



Research paper / Praca doświadczalna

Study of the effect of accelerated ageing on the properties of modified nitrocellulose propellants *Badanie wpływu przyspieszonego starzenia na właściwości prochów nitrocelulozowych modyfikowanych*

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Abstract: The study investigated the stability of nitrocellulose (NC) powders modified with nitroglycerine (NG) and/or polyos 250 (polyester polyol) or centralite I (CI) and determined the changes in physicochemical properties before and after accelerated ageing. Six NC modified powders stabilized with diphenylamine (DPA) or CI were tested. Accelerated ageing of the powders was carried out in accordance with AOP-48, under isothermal heating at 71 °C for 35 days, which corresponds to storing the powders at 25 °C for 10 years. The initial powder samples and those aged under the above conditions were examined by high-performance liquid chromatography (HPLC) for loss of initial stabilizer (DPA or CI), calorimetry, and manometric bomb. The geometric changes of gunpowder grains and their densities, were also compared before and after accelerated ageing. Tests on the stability of the powders by means of heat flow microcalorimetry (HFC) conducted in accordance with STANAG 4582 at 90 °C for 3.43 days, showed that the tested powders did not exceed the permissible limit of a released heat power of 350 μW/g, which means that they should be stable for the next 10 years of storage at 25 °C. This diagnosis was confirmed by chromatographic (HPLC) analyses of stabilizer loss. After accelerated ageing, the content of modifiers and stabilizers was lower compared to the initial powders. Ageing at elevated temperatures did not change the geometry of the aged powders relative to the starting powders. For most of the tested powders, accelerated ageing resulted in a slight increase in calorific value relative to the starting powders. Comparable helium density values were obtained for the powders before and after ageing, all of which were within error limits. Accelerated ageing did not significantly affect the changes in dynamic vivacity between the aged and initial powders. The tested NC modified powders should not change their properties enough during 10 years of storage at 25 °C to become unstable, i.e. unsafe when stored and/or to fail to meet ballistic requirements.

Streszczenie: *Celem pracy było badanie stabilności nitrocelulozowych (NC) prochów modyfikowanych nitrogliceryną i/lub poliosem 250 (poliolem poliestrowym) albo centralitem I (CI) oraz określenie zmian właściwości fizykochemicznych przed i po przyspieszonym starzeniu. Badaniom poddano 6 NC prochów modyfikowanych stabilizowanych difenylaminą (DFA) lub CI. Sztuczne starzenie prochów przeprowadzono według normy AOP-48, w ramach izotermicznego ogrzewania w 71 °C przez 35 dni, co odpowiada przechowywaniu prochów w temperaturze 25 °C przez 10 lat. Wyjściowe próbki prochów oraz starzone w ww. warunkach badane były za pomocą wysokosprawnej chromatografii cieczowej (HPLC) pod kątem ubytków stabilizatora wyjściowego (DFA albo CI), kalorymetrii, bomby manometrycznej. Porównano również przed i po przyspieszonym starzeniu zmiany geometryczne ziaren prochowych i ich gęstości. Badania stałości prochów za pomocą mikrokalorymetrii przepływowej (HFC) prowadzone według STANAG-u 4582 w temp. 90 °C przez 3,43 doby wykazały, że badane prochy nie przekroczyły dopuszczalnego limitu wydzielonej mocy cieplnej wynoszącego 350 μW/g, co oznacza, że powinny być stabilne przez następne 10 lat przechowywania w temperaturze 25 °C. Diagnozę tę potwierdziły analizy chromatograficzne (HPLC) w zakresie ubytków stabilizatorów. Po przyspieszonym starzeniu zawartość modyfikatorów i stabilizatorów uległa obniżeniu w stosunku do prochów wyjściowych. Starzenie w podwyższonej temperaturze nie wpłynęło na zmianę geometrii prochów starzonych w stosunku do prochów wyjściowych. Dla większości badanych prochów, przyspieszone starzenie spowodowało nieznaczne podwyższenie kaloryczności względem prochów wyjściowych. Uzyskano porównywalne wartości gęstości helowej dla prochów przed i po starzeniu, wszystkie mieściły się w granicach błędu. Przyspieszone starzenie nie wpłynęło znacząco na zmiany żywości dynamicznej pomiędzy prochami starzonymi i wyjściowymi. A zatem, badane NC prochy modyfikowane nie powinny zmienić na tyle swoich właściwości w trakcie 10 lat przechowywania w temperaturze 25 °C, aby stać się niestabilne, tj. niebezpieczne podczas przechowywania i/lub aby nie spełnić wymogów balistycznych.*

Keywords: *nitrocellulose powders, accelerated ageing, HFC, HPLC, stabilizer loss*

Słowa kluczowe: *prochy nitrocelulozowe, przyspieszone starzenie, HFC, HPLC, ubytek stabilizatora*

1. Introduction

To change the properties of nitrocellulose (NC) powders (single base), modification processes are performed on its combustible layer [1-3]. These processes involve the introduction of the modifying substance(s) into the outside layers of NC powder by diffusion. Such processes change various physicochemical properties, including ballistic properties. These properties are also influenced by other parameters, such as nitrogen content [4] or volatile component content. NC powders are hygroscopic, so it is important that their volatile components, most often water or process solvents (diethyl ether, ethyl alcohol), remain unchanged during storage.

During storage, NC powders are subject to natural ageing processes. NC is subject to deterioration, of which the main cause is the instability of nitrate groups in the polymer. Nitrate groups ($-\text{O}-\text{NO}_2$) have a low binding energy, so they are easily ruptured, which causes the release of products in the form of nitrogen oxides. Nitrogen dioxide (NO_2), due to its reactivity, catalyses a series of exothermic reactions that may lead to the self-ignition of NC (and thus, powder). Decomposition products may lead to changes in the combustion heat value and the ballistic properties of the powder. To neutralise NC decomposition products and extend powder storage time, stabilizers are introduced into their composition [1]. The stabilizer is consumed during storage, which may accelerate the auto-catalytic reactions responsible for NC degradation. For this reason, the stability of NC powders must be monitored during their storage. There are several methods of determining the stability of NC powders, e.g. the Bergmann-Junk Test or Abel Test, the measurement of stabilizer loss using analytic techniques, in particular chromatography, or heat flow microcalorimeter (HFC) testing [5-7].

The changes in NC powder properties during production and storage are referred to as ageing. Ageing is a complex process, in which a series of physical and chemical processes occur. Physical processes may include e.g. the diffusion of liquid nitrate esters. The ageing and decomposition of powders is accompanied by a series of phenomena, such as the release of gas, reduction of the molecular weight of NC, reduction in the original concentration of stabilizer or heat generation (exothermic reactions) [8]. These phenomena occur during ageing and may be used to evaluate the stability of the powder, to investigate the kinetics of its decomposition and to evaluate its storage period. Considering the fact that these processes are very slow under typical (natural) conditions (the storage period of powder is usually longer than 20 years), the duration of many tests aimed at evaluating changes in material parameters which occur at room temperature would be significantly longer. To shorten the test duration, artificial (accelerated) ageing of powder, i.e. at increased temperature, is carried out.

One of these tests is the stabilizer loss test [9]. This enables the time to full reaction (full loss) of the initial stabilizer, to be determined. Such tests are performed by artificially ageing at a single temperature or at different temperatures. Ageing at a single temperature is sufficient to determine if the powder is stable enough to store for 10 years at room temperature (25 °C). This is applicable to powders made of well-known and generally used components. For new powder compositions, particularly with new stabilizers and/or different components introduced, more elaborate tests are required, such as multi-stage ageing. In Allied Publication NATO AOP-48 [10], powder stability evaluation criteria are given based on stabilizer content loss and its transformation products. It also includes information on stabilizers:

- diphenylamine (DPA),
- 2-nitrodiphenylamine (2-NDPA),
- 1,3-diethyl-1,3-diphenylurea (ethyl centralite, centralite I, CI),
- 1,3-dimethyl-1,3-diphenylurea (methyl centralite, centralite II),
- 3-methyl-1,1-diphenyl-urea (acardite II),
- 4-nitro-*N*-methylaniline,

as well as the products produced during the storage of powder. It also describes the method of sample preparation for HPLC analysis and the preparation procedure for the artificially aged powder samples to test for stability. According to [10], powder with added stabilizer is considered as being stable and compliant with NATO requirements if it still contains at least 0.2% by weight of stabilizer after 10 years of storage under isothermal conditions at a temperature of 25 °C and if the maximum relative stabilizer loss does not exceed 80%.

Other powder stability tests are microcalorimetry measurements. In Standardisation Agreement NATO STANAG 4582 [11], powder stability evaluation criteria are given based on heat flow microcalorimeter (HFC) measurements. The parameter measured in this technique is the released heat power. The test temperature should be in the range of 60 °C to 90 °C. To shorten the duration of the test, temperatures closer to the upper limit are recommended. The duration depends on the selected temperature and corresponds to 10 years of storage of the powder at 25 °C. The maximum permissible heat flow limit, corresponding to the test temperature in use, is considered as the criterion of adequate chemical stability. According to [11], it is considered that the powder will remain stable for 10 years of storage at 25 °C if the maximum heat flow during accelerated ageing for 3.43 days at a temperature of 90 °C does not exceed a thermal poweroutput of 350 μ W/g.

The techniques described are suitable for evaluating the stability of NC powders. It is also important to evaluate the changes in physicochemical and ballistic properties resulting from ageing. The purpose of the study was to complete the accelerated ageing process on modified NC powders to compare their physicochemical properties before and after ageing. The properties tested were for powders with one of two of the above-named stabilizers, i.e. DPA or CI.

2. Experimental part

2.1. Powders used for testing

Single base modified powders stabilized with DPA or CI manufactured by MESKO S.A. were selected for testing. Table 1 shows their composition. Nitroglycerine (NG) and CI (added in greater volumes to serve a dual function, namely stabilizer and modifier) and Polyos P250 (polyester polyol) were used as modifiers. NG, a chemical compound with positive oxygen balance, contributes to an increased calorific content of a powder, Polyos P250 reduces the diffusion of small particle components (including NG) from the powder grain. CI, as a NC plasticizer, decreases the porosity of the subsurface layers of powders and reduces the calorific output. 2-NDPA was also added to all the modification processes, as a penetration depth indicator.

Table 1. Stabilizers and modifiers used in test powders

Powder name	Stabilizer type (content 1 wt.%)	Modifier type and content ([wt.%])
P1	CI	polyos P250 (0.5)
P2		CI (2)
P3		NG (2.9), polyos P250 (1.9)
P4	DPA	NG (7.3), polyos P250 (0.9)
P5		NG (4.1), polyos P250 (0.9)
P6		NG (7.3), polyos P250 (0.9)

2.2. Accelerated ageing of powders in a drying chamber

The accelerated ageing of powders was performed as per [10]. This corresponds to the storage of powder for 10 years at a temperature of 25 °C. The process is performed in a drying chamber, SML-32/250, at a temperature of 71 °C. Powder samples (20.00 g) were weighed into glass vessels using an analytical balance. The glass vessels were closed with metal nuts with plastic sealing. The samples were subject to ageing for 35 days.

2.3. Test methods

2.3.1. Investigation of powder grain geometry

The geometrical parameters of the prepared powder grains were analysed using a Delta Optical Smart 5M PRO microscope. 100 grains of each powder type were selected at random and their width (d_z) and length (l) measured. The powder grains were then cut with a scalpel along the tubular axis and the following parameters were measured:

- inner wall diameter (d_k),
- combustible layer thickness (d_{vp}) and
- modified layer thickness (d_{vm}).

Figure 1 shows the geometrical measurements for the grain (Figure 1a) and its cross-section (Figure 1b).

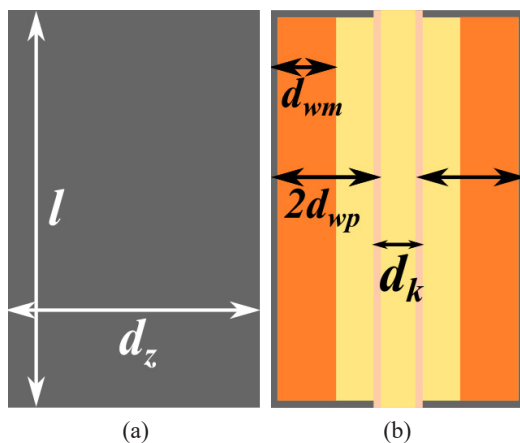


Figure 1. Measurement of grain geometry (a) and its cross-section (b), including the length (l), outside diameter (d_z), inner wall diameter (d_k), double thickness of the combustible layer ($2d_{wp}$) and the modified layer (d_{wm})

2.3.2. Powder density test

The density of the modified powders was determined using a Micromeritics AccuPyc 1330 helium pycnometer. The measurement vessel was filled to approx. 2/3 of its volume with the test sample. Two series of 10 measurements each were performed at a temperature of 25 °C. The average of the measurements was taken.

2.3.3. Powder calorific value test

The powder combustion heat (calorific value) was determined using a IKA C2000 basic calorimeter. The measurements were performed twice under reduced pressure (3-4 hPa) each sample having a mass of 2 g (measured to 0.0002 g accuracy). The powders were ignited using a resistance wire with a known calorific value of 2.69 J/cm. Before the powder sample measurements, the calorimetric constant of the device was determined using a NC-NG powder with a known calorific value (4922 J/g).

2.3.4. Powder dynamic vivacity test

A manometric bomb with a fixed capacity of 25 cm³ (loading density $\Delta = 160$ kg/m³) was used to test the dynamic vivacity of the powders. The measurements were performed as per STANAG 4115 [12]. Two measurements were performed for each powder. 200 mg of gunpowder was used as an igniter.

Pressure change over time was recorded. In interpreting the results (to determine the dynamic vivacity), the parameter α was defined as the ratio of the instant pressure to the maximum pressure (p/p_{max}). The dynamic vivacity (Γ) was calculated using the following equations:

$$\Gamma = \frac{d\alpha}{dt} \cdot \frac{1}{p} \quad (1)$$

$$\alpha = \frac{p}{p_{max}} \quad (2)$$

where: $\frac{d\alpha}{dt}$ – gas production rate, p – instant pressure, p_{max} – maximum pressure.

2.3.5. Powder microcalorimetry test (HFC)

To evaluate the stability of the powders samples as per STANAG 4582 [11], heat flow microcalorimetry (HFC) was used. The measurements were performed on a TAMIII, made by TA Instruments, by placing the test samples in glass vials with a volume of 4.3 cm³. The vials were completely filled with powder and sealed.

The measurements were performed as per STANAG 4582 [11], at the highest permitted constant test temperature of 90 °C. The powders were subjected to ageing for a minimum of 3.43 days following a release of 5 J/g. It is considered that powder is stable for 10 years of storage at a temperature of 25 °C if the test sample does not release heat power above 350 μW/g over 3.43 days.

2.3.6. Determining stabilizer and modifier content using high performance liquid chromatography

The stabilizer and modifier contents of the prepared samples were determined using high performance liquid chromatography (HPLC), as per STANAG 4620 [10]. For test purposes, an Agilent 1260 Infinity liquid chromatograph was used. Into 100 cm³ measuring flasks, 200 ±2 mg test powder samples and 50 cm³ of acetonitrile were added. The flasks were shaken every 15 min for 4 h to dissolve the samples completely. During that time, the flasks were stored in a dark place. 10 cm³ of 2% calcium chloride water-based solution was then added to the flasks to precipitate the NC and filled with water to the volumetric line. The flasks were then shaken every 15 min for 1 h. For analytical purposes, 1.5 cm³ of the filtered solution were drawn using a disposable syringe filter with a pore size of 0.45 μm. Every prepared propellant was analysed three times.

3. Results and discussion of the results

3.1. CI-stabilized powders

First, powders were analysed using a TAMII flow microcalorimeter to ensure their stability and thus the validity of their ageing and for further testing. The measurement is based on the rate of heat generation, caused by powder decomposition. The heat generation rate is the general effect and applies both to a decreased combustion heat and a spontaneous heating capacity. Figure 2 shows the HFC curves for CI-stabilized powders. In accordance with the material stability requirements of STANAG 4582 [11], conditioning lasts for 3.43 days and the powder sample must not exceed the heat power limit of 350 μW/g.

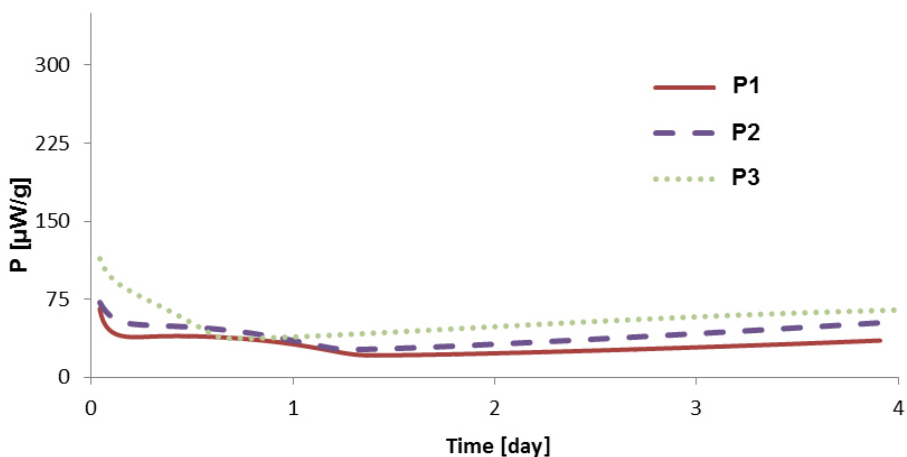


Figure 2. HFC curves for CI-stabilized powders (ageing conditions: 90 °C, 3.43 days)

Figure 2 shows that the limit of 350 $\mu\text{W/g}$ after 3.43 days of heating at 90 °C had not been exceeded thereby meeting the conditions specified in STANAG 4582 [11]. This means the tested powders should be stable and thus safe to store for 10 years at a temperature of 25 °C.

The second test determining the stability of NC powders is the stabilizer loss test in accordance with Allied Publication NATO AOP-48 [10]. NC-based powders may be considered as stable for 10 years at a temperature of 25 °C if they meet the following two criteria. First, the maximum stabilizer loss during ageing (in % relative to its initial content) should be up to 80%. Second, the minimum stabilizer content after ageing should be no lower than 0.2%. Table 2 presents the result of stabilizer and selected modifier contents tests for initial powders and powders after accelerated ageing (at the temperature of 71 °C for 35 days).

Table 2. HPLC analysis results for initial powders and powders after ageing, CI-stabilized

Powder name	Tested powder component	Amount [wt.%]		Loss of the test substance [%]
		Before ageing	After ageing	
P1	CI	1.01	0.89	11.88
	2-NDPA	0.09	0.02	77.78
P2	CI	3.73	3.04	18.50
	2-NDPA	0.02	0.01	50.00
P3	NG	0.96	0.61	36.46
	CI	0.86	0.67	22.09

In all the powders analysed, the amounts of the tested substance decreased, as expected. For powder P1 after ageing, the CI loss was 0.11 wt.%, which corresponded to 11.88%. For 2-NDPA, the loss of 0.06 wt.% or 77.78% was observed. For powder P2, the CI amount decreased by 0.69 wt.% CI, which constituted a 18.50% loss. For 2-NDPA, the amount determined was 0.01%_{w/w} less after ageing, which corresponded to 50%. For powder P3, the amount of the modifier NG decreased by 0.19 wt.% in relation to the initial powder, while the CI stabilizer content decreased by 0.35 wt.% or 22.09%. By comparing the results, the modified powder stability may be confirmed. An 80% stabilizer loss was not observed for any of the powders. Considering the modifiers used, it can be concluded that when added to NG, powder P3, contributes to a higher stabilizer consumption during the ageing process. For this powder, the loss is two times greater compared to powder P1, in which only polyos P250 is used as the modifier.

Table 3 presents the geometrical dimensions of powder grains before and after accelerated ageing. It was found that the ageing process has no significant effect on the powder grain geometry. Similarly, there does not appear to be a significant effect on the thickness of the modified layer. For every tested powder, it is greater than for the powder before ageing. However, given the errors in determining this parameter, it can be said that the modified layer thickness is not affected either. This indicates that the introduced components do not penetrate deeply into the grain during artificial ageing. Table 4 presents the combustion heat values and helium density of the powder before the ageing process, compared to the results after artificial ageing.

Table 3. Geometrical dimensions of CI-stabilized powder grains before and after ageing

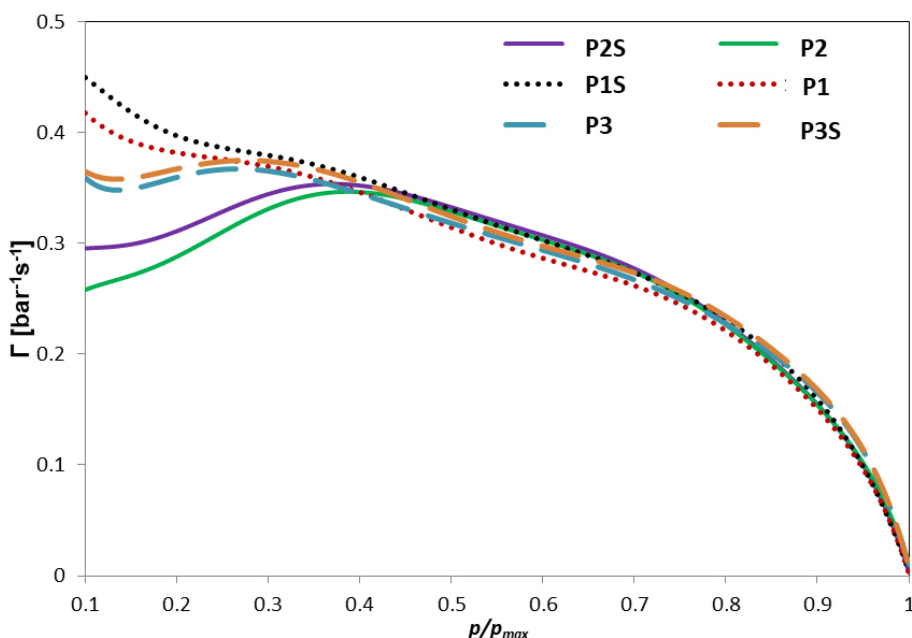
Powder		Size [mm]				
		<i>l</i>	<i>d_z</i>	<i>d_k</i>	<i>2d_{vp}</i>	<i>d_{wm}</i>
P1	before ageing	2.13 ±0.30	1.25 ±0.04	0.15 ±0.06	0.57 ±0.05	0.14 ±0.02
	after ageing	2.18 ±0.30	1.28 ±0.05	0.15 ±0.05	0.60 ±0.10	0.17 ±0.05
P2	before ageing	2.01 ±0.26	1.23 ±0.04	0.20 ±0.03	0.51 ±0.06	0.05 ±0.01
	after ageing	2.06 ±0.24	1.26 ±0.05	0.20 ±0.02	0.58 ±0.09	0.08 ±0.06
P3	before ageing	2.09 ±0.32	1.26 ±0.05	0.16 ±0.03	0.55 ±0.08	0.06 ±0.01
	after ageing	2.14 ±0.28	1.29 ±0.06	0.18 ±0.03	0.52 ±0.07	0.07 ±0.02

Table 4. Combustion heat and density of CI-stabilized powders before and after ageing

Powder		Combustion heat [J/g]	Density [g/cm ³]
P1	before ageing	4098 ±2	1.643 ±0.002
	after ageing	4126 ±3	1.638 ±0.004
P2	before ageing	3749 ±14	1.611 ±0.004
	after ageing	3815 ±13	1.605 ±0.004
P3	before ageing	4065 ±2	1.630 ±0.001
	after ageing	4120 ±14	1.634 ±0.002

The combustion heat of all the tested samples increased after artificial ageing. The calorific value was observed to increase by 28 J/g for powder P1, by 66 J/g for powder P2 and by 55 J/g for powder P3. The combustion heat change may be influenced by different factors, including the loss of small particle components or changes in the stabilizer. They may explain the differences in the resulting combustion heat values. For helium density, no significant effect of the artificial ageing process was observed on the obtained values. Within error limits, the values obtained for powders before and after the artificial ageing process are consistent.

One of the most important parameters of a powder are its ballistic properties, because any change in them will cause changes in the operational parameters of a munition. Figure 3 plots show the dependency of the dynamic vivacity on the parameter p/p_{max} for powders before and after ageing.

**Figure 3.** Changes in dynamic vivacity of initial CI-stabilized powders compared to artificially changed powders

Powder P1, before and after ageing (P1S) – dotted lines – burns with a decreasing combustion surface, which is degressive burning. The remaining powders, however, burn progressively to the pressure values p/p_{max} approx. 0.35. The lowest dynamic vivacity is shown by powder P2, in which only CI was used as

a modifier. Powder P1 with the highest dynamic vivacity was modified with polyos P250. The smallest difference in dynamic vivacity of the initial powder and the aged powder may be observed for powder P3. By comparing the powders before and after artificial ageing, it can be seen that artificial ageing had no significant influence on the dynamic vivacity. It was slightly higher for the initial powders, which may be related to the elimination of the volatile components during conditioning of the powder.

3.2. Diphenylamine-stabilized powders

Figure 4 shows the HFC curves for DPA-stabilized powders. In accordance with the material stability requirements of STANAG 4582 [11], the conditioning lasts for 3.43 days and the powder sample must not exceed the released heat power limit of 350 $\mu\text{W/g}$. Powders P4, P5 and P6 meet the requirements of STANAG 4582. This means that they will be stable and safe to store for at least 10 years at a temperature of 25 $^{\circ}\text{C}$.

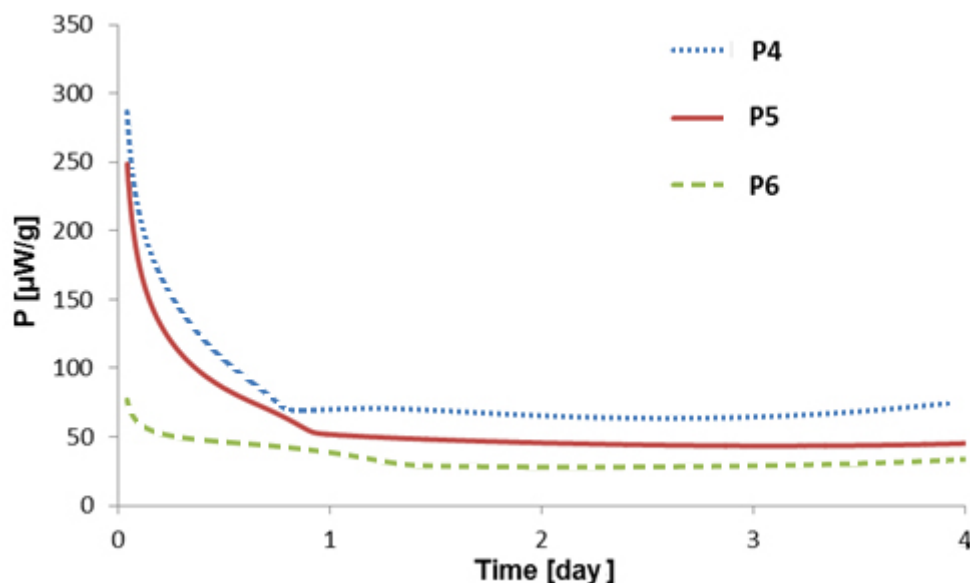


Figure 4. HFC curves for DPA-stabilized powders

For DPA-stabilized powders, a stabilizer loss test was also performed as per NATO AOP-48. Table 5 summarises the determined quantities of stabilizer and NG of the tested powders. Analysis of the results in Table 5, shows losses in both NG and DFA after conditioning. The difference in NG content in powders after ageing is 0.76 wt.% for powder P4, corresponding to 12.00%, 0.69 wt.% or 23.79% for P5, 0.31 wt.% or 4.68% for P6. Since NG is a volatile compound, it may evaporate during the ageing process. For DPA, all powders are characterised by a stabilizer loss lower than 80% with their concentration being equal to or higher than 0.2%. However, DPA loss is much greater than for powders with CI. For DPA, its derivatives also have a stabilizing effect [13]. This affects the HFC test result, where the powder is stable and compliant with STANAG 4582. Table 6 summarises the geometrical dimensions of the grains. Artificial ageing had no effect on changes in grain geometry. All measurements are within error limits. The values are similar to that of the modified layer thickness. The differences in these values are within error limits. The modified layer thickness is insignificantly greater after ageing indicating that the modifier, under the influence of temperature diffused into the grain and did not remain on the outside.

Table 5. HPLC analysis results for initial powders and powders after ageing, DPA-stabilized.

Powder name	Tested powder component	Amount [wt.%]		Loss of the tested substance [%]
		Before ageing	After ageing	
P4	NG	6.33	5.57	12.00
	DPA	0.81	0.25	69.13
P5	NG	2.99	2.30	23.79
	DPA	0.95	0.50	48.39
P6	NG	6.63	6.32	4.68
	DPA	0.75	0.20	73.33

Table 6. Geometrical dimensions of DPA-stabilized powder grains before and after ageing

Powder		Size [mm]				
		l	d_z	d_k	$2d_{wp}$	d_{wm}
P4	before ageing	1.64 ±0.25	1.30 ±0.05	0.18 ±0.05	0.58 ±0.06	0.08 ±0.03
	after ageing	1.49 ±0.22	1.28 ±0.07	0.19 ±0.04	0.56 ±0.07	0.10 ±0.04
P5	before ageing	1.62 ±0.29	1.34 ±0.06	0.20 ±0.06	0.52 ±0.08	0.08 ±0.03
	after ageing	1.60 ±0.27	1.32 ±0.06	0.18 ±0.05	0.53 ±0.05	0.10 ±0.03
P6	before ageing	1.62 ±0.26	1.38 ±0.04	0.16 ±0.03	0.58 ±0.09	0.11 ±0.03
	after ageing	1.60 ±0.19	1.36 ±0.04	0.16 ±0.03	0.58 ±0.06	0.14 ±0.04

Figure 5 shows the comparative photos of a cross-section of powder grain P6 before artificial ageing (Figure 5a) and after (Figure 5b). It can be seen that the modified layer thickness did not change significantly and remained within error limits. The colour of the powder grain after ageing changed, but this is connected to the formation of diphenylamine derivatives, whose colour is darker.

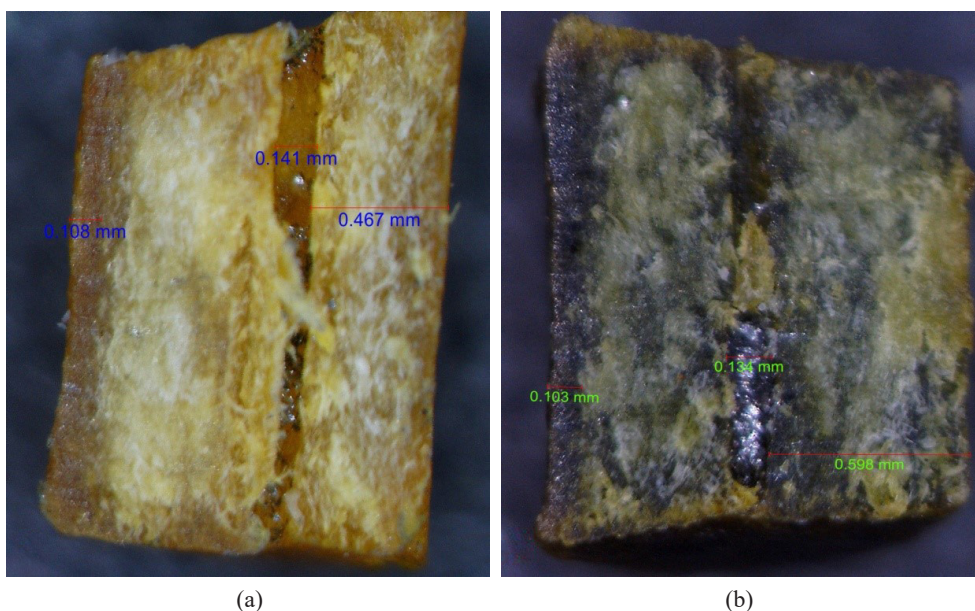
**Figure 5.** Cross-section of powder grain P6: before (a) and after (b) ageing

Table 7 shows the combustion heat and helium density results of the powders before and after ageing. Combustion heat, after artificial ageing, did not change and remained within error limits. The conditioning had an insignificant effect on the calorific value increase, not exceeding 1%. This increase was 0.22% for powder P4, 0.54% for P5, 0.62% for P6. The increases may result from the elimination of small particle substances, which decrease the combustion heat. For helium density, there was no significant effect by the artificial ageing process on the change in this parameter.

Table 7. Combustion heat and density of initial powders and powders after ageing, DPA-stabilized

Powder		Combustion heat [J/g]	Density [g/cm ³]
P4	before ageing	4214 ±2	1.631 ±0.001
	after ageing	4223 ±2	1.626 ±0.001
P4	before ageing	4008 ±3	1.636 ±0.001
	after ageing	4029 ±7	1.627 ±0.002
P5	before ageing	4274 ±4	1.631 ±0.004
	after ageing	4300 ±7	1.636 ±0.002

Comparison of the dependency of the dynamic vivacity on the parameter p/p_{max} for DPA-stabilized powders before and after artificial ageing is presented in Figure 6. All the powders are characterised by the dynamic vivacity decreasing with e increasing p/p_{max} , which is regressive burning. The ageing process had no effect on the change in powder burning type. Powders P4, P5 and P6 were modified using different amounts of NG and depositing polyos P250 on the surface. Based on the analysis of the plot, it is noted that the difference in the amount of modifier had no effect on the dynamic vivacity. During conditioning, the amount of modifiers in powders decreased insignificantly, which influenced the difference in vivacity between initial powders and powders after ageing.

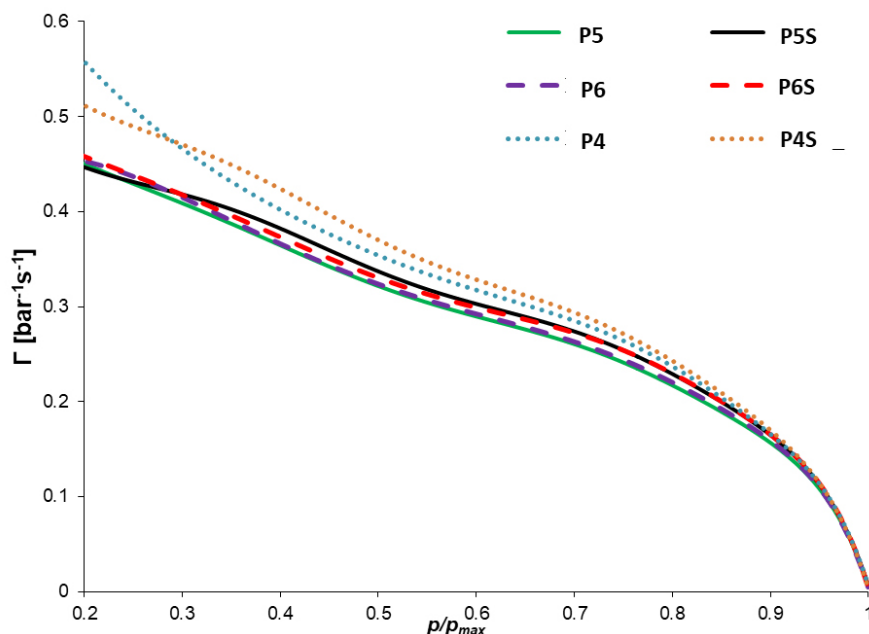


Figure 6. Changes in dynamic vivacity of initial powders compared to artificially aged powders, DPA-stabilized

4. Summary and conclusions

- ◆ Artificial ageing processes were conducted on modified NC powders using two methods, i.e. at a temperature of 71 °C for 35 days as per AOP-48 [10] and at a temperature of 90 °C for 3.43 days using HFC as per STANAG 4582 [11].
- ◆ Based on the phase of HFC curves, all tested powders will be stable for the next 10 years of storage at 25°C. This conclusion was confirmed by the stabilizer loss tests as per AOP-48 [10].
- ◆ The properties of the modified powders were investigated during artificial ageing. Ageing at elevated temperature did not change the geometry of the powders. The modified layer thickness increased insignificantly for aged powders, however this change remained within measurement error limits. No effect of either the stabilizer, or the modifier type on the tested physicochemical and ballistic properties was observed.
- ◆ For most of the tested powders, CI- or DPA-stabilized, ageing at elevated temperature resulted in a slight increase in calorific value relative to the initial powders.
- ◆ For most non-aged (initial) powders, the resulting helium density values were comparable and all within error limits.
- ◆ For ballistic properties, no significant changes in the dependency of the dynamic vivacity on the parameter p/p_{max} were observed. Powders modified with NG/polyos P250 were distinguished by the least differences in dynamic vivacity relative to the initial powder. It means that modified NC powders should not change their ballistic properties over 10 years of storage at a temperature of 25 °C.

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