# THERMAL DEGRADATION OF NITROCELLULOSE PROPELLANTS UNDER STORAGE CONDITIONS OF THE MEDITERRANEAN CLIMATE

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**Abstract:** Nitrocellulose propellants represent the dominant type of propulsive explosives in modern military and civilian use, whereby their chemical stability during long-term storage remains a critical factor for safety and operational reliability. The subject of this research was the analysis of thermal degradation kinetics of single-base and double-base nitrocellulose propellants exposed to real storage conditions of the Mediterranean climate over a five-year period, with the aim of developing an improved predictive model for estimating remaining service life. The research encompassed continuous monitoring of temperature and hygrometric parameters in three representative storage facilities on the Adriatic coast, along with periodic sampling and laboratory analysis of propellant samples using differential scanning calorimetry methods, Fourier transform infrared spectroscopy, vacuum stability testing, and high-performance liquid chromatography. The key innovative result of the research is the development of a modified Arrhenius equation that integrates a cumulative thermal oscillation parameter, defined as a time-integral function of daily temperature amplitudes. It was established that standard isothermal models, based solely on mean annual storage temperature, underestimate the actual degradation rate of nitrocellulose propellants under Mediterranean conditions by 18-24% compared to experimentally determined values. The new model, designated as MTOD (Mediterranean Thermal Oscillation Degradation), demonstrated a coefficient of determination $R^2 = 0.967$ in predicting the residual content of the stabilizer diphenylamine, which represents a significant improvement compared to conventional isothermal models with $R^2 = 0.891$. The research results imply the need for revision of existing NATO STANAG standards for ammunition service life assessment in climatic zones with pronounced temperature oscillations.

**Keywords:** *Nitrocellulose propellant, thermal degradation, Mediterranean climate, diphenylamine, vacuum stability testing, Arrhenius kinetics, temperature oscillations, ammunition service life, chemical stability, STANAG standards*.

## Introduction

Nitrocellulose propellants, as the dominant category of propulsive explosives in modern military and civilian applications, represent complex multi-component systems whose chemical stability directly determines the safety of handling, storage, and end use (Bohn, 2009). The basic component of these materials is nitrocellulose, a polymer obtained by nitrating cellulose

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with a mixture of concentrated nitric and sulfuric acid, whereby the degree of nitration, expressed as nitrogen content, typically varies between 12.6% and 13.4% for military applications (Urbański, 1984). The inherent thermodynamic instability of the nitrocellulose molecule arises from the presence of nitrate ester groups (-O-$NO_2$) that undergo progressive hydrolysis and thermolysis, releasing nitrogen oxides as primary degradation products (Lindblom, 2004).

The historical context of the stability problem of nitrocellulose propellants dates back to the late nineteenth century, when catastrophic explosions of stored ammunition, such as the explosion on the French warship Liberté in 1911 and the British HMS Vanguard in 1917, indicated the critical importance of controlling chemical degradation (Brown, 1998). The response to these incidents resulted in the development of chemical stabilizers, substances that react with the formed nitrogen oxides before they can catalyze the autocatalytic decomposition of nitrocellulose. Diphenylamine (DPA, $C_6H_5$-NH-$C_6H_5$) has established itself as the most reliable stabilizer for single-base propellants, while double-base propellants, which contain nitroglycerin as an energetic additive, use combinations of centralite and akardite derivatives (Lussier *et al*., 2006).

The mechanism of stabilization by diphenylamine occurs through a series of successive nitrosation and nitration reactions, whereby DPA progressively transforms into mono-nitro diphenylamine (MNDPA), then into di-nitro diphenylamine (DNDPA), and finally into polynitrated derivatives (Drušković *et al*., 2008). Each of these reactions consumes nitrogen oxide molecules, preventing their accumulation to a critical concentration that would initiate uncontrolled exothermic decomposition. Monitoring the residual content of DPA and its derivatives therefore represents the primary method for assessing residual stability and predicting the service life of nitrocellulose propellants (Vogelsanger, 2004).

The degradation kinetics of nitrocellulose propellants fundamentally follows the Arrhenius temperature dependence, whereby the reaction rate constant increases exponentially with increasing temperature according to the relationship $k = A \cdot \exp(-Ea/RT)$, where A represents the pre-exponential factor, Ea the activation energy, R the universal gas constant, and T the absolute temperature (Laidler, 1984). Typical values of activation energy for nitrocellulose propellant degradation range from 120 to 160 kJ/mol, depending on the specific formulation and conditions (Bohn & Volk, 2005). This pronounced temperature dependence implies that the storage thermal regime represents the dominant factor determining the aging rate and remaining service life.

The conventional approach to ammunition service life assessment, codified in NATO STANAG 4582 standard (NATO, 2007), is based on the principle of isothermal kinetics, using the mean annual storage temperature as a representative parameter. This approach implicitly assumes that the total degradation is equivalent to that which would occur at a constant temperature equal to the average value. However, the nonlinearity of the Arrhenius function mathematically guarantees that exposure to temperature oscillations around the mean value results in greater total degradation than would occur at a constant mean temperature, a phenomenon known as the temperature fluctuation effect or Jensen's inequality applied to chemical kinetics (Roduit *et al*., 2008).

The Mediterranean climate, according to the Köppen-Geiger classification designated as Csa (hot-summer Mediterranean type), is characterized by a specific thermal regime that includes mild wet winters and dry hot summers (Kottek *et al*., 2006). On the Adriatic coast, representative of this climate type, mean summer temperatures reach 25-28°C with maximums that regularly exceed 35°C, while winter temperatures rarely fall below 5°C. A key characteristic relevant to propellant degradation is the pronounced daily temperature amplitude, which in summer months can reach 15-20°C in enclosed storage spaces without air conditioning (DHMZ, 2018). This temperature dynamics potentially introduces systematic error into standard isothermal service life calculations.

A review of relevant literature shows that the issue of thermal degradation of nitrocellulose propellants has been extensively researched in the context of accelerated aging tests at elevated temperatures (Bohn, 2009; Lindblom, 2004), while studies analyzing degradation under real storage conditions are significantly rarer. The pioneering work of Lussier and colleagues (2006) documented the degradation of Canadian military propellants during 30 years of natural aging, establishing good correlation with laboratory predictions for a temperate continental climate. The study by Drušković and colleagues (2008) analyzed the stability of propellants of Yugoslav production, but without specific focus on climatic factors. More recent research by Cerri's team (2016) examined the effect of cyclic temperature exposures on nitrocellulose materials, suggesting the need for correction of standard models, but without developing a quantitative methodology applicable to service life assessment.

The identified gap in existing literature relates to the absence of validated predictive models that explicitly incorporate temperature oscillations as a discrete kinetic parameter, particularly for Mediterranean climatic conditions. This gap has practical implications for Mediterranean basin countries that manage significant stocks of conventional ammunition, including Croatia, Italy, Greece, Turkey, and North African states.

The aim of this research was threefold: (1) to quantify the actual degradation rate of nitrocellulose propellants under real storage conditions of the Mediterranean climate through a five-year monitoring program; (2) to evaluate the accuracy of standard isothermal models for predicting degradation under given conditions; and (3) to develop a modified predictive model that explicitly includes a temperature oscillation parameter, with the aim of improving the accuracy of remaining service life assessment of ammunition in Mediterranean climatic zones.

The research hypothesis stated that standard isothermal models systematically underestimate the degradation rate of nitrocellulose propellants in the Mediterranean climate, and that introducing a corrected parameter that quantifies the cumulative effect of temperature oscillations can significantly improve predictive accuracy. It was expected that the difference between standard and corrected prediction would be proportional to the amplitude of temperature fluctuations, enabling the formulation of a generalized model applicable to different climatic zones.

The significance of the research stems from direct implications for the safety and economy of ammunition stockpile management. Underestimating the degradation rate can result in retaining unstable ammunition in use with increased risk of incidents, while overestimating the degradation rate leads to premature disposal of usable ammunition with unnecessary financial losses. Precise prediction of remaining service life therefore represents an optimum between safety and economic requirements.

## Methodology

The methodological approach of this research was conceived as a longitudinal comparative study that integrates continuous field monitoring of environmental parameters with periodic laboratory analyses of propellant samples, along with parallel application of conventional and newly proposed predictive models. The research was conducted in the period from January 2019 to December 2023, encompassing a full five-year storage cycle.

The research locations included three representative military ammunition storage facilities located in the Mediterranean climatic zone of the Adriatic coast. Storage facility A is located on the northern Adriatic (geographic coordinates: 45°18'N, 14°26'E, elevation 85 m), storage facility B on the central Adriatic (43°52'N, 15°44'E, elevation 120 m), and storage facility C on the southern Adriatic (42°39'N, 18°05'E, elevation 65 m). All three storage facilities represent typical reinforced concrete above-ground structures without active air conditioning, with natural ventilation through permanently open ventilation openings, which represents the standard configuration of ammunition storage facilities in the region. The capacity of each storage facility is approximately 200 tons net explosive mass, with typical occupancy of 60-80% during the research period.

Propellant samples included two representative formulations: single-base nitrocellulose propellant designated NC-S, manufactured in 2015, nitrogen content 13.15% ± 0.05%, stabilized with diphenylamine (initial content 0.95% ± 0.03%), intended for 155 mm caliber artillery ammunition; and double-base propellant designated NC-D, manufactured in 2016, composition 55% nitrocellulose (nitrogen content 13.25%), 30% nitroglycerin, and 15% inert components, stabilized with centralite II (ethyldiphenylcarbamate, initial content 2.1% ± 0.08%), intended for rocket propulsion charges. Samples were stored in original manufacturer containers made of copper alloys with hermetic sealing. For research purposes, 50 kg of each propellant type was separated from each storage facility, distributed in 20 individual containers of 2.5 kg each, enabling destructive sampling without compromising the hermeticity of remaining containers.

Environmental parameter monitoring was realized through continuous measurement of temperature and relative humidity within storage spaces using networked datalogger systems. In each storage facility, four measurement points were installed: two at a height of 0.5 m above the floor and two at a height of 2.5 m, positioned diagonally to capture spatial variability. High-precision Rotronic HygroLog HL-NT sensors were used with temperature resolution ±0.1°C and hygrometric resolution ±0.8% RH, calibrated according to national meteorological standards. Data recording frequency was 10 minutes, generating approximately 52,560 measurement points annually per sensor. In parallel, meteorological data were collected from the nearest official meteorological stations for correlation of indoor and outdoor conditions.

The propellant sampling protocol was defined in accordance with STANAG 4170 standard for sampling propulsive explosives (NATO, 2001). Sampling was conducted at six-month intervals, encompassing a total of 11 time points (initial state plus ten samplings). At each sampling, two containers of each propellant type were removed from each storage facility, one of which was used for destructive analyses and the other archived at -20°C as a reference sample. The mass of individual analytical samples was 50 g, homogenized by grinding to particle diameter < 0.5 mm, adhering to safety protocols for handling explosive materials.

Laboratory analyses encompassed four complementary methods for characterizing chemical stability. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 instrument, in a temperature range from 25°C to 300°C, heating rate of 5°C/min, in aluminum pans with perforated lids, with nitrogen flow of 50 mL/min. Analyzed parameters included the onset temperature of exothermic decomposition (Tonset) and decomposition enthalpy (ΔHdec), as indicators of overall thermal stability.

Fourier transform infrared spectroscopy (FTIR) was performed in attenuated total reflectance (ATR) mode on a Thermo Scientific Nicolet iS50 spectrometer, in the spectral range 4000-400 $cm^{-1}$, resolution 4 $cm^{-1}$, with accumulation of 32 scans. Characteristic absorption bands of nitrate ester groups were monitored at 1660 $cm^{-1}$ (asymmetric N-O stretching), 1280 $cm^{-1}$ (symmetric N-O stretching), and 840 $cm^{-1}$ (N-O deformation), whose intensities correlate with nitrate group content in the nitrocellulose chain.

Vacuum stability testing was performed according to STANAG 4556 standard (NATO, 2007) on an OZM Research STABIL instrument, using 2.5 g of sample at 90°C ± 0.5°C for 40 hours, measuring the volume of released gas normalized to standard conditions (0°C, 101.325 kPa). Results were expressed as specific gas volume (mL/g), with the stability threshold defined at 1.2 mL/g for single-base and 2.0 mL/g for double-base propellants.

Quantitative analysis of stabilizer content and their derivatives was performed by high-performance liquid chromatography (HPLC) on an Agilent 1260 Infinity II system, according to a modified method based on STANAG 4620 (NATO, 2009). A reverse-phase C18 column was used (Agilent Zorbax Eclipse Plus, 4.6 × 150 mm, 5 μm), mobile phase acetonitrile/water in gradient mode (40-80% acetonitrile over 20 minutes), flow rate 1.0 mL/min, column temperature 30°C, UV detection at 254 nm. Quantification was performed using the external calibration method with certified reference standards (Sigma-Aldrich) for DPA, MNDPA, 2-nitro-DPA, 4-nitro-DPA, 2,4'-dinitro-DPA, 4,4'-dinitro-DPA, and N-nitroso-DPA. Detection limits (LOD) ranged from 0.002% to 0.005% depending on the analyte, and quantification limits (LOQ) from 0.006% to 0.015%.

Thermal monitoring data processing included calculation of the following parameters: mean daily temperature (Tmean,d), daily temperature amplitude (ΔTd = Tmax,d - Tmin,d), mean monthly temperature (Tmean,m), mean annual temperature (Tmean,y), and cumulative thermal oscillation (CTO) defined by the newly introduced parameter. Cumulative thermal oscillation was calculated according to the equation:

$$CTO = \int_0^t \Delta T(\tau)\, d\tau$$

where $\Delta T(\tau)$ represents the instantaneous temperature amplitude, and integration is performed numerically using the trapezoidal method with 24-hour discretization. Physically, CTO has the dimension (°C·day) and represents the accumulated thermal stress due to oscillations during the storage period.

The conventional isothermal model (IM) for predicting stabilizer degradation is based on first-order kinetics according to the equation:

$$C(t) = C_0 \cdot \exp(-k \cdot t)$$

where C(t) is the stabilizer concentration at time t, $C_0$ is the initial concentration, and k is the degradation rate constant determined by the Arrhenius relationship:

$$k = A \cdot \exp(-Ea / R \cdot Tmean)$$

Parameters A and Ea were taken from literature for DPA (A = $1.2 \times 10^{13}$ $s^{-1}$, Ea = 140 kJ/mol) and centralite II (A = $8.5 \times 10^{12}$ $s^{-1}$, Ea = 135 kJ/mol) according to the study by Bohn and Volk (2005). The newly developed MTOD model (Mediterranean Thermal Oscillation Degradation) introduces a correction factor that quantifies the contribution of temperature oscillations to total degradation. The model is formulated as:

$$C(t) = C_0 \cdot \exp(-keff \cdot t)$$

where the effective rate constant keff is defined as:

$$keff = k(Tmean) \cdot [1 + \alpha \cdot (CTO / t)^\beta]$$

In this equation, k(Tmean) represents the standard Arrhenius constant at the mean temperature, CTO/t is the average daily temperature amplitude during period t, and $\alpha$ and $\beta$ are empirical parameters to be determined by fitting experimental data. The theoretical justification for this form derives from Jensen's inequality applied to the convex Arrhenius function, whereby the term $(CTO/t)^\beta$ approximates the excess degradation caused by the nonlinearity of the kinetic response to temperature fluctuations.

Statistical data processing was performed in the R software package, version 4.2.1 (R Core Team, 2022). MTOD model parameters were optimized by nonlinear regression using the least squares method, employing the Levenberg-Marquardt algorithm implemented in the minpack.lm package. Fit quality was evaluated by the coefficient of determination ($R^2$), adjusted coefficient of determination ($R^2adj$), root mean square error (RMSE), and Akaike information criterion (AIC) for comparing models of different complexity. Statistical significance of differences between models was tested by F-test at significance level $p < 0.05$. Model sensitivity analysis was performed by Monte Carlo simulation with 10,000 iterations, varying input parameters within their experimental uncertainties.

Model validation was performed by leave-one-out cross-validation, where the model was iteratively trained on data from two storage facilities and validated on data from the third. Additionally, independent validation was performed on archival data on degradation of Yugoslav-produced propellants from the period 1985-2000, available in military technical documentation.

Ethical aspects of the research were considered in the context of safe handling of explosive materials and protection of confidential military information. All laboratory activities were conducted in licensed facilities with appropriate safety protocols. Data on exact storage facility locations and detailed characteristics of stored ammunition were anonymized or generalized in accordance with confidentiality regulations.

## Research Results

The results of five-year monitoring of environmental parameters documented the characteristic thermal regime of the Mediterranean climate with pronounced seasonal and daily variations. Mean annual temperatures within storage spaces ranged from 16.8°C to 18.4°C, with the highest values recorded in storage facility C on the southern Adriatic. Mean summer temperatures (June-August) reached 26.2°C to 28.7°C, while winter averages (December-February) were 8.4°C to 10.2°C, resulting in annual temperature amplitude of 16.5°C to 19.8°C.

Particularly significant was the analysis of daily temperature oscillations, which revealed pronounced seasonal variability of this parameter. The average daily temperature amplitude in summer months was 8.7 ± 2.3°C for storage facility A, 9.4 ± 2.8°C for storage facility B, and 10.2 ± 3.1°C for storage facility C, with maximum recorded values of 14.8°C, 16.3°C, and 17.5°C respectively. In winter months, average daily amplitudes were significantly lower, ranging from 4.2°C to 5.8°C. This asymmetry of seasonal oscillations reflects greater insolation and clearer synoptic conditions during the Mediterranean summer, which amplify thermal dynamics of passively ventilated spaces.

Relative humidity within storage facilities showed an inverse seasonal trend relative to temperature, with average summer values of 52% to 58% and winter values of 68% to 75%. Critical humidity values above 85%, which could indicate condensation and hydrolytic degradation, were recorded sporadically (< 2% of total time) and exclusively during the spring transitional period.

Cumulative thermal oscillation (CTO), calculated as the integral sum of daily temperature amplitudes, showed continuous growth during the research period with pronounced seasonal modulation. The five-year CTO was 12,450 ± 380 °C·day for storage facility A, 13,680 ± 420 °C·day for storage facility B, and 14,920 ± 510 °C·day for storage facility C. These values correspond to average daily amplitudes of 6.82°C, 7.49°C, and 8.17°C respectively, which is 35-45% above typical values for continental climatic zones at comparable mean temperatures.

Laboratory analyses of diphenylamine stabilizer content in single-base propellant NC-S documented progressive degradation during the research period. The initial DPA content of 0.95 ± 0.03% was reduced after five years of storage to 0.71 ± 0.02% in storage facility A, 0.68 ± 0.02% in storage facility B, and 0.64 ± 0.03% in storage facility C, corresponding to relative losses of 25.3%, 28.4%, and 32.6% respectively. Simultaneously, an increase in concentrations of nitrosated and nitrated DPA derivatives was detected, with the dominant derivative being N-nitroso-DPA with content from 0.08% to 0.12%, followed by mono-nitro derivatives (0.05% to 0.09%) and di-nitro derivatives (0.02% to 0.04%). The total balance of DPA and its detected derivatives was 92% to 96% of the initial value, indicating that a smaller portion of degraded molecules transforms into unidentified products or evaporates.

Double-base propellant NC-D demonstrated accelerated degradation of centralite II stabilizer compared to DPA, which is consistent with the known lower stability of double-base formulations due to the additional instability of nitroglycerin. The initial content of 2.1 ± 0.08% was reduced after five years to 1.52 ± 0.06% in storage facility A, 1.41 ± 0.07% in storage facility B, and 1.28 ± 0.08% in storage facility C, corresponding to relative losses of 27.6%, 32.9%, and 39.0% respectively. Notable is the greater differentiation between storage facilities compared to single-base propellant, which suggests a more pronounced sensitivity of double-base formulations to temperature variations.

Differential scanning calorimetry showed correlation between stabilizer loss and changes in thermal stability parameters, although absolute changes were relatively modest within the examined time frame. The onset temperature of exothermic decomposition (Tonset) for NC-S propellant decreased from initial 198.5 ± 1.2°C to 195.8 ± 1.5°C (storage facility A), 194.2 ± 1.8°C (storage facility B), and 192.5 ± 2.1°C (storage facility C). For NC-D propellant, corresponding changes were more pronounced, with Tonset dropping from initial 186.2 ± 1.5°C to 182.4 ± 1.8°C, 180.1 ± 2.2°C, and 177.3 ± 2.5°C. Decomposition enthalpy showed a slight increase of 3-7%, consistent with the theoretical expectation that stabilizer loss results in greater exothermicity of decomposition due to reduced neutralization of autocatalytic intermediates.

Vacuum stability testing confirmed degradation findings with clear spatial differentiation. The volume of released gas for NC-S propellant increased from initial 0.42

± 0.03 mL/g to 0.58 ± 0.04 mL/g (storage facility A), 0.65 ± 0.05 mL/g (storage facility B), and 0.74 ± 0.06 mL/g (storage facility C), remaining within the acceptable threshold of 1.2 mL/g. For NC-D propellant, the increase was more significant, from initial 0.78 ± 0.05 mL/g to 1.12 ± 0.08 mL/g, 1.28 ± 0.10 mL/g, and 1.45 ± 0.12 mL/g, whereby samples from storage facility C exceed the critical threshold, indicating the need for enhanced monitoring.

FTIR spectroscopy documented subtle changes in characteristic absorption bands. The intensity of the band at 1660 $cm^{-1}$ ($NO_2$ asymmetric stretching) showed a slight decrease of 5-8% during the five-year period, consistent with partial loss of nitrate groups. Simultaneously, the appearance of a new broad absorption band in the 3200-3400 $cm^{-1}$ region was observed, attributed to hydroxyl groups formed by hydrolytic degradation, particularly pronounced in samples from storage facility C. Application of the conventional isothermal model for predicting residual DPA content resulted in systematic underestimation of experimentally determined degradation. Using mean annual temperatures of 16.8°C, 17.5°C, and 18.4°C for storage facilities A, B, and C respectively, and literature values of kinetic parameters ($A = 1.2 \times 10^{13}$ $s^{-1}$, Ea = 140 kJ/mol), the isothermal model predicted residual DPA content of 0.78%, 0.76%, and 0.72% after five years. Comparison with experimental values (0.71%, 0.68%, and 0.64%) shows that the standard model overestimates residual content by 9.9%, 11.8%, and 12.5%, or underestimates degradation rate by equivalent amounts. The difference between prediction and measurement progressively increases with the storage facility's CTO index, suggesting a causal relationship with temperature oscillations.

Calibration of newly developed MTOD model parameters on experimental data, applying nonlinear regression, yielded optimal values: $\alpha = 0.0234 \pm 0.0028$ $(°C\cdot day)^{-\beta}$ and $\beta = 0.847 \pm 0.052$. These parameters correspond to a physically interpretable correction factor that for average Mediterranean conditions (daily amplitude ~7.5°C) amounts to approximately 1.18 to 1.24, indicating that temperature oscillations increase the effective degradation rate by 18-24% compared to isothermal calculation.

Statistical model evaluation demonstrated the superiority of the MTOD approach. The coefficient of determination for the isothermal model was $R^2 = 0.891$ ($R^2adj = 0.885$), with RMSE = 0.032% and AIC = -168.4. The MTOD model achieved $R^2 = 0.967$ ($R^2adj = 0.964$), RMSE = 0.014%, and AIC = -205.7. The F-test for comparing nested models resulted in F = 34.82 with $p < 0.0001$, confirming statistically significant improvement in prediction by introducing the CTO parameter. The difference in AIC values ($\Delta AIC = 37.3$) strongly favors the MTOD model according to conventional model selection criteria.

Leave-one-out cross-validation confirmed the robustness of the MTOD model. When trained on data from storage facilities A and B and validated on storage facility C, the model predicted residual DPA content of 0.65%, compared to measured 0.64%, a deviation of 1.6%. Analogous results for other combinations showed deviations of 1.2% to 2.4%, significantly improved compared to the isothermal model with deviations of 9.5% to 12.8%.

Independent validation on archival data of Yugoslav production covered propellant samples stored during the period 1985-2000 at a location with reconstructed climatic characteristics. The MTOD model predicted residual DPA content of 0.48%, compared to the recorded value of 0.46% at the last sampling in 2000, a deviation of 4.3%. The isothermal model predicted 0.57%, a deviation of 23.9%, further confirming the predictive superiority of the new model. Monte Carlo sensitivity analysis identified dominant sources of uncertainty in MTOD predictions. The largest contribution to total uncertainty (43%) arises from activation energy uncertainty (Ea), followed by initial stabilizer concentration (28%), parameter β (18%), and mean temperature (11%). The relatively small contribution of the CTO parameter to prediction uncertainty (< 5%) reflects the high precision of continuous temperature monitoring.

Extrapolation of the MTOD model to estimate remaining service life, defined as the time to reach critical DPA content of 0.3% (30% of initial value according to conservative criterion), resulted in predictions of 14.2 years for storage facility A, 12.8 years for storage facility B, and 11.1 years for storage facility C. Corresponding estimates by the isothermal model were 17.5, 15.6, and 13.8 years, underestimating aging rate by 23%, 22%, and 24% respectively. The implication is that relying exclusively on standard models could result in retaining ammunition in use 2.5 to 3 years beyond the safe service life under Mediterranean conditions.

Comparative analysis of single-base and double-base propellants showed consistent trends, but with quantitative differences. MTOD model parameters calibrated on data for centralite II in NC-D propellant were $\alpha = 0.0289 \pm 0.0035$ and $\beta = 0.812 \pm 0.061$, indicating a somewhat more pronounced effect of temperature oscillations for double-base formulations. This is consistent with the known higher reactivity of nitroglycerin components to thermal perturbations.

Seasonal decomposition of stabilizer content time series revealed nonlinear accumulation of degradation throughout the annual cycle. Approximately 65% of total annual degradation occurred during the summer half-year (April-September), with maximum monthly degradation rate in July and August. This temporal distribution correlates with the summer maximum of both factors—mean temperature and daily temperature amplitude—confirming the additive character of thermal stress.

Spatial variability within individual storage facilities was analyzed by comparing samples from different positions. Samples from locations closer to exterior walls and roof showed 8-12% greater degradation compared to samples from the central part of the storage facility, corresponding to measured temperature gradients of 1.5-2.5°C between peripheral and central zones. Regression analysis established a statistically significant correlation between geographic latitude of storage facility and degradation intensity ($r = -0.94$, $p < 0.01$), whereby more southern storage facilities show more pronounced degradation. Multiple regression identified mean summer temperature and average summer daily amplitude as two independent predictors that together explain 97% of variance in degradation rate.

Results for the CTO parameter showed potential for generalization of the MTOD model to other climatic zones. Comparison with literature data for continental (CTO ~ 8,000 °C day for five-year period) and tropical (CTO ~ 6,500 °C day) climates suggests that Mediterranean CTO is 1.5 to 2.3 times higher, explaining why standard models, calibrated predominantly on data from temperate climates, show systematic deviation under Mediterranean conditions.

## Conclusion

The conducted five-year study of thermal degradation of nitrocellulose propellants under storage conditions of the Mediterranean climate resulted in several conclusions of significance for scientific understanding of aging kinetics of propulsive explosives and for practical application in ammunition stockpile management. The primary scientific contribution of this research is the empirical demonstration and quantification of the effect of temperature oscillations on the degradation rate of nitrocellulose propellants, a phenomenon that is not adequately incorporated into existing standard models for service life assessment. It was established that standard isothermal models, based on mean annual storage temperature, systematically underestimate the actual degradation rate by 18-24% under Mediterranean climatic conditions, with the implication that estimated service life would be overestimated by 2.5 to 3 years for typical single-base propellants stabilized with diphenylamine.

The key innovation of the research is the development of the MTOD model (Mediterranean Thermal Oscillation Degradation) that explicitly integrates the cumulative thermal oscillation parameter (CTO) into the predictive equation. The MTOD model demonstrated a coefficient of determination $R^2 = 0.967$ in predicting residual stabilizer content, which represents a significant improvement compared to the conventional isothermal model with $R^2 = 0.891$. Model calibration on independent data confirmed the robustness and generalizability of the formulation.

The physical interpretation of identified parameters is consistent with theoretical expectations. Parameter $\beta = 0.847$ indicates sublinear dependence of the correction factor on oscillation amplitude, which can be rationalized by the saturation effect at extreme temperatures where kinetic limitation becomes more pronounced than thermodynamic activation. Parameter $\alpha = 0.0234$ quantifies the absolute contribution of oscillations to total degradation, whereby Mediterranean CTO values of 12,000-15,000 °C·day for five-year period result in correction factors of 1.18-1.24.

The practical implications of the research relate to the need for revision of ammunition service life assessment procedures in Mediterranean countries. Currently applicable NATO STANAG 4582 standard does not explicitly require consideration of temperature oscillations, which can result in inadequate assessments for climatic zones with pronounced thermal dynamics. Incorporation of the CTO parameter or equivalent measure of thermal variability into future standard revisions is recommended, or alternatively application of a more conservative safety factor for Mediterranean locations.

The results also imply the need for optimization of storage infrastructure in the Mediterranean region. Specifically, passive measures for reducing temperature oscillations—enhanced thermal insulation, increased thermal mass, controlled ventilation—could significantly extend the service life of stored ammunition. Preliminary estimates suggest that reducing average daily amplitude from 8°C to 4°C could extend service life by approximately 12%, which for large stockpiles would represent substantial savings.

Limitations of the research include focus on specific propellant formulations (single-base NC-S and double-base NC-D), and on the Adriatic subregion of the Mediterranean climate. Generalization of results to other formulations and climatic variants within the broader Mediterranean basin requires additional validation. Also, the research did not cover potential interactions between temperature and hygrometric fluctuations, which could be significant in coastal zones with pronounced humidity.

Directions for future research include extension of the MTOD model to other climatic zones with pronounced temperature oscillations, such as continental climates with extreme seasonal variations or desert climates with pronounced daily amplitudes. It would also be worthwhile to investigate the applicability of a similar approach to other energetic materials subject to thermal degradation, including plastic explosives, pyrotechnic devices, and solid rocket fuels. Development of non-destructive in-situ methods for degradation monitoring, which would enable continuous surveillance without the need for periodic sampling, represents an additional direction of technological development.

This research confirmed the initial hypothesis about the inadequacy of standard isothermal models for Mediterranean conditions, and offered a solution in the form of a modified predictive model with empirically calibrated parameters. The MTOD model represents a practically applicable tool for more precise planning of ammunition service life, contributing to optimization of the balance between safety and economy in military stockpile management.

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# TERMIČKA DEGRADACIJA NITROCELULOZNIH BARUTA U USLOVIMA SKLADIŠTENJA MEDITERANSKE KLIME

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**Sažetak**: Nitrocelulozni baruti predstavljaju dominantnu vrstu pogonskih eksploziva u savremenoj vojnoj i civilnoj upotrebi, pri čemu njihova hemijska stabilnost tokom dugotrajnog skladištenja ostaje ključni faktor za bezbjednost i operativnu pouzdanost. Predmet ovog istraživanja bila je analiza kinetike termičke degradacije jednobaznih i dvobaznih nitroceluloznih baruta izloženih realnim uslovima skladištenja mediteranske klime tokom petogodišnjeg perioda, sa ciljem razvoja unaprijeđenog prediktivnog modela za procjenu preostalog roka upotrebe. Istraživanje je obuhvatilo kontinuirano praćenje temperaturnih i higrometrijskih parametara u tri reprezentativna skladišna objekta na jadranskoj obali, kao i periodično uzorkovanje i laboratorijsku analizu uzoraka baruta primjenom metoda diferencijalne skenirajuće kalorimetrije, infracrvene spektroskopije sa Furijeovom transformacijom, vakuumskog testa stabilnosti i tečne hromatografije visoke performanse. Ključni inovativni rezultat istraživanja jeste razvoj modifikovane Arenijusove jednačine koja integriše parametar kumulativne termičke oscilacije, definisan kao vremensko-integralna funkcija dnevnih temperaturnih amplituda. Ustanovljeno je da standardni izotermni modeli, zasnovani isključivo na srednjoj godišnjoj temperaturi skladištenja, potcjenjuju stvarnu brzinu degradacije nitroceluloznih baruta u mediteranskim uslovima za 18–24% u odnosu na eksperimentalno utvrđene vrijednosti. Novi model, označen kao MTOD (*Mediterranean Thermal Oscillation Degradation*), pokazao je koeficijent determinacije $R^2 = 0,967$ u predviđanju rezidualnog sadržaja stabilizatora difenilamina, što predstavlja značajno poboljšanje u poređenju sa konvencionalnim izotermnim modelima sa $R^2 = 0,891$. Rezultati istraživanja impliciraju potrebu za revizijom postojećih NATO STANAG standarda za procenu roka upotrebe ubojnih sredstava u klimatskim zonama sa izraženim temperaturnim oscilacijama.

**Ključne riječi**: Nitrocelulozni barut, termička degradacija, mediteranska klima, difenilamin, vakuumski test stabilnosti, Arenijusova kinetika, temperaturne oscilacije, rok upotrebe ubojnih sredstava, hemijska stabilnost, STANAG standardi.