

DETERMINATION OF STABILIZER CONTENT AND PREDICTION OF THE SERVICE LIFE OF A SINGLE-BASE PROPELLANT USING ACCELERATED AGEING

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Abstract: The chemical stability of a single-base propellant was assessed through quantifying its stabilizer content and predicting its safe service life through the accelerated ageing method. The main goal was to evaluate the rate of stabilizer depletion at elevated temperatures and, based on these results, to predict the chemical stability of the propellant under standard storage conditions. According to NATO and other national military standards, storage temperatures are typically assumed to be around 20°C. Propellant samples with an initial diphenylamine stabilizer concentration of approximately 2 wt.% underwent a treatment of thermal ageing at 100°C and 110°C for varying beforehand set intervals. Following each ageing interval, the residual stabilizer and its reaction derivatives were analyzed using high-performance liquid chromatography. The experimental data were used to determine the degradation of the amount of the stabilizer and to estimate the service life of the propellant. The results captured a gradual decrease in stabilizer content with increasing ageing time, and temperature was shown to significantly affect the degradation rate. Explosive materials are incorporated in different types of ammunition and explosive devices, which requires a safe life service of 20–30 years counting from the day of its development. Based on the results, the propellant is expected to maintain chemical stability for approximately 44 years under normal, expected storage conditions. High-performance liquid chromatography was validated as a reliable and accurate analytical technique for assessing stabilizer depletion and evaluating the chemical stability of single-base propellants. These results may support enhanced quality control procedures, improved storage safety, and more knowledgeable decisions concerning the continued use or timely withdrawal of ammunition from service. The chromatographic analyses enabled quantitative determination of the stabilizer diphenylamine together with its major degradation products, including N-nitrosodiphenylamine and nitrated derivatives, providing evaluation of the total stabilizer descending throughout the ageing process. The accelerated ageing approach combined with the Arrhenius relationship proved suitable for predicting the long-term behavior of the investigated propellant under standard storage conditions. The captured results lead us to conclusion that the critical stabilizer level established to 50% of the initial concentration can be referred to as a practical criterion for estimating the remaining safe service life. The predicted service life should be taken in consideration as an approximation because practical storage conditions, packaging characteristics, propellant mass, and environmental factors may influence the actual ageing rate. Nevertheless, the presented methodology provides a rapid and reliable approach for routine surveillance of ammunition stocks and evaluation of propellant chemical stability. The proposed analytical procedure can therefore assist military and industrial laboratories in planning periodic inspections and identifying propellants approaching the end of their safe storage period. The findings of this study contribute to improving ammunition safety, optimizing storage management, and supporting evidence-based decisions regarding maintenance or disposal of ageing energetic materials. The developed approach may also serve as a useful basis for future investigations involving other types of propellants and stabilizer systems under accelerated ageing conditions.

Keywords: chemical stability, service life, diphenylamine, accelerated ageing

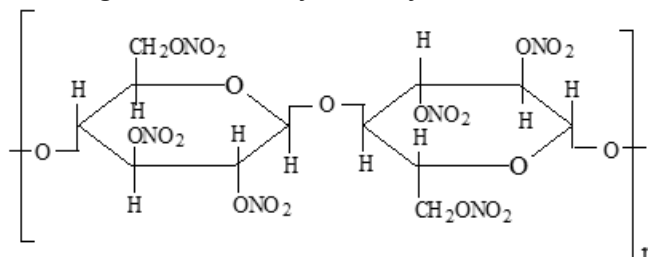
1. INTRODUCTION

Propellant explosives, including all types of propellants, contain one or more nitrate esters whose chemical, mechanical, and ballistic evolution is the subject of stability studies in both scientific research and engineering practice (Hristovski, 1994; Smileski, 1998).

These energetic materials are characterized by two fundamental properties: sensitivity, defined as their ability to respond to external stimuli, and stability, which represents their capability to preserve their original chemical, mechanical, physical, ballistic, and other performance characteristics within specified limits throughout their intended service life. Consequently, stability is evaluated primarily from the standpoint of the reliability and safe performance of explosive materials, whether incorporated into ammunition systems or stored separately (Pavlović & Duilo, 1983). Explosive materials are incorporated into a wide range of conventional and rocket ammunition, mines, and other military systems, for which reliable performance is required even after 20–30 years of storage.

The chemical stability of explosive materials refers to their ability to remain chemically unchanged during storage and service in ammunition under temperatures ranging from -30°C to $+60^{\circ}\text{C}$ over extended periods, without undergoing chemical decomposition. However, esters, and particularly nitrate esters, are inherently unstable compounds that undergo spontaneous self-decomposition. The rate of this reaction increases with temperature and follows the well-known Arrhenius relationship. Nitrocellulose, the principal constituent of single-base propellants, therefore exhibits thermal decomposition. This decomposition is a complex process that is believed to be catalyzed by its own decomposition products, particularly reactive nitrogen oxides (Bergens & Danielsson, 1995a).

Figure 1. Structural formula of nitrocellulose



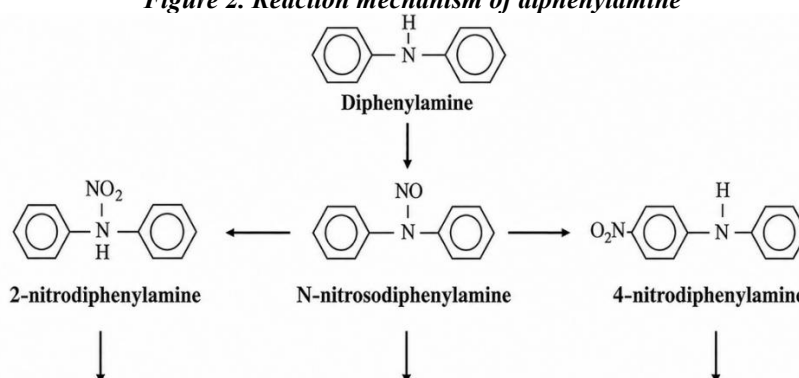
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The most widely applied method for stabilizing nitrocellulose-based propellants is the addition of diphenylamine, which reacts with nitrogen oxide decomposition products, forming nitrated derivatives of diphenylamine. Alternatively, stabilization may be accomplished by incorporating mixtures of two stabilizers, such as diphenylamine and centralite, in appropriate proportions. Nitrocellulose propellants used in ammunition generally contain between 1 and 3 wt.% stabilizer.

Because the stabilizer acts as the primary scavenger of nitrogen oxides generated during nitrocellulose decomposition, its residual concentration is considered an appropriate indicator of propellant ageing. Consequently, determination of the remaining stabilizer content has become one of the principal methods for assessing the chemical stability of propellants during storage. Once the stabilizer concentration decreases by more than 50% of its initial value, the propellant is generally regarded as chemically unstable and unsuitable for further use (O'Keef, 1995).

The reaction mechanism between diphenylamine and the products of nitrocellulose denitration proceeds through substitution of hydrogen atoms in diphenylamine by nitroso species originating from nitrocellulose decomposition. Initially, N-nitrosodiphenylamine is formed, followed by several nitrated intermediates and derivatives (Figure 2), which are also considered to possess stabilizing properties (Bergens & Danielsson, 1995b).

Figure 2. Reaction mechanism of diphenylamine



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Determination of the total stabilizer content, including diphenylamine and its nitrated derivatives, yields valuable information for predicting the safe storage life of propellants. This requires analytical techniques that are both rapid and highly accurate. Classical analytical methods do not satisfy these requirements because the analyses require several days and involve exposure of the propellant to elevated temperatures, thereby inducing accelerated ageing by mechanisms that remain not fully understood. Gas chromatography was for many years the principal method used for stabilizer determination. Although sufficiently rapid, this technique has major limitations for this application. Before entering the chromatographic column, the analytes must be vaporized,

which may result in partial or complete decomposition of thermally unstable compounds (Jelisavac et al., 2001). For example, the thermally unstable compound N-nitrosodiphenylamine decomposes to diphenylamine during analysis (Sopranetti & Reich, 1979), preventing accurate quantification of diphenylamine and its derivatives. In recent years, this constraint has largely been overcome through the application of high-performance reversed-phase liquid chromatography, which enables analyses to be performed at substantially lower temperatures, thereby minimizing thermal decomposition during measurement.

2. EXPERIMENTAL

A single-base propellant containing 2 wt.% diphenylamine as the initial stabilizer was investigated in this study. The residual stabilizer content following thermal aging at 100°C and 110°C was determined by high-performance liquid chromatography (HPLC).

Thermal aging was carried out using laboratory heating blocks. Approximately 5 g of propellant was placed in individual test tubes and exposed to temperatures of 100°C and 110°C. At 12-hour intervals, one test tube was removed from each heating block, and the propellant sample was transferred to a clean vessel containing 80 mL of dichloromethane to extract the remaining stabilizer. The extraction procedure was performed over a period of 12 h.

Chromatographic analyses were performed using an Agilent high-performance liquid chromatograph equipped with a UV detector and an RP-C8 analytical column (3 × 150 mm, Bondesil stationary phase, 2.7 µm particle size).

All measurements were performed at a column temperature of 30°C, with an injection volume of 1 µL and UV detection at 254 nm. The mobile phase consisted of 60% methanol and 40% water, delivered at a flow rate of 0.500 mL min⁻¹.

Each experiment was repeated several times to verify the reproducibility and accuracy of the analytical results.

3. RESULTS AND DISCUSSION

The obtained results for stabilizer determination enabled an evaluation of the kinetics of stabilizer depletion during accelerated ageing of the single-base propellant. By comparing the changes in stabilizer concentration at 100°C and 110°C, the influence of temperature on the rate of chemical degradation was assessed. Furthermore, application of the Arrhenius equation allowed extrapolation of the experimental data and prediction of the safe service life of the investigated propellant under normal storage conditions.

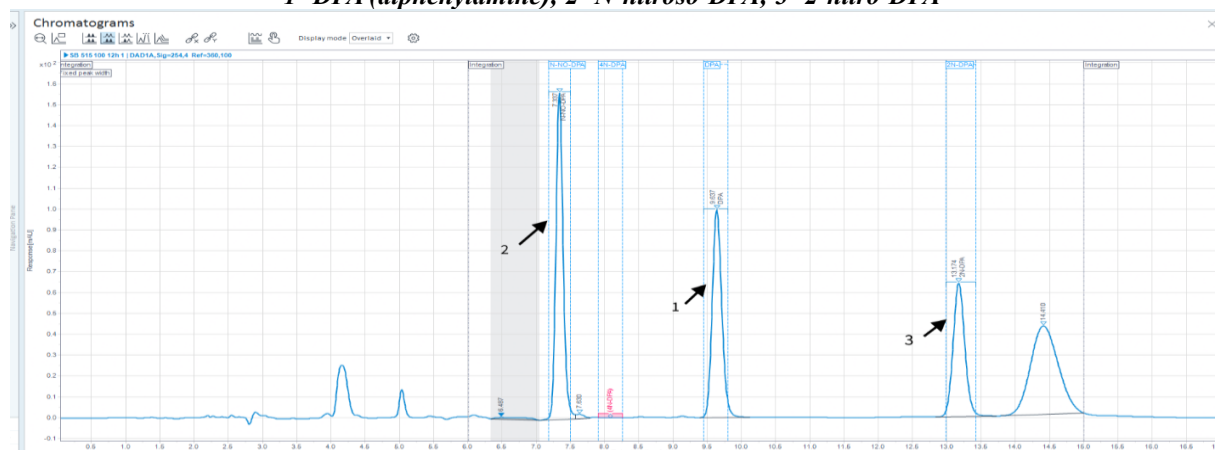
The chromatographic results obtained by high-performance liquid chromatography are presented as chromatograms in Figures 3 and 4.

The chromatograms shown in Figure 3 clearly demonstrate the presence of diphenylamine (Peak 1) in the analyzed propellant, with a retention time of approximately 9–10 minutes. In addition to the parent stabilizer, several nitrated derivatives of diphenylamine were identified. Prior to quantitative analysis, calibration curves were established for all analyzed compounds.

Quantitative determination revealed that the total stabilizer content remained above 50% of its initial value after 12 h of thermal treatment at 100°C (Table 1). After 24 h, however, the total stabilizer content decreased to approximately 48% of the initial concentration, suggesting considerable stabilizer consumption.

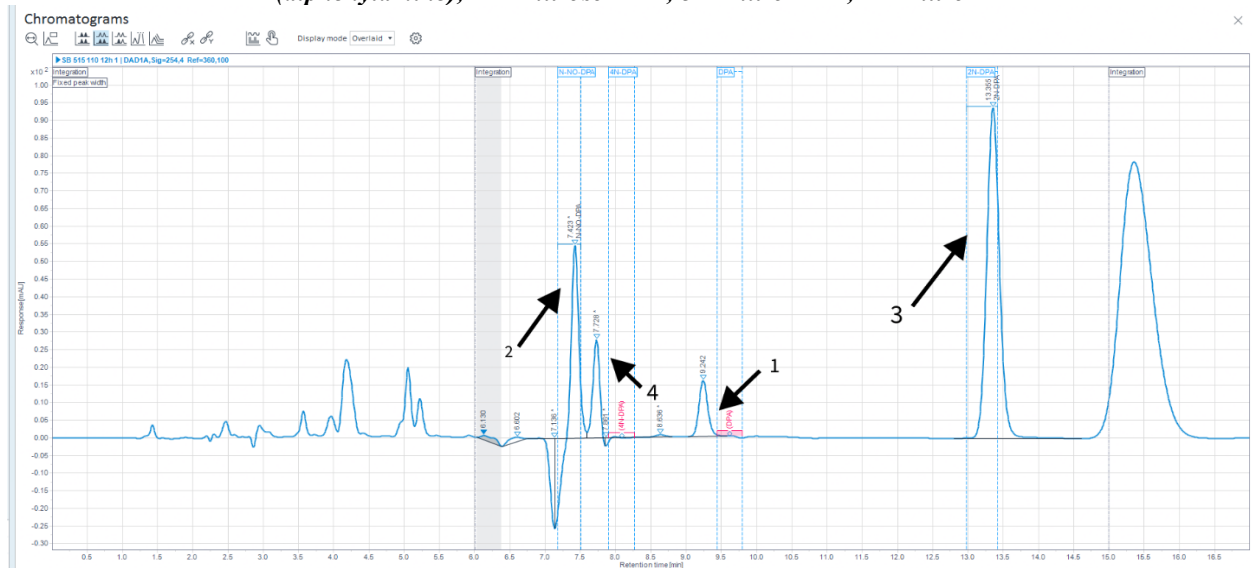
Furthermore, the results presented in Figure 5 indicate the thermal instability of certain diphenylamine derivatives. Such fluctuations promote reverse reactions, particularly during the period between 12 and 24 h of thermal treatment, influencing the observed concentration profiles of individual degradation products.

Figure 3. Chromatogram of diphenylamine and its derivatives from 0 to 12 h treatment at 100°C
1- DPA (diphenylamine); 2- N-nitroso-DPA; 3- 2-nitro-DPA



Source: created by the authors based on experimental results

Figure 4. Chromatogram of diphenylamine and its derivatives from 0 to 12 h treatment at 110°C
1- DPA (diphenylamine); 2- N-nitroso-DPA; 3- 2-nitro-DPA; 4- 4-nitro-DPA



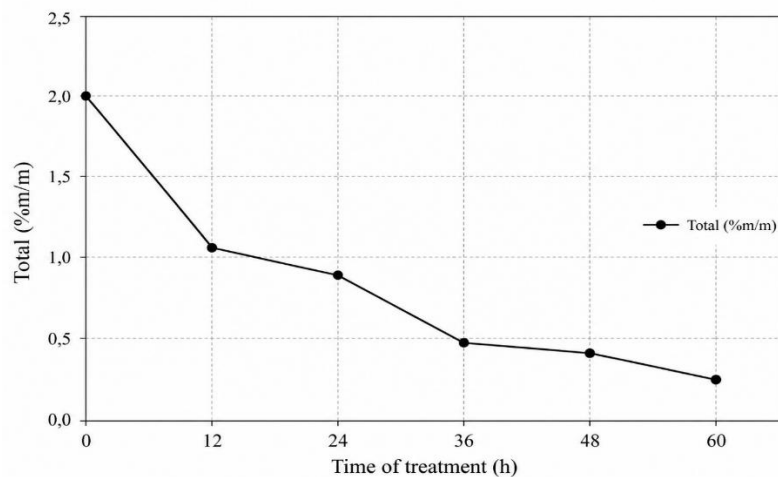
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Table 1. Content of the stabilizer after treatment of the gunpowder from 0 to 60 h at a temperature of 100°C

Time of treatment [h]	DPA [%m/m]	N-nitroso-DPA [%m/m]	2-nitro-DPA [%m/m]	4-nitro-DPA [%m/m]	Total stabil. [%m/m]
0h	1,766	0,212	0,022	0	2
12h	0,338	0,439	0,283	0	1,060
24h	0,011	0,645	0,202	0,036	0,9
36h	0,092	0,102	0,146	0,141	0,481
48h	0,025	0,147	0,123	0,127	0,422
60h	0,01	0,091	0,114	0,035	0,250

Source: created by the authors based on experimental results

Figure 5. Diagram of the loss of the stabilizer in the gunpowder during treatment at 100°C



Source: created by the authors based on experimental results

The experimentally determined time required for depletion of 50% of the initial stabilizer content was substituted into Equation (1), yielding an estimate of the service life of the propellant under standard storage conditions.

$$D_{50(20^{\circ}\text{C})} = \frac{d_{\{50\}} T \cdot \gamma_{\{10\}}^{\left\{\frac{T-20}{10}\right\}}}{365}$$

Where:

- D_{50} (20°C) is the time required for consumption of 50% of the initial stabilizer content at a storage temperature of 20°C;
- γ_{10} is the temperature acceleration coefficient describing the increase in decomposition rate for every 10 K increase in temperature;
- $d_{50}(T)$ is the time required for depletion of 50% of the stabilizer at the accelerated ageing temperature (100°C).

$$D_{50(20^{\circ}\text{C})} = \frac{1 \cdot 3,35^{\left(\frac{100-20}{10}\right)}}{365} = 43,45 \text{ years.}$$

The calculated value indicates that the investigated propellant would remain chemically stable for approximately 44 years under normal storage conditions.

Nevertheless, this prediction should be interpreted with caution because the calculation does not account for several important factors impacting long-term ageing, including the mass of the propellant, packaging characteristics, and the storage environment, all of which may markedly influence the actual degradation rate.

4. CONCLUSIONS

The experimental results confirmed that the stabilizer content in the investigated single-base propellant gradually decreases with increasing thermal ageing time. High-performance liquid chromatography proved to be a reliable and accurate quantitative analytical method for monitoring stabilizer depletion and evaluating the chemical stability of energetic materials. Application of accelerated ageing combined with the Arrhenius approach permitted prediction of the safe service life of the investigated propellant under normal storage conditions. Based on the obtained results, the propellant is expected to retain its chemical stability for approximately 44 years, corresponding to the point at which the total stabilizer content decreases to 50% of its initial concentration. However, this prediction should be regarded as an approximation because it does not incorporate the influence of practical storage conditions, such as propellant mass, packaging configuration, or surrounding conditions.

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