilizer consumption and heat generation was studied and it was shown that heat production does not increase substantially until the stabilizer has been consumed almost completely. For pure nitrocellulose at 70°C violent degradation will start after 2-4 days (Lindblom and Paulsson, 1998). Therefore, as the sample exhibits excellent thermal properties, it probably indicates that even though all the parent DPA is almost consumed, the remaining daughter stabilizer continues to protect the propellant from possible self-ignition for a long period of time. Also, some researchers assumed that chemical reaction occurs between nitrocellulose and diphenylamine forming some form of complex which is difficult to extract (Curtis and Rogash, 1987; Lindblom, 2002).

The satisfactory stability of the tested single base propellant may be explained by the presence of inorganic stabilizers, such as magnesium oxide and calcium carbonate (Jelisavac et al., 2014). These salts stabilize nitrocellulose by neutralizing acids that would otherwise accelerate the hydrolysis of the O-NO_2 bond. In order to examine the presence of inorganic stabilizers, the single

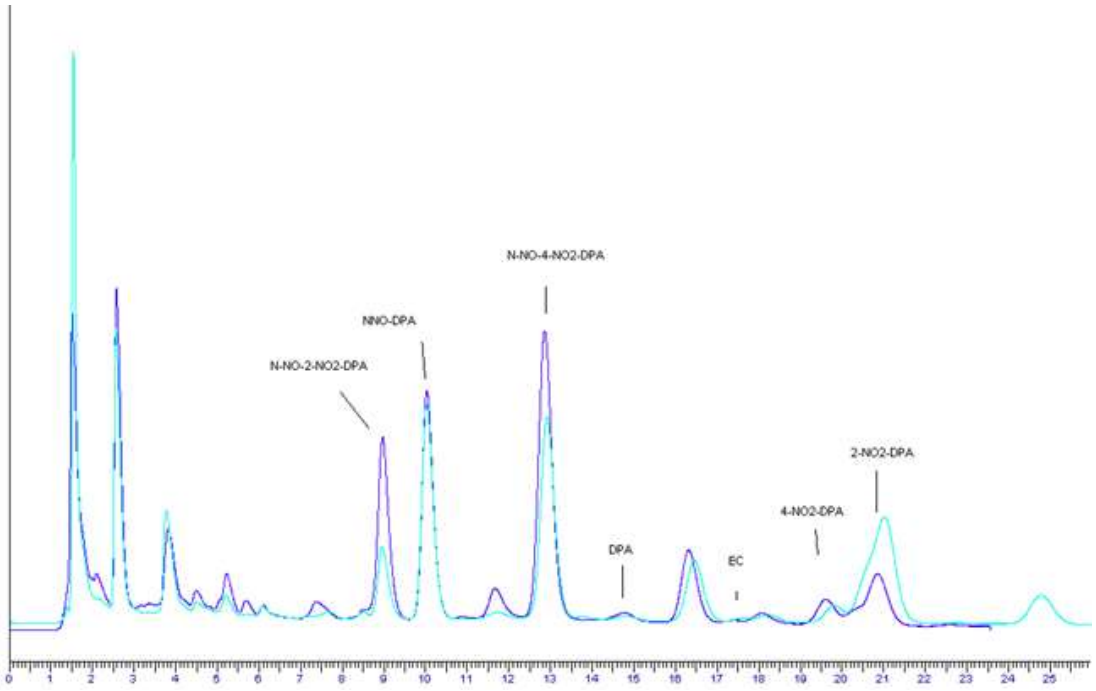

Figure 2. Chromatograms of sample before aging (green) and after ageing at 80 °C for 24 days (blue)

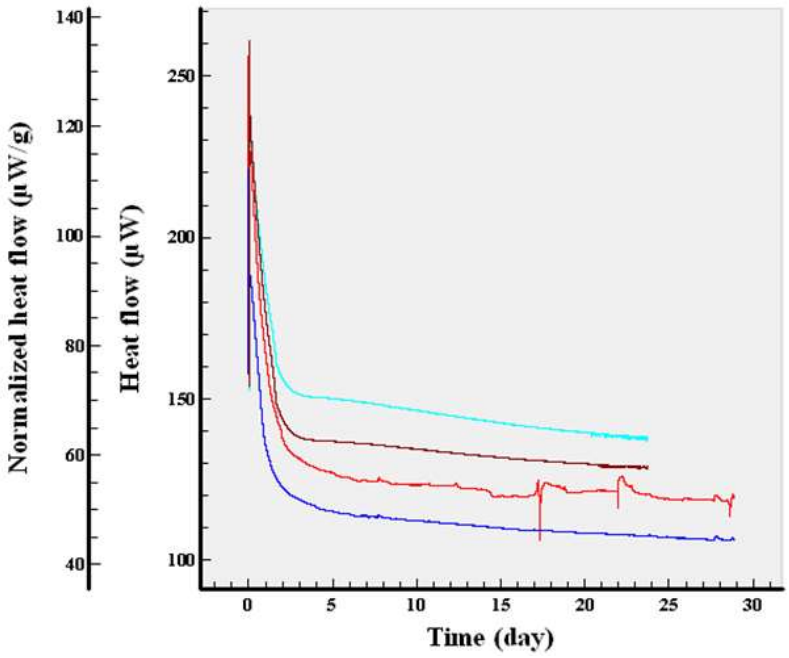

Figure 3. Heat flow curves in (µW/g) of the sample, four measurements.

base propellant sample was analyzed by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX). The results of SEM/EDX analysis showed only the presence of C, O and N and traces of Si (Figure 4). Therefore, the thermal stability of the sample cannot be explained by the presence of inorganic stabilizers. The morphology of the nitrocellulose sample was studied with scanning electronic microscopy (SEM). Figure 5 revealed very damaged and ruptured nitrocellulose fiber structure.

Figure 4. EDX spectrum of the sample.

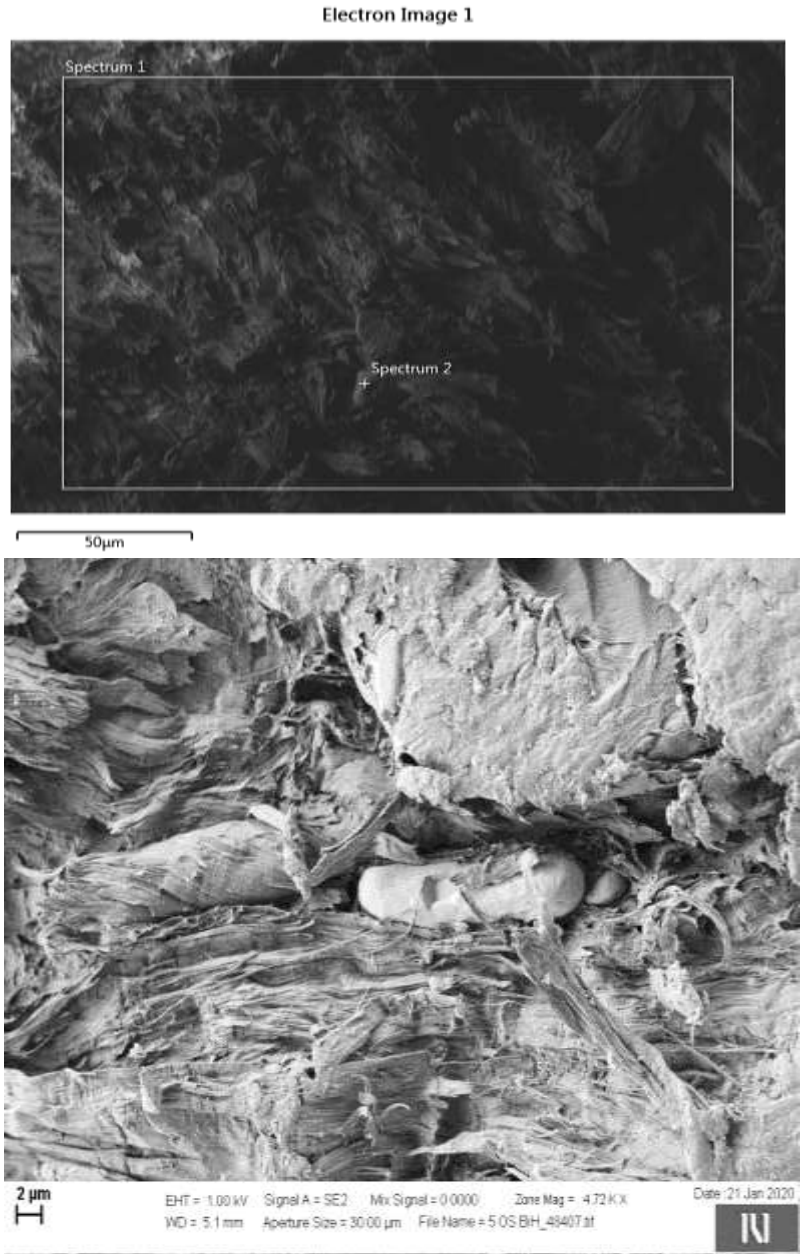

Figure 5. SEM images of tested sample.

Conclusion

The ageing process in NC based propellants changes the important properties of propellants such as stabilizer content, heat of reaction, heat capacity and other properties. Ageing of propellant limits the safe service lifetime and increases the possibility of self-ignition. In this work, the chemical stability of single base propellant, which has been naturally aged for 42 years was analyzed. The circumstances in which the propellant has been stored were unknown. The HPLC analysis showed traces of the DPA stabilizer and degradation products in amount less than required 0.2%. That confirmed VST result where released gases were more than 2 ml/g and classifies the sample as very unstable sample.

Surpassingly, mass loss of the tested propellant sample, after artificially aging at 80°C in duration of 28 days, was less than required 3% mass loss. The sample also demonstrated very good thermal properties measured using HFC. The heat flow limit of ≤114 μW/g was not exceeded and the sample meet the requirements laid down in STANAG 4582, which means that it is chemically stable when stored at 25°C for 10 years. The results are contradictory because although there was almost no stabilizing action of diphenylamine and its nitrated derivatives, the sample showed good thermal properties.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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