Research paper / Praca doświadczalna

Modification of the burning layer of nitrocellulose powders with liquid nitroesters
Modyfikacja warstwy palnej prochów nitrocelulozowych za pomocą ciekłych nitroestrów

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Abstract: The article describes the use of liquid nitroesters (nitroglycerine, dinitrodiethyleneglycol and dinitrotriethyleneglycol) as modifiers of the burning layer of nitrocellulose powders. The properties of the modified powder were determined and compared with those of the base powder. The modification process did not change the powder's geometry. The increase in heat of combustion is obtained by using a larger amount of nitroglycerine (from 6 to 8 phr) or by using dinitrotriethyleneglycol without an inert polymer. By using the appropriate composition and type of modifiers, a similar intensity of gas formation was obtained for different nitroesters. A faster loss of the stabilizer was observed for the powders with nitroglycerine. All modified powders will be stable for 10 years of storage at 25 °C.

Streszczenie: W artykule opisano zastosowanie ciekłych nitroestrów (nitrogliceryny, dinitrodietylenoglikolu i dinitrotrietylenoglikolu) jako modyfikatorów warstwy palnej prochów nitrocelulozowych. Określono właściwości prochów modyfikowanych i porównano je z prochem bazowym. Stwierdzono, że proces modyfikacji nie wpływa na zmianę geometrii prochów. Wzrost kaloryczności uzyskuje się przy zastosowaniu większej ilości nitrogliceryny (od 6 do 8 phr) lub zastosowaniu dinitrotrietylenoglikolu bez inertnego polimeru. Stosując odpowiedni skład i rodzaj modyfikatorów uzyskano zbliżoną intensywność powstawania gazów dla różnych nitroestrów. Dla prochów z nitrogliceryną zaobserwowano szybszy ubytek stabilizatora. Wszystkie modyfikowane prochy będą stabilne przez 10 lat składowania w temperaturze 25 °C.

Keywords: nitrocellulose powders, nitroglycerine, dinitrotriethyleneglycol, dinitrodiethyleneglycol, ballistic properties
Słowa kluczowe: prochy nitrocelulozowe, nitrogliceryna, dinitrotrietylenoglikol, dinitrodietylenoglikol, właściwości balistyczne

1. Foreword

Single-base nitrocellulose-based propellants have a porous structure determined by the structure of the fibrous nitrocellulose (NC) [1]. Also, they burn in layers which enables the emission rate of gases produced

when burning the propellant charge, to be controlled. One disadvantage of single-base propellants is their low calorific value and non-uniform combustible layer resulting in deviations from the geometric burning law. Introducing energetic components to the combustible charge changes its calorific value and dynamic vivacity [2], the process is referred to as a modification process and is used to improve ballistic properties, by introducing a substance to the structure of the combustible layer which slows down the burning rate at the initial stage. These substances are referred to as phlegmatizing agents or burn rate modifiers. Proper modifier selection and distribution in the combustible layer yields modified propellants showing the expected ballistic properties. The concentration of phlegmatizing agents in the combustible layer depends on the depth they are introduced at – the highest amount of the burn rate modifier should be in the outer combustible layer and the lowest – further in the propellant grain. An increase or decrease in calorific value depends on the oxygen balance of the modifier used. Using a modifier with an oxygen balance higher than the oxygen balance of the NC used in production of the propellant, will increase the calorific value of the modified propellant. The modification process involves introducing the components into the propellant structure by diffusion. During the modification process, in the first stage, the modifier is applied to the surface. In the second stage, the modifier penetrates the nitrocellulose structure of the propellant by diffusion and modifies the composition of the combustible layer, pore filling ratio and the gross calorific value. Changes in those parameters affect the gas emission rates and enables constant pressure to be maintained as the projectile moves inside the barrel.

Literature discusses two main modification process methods namely, a dry coating process [3-6] and processes involving a dispersing medium. The former consists of placing the propellant and the modifier together in a polishing drum. The temperature is selected based on the melting temperature of the modifier. The biggest advantage of this method is that no solvents are used and it is environmentally-friendly. The main disadvantage is grain adhesion at the cooling stage. The latter uses a dispersing medium (water [7, 8] or organic solvents [9, 10]). The process involves introducing the phlegmatizing agents into the structure of the combustible layer by diffusion. The method provides reproducibility of the ballistic parameters of modified propellants, as well as uniform distribution of the modifiers over the grain surface.

Liquid nitrate esters including nitroglycerine (NG), dinitrodiethylene glycol (DNDG) and dinitrotriethylene glycol (DNTG) are good NC plasticizers, also used in the production of double-base propellants, and as burn rate modifiers in single-base propellants. NG can be introduced into the combustible layer structure of propellants using different methods. The first processes described in the literature involve its introduction into the combustible layer by diffusion [7, 11]. Another proposed method is surface modification of the propellant involving spray coating the grain surface with a modifier solution [12]. The modification processes using other liquid DNDG and DNTG nitrate esters were carried out using a dispersing medium method [10]. A mixture of water and organic solvent was used as a dispersing medium. The modifier was added as a 50% solution dispersing medium.

In the Department of High-Energetic Materials (ZMW), Faculty of Chemistry, Warsaw University of Technology, systematic research was carried out involving single-base propellants [13, 14], NC interactions with liquid nitrate esters [15] and modification of the combustible layer of NC-based propellants. The article presents the modification processes using liquid nitrate esters: NG, DNDG and DNTG and compares the properties of the resulting propellants.

2. Experimental section

2.1. Raw materials used in the modification process

A single-perforated NC based propellant stabilised with diphenylamine, manufactured by Mesko S.A.:
– length 1.88 ±0.30 mm,
– diameter 1.31 ±0.09 mm,
– combustible layer thickness 0.50 ±0.05 mm,

–   perforation diameter 0.34 ±0.05 mm,

was used in the modification processes. In the article, the propellant is referred to as 5/1. Distilled water was used as the dispersing medium in the modification processes. The following modifiers were used:

–   NG (Mesko S.A.),
–   DNTG (synthesised at the ZMW, purity determined using chromatography to be at least 95%),
–   DNDG (synthesised at the ZMW, purity determined using chromatography to be at least 95%),
–   2-nitrodiphenylamine (2-NDPA synthesised at the ZMW, melting point 76 °C),
–   Polios 250 (P250, Purinova, polyester based on carboxylic acid and glycol mixture, molecular mass determined using 893 Da gel chromatography, molecular composition determined based on molecular analysis: 57.45% C, 8.00% H, 34.55% O), and
–   Polios 420 (P420, Purinova, a polyester based on carboxylic acid and glycol mixture, molecular mass determined using 507 Da gel chromatography, molecular composition determined based on molecular analysis: 55.40% C, 8.07% H, 36.53% O).

The modifier solutions were prepared in ethanol (96%, Zakłady Produkcyjne Solanum, Poland).

2.2. Modification process instrumentation

The modification processes were carried out in a glass reactor with cooling-heating jacket (operating at a temperature range of ambient to 95 °C) with a convex, ellipsoidal bottom, 25 dm^3 volume with turbine mixer and three profiled blades. The system was fitted with a 10 dm^3 dispenser with valve, 20 dm^3 collector, a water cooled condenser and a vacuum pump. The system can operate in two modes: manual and automatic. The software controls mixer speed, dispensing rate and reactor pressure. The temperature is controlled by a Pt100 sensor inside the reactor.

2.3. General description of the modification process

A general description of the modification process is presented below. A propellant was placed inside a reactor in a dispersing medium (water) and conditioned at a specific temperature (from 20 to 50 °C, depending on the process). The modifiers were introduced by dispensing them into an ethanol solution. In the presented methods, dispensing is a two-stage process: nitrate ester with 2-NDPA (used as a dye to determine the thickness of a modified layer) was dispensed first, followed by a polymer solution. A dispensing rate ensuring the best conditions for modifier deposition on the propellant grains, was selected. The propellant was conditioned in the presence of the modifier in solution. The ethanol was distilled under reduced pressure. The last stage in the reactor was cooling to ambient temperature. The propellant was dried and graphite-coated. Table 1 shows the composition of modifiers used in each process. The composition is expressed in phr (parts per hundred) – one part modifier per 100 parts propellant.

Table 1.   Modifier compositions

Propellant name	Content [phr]					
	NG	DNTG	DNDG	2-NDPA	P250	P420
M1	2.3	–	–		1.0	–
M2	8.0	–	–		1.0	–
M3	6.6	–	–		2.0	–
M4	–	2.5	–	0.2	–	–
M5	–	3.0	–		–	0.2
M6	–	–	1.0		1.0	–
M7	–	–	3.0		1.0	–

2.4. Test methods

2.4.1. Analysing the grain geometry

For the tested propellants, length, diameter and thickness of the modified layer and perforation width of randomly selected grains, cut with a scalpel along the perforation, were determined using an optical microscope.

2.4.2. Determining density of the propellant

Density of the analysed propellants was determined using a Micromeritics AccuPyc 1340 gas displacement pycnometry system. The measurements were carried out at 25 °C. For each propellant, 3 series of 10 measurements were carried out and the arithmetic mean of 30 measurements determined.

2.4.3. Determining calorific value of the propellants

The calorific value (Q_s) of the propellants was determined using a IKA C2000 basic calorimeter. A resistance wire with a known calorific value of 2.69 J/g was used for ignition. The measurements were carried out under reduced pressure and were carried out twice for each propellant. The calorimeter constant determination was based on a NC-NG propellant of known calorific value (4922 J/g).

2.4.4. Analysing the dynamic vivacity of the propellants

The dynamic vivacity of the propellants was determined using a manometric bomb with a volume of 25 cm^3, in accordance with STANAG 4115 [16]. A black powder primer was used to initiate the ignition. The changes in pressure with time were recorded. Two measurements were carried out for each propellant at a packing density of $\Delta = 160$ kg/m^3.

An α parameter, determined by the ratio of pressure to the maximum pressure (p/p_{max}) was introduced to interpret the results. The dynamic vivacity (Γ) of propellant was determined using the following equations:

$$\Gamma = \frac{d\alpha}{dt} \cdot \frac{1}{p} \tag{1}$$

$$\alpha = \frac{p}{p_{max}} \tag{2}$$

where: $\frac{d\alpha}{dt}$ – gas production rate, p – pressure, p_{max} – maximum pressure.
A characteristic dynamic vivacity was also determined using the following equation:

$$\Gamma_{ch} = \frac{\sum \Gamma_i}{n} \tag{3}$$

where: Γ_{ch} – characteristic dynamic vivacity, $\sum \Gamma_i$ – total dynamic vivacity for $\alpha = \{0.3; 0.4; 0.5; 0.6; 0.7\}$, n – total number of Γ_i parameters.

2.4.5. Analysing stability of the propellants

Stability of the propellants was measured using a TAMIII heat flow microcalorimeter by TA Instruments. The propellants were placed in 4.3 ml glass ampules, filling the entire volume of the ampules. The measurements were carried out in accordance with STANAG 4582 [17] at 90 °C.

3. Results and discussion

Introducing a modifier into the combustible layer of a propellant changes its ballistic properties. Choosing the right modifiers can affect the gas production rate and improve the performance of propellants. The properties of propellants using liquid nitrate esters: NG, DNDG and DNTG as burn rate modifiers, are compared below.

Table 2 shows the numerical data for propellant grains with modified geometry and for the base propellant. A comparison of the numerical data shows that for all the modified propellants analysed, no significant change in length and diameter of the grain and perforation diameter was observed which indicates that the modifier penetrated the pores of the NC matrix.

In the modification process, 2-NDPA, a bright orange substance, is added along with the modifier. Adding a dye with the modifier allows the thickness of the modified layer to be determined (modified layer thickness – *GWM*). 2-NDPA also stabilises NC. Figure 1 shows the propellant fracture. Orange layers, visible in the picture (outside of the grain and from the perforation side) are the modified layers.
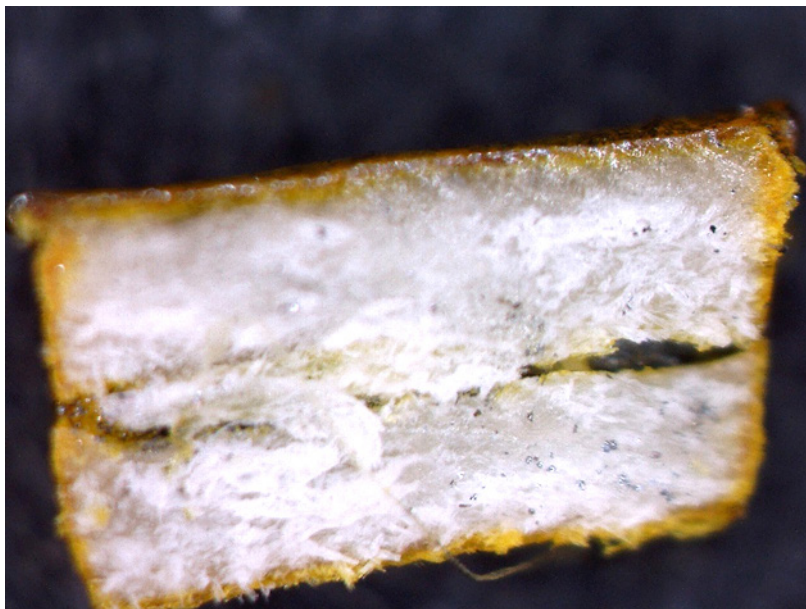
Figure 1. Image of M1 propellant grain fracture; orange layer corresponds to the thickness of the modified layer

Table 2. Average values *L* – length, *D* – diameter, *d* – perforation diameter and *GWM*

Propellant name	*L* [mm]	*D* [mm]	*d* [mm]	*GWM* [μm]
5/1	1.88 ±0.30	1.31 ±0.09	0.34 ±0.05	–
M1	1.86 ±0.18	1.36 ±0.07	0.28 ±0.06	60
M2	1.83 ±0.23	1.30 ±0.08	0.33 ±0.08	100
M3	1.86 ±0.22	1.36 ±0.09	0.34 ±0.05	80
M4	1.80 ±0.22	1.35 ±0.10	0.36 ±0.05	80
M5	1.82 ±0.26	1.30 ±0.05	0.37 ±0.08	80
M6	1.82 ±0.27	1.31 ±0.05	0.31 ±0.05	80
M7	1.83 ±0.29	1.34 ±0.01	0.31 ±0.05	120

Table 2 shows the *GWM* values for modified propellants. The comparison included the layer thickness of the outer grain section only. The modified layer thickness from the perforation side is significantly lower. The highest amount of NG (8.0 phr) was used in the modification of M2 propellant. The modified layer thickness *GWM* of this propellant is 100 μm. The lowest *GWM* was observed for M1 propellant using the least amount of NG (2.3 phr). Using both 2.5 or 3.0 phr of DNTG, and 0.2 phr P420, yielded the same thickness of the modified layer (80 μm). The same thickness was observed for M3 propellant using 6.6 phr NG and 2.0 phr Polios P250. For DNDG-modified propellants, the thickness of the modified layer was determined to be 80 μm for 1.0 phr and 120 μm for 3.0 phr of the modifier. This validates the conclusion that the higher the modifier content, the higher the thickness of the modified layer. Similar amounts of liquid nitrate esters were used in the modification processes of M1 (NG – 2.3 phr), M5 (3.0 phr DNTG) and M7 (3.0 phr DNDG) propellants. Comparison of the *GWM* values for these propellants showed that the highest *GWM* was obtained for the propellant modified with DNDG, followed by those modified with DNTG and NG.

Other properties of the modified propellants, including calorific value, density or characteristic dynamic vivacity, were also analysed. Table 3 shows the obtained values. The values were compared with the values obtained for the base propellant.

**Table 3.** Properties of the modified propellants and the base propellant

Propellant name	Q_s [J/g]	ρ [g*cm^{-3}]	Γ_{ch} [bar^{-1}*s^{-1}]
5/1	3987 ±14	1.643 ±0.002	0.376
M1	3978 ±33	1.625 ±0.001	0.317
M2	4059 ±15	1.609 ±0.003	0.359
M3	4012 ±9	1.609 ±0.004	0.360
M4	4054 ±25	1.618 ±0.006	0.369
M5	3961 ±16	1.615 ±0.003	0.364
M6	3949 ±9	1.620 ±0.001	0.358
M7	3978 ±9	1.626 ±0.001	0.322

The calorific value of the base propellant is 3987 J/g. An increase in calorific value was observed for M2, M3, and M4 propellants. The increase in the calorific value for M2 and M3 propellants is attributed to their higher NG content. The addition of 8.0 phr NG (M2) increased the calorific value by 72 J/g, and at 6.0 phr NG (M3) increased it by 25 J/g. The calorific value of the M4 propellant is a result of using only DNTG in the modification process. In the modification process of M5 propellant, a similar amount of DNTG was used and a polymer, Polios P420, was added in the last stage. Adding a small amount of the polymer (0.2 phr) reduced the calorific value by 93 J/g. For DNDG-modified propellants, the calorific value was reduced (M6) or not affected (M7) compared to the base propellant. Changes in the calorific value are a result of the oxygen balance of the modifiers used. A correct ratio of high-energy modifier to inert modifier will not affect the calorific value of the propellant but only modify its gas production rate.

As a result of the processes, the density determined using a helium pycnometer, has decreased in all the propellants with M2 and M3 propellants showing the lowest density. DNTG-modified propellants (M4 and M5) show similar densities. The highest density was observed for M1 propellant which contains the least amount of NG, and M7 propellant containing 3.0 phr DNDG. The characteristic dynamic vivacity was similar for all the propellants at approximately 0.36 bar^{-1}·s^{-1} with the M1 and M7 propellants showing the lowest values. Figure 2 shows the relationship between the dynamic vivacity and the p/p_{max} parameter of the propellants.
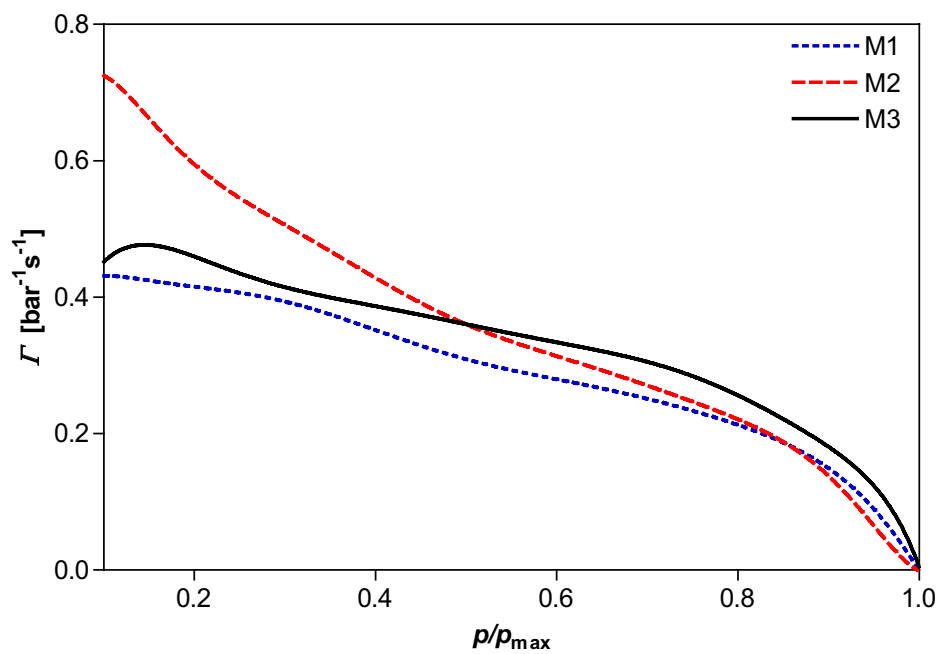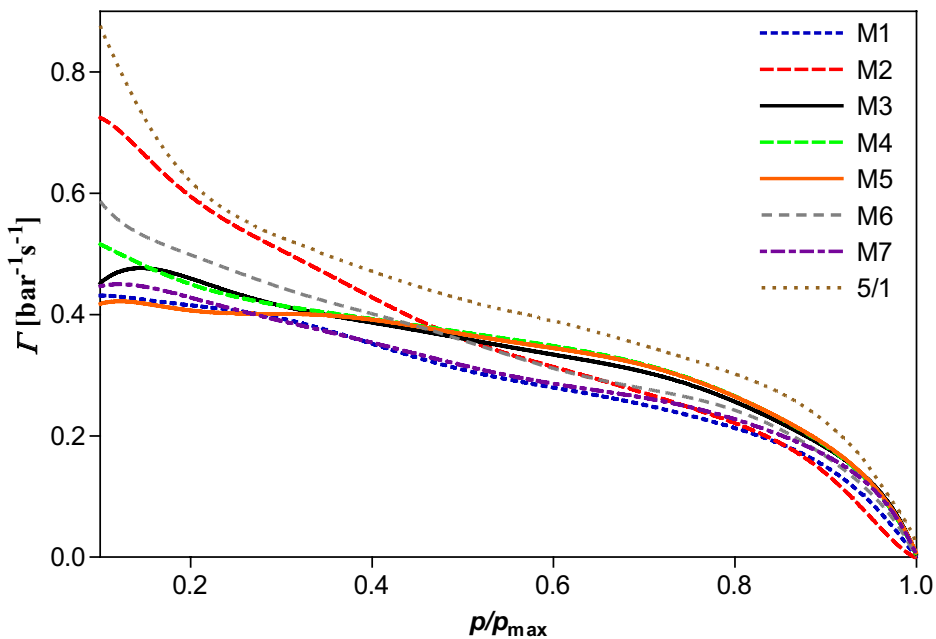
a)
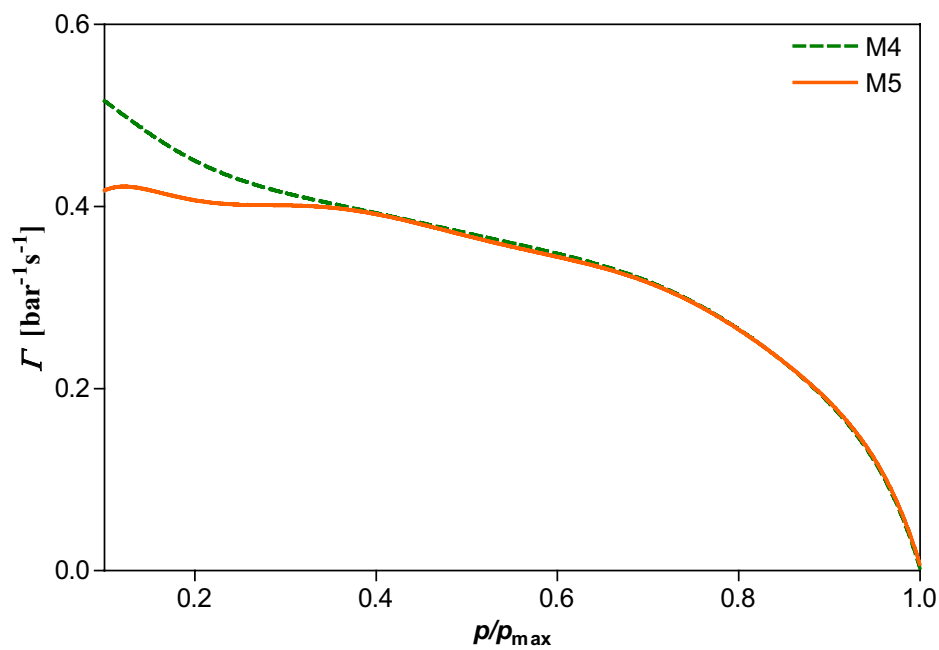
b)
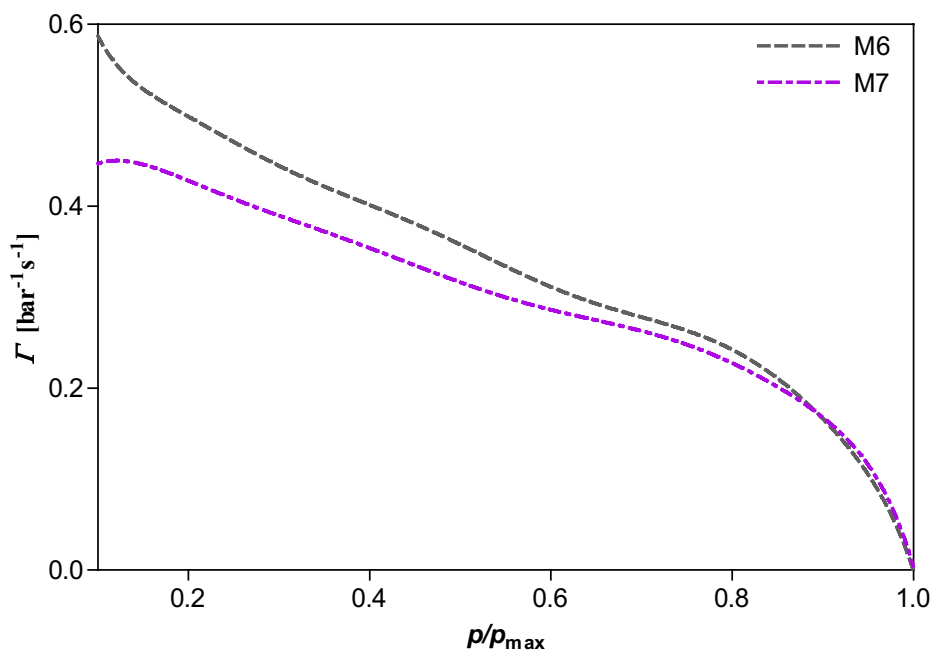
c)

d)

Figure 2. The relationship between dynamic vivacity and the p/p_{max} parameter for: a) NG-modified propellants (M1, M2 and M3), b) DNTG-modified propellants (M4 and M5), c) DNDG-modified propellants (M6 and M7), d) comparison of all modified propellants with the base propellant

In the initial burning stage (up to $p/p_{max} \approx 0.5$), M2 propellant (Figure 2a) with the highest NG content, shows the highest vivacity. M1 and M3 propellants show a similar relationship of the dynamic vivacity. M1 propellant shows the lowest dynamic vivacity. DNTG-modified propellants (Figure 2b) differ with the relationship between dynamic vivacity and the p/p_{max} parameter, only at the initial burning stage (up to $p/p_{max} \approx 0.4$). M4 propellant, at the initial stage, burns with a higher intensity compared to M5 propellant with a polymer layer deposited on its surface. The difference in DNDG modifier content affected the gas production rate (Figure 2c). The propellant with lower DNDG content (M6) shows lower vivacity than M7 propellant, and shows similar burning properties at the final stage (from $p/p_{max} \approx 0.92$). A higher amount of DNDG resulted in better packing of the combustible layer pores, reducing the vivacity which is consistent with the determined *GWM* values; for M7 propellant the *GWM* value is higher than for M6 propellant. Comparison of the modifiers shows that M1 and M7 propellants are characterised by similar dynamic vivacity. M3 and M4 propellants also show a similar relationship indicating the possibility of replacing NG with DNDG and DNTG nitrate esters, providing a lower environmental impact, in the modification processes.

To determine their stability, the propellants were analysed using heat flow microcalorimetry in accordance with STANAG 4582 [17]. The results obtained from heat flow microcalorimetry can be represented as a relationship between the calorific value (*P*) and time (*t*) (Figure 3). Another option is representing it as a relationship between the accumulated heat (*Q*) and time (*t*), expressed as:

$$Q = tk_Q + c \tag{4}$$

where: is the generated heat rate constant, *c* is a constant. It is a two-stage relationship for diphenylamine (DPA)-stabilised propellants [18]. The first stage is related to a decomposition process controlled by DPA and the second stage – to a decomposition process not controlled by DPA. Using this equation, constant rates for the first stage and for the second stage, Q_{tr} and t_{tr} parameters – a point of intersection between the two stages was determined, see Table 4. Point t_{tr} corresponds with a good approximation to a complete reaction of DPA in the propellant sample.

Table 4. List of rate constants, k_Q^1, k_Q^2, Q_{tr} and t_{tr} parameters for the modified propellants and base propellant

Propellant name	k_Q^1	k_Q^2	Q_{tr} [J/g]	t_{tr} [day]
5/1*	3.39	11.72	23.37	6.3
M1	2.72	8.08	28.82	9.3
M2	6.98	9.10	16.34	1.9
M3	4.40	5.37	17.04	2.8
M4	2.72	5.73	19.86	6.2
M5	3.53	6.83	25.62	6.4
M6	2.81	7.46	23.49	7.4
M7	2.50	6.95	23.09	8.1

* data from [18]

Comparison of t_{tr} parameter for modified propellants shows that using a higher amount of NG (M2 and M3 propellant) uses up the stabiliser to a greater extent compared to the other propellants and the base propellant. Using DNTG and depositing a layer of the second modifier to the propellant surface does not affect the loss of stabiliser (M4 and M5 propellants) which, in this case, is similar to the base propellant. The stabiliser loss was slowest in the M1 propellant. The stabiliser loss for DNDG-modified propellants (M6 and M7) is 7.4 days and 8.1 days, respectively and is longer than that observed for the base propellant.
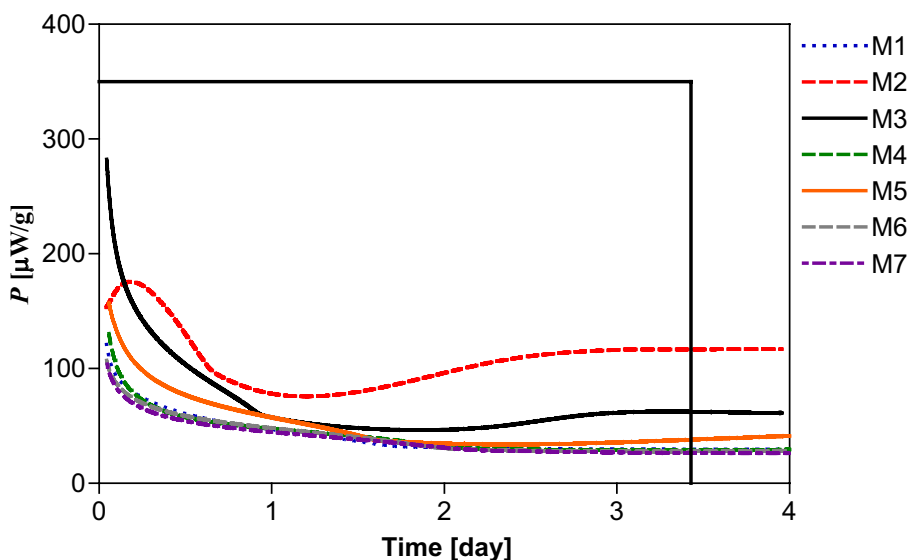
Figure 3. HFC curves for modified propellants

STANAG 4582 [17] is used to determine if the analysed propellant will be stable over 10 years of storage at 25 °C. At 90 °C, the temperature at which the propellants are analysed, the heat flow must not exceed 350 μW/g in 3.43 days. Figure 3 shows the relationship between heat flow and time for the modified propellants. All analysed propellants meet the STANAG 4582 requirements, since the heat flow does not exceed the assumed value over the given time. The propellants can be safely stored for 10 years at 25 °C.

4. Summary

♦ Liquid nitrate esters (NG, DNTG and DNDG) are good modifiers of single-base nitrocellulose-based propellants. The nitrate ester used depends on the properties required for the modified propellant. NG increases the calorific value of the propellant but also causes high-intensity propellant burning in its initial phase. Choosing the right NG-polymer (M1 propellant) ratio did not result in a change to calorific value compared to the base propellant; a similar relationship has been observed for DNDG-modified propellants. Using DNTG without an inert modifier will increase the calorific value compared to the base propellant.

♦ Gas production rate differs depending on the type and amount of modifier used. Choosing the right amount and type of modifier will yield similar dynamic vivacity correlations. The modifier type affects the DPA loss rate. The stabiliser is used up at the highest rate in propellants with the highest NG content. Using DNDG or DNTG does not increase the stabiliser loss rate compared to the base propellant.

♦ All modified propellants will remain stable for 10 years at 25 °C. The analyses show that NG can be substituted with other nitrate esters provided that the right amount of modifier is used.

Acknowledgements

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