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# Modification of AOP-48 Ed.2 Extrapolation Expression by Introduction of Real Storage t-T Conditions of Naturally Aged Nitrocellulose Gun Powder

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**Comparison of the results of gunpowder chemical stability assessment by procedures based on natural and accelerated aging was performed. It was achieved by introducing some of modification in extrapolation expression of NATO standard AOP-48 Ed. 2. Real storage conditions of naturally aged nitrocellulose gunpowder from collection KB-1 under the continental and from collection KB-2 under the Mediterranean climate, instead of standard AOP-48 Ed. 2 conditions, 10 years at 25°C, were introduced in mentioned extrapolation expression. Based on the analysis of the results, it can be concluded that the depletion of the stabilizer in each of the temperature-time loads of accelerated aging of the NC, NCD and NGB powder is greater than the depletion of the stabilizer in the equivalent temperature-time conditions of natural aging of the same types of powders stored 25 years in collections KB-1 and KB-2. Exception are NC powders stored 25 years in KB-2 collection because of faster dynamics of their decomposition under the extreme Mediterranean climate conditions. Increased stabilizer depletion in accelerated and then in naturally aged powder is preferable because it provides an increased degree of safety and precautions during assessment of chemical stability of the powder by NATO standard AOP-48 Ed. 2. In this way, the possibility of applying the AOP-48 Ed. 2 standard to the nitrocellulose based powders of domestic production which were stored under the conditions of continental and Mediterranean climate, was verified.**

*Key words*: **AOP-48 Ed.2, nitrocellulose based gunpowder, chemical stability, natural aging, accelerated aging liquid chromatography.**

## Introduction

WITH the aim of improvement of domestic methodology of chemical stability assessment prescribed by SORS 8069/91 standard [1], equivalent to the NATO standard AOP-48, Ed.2 was applied [2].This standard is based on isothermal single-temperature ageing of powders and has the ability to predict dynamic of powder ageing process and to guarantee that propellant will remain chemically stable if stored at ambient temperatures 25°C for minimum of 10 years.

NATO standard AOP-48, Ed.2, uses extrapolation expression (1) which presents the Arrhenius's modified equation [2-7], addopted from NATO standard STANAG 4582 [8].

$$t_T = t_s e^{\frac{E_1\left(\frac{1}{T_t}-\frac{1}{T_{60}}\right)+E_2\left(\frac{1}{T_{60}}-\frac{1}{T_S}\right)}{R}} \quad (1)$$

where are:

$t_T$ - time of duration of single temperature test at $T_T$, days

$t_S$ - time of storage at $T_S$, days; (according AOP-48 Ed.2: 10 years = 3652,5 days for $T_S$ = 25°C),

$E_1$ - activation energy for heat generation caused by thermal decomposition of propellants at temperatures higher then 60°C, J/ mol, $E_1$ = 120 kJ/mol, empiric values,

$T_T$ - temperature of single temperature test, K,

$T_{60}$ - temperature of changing of the activation energy for NC thermal decomposition, 60°C = 333,15 K,

$T_S$ - temperature of storage, (according AOP-48 Ed. 2: 25°C= 298,15 K),

$R$ - universal gas constant, R= 0,008314 kJ/(K·mol),

$E_2$ - activation energy for heat generation caused by thermal decomposition of propellants in temperature range from 25 °C to 60°C, J/ mol, $E_2$ = 80 kJ/mol, empiric values.

The corresponding ageing times which are considered equivalent to 10 years of isothermal storage at 25°C at temperature 60°C, 65.5°C, 70°C and 80°C calculated according extrapolation expression (1) are respectively: 123, 60.9, 34.8 and 10.6 days [2,9,10].

Test conditions ensure sufficient chemical stability of powder for minimum 10 years of isothermal storage at 25°C.

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However, in practice, an isothermal storage is not often realized, so extrapolation expression accords to STANAG 4582 (2) for non isothermal storage conditions, below the $T_s$=50 °C, exists [8].

$$t_{25} = t_s e \frac{E_2 \left( \frac{1}{T_{25}} - \frac{1}{T_S} \right)}{R} \tag{2}$$

$T_s$ - temperature of storage, K,

$t_s$ time of storage at $T_S$, years,

$t_{25}$ time of storage at 298.15 K, years,

$E_2$ activation energy for heat generation caused by thermal decomposition of propellants for storage conditions below 50°C, 80 kJ/mol (empiric value).

There is also an example of using value of activation energy, $E_2 = 80\,\text{kJ/mol}$ for non-isothermal storage of propellant at temperatures from 15°C to 40°C [8].

Therefore, in this article in order to predict the dynamics of the aging process of powder at an average storage temperature 15°C in Continental and 20°C in Mediterranean climate conditions, the activation energy for heat generation caused by thermal decomposition of powder, $E_2 = 80\,\text{kJ/mol}$ was used.

Domestic methodology of chemical stability control, based on the determination of the stabilizer content in naturally aged samples of powders and propellants according SORS 8069/91 standard was essentially different from the procedure prescribed by AOP-48, Ed.2 standard.

In the laboratory of TRZ (Technical Overhaul Centre) in Kragujevac, beside periodical assessment of chemical stability of naturally aged NC powder from collection KB-1 under the continental climate conditions (Kragujevac), periodical assessment of chemical stability of the same naturally aged NC powders from collection KB-2 under the conditions of the Mediterranean climate (Sasovici), were carried out years ago [11-13].

Contents of diphenylamine effective (mass %) is calculated by equation (3):

$$\text{DPA}_{\text{eff}} = \text{DPA} + 0.85 \cdot \text{NNODPA} \tag{3}$$

where:

$DPA_{eff}$ - contents of diphenylamine effective,

$DPA$ - contents of diphenylamine,

$NNODPA$ - contents of N-nitrosodiphenylamine.

By equation (4) relative depletion of of diphenylamine effective,$D_{DPAeff}$ (mass %) is calculated [2,5,6]:

$$D_{DPAeff} = \frac{\left( DPA - DPA_{eff} \right) \cdot 100}{DPA_0} \tag{4}$$

where are:

$D_{DPAeff}$ - relative depletion of of diphenylamine effective,

$DPA_0$ - initial contents of diphenylamine.

## Experemental part

In this paper the temperature of 15°C was used as the average annual temperature in the KB-1 powder collection under the continental climate conditions (average annual temperature in the M-40 type of warehouses in the continental part of the country is 15°C). The temperature of 20°C was used as the average annual temperature in the KB-2 collection (the average annual temperature under the conditions of the Mediterranean climate in Sasovici) [6,11,14].

In the naturally aged NC, NCD and NGB powders stored for 15 and 25 years in collections KB-1 and KB-2, periodical HPLC measuring of the contents of the stabilizer remained, were carried out [6,11,15].

Introduction of necessary modifications in extrapolation expression (1) was carried out. Instead of the AOP-48 powder and propellants storage conditions (10 years at 25°C), real storage conditions of naturally aged nitrocellulose powders from KB-1 and KB-2, were used: storage temperatures $T_s$=15°C and 20°C and storage times, $t_S$=15 years and 25 years. According to the modified expression (1), the times of duration of accelerated aging test of gunpowders, $t_T$ for each of selected test temperature, $T_T$, were calculated. The samples of NCD-19, NCD-21, NC-40, NC-27 and NGB-051 gunpowders were artificially aged in heating tubes within thermal blocks at 80°C, 70°C, 65.5°C and 60°C.

The values of the stabilizer contents of DPA and NNODPA in tested NC and NCD samples for calculated ($t_T$, $T_T$) test conditions, were determined by procedures which are described in literature [5,6,11,15]. The contents of stabilizer ethyl centralite in NGB-051 powder were determined, too.

Liquid chromatograph „Waters 1525 EF Binary HPLC Pump" with a thermostat for column heating, the manual injector „Rheodine Model 7125", and the photodiode array detector „Waters 2998 PDA" were used for these experiments. Liquid chromatographf „LDC/ Milton Roy 3000" in the laboratory in TRZ Kragujevac was used for these experiments, too.

Comparison of the results of gunpowder chemical stability assessment by procedures based on natural and accelerated aging was performed.

## Results and discussion

The results of periodical control of chemical stability of different types of nitrocellulose based NCD gunpowders by determination of the contents of stabilizer using of high performance liquid chromatography (HPLC) method were presented in Tables 1 and 2. The contents of the DPA, NNODPA, an effective stabilizer $DPA_{eff}$, (3) and relative depletion of effective stabilizer (4) in naturally aged NCD powders were shown. NCD powders were naturally aged in period 25 years under the conditions of: the continental climate at the temperature of 15°C and the Mediterranean climate at the temperature of 20°C [6,11].

**Table 1.** Stabilizer consumption in NCD powders naturally aged for 25 years under the continental climate conditions in KB-1 at 15°C

| NCD powders | Series MBL | years of storage in KB-1 | DPA0, mass % | DPA, mass% | NNODPA, mass% | DPAeff, mass% | relative depletion of DPAeff, % |
|---|---|---|---|---|---|---|---|
| NCD-11 | 8458 | 25 | 1.38 | 1.03 | 0.03 | 1.06 | 23.51 |
| NCD-11 | 7949 | 25 | 1.31 | 1.07 | 0.03 | 1.10 | 16.37 |
| NCD-11 | 7951 | 25 | 1.40 | 1.11 | 0.03 | 1.14 | 18.89 |
| NCD-21 | 7949 | 25 | 1.27 | 1.11 | 0.02 | 1.13 | 11.26 |
| NCD-21 | 7950 | 25 | 1.49 | 1.20 | 0.02 | 1.22 | 18.32 |
| NCD-11 | 7643 | 25 | 1.35 | 1.07 | 0.07 | 1.13 | 16.33 |
| NCD-11 | 7644 | 25 | 1.29 | 1.04 | 0.08 | 1.11 | 14.11 |
| Average value of $D_{DPAeff}$ of NCD powder, naturally ageing conditions: 25 years at 15°C in KB-1, % | | | | | | | **17.67** |

**Table 2.** Stabilizer consumption in NCD powders naturally aged for 25 years under the Mediterranean climate conditions in KB-2 at 20°C

| NCD powders | series MBL | years of storage in KB-1 | $DPA_0$, mass% | DPA, mass% | NNODPA, mass% | $DPA_{eff}$, mass% | relative depletion of $DPA_{eff}$, % |
|---|---|---|---|---|---|---|---|
| NCD-11 | 7847 | 25 | 1.50 | 1.11 | 0.20 | 1.28 | 14.67 |
| NCD-11 | 7949 | 25 | 1.31 | 0.98 | 0.03 | 1.01 | 23.24 |
| NCD-11 | 7950 | 25 | 1.48 | 1.04 | 0.03 | 1.07 | 28.01 |
| NCD-11 | 7951 | 25 | 1.40 | 0.99 | 0.03 | 1.02 | 27.46 |
| NCD-11 | 8458 | 25 | 1.38 | 1.04 | 0.04 | 1.07 | 22.17 |
| NCD-21 | 7949 | 25 | 1.27 | 0.63 | 0.07 | 0.69 | 45.71 |
| NCD-21 | 7950 | 25 | 1.49 | 0.64 | 0.02 | 0.66 | 55.91 |
| NCD-11 | 7643 | 25 | 1.35 | 1.07 | 0.07 | 1.13 | 16.33 |
| NCD-11 | 7644 | 25 | 1.29 | 1.04 | 0.08 | 1.11 | 14.11 |
| NCD-11 | 7847 | 25 | 1.50 | 1.11 | 0.13 | 1.22 | 18.63 |
| NCD-11 | 7949 | 25 | 1.31 | 0.97 | 0.07 | 1.03 | 21.41 |
| NCD-11 | 7950 | 25 | 1.48 | 1.04 | 0.09 | 1.12 | 24.56 |
| NCD-11 | 7951 | 25 | 1.40 | 0.99 | 0.09 | 1.07 | 23.82 |
| NCD-11 | 7952 | 25 | 1.46 | 1.02 | 0.10 | 1.11 | 24.32 |
| NCD-11 | 8053 | 25 | 1.39 | 1.08 | 0.11 | 1.17 | 15.58 |
| NCD-27 | 7601 | 25 | 1.49 | 1.13 | 0.11 | 1.22 | 17.89 |
| NCD-27 | 7602 | 25 | 1.46 | 1.10 | 0.11 | 1.19 | 18.25 |
| NCD-27 | 7603 | 25 | 1.41 | 1.05 | 0.12 | 1.15 | 18.30 |
| NCD-27 | 7604 | 25 | 1.28 | 1.17 | 0.10 | 1.26 | 1.95 |
| NCD-27 | 7605 | 25 | 1.41 | 1.21 | 0.10 | 1.30 | 8.16 |
| NCD-27 | 7606 | 25 | 1.46 | 1.21 | 0.10 | 1.30 | 11.30 |
| NCD-27 | 7607 | 25 | 1.44 | 1.20 | 0.11 | 1.29 | 10.17 |
| NCD-27 | 7608 | 25 | 1.44 | 1.00 | 0.15 | 1.13 | 21.70 |
| NCD-27 | 7609 | 25 | 1.50 | 0.61 | 0.23 | 0.81 | 46.30 |
| NCD-27 | 7910 | 25 | 1.38 | 0.54 | 0.25 | 0.75 | 45.47 |
| NCD-21 | 7641 | 25 | 1.49 | 1.09 | 0.11 | 1.18 | 20.57 |
| NCD-21 | 7642 | 25 | 1.39 | 1.08 | 0.1 | 1.17 | 16.19 |
| NCD-21 | 7846 | 25 | 1.5 | 1.00 | 0.15 | 1.13 | 24.83 |
| NCD-21 | 7948 | 25 | 1.4 | 0.70 | 0.15 | 0.83 | 40.89 |
| NCD-21 | 7949 | 25 | 1.27 | 0.63 | 0.21 | 0.81 | 36.34 |
| NCD-21 | 7950 | 25 | 1.49 | 0.64 | 0.2 | 0.81 | 45.64 |
| NCD-21 | 7951 | 25 | 1.5 | 0.63 | 0.19 | 0.79 | 47.23 |
| NCD-21 | 7952 | 25 | 1.48 | 0.42 | 0.21 | 0.60 | 59.56 |
| NCD-21 | 8053 | 25 | 1.46 | 0.74 | 0.18 | 0.89 | 38.84 |
| NCD-21 | 8054 | 25 | 1.35 | 0.64 | 0.2 | 0.81 | 40.00 |
| Average values of $D_{DPAeff}$ of NCD powder, naturally ageing conditions: 25 years at 20°C in KB-2, % | | | | | | | **27.01** |

By modifications of equation (1), the time of duration of the experiment $t_T$ at the test temperature $T_T$, which leads to the same degree of decomposition as those obtained during real storage period $t_S$ at an ambient storage temperature $T_s$, can be calculated for a temperature of test above 60°C. The results of DPA consumptions in naturally and artificially aged NCD powder are presented in Table 3. The test times, $t_T$, at different test temperatures, $T_T$, were calculated by introducing the conditions of naturally aging of different types of NCD powders ($t_S$, $T_S$): 25 years at 15°C in KB-1 collection and 25 years at 20 °C in KB-2 collection.

**Table 3.** DPA consumptions in NCD powder naturally aged for 25 years in KB-1 and KB-2 and artificially aged in equivalent test conditions ($t_T$, $T_T$) according (1)

| | KB-1 | KB-2 | KB-1 | KB-2 | |
|---|---|---|---|---|---|
| Single heating test temperature ($T_T$), °C | 65.5 | | 80 | | sample of powder |
| Test time ($t_T$), days | 49.66 | 87.78 | 8.63 | 15.25 | |
| $DPA_{eff}$, mass % | 0.88 | 0.69 | 0.84 | 0.74 | NCD -21 |
| $D_{DPAeff}$, % | 31.25 | 46.09 | 34.38 | 42.19 | |
| $DPA_{eff}$, mass % | 0.88 | 0.78 | 0.85 | 0.78 | NCD -19 |
| $D_{DPAeff}$, % | 23.48 | 32.17 | 26.09 | 32.17 | |
| average $D_{DPAeff}$, % | 27.37 | 39.13 | 30.24 | 37.13 | NCD powders |
| collection of powder | | | | KB-1 | KB-2 |
| Average DDPAeff, for artificially ageing of NCD powder in temperature interval from 65.5 to 80°C, % | | | | 28.80 | 38.13 |
| Average DDPAeff, for naturally ageing of NCD powder 25 years at 15°C from KB-1 and at 20°C from KB-2, % | | | | 17.67 | 27.01 |

In Table 4, in the same way by modification of expression (1), the test times, $t_T$ for selected test temperatures, $T_T$, were recalculated by introducing the conditions of natural aging of different types of NC powders ($t_S$, $T_S$): 15 years at 15°C in KB-1 collection and 15 years at 20°C in KB-2 collection.

**Table 4.** DPA consumptions in NC powder: naturally aged 15 years in KB-1 and KB-2 and artificially aged in equivalent test conditions ($t_T$, $T_T$) according (1)

| | KB-1 | KB-2 | KB-1 | KB-2 | KB-1 | KB-2 | KB-1 | KB-2 | |
|---|---|---|---|---|---|---|---|---|---|
| Single heating test temperature ($T_T$), °C | 60 | | 65.5 | | 70 | | 80 | | NC powder |
| Test time ($t_T$), days | 60.22 | 106.44 | 29.80 | 52.67 | 17.04 | 30.12 | 5.18 | 9.15 | |
| $DPA_{eff}$, mass % | 1.08 | 0.95 | - | - | - | - | 1.02 | 0.86 | NC-27 |
| $D_{DPAeff}$, % | 18.18 | 28.03 | - | - | | - | 22.72 | 34.85 | |
| $DPA_{eff}$, mass % | - | - | 0.76 | 0.65 | 0.83 | 0.64 | 0.89 | 0.74 | NC-40 |
| $D_{DPAeff}$, % | - | - | 28.30 | 38.68 | 21.37 | 39.62 | 16.04 | 30.19 | |
| average $D_{DPAeff}$, % | 18.18 | 28.03 | 28.30 | 38.68 | 21.37 | 39.62 | 19.38 | 32.52 | NC powder |
| collection of powder | | | | | | | | KB-1 | KB-2 |
| Average $D_{DPAeff}$, for artificially ageing of NC powder in temperature interval from 60 to 80°C, % | | | | | | | | **21.81** | **34.71** |
| Average $D_{DPAeff}$, for naturally ageing of NC powder 15 years: at 15°C from KB-1 and at 20°C from KB-2, % | | | | | | | | **16.72** | **23.02** |

In Table 5, in the same way by modification of expression (1), the test times, $t_T$ for selected test temperatures, $T_T$, were recalculated by introducing the conditions of natural aging of different types of NC powders ($t_S$, $T_S$): 25 years at 15°C in KB-1 collection and 25 years at 20°C in KB-2 collection [15].

**Table 5.** DPA consumptions in NC powder: naturally aged 25 years in KB-1 and KB-2 and artificially aged in equivavent test conditions ($t_T$, $T_T$) according (1)

| | KB-1 | KB-2 | KB-1 | KB-2 | KB-1 | KB-2 | KB-1 | KB-2 | |
|---|---|---|---|---|---|---|---|---|---|
| Single heating test temperature ($T_T$), °C | 60 | | 65,5 | | 70 | | 80 | | NC powder |
| Test time ($t_T$), days | 100.4 | 177.4 | 49.7 | 87.78 | 28.40 | 50.19 | 8.63 | 15.25 | |
| $DPA_{eff}$, mass % | 0.96 | 0.484 | - | - | - | - | 0.87 | 0.78 | NC-27 |
| $D_{DPAeff}$, % | 27.27 | 36.36 | - | - | - | - | 34.09 | 40.91 | |
| $DPA_{eff}$, mass % | - | - | 0.66 | 0.56 | 0.67 | 0.42 | 0.77 | 0.59 | NC-40 |
| $D_{DPAeff}$, % | - | - | 37.74 | 47.17 | 36.79 | 60.38 | 27.36 | 44.34 | |
| average $D_{DPAeff}$, % | 27.27 | 36.36 | 37.74 | 47.17 | 36.79 | 60.38 | 31.20 | 42.63 | NC-powder |
| collection of powder | | | | | | | | KB-1 | KB-2 |
| Average value of $D_{DPAeff}$, for artificially ageing of NC powder in temperature interval from 60 to 80°C, % | | | | | | | | **33.25** | **46.64** |
| Average value of $D_{DPAeff}$ for naturally ageing of NC powders 25 years: at 15°C from KB-1 and at 20°C from KB-2, % | | | | | | | | **17.20** | **81.40** |

Table 6 shows the times of accelerated aging, $t_T$ of tested powder NGB-051 at selected test temperatures: 80°C and 65.5°C and 60°C which were calculated according to the equation (1) with the introduction of the mentioned necessary modifications related to the real storage conditions. Table 6. also contains the results of determining the relative depletion of stabilizer, $D_{CI}$ in the accelerated aged of NGB-051 powder at the test temperature $T_T$ at test time $t_T$, calculated by the modification of expression (1).

**Table 6.** CI consumptions in NGB powder: naturally aged for 25 years in KB-1 and KB-2 and artificially aged in equivavent test conditions ($t_T$, $T_T$) according (1)

| | KB-1 | KB-2 | KB-1 | KB-2 | |
|---|---|---|---|---|---|
| Single heating test temperature ($T_T$), °C | 65,5 | | 80 | | sample |
| Test time ($t_T$), days | 49.66 | 87.78 | 8.63 | 15.25 | |
| CI, mass % | 1.24 | 0.94 | 1.12 | 0.78 | NGB-051 |
| DCI, % | 19.48 | 38.96 | 27.27 | 49.35 | |
| collection of powder | | | | KB-1 | KB-2 |
| Average DCI, for artificially ageing of NGB powder in temperature interval from 65.5 to 80 oC, % | | | | 23.38 | 44.16 |
| Average DCI for naturally ageing of NGB powders: 25 years at 15°C from KB-1 and 25 years at 20°C from KB-2, % | | | | 10.89 | 11.80 |

With the aim of comparison of the results of chemical stability assessment, which were based on two essentially different approaches (natural and artificial ageing of powders), all results were presented in Figures 1 and 2.

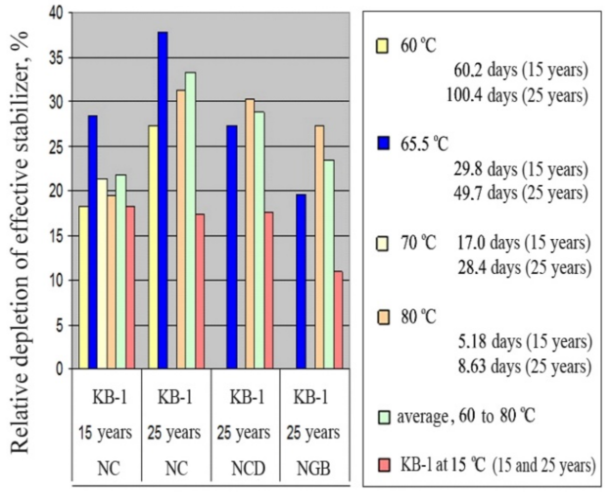


**Figure 1.** Comparison of stabilizer consumptions in naturally (KB-1) and accelerated aged NC, NCD and NGB powder

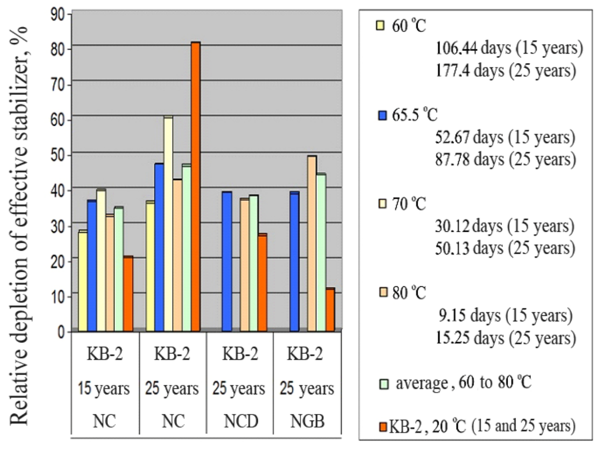


**Figure 2.** Comparison of stabilizers consumption in naturally (KB-2) and accelerated aged NC, NCD and NGB powder

In Figures 1 and 2, all results of stabilizer consumption in naturally aged (under the continental and Mediterranean climate conditions) and artificially aged NC, NCD and NGB powders were presented.

The analysis of the results showed that depletion of the stabilizer in NC, NCD and NGB nitrocellulose based powders, in each of the temperature-time (*T-t*) accelerated aging loads is greater than in the equivalent (*T-t*) conditions of natural aging of the same types of powders of age 15 and 25 years, from collection KB-1 and KB-2. Exception are NC powders stored for 25 years in KB-2.

Increased stabilizer depletion in accelerated and then in naturally aged powders is preferable because it provides an increased degree of safety and precautions during assessment of chemical stability of the powder by NATO standard AOP-48 Ed.2.

In this way, the possibility of applying the standard AOP-48 Ed.2 to the NCD, NC and NGB powders of domestic production which were stored for 25 years under the conditions of continental climate in KB-1 collection, and for NCD and NGB powder which were stored for 25 years under the conditions of Mediterranean climate in KB-2 collection, was verified.

However, this conclusion does not apply to NC powder storage for 25 years in KB-2 collection. By analyzing the results presented in Table 5, Figures 1 and 2, it can be seen :

- there is significantly higher relative depletion of $DPA_{eff}$ in naturally aged NC powder from collection KB-2 ($D_{DPAeff}$ = 81.48 %) than in equivalent *T-t* conditions of accelerated aging of the same type of NC powder ($D_{DPAeff}$ = 46.64 %);
- there is significantly higher relative depletion of $DPA_{eff}$ in naturally aged NC powder (25 years) from collection KB-2 ($D_{DPAeff}$ = 81.48 %) than in collection KB-1 ($D_{DPAeff}$ = 17.36 %) [15].

This can be explained by extreme conditions of the Mediterranean climate to which the samples of NC powder were exposed in collection KB-2 .

After a certain storage period, especially under conditions of the Mediterranean climate in KB-2, some of the series of all types of NC gunpowders show a sudden decrease in chemical stability [6,11,15]. For most gunpowder this is a period of 15 to 20 years, and for extremely stable gunpowder this is a period of 25 to 30 years. An example is NC-27 MBL 8768 gunpowder, which consumes about 0.52% DPA for 19 years of storage in KB-1 at 15° C, while after 18 years, or approximately the same period, the same series of gunpowder in KB-2 loses all stabilizer contents. Sudden and high DFAef consumption that occurs with old NC gunpowder from KB-2 is a consequence of the influence on the chemical stability of gunpowder of more extreme conditions of the Mediterranean climate and factors such as: higher temperature, relative humidity in the warehouse, moisture content of gunpowder, acidity, influence of salt, light etc.

So, NATO standard AOP-48 Ed.2 can be applied for:
- different type of nitrocellulose based gunpowder;
- gunpowder stored in different climatic conditions of storage;
- gunpowder of different ages and
- gunpowder exposed to different temperature-time loads of accelerated aging.

By confirming the possibility of applying the mentioned AOP-48 Ed.2 extrapolation method to gunpowder from domestic collections, a prerequisite for the application of the modern, wide-world method of chemical stability assessment based on the accelerated aging process to the test gunpowder has been achieved.

## Conclusion

Comparison of the results of gunpowder chemical stability assessment, by the procedure based on two essentially different approaches (natural and accelerated aging), was performed. It was achieved by introducing some of modification in AOP-48 Ed.2 extrapolation expression. Instead of powder storage conditions (10 years at 25 °C), the real conditions of natural aging for 15 and 25 years of nitrocellulose based powders in continental conditions (15°C) and Mediterranean climate (20°C) were introduced. In this way, it was possible to connect different equivalent time-temperature loads of natural and accelerated aging of NC, NCD and NGB powders, in which approximately the same degree of decomposition is expected, namely approximately the same depletion of stabilizers.

By analyzing the results presented, it can be concluded (with the exception of NC powders stored for 25 years in powder collection KB-2) that the depletion of the stabilizer in each of the temperature-time loads of accelerated aging of the NC, NCD and NGB powders is greater than the depletion of the stabilizer in the equivalent temperature-time conditions of natural aging of the same types of powders stored for 25 years in collection KB-1 under the continental climate conditions. Increased DPA depletion in accelerated related to naturally aged powder is preferable, because it provides an increased degree of safety and precautions during assessment of chemical stability of the nitrocellulose based powder by AOP-48 Ed.2.

In this way, the possibility of applying the NATO standard AOP-48 Ed.2 to the NCD and NGB powders of domestic production stored for 25 years in collections KB-1 and KB-2, and NC powders stored for 25 years in KB-1 and 15 years in KB-2 collection, was verified.

Standard AOP-48 Ed.2 is not able to predict dynamics of stabilizer depletion of naturally aged NC powder stored for 25 years in collection KB-2 under the Mediterranean climate conditions, because of significantly higher relative depletion of $DPA_{eff}$ in naturally aged NC powder stored for 25 years in collection KB-2 than in equivalent T-t conditions of accelerated aging of the same type of NC powder. Rapid depletion of $DPA_{eff}$ which occurs in the old NC powders from KB-2 is due to the impact of conditions of the Mediterranean climate and factors, such as: higher temperature, relative humidity of the air in the storage, moisture content in the powders, acidity and salt on the chemical stability of the powders.

Under the conditions of the Mediterranean climate in KB-2 powder collection, there is a faster dynamics of NC powder decomposition and stabilizer depletion than in the same NC powders stored under the conditions of continental climate in KB-1 powder collection.

Thus, there is significantly higher relative depletion of $DPA_{eff}$ in naturally aged NC powder stored for 25 years in collection KB-2 than in KB-1. In this way, by storing of the same powder in both collection KB-1 and KB-2, and by periodical measuring of stabilizer depletion, it is possible not only to monitor, but also on the base results from KB-2, to predict the dynamics of the aging process and chemical stability of NC powder during storage in KB-1.

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# Modifikacija AOP-48 Ed. 2 ekstrapolacionog izraza uvođenjem realnih t-T uslova skladištenja prirodno starenih nitroceluloznih baruta

**Izvršeno je upoređivanje rezultata ocene hemijske stabilnosti baruta postupcima zasnovanim na prirodnom i veštačkom starenju. To je postignuto uvođenjem nekih izmena u ekstrapolacioni izraz NATO standarda AOP-48 Ed. 2. Realni uslovi skladištenja prirodno starenih nitroceluloznih baruta iz kolekcije KB-1 u kontinentalnim i iz kolekcije KB-2 u mediteranskim klimatskim uslovima, uvedeni su u pomenuti ekstrapolacioni izraz umesto uslova 10 godina na 25 °C datih u AOP-48 Ed. 2 standardu. Na osnovu analize rezultata može se zaključiti da je potrošnja stabilizatora u svakom od temperaturno-vremenskih ciklusa veštačkog starenja NC, NCD i NGB baruta, veća od potrošnje stabilizatora u ekvivalentnim temperaturno-vremenskim uslovima prirodnog starenja istih vrsta baruta čuvanih 25 godina u kolekcijama KB-1 i KB-2. Izuzetak su NC baruti čuvani 25 godina u kolekciji KB-2 zbog ubrzane dinamike njihove razgradnje u ekstremnim mediteranskim klimatskim uslovima. Veća potrošnja stabilizatora u veštački, nego u prirodno starenim barutima je poželjna, jer pruža povećan stepen sigurnosti i meru opreza tokom procene hemijske stabilnosti baruta prema NATO standardu AOP-48 Ed. 2. Na ovaj način, verifikovana je mogućnost primene standarda AOP-48 Ed 2. na nitrocelulozne barute domaće proizvodnje, čuvane u uslovima kontinentalne i mediteranske klime.**

*Ključne reči:* **AOP-48 Ed.2, nitrocelulozni barut, hemijska stabilnost, prirodno starenje, veštačko starenje, tečna hromatografija.**