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Research paper / Praca doświadczalna

Methods of modifying single base propellants using centralite I, dibutyl phthalate and rosin Metody modyfikacji prochów jednobazowych z wykorzystaniem centralitu I, ftalanu dibutylu i kalafonii

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Abstract: Modification processes were carried out using combustion modifiers such as centralite I, dibutyl phthalate (DBP) and rosin. Modifications were carried out using three methods: water, alcohol and suspension. The effect of the amount and type of combustion modifiers and the method of their introduction on the change in the properties of the powders, was studied. The effective introduction of rosin without intergrain adhesion can be achieved using only the alcohol method. It was found that the geometry of the powders after modification did not change. The method of conducting the process affects the thickness of the modified layer in the range of 12 to 24%. In propellants modified by the alcohol method with rosin, a reduction in dynamic vivacity and an increase in bulk density were observed relative to the original propellant. All modification processes reduced the calorific value relative to the original propellant. Modifications carried out from an aqueous suspension reduce dynamic vivacity relative to the original propellant at the initial stage of combustion.

Streszczenie: Przeprowadzono procesy modyfikacji stosując takie modyfikatory spalania jak: centralit I, fialan dibutylu (DBP) i kalafonia. Modyfikacje prowadzono trzema metodami: wodną, alkoholową i zawiesinową. Zbadano wpływ ilości i rodzaju modyfikatorów spalania oraz metody ich wprowadzania na zmianę właściwości prochów Efektywne wprowadzenie kalafonii bez adhezji międzyziarnowej można osiągnąć stosując jedynie metodę alkoholową. Stwierdzono, że geometria prochów po modyfikacji nie uległa zmianie. Sposób prowadzenia procesu wpływa na grubość warstwy zmodyfikowanej w zakresie od 12 do 24%. W prochu modyfikowanym metodą alkoholową z kalafonią zaobserwowano obniżenie żywości dynamicznej oraz zwiększenie gęstości usypowej względem prochu bazowego. Wszystkie procesy modyfikacji wpłynęły na obniżenie kaloryczności względem prochu bazowego. Modyfikacje prowadzone z zawiesiny wodnej obniżają żywość dynamiczną względem prochu bazowego w początkowym etapie spalania.

Keywords: modification of combustible layer, change of powder properties, rosin, centralite I, dibutyl phthalate

Słowa kluczowe: modyfikacja warstwy palnej, zmiana właściwości prochu, kalafonia, centralit I, ftalan dibutylu

1. Introduction

The single-base propellants currently manufactured in Poland do not meet the requirements for propellants for NATO ammunition. A major disadvantage is the low heat of combustion and high hygroscopicity affecting the change in ballistic performance during storage. In addition, single-base propellants have a regressive combustion character. The amount of energy is limited by the content of nitrocellulose, the main ingredient in the propellants. Improvements in ballistic performance can be achieved by modifying the structure of the combustible layer by introducing substances into the propellant which reduce porosity, resulting in a reduction in the rate of gas generation in the initial stage of combustion. The modified layer shows less hygroscopicity and is more resistant to changing conditions during storage. Modifier in the combustible layer should be distributed unevenly [1]. The even introduction of the modifier into the combustible layer results in a decrease in the burning rate. This then leads to a regressive combustion of such a propellant [2]. Determining the correct amount of combustion modifier, as well as the depth to which they should be introduced, makes it possible to obtain propellants with the expected ballistic parameters. Another proposed method for obtaining propellants with altered ballistic parameters is by using gradient denitration. This involves the removal of nitro groups from the outer surface of the propellant [3].

One method for the modification process is the introduction of modifiers using a solvent. The dispersion medium can be water [4] or organic solvents [5]. The process involves the diffusion of a phlegmatiser into the combustible layer of the propellant. The most significant advantage of this technology is the reproducibility of the ballistic properties of the modified propellant. This is possible due to a more uniform distribution of modifiers on the grain surface [6]. Various combustion rate modifiers can be introduced by this method and descriptions of modifications with:

- 1,3-diethyl-1,3-diphenylurea (centralite I) [7],
- dibutyl phthalate (DBP) [8],
- 2,4-dinitrotoluene [9],
- propane-1,2,3-triol triazotate [10],
- diethylene glycol diazotate [11],
- triethylene glycol diazotate [11] and other [12]

can be found. Książczak *et al.*, applying various modification methods and using different modifiers, developed modified propellants which meet the ballistic requirements for different types of ammunition [13-15]. Analysing the literature reports, it can be concluded that ballistic parameter adjustment can be achieved by changing the type of modifier and its concentration, the time and type of modification method, and changing the process guidance parameters.

The aim of this study was to carry out a modification process using different modifiers of the combustible layer with the use of three different modification methods. The modifiers used included: centralite I, DBP and rosin. It was examined how the methods and modifiers used changed the physico-chemical and ballistic properties of the modified propellants.

2. Experimental part

2.1. Raw materials used in the modification process

Modification processes were carried out on nitrocellulose single-channel propellant with a grain length of 1.68 ± 0.31 mm, a diameter of 0.74 ± 0.04 mm, a combustible layer thickness of 0.31 ± 0.02 mm, and

a channel diameter of 0.12 ±0.02 mm. The propellant was manufactured by Mesko S.A. Centralite I was used as a stabiliser. Hereafter, the propellant will be referred to as WTwaC1 propellant. The modification processes were carried out using two dispersion media: distilled water and 99.8% fully denatured ethanol (from Hurtownia Odczynników Chemicznych, Butra, Poland). The following were used as combustion modifiers: centralite I (Mesko S.A.), DBP with a purity of 98% (POCH S.A.), rosin (Biomus Sp. z o.o.) and graphite (Mesko S.A.). 2-Nitrodiphenylamine (2-NDPA with a purity of 99.7% synthesised at the Department of High Energy Materials, Warsaw University of Technology) was used as an indicator of the depth of penetration of the modifier.

2.2. Instruments for the modification process

All modification processes were carried out in the same setup. The system included a 500 ml flat-bottom glass cylindrical reactor vessel. A five-necked lid housing a thermometer, a mechanical stirrer and a distillation column fed by tap water. The stirrer was placed 0.5 cm from the bottom of the vesselr. The system was fitted with a vacuum pump with a KNF Lab SC920 controller and a Huber Minichiller thermostat. The vessel was housed in a WSL TPP 100-4/200 thermostat, using distilled water as the medium.

Graphitisation of the modified propellants was carried out in a Heidolph Hei-VAP Adventage rotary evaporator. The evaporator equipment included the following: water bath, spiral cooler, vacuum pump with KNF Lab SC920 wireless controller, Huber Minichiller thermostat, 500 ml ribbed flask and a 1000 ml round-bottom flask (receiver).

2.3. General description of the modification process

The modification processes were carried out using three methods: water, alcohol and suspension.

Water method (W). 250 ml of water and 50 g of source propellant were introduced into the reactor vessel, and the system was then conditioned at 50-70 °C for 1.5-3 h while maintaining continuous stirring (400 rpm). The alcoholic modifier solution was then dosed at the appropriate rate. The next step was to distil the solvent under reduced pressure. If the solution became cloudy, salting out was used. A certain amount of inorganic salt – potassium sulphate or sodium chloride – was introduced into the vessel. The purpose of salting out was to reduce the solubility of the modifier in the solution to ensure greater efficiency of penetration into the combustible layer of the propellant. The system was cooled to T = 25 °C. The propellant was then drained and pre-dried at T = 60 °C for 15 min. They were graphitised in a rotary evaporator at T = 60 °C at 60 rpm. The graphitised propellants were dried in a flow dryer at T = 60 °C to constant mass.

Alcohol method (A). 250 ml of ethanol, 50 g of source propellant and a modifier were introduced into the vessel. The system was then conditioned at T = 50 °C for 3 h at 600 rpm. The next step was the dosage of water to reduce the solubility of the modifier in ethanol. The remaining operations were carried out in the same way as in the water method.

Suspension method (Z). 50 g of propellant, 250 ml of distilled water and the appropriate amount of modifier were introduced simultaneously into the vessel. The system was conditioned for 3 h with continuous stirring (400 rpm). Further operations were identical to the water and alcohol methods.

Table 1 shows the modifier compositions used in each process. The compositions are given in parts per hundred (phr) – one part of modifier per 100 parts of propellant. In each modification, 0.2 phr 2-NDPA was used as an indicator of modifier penetration into the combustible layer. In the graphitisation processes, 0.2 phr of graphite was introduced.

Process	Centralite I [phr]	DBP [phr]	Rosin [phr]	K ₂ SO ₄ [g]	NaCl [g]	Modification method*)
P1	3.0	_	-	-	_	W
P2	2.1	_	_	_	_	Z
Р3	_	2.0	-	2.5		Z
P4	3.0	_	-	2.5	_	W
P5	_	_	3.0	-	1.0	W
P6	_		3.0	_		A

Table 1. Modifier compositions used

The P1 process used an approximately 5% solution of centralite I in ethanol with 2-NDPA, and the P4 process used approximately 10%. For processes P3, P4 and P5, salting out with NaCl and K₂SO₄ was used due to high turbidity in the vessel. The P5 process used approximately 10% rosin in ethanol. During the cooling stage, it was noticed that the propellant grains stick together due to the high surface adhesion (Figure 1). An attempt was made to mechanically separate the grains by reintroducing them into a reactor with a mechanical stirrer. This did not yield satisfactory results. Due to the high adhesion of the grains, they were not tested further. The method of introducing rosin into the combustible layer of the gunpowder was changed using the alcohol method – the P6 process. To precipitate the modifier, water was dosed into the system.



Figure 1. Glued propellant grains after P5 modification with 3 phr rosin

2.4. Test methods

2.4.1. Grain geometry test

The geometric parameters of the modified propellants were determined using a Delta Optical Smart 5M PRO optical microscope. For those tested, the width (d_z) and length (I) of 100 randomly selected grains were measured. The grains of the modified grains were sectioned to determine the diameter of the channel (d_k) , the thickness of the combustible layer (d_{wp}) and that of the modified layer (d_{wm}) . The cut was made with a scalpel along the channel. In Figure 2, the geometric measurement methodology for the grain (A) and its cross-section (B) is shown.

^{*} W – water method, A – alcohol method, Z – suspension method

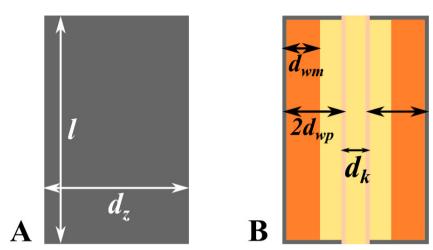


Figure 2. Methodology for measuring grain geometry (A) and its cross-section (B) including the method of measuring l, d_z , d_k , $2d_{wp}$ and d_{wm}

2.4.2. Propellant density test

The densities of the propellants following modification were determined using a Micromeritics AccuPyc 1330 helium pycnometer, filling approximately two-thirds of the volume of the measuring vessel with the test material. For each sample, 2 series of 10 measurements were taken at 25 °C. The density value determined is the average of the measurements taken.

2.4.3. Combustion heat testing of the propellants

The calorific value of the modified propellants was tested using an IKA C2000 basic calorimeter. Measurement of the heat of combustion was carried out at a reduced pressure of 3-4 mbar. A resistance wire with a heat of combustion of 2.69 J/cm was used as the igniter. Each propellant was measured twice. The calorimetric constant was determined using a double-base propellant with a known heat of combustion of 4922 J/g.

2.4.4. Testing the dynamic vivacity of propellants

Dynamic vivacity testing was performed using a 25 cm³ fixed volume manometric bomb, in accordance with STANAG 4115 [16]. Ignition was carried out using a black gunpowder igniter and 200 mg of black gunpowder was used for testing. The change in pressure over time was recorded. For each propellant, 2 measurements were made at a charge density of $\Delta = 160 \text{ kg/m}^3$.

In order to interpret the results, a parameter α was introduced, defined as the ratio of pressure to maximum pressure (p/p_{max}) . The dynamic vivacity (Γ) is described by the 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 release rate, p – pressure, p_{\max} – maximum pressure. In addition, the characteristic dynamic vivacity was defined by the equation:

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

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

Dynamic vivacity graphs were also drawn up for p/p_{max} values equal to: 0.3, 0.4, 0.5, 0.6 and 0.7 to accurately describe the combustion characteristics of the propellants. The resulting points are described by the linear equation (Equation 4).

$$\Gamma = A \frac{p}{p_{\text{max}}} + B \tag{4}$$

where: A – directional coefficient of the straight line (progressivity coefficient), B – free expression.

2.4.5. Bulk density test

Tests were carried out for all modified propellants. The volume of the vessel was 3.1840 ± 0.0078 cm³. As much propellant as possible was poured into the vessel, in such a way as to allow the shell pin to close freely. The result of the bulk density measurement is the arithmetic average of the three measurements.

2.4.6. Determination of modifiers by high-performance liquid chromatography

Modifier content was determined by high-performance liquid chromatography (HPLC). An Aglient 1260 Infinity liquid chromatograph was used. The analysis was performed in accordance with STANAG 4620 [17]. 200 ± 2 mg of propellant was introduced into 100 ml volumetric flasks. 50 ml of acetonitrile was added to the flasks. To dissolve the propellant completely, the flasks were agitated every 15 min for 4 h. The propellant samples were stored in a darkened area. 10 ml of a 2% aqueous solution of calcium chloride $CaCl_2$ was added to the flasks (to precipitate nitrocellulose – NC). The flasks were topped up to the mark with water and agitated in the same way for 1 h. Samples (1.5 ml) were taken for analysis and filtered through a disposable syringe filter with a pore size of 0.45 μ m. Each sample was analysed three times.

3. Results and discussion of the results

The use of different combustion modifiers allows the properties of single base propellants to be altered in different ways. Properties are also influenced by how the modification process is carried out. The use of centralite I, DBP and rosin as combustion modifiers using different modification methods is compared below. Table 2 summarises the data for the geometric parameters of the grains. The determination of these parameters was carried out to test the effect of the modification on the grain size and the penetration depth of the modifier.

Table 2. Geometrical parameters of grams after meanitations						
Powder	Dimension [mm]					
rowaer	L	d_z	d_k	$2d_{wp}$	d_{wm}	
WTwaC1	1.68 ± 0.31	0.74 ± 0.04	0.12 ± 0.02	0.31 ± 0.05	_	
P1	1.43 ±0.28	0.73 ± 0.04	0.11 ± 0.02	0.31 ± 0.05	0.04 ± 0.02	
P2	1.65 ±0.21	0.81 ± 0.04	0.13 ± 0.03	0.33 ± 0.05	0.06 ± 0.02	
Р3	1.53 ±0.25	0.73 ± 0.04	0.08 ± 0.03	0.25 ± 0.07	0.03 ± 0.01	
P4	1.58 ±0.25	0.77 ± 0.04	0.15 ±0.04	0.30 ± 0.05	0.04 ± 0.02	
P6	1.63 ±0.27	0.77 ± 0.05	0.17 ± 0.04	0.33 ± 0.06	0.08 ± 0.02	

Table 2. Geometrical parameters of grains after modifications

The modification processes reduced the mean value of the grain length, but when the standard deviation taken into account, the length did not change. The grain diameter values are within the standard deviation of the source grains. The highest percentage of modified layer width to combustible layer width was obtained for propellant P6 (rosin, alcohol method), at 24%. The lowest percentage of modified layer was obtained for the P3 process (12%), indicating that the use of the suspension method for DBP resulted in a not very deep penetration of the modifier. For the second process performed using the suspension method (P2), the combustible layer accounts for 18%. This means that centralite I is easier to introduce using this method. For processes P1 and P4, where different modifier concentrations in ethanol were used, the combustible layer represents 13%. It should be noted that the flammable layer on the channel face does not undergo a modification process. Phlegmatisation of the surface on the channel face is achieved by applying variable pressure during the process. In the initial stage of the process, the pressure in the system should be lowered to decongest the channel and introduce the modifier solution. Variable pressure was not used in the processes carried out, and therefore access of the modifying solution to the inner part of the channel was hindered and did not result in modification. Figure 3 shows an example of a grain after modification and its cross-section. Table 3 summarises the determined values of the heat of combustion, specific density and bulk density of the tested samples. The resulting heat values were compared with the WTwaC1 source propellant.



Figure 3. Example of grain and its cross-section for propellant P1

Propellant	Combustion heat [J/g]	Density [g/cm ³]	Bulk density [g/cm ³]
WTwaC1	4168 ±1	1.623 ± 0.004	0.877 ± 0.015
P1	3781 ±36	1.623 ±0.003	0.891 ±0.008
P2	4007 ±1	1.632 ± 0.004	0.859 ± 0.020
P3	3960 ±2	1.619 ± 0.003	0.872 ± 0.013
P4	3768 ±6	1.610 ± 0.004	0.865 ± 0.004
P6	3567 ±8	1.619 ± 0.003	0.932 ± 0.023

Table 3. Summary of properties tested for modified and source propellants

All modifications reduced the calorific value relative to the source propellant. Modification with DBP (P3) has a calorific value approximately 50 J/g lower than modification with centralite (P2), carried out in the same way. Rosin-modified P6 propellant shows the lowest heat of combustion. The P1 process carried out with about 5% modifier solution has a similar heat of combustion to the P4 process, where a higher concentration of modifier solution (10% approx) was used.

Modification processes P1, P3, P6 did not affect the density value compared to the source propellant. Powder P2 has a higher density relative to the WTwaC1 source propellant. Powder P4 has the lowest density value. Powder P3, modified with DBP, has the same density as propellant modified with rosin (P6), while its density is lower than P2, modified in the same way.

Powders modified with centralite I and DBP show a lower bulk density compared to the reference propellant. The highest bulk density value was obtained for rosin-modified P6 propellant. The reason for this may be not only the type of modifier used but also the way the process is conducted. The use of ethanol as a dispersing medium and the water dosing led to a more efficient deposition of the modifier on the surface of the gunpowder grain compared to water-based processes, to which alcoholic modifier solution was dosed or the propellant in the modifier solution, directly conditioned.

Figure 4 shows the changes in the vivacity of the modified propellants. The results were compared with the source propellant WTwaC1, which burns regressively. All modified propellants burn progressively in the initial stage of combustion up to a p/p_{max} parameter value of around 0.40. Changing the alcohol concentration does not affect the dynamic vivacity of P1 and P4. Modification from a P2 aqueous suspension reduced the dynamic vivacity relative to WTwaC1 to $p/p_{max} = 0.40$. Modifications P3 and P6 reduced dynamic vivacity relative to WTwaC1, over the entire tested range. For a value of $p/p_{max} = 0.20$, the vivacity of DBP -modified propellant is 0.2 bar⁻¹·s⁻¹ higher than that of rosin-modified gunpowder. The characteristic dynamic vivacity and coefficients of Equation 4 were also determined. The results are shown in Table 4.

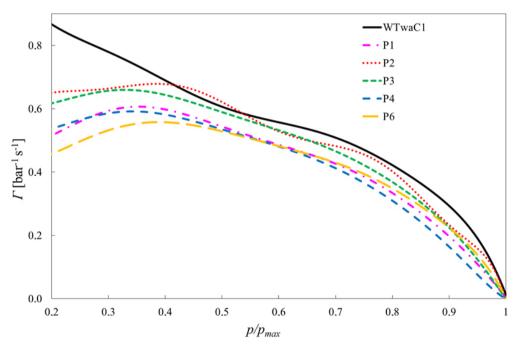


Figure 4. Variations in dynamic vivacity for modified propellants

Table 4. Characteristic dynamic vivacity and coefficients of Equation 4

•	,	1	
Powder	Γ_{ch} [bar ⁻¹ ·s ⁻¹]	A	<i>B</i> [bar ⁻¹ ⋅s ⁻¹]
WTwaC1	0.63	-0.674	0.966
P1	0.53	-0.446	0.753
P2	0.60	-0.513	0.852
P3	0.58	-0.493	0.824
P4	0.52	-0.447	0.743
P6	0.51	-0.257	0.614

Powders P1 and P4, which differ in the amount and concentration of the dosed modifier solution, show a similar value for the A parameter (progressivity coefficient) including a characteristic dynamic vivacity. The use of ethanol as a dispersion medium (P6) resulted in the lowest characteristic dynamic vivacity. Powders from the suspension method – P2 and P3 – are characterised by similar values of progressivity and characteristic dynamic vivacity. The effectiveness of the introduction of modifiers was also tested; the results of the determined amounts are shown in Table 5. The proposed determination method could not be used to determine the rosin content.

Table 5. Determined amounts of modifiers

Powder	Centralite I [phr]	DBP [phr]	2-NDPA [phr]	Added number of modifiers [phr]
WTwaC1	1.0	_	_	_
P1	3.7	_	0.2	3.0 Centralite I
P2	2.6	_	0.2	2.1 Centralite I
Р3	1.1	1.5	0.1	2.0 DBP
P4	3.7	_	0.2	3.0 Centralite I

Modification processes with centralite I led to effective embedding of the modifier in the grains. The increased amount of determined modifier, relative to the amount added, is due to the fact that centralite I acts as a stabiliser and is a component of the source material. The largest amount of centralite was introduced into P2. A smaller amount of the determined modifier in relation to the amount added is shown by P3, modified with DBP which is obtained by the suspension method.

4. Summary

- Processes were carried out to modify the combustible layer of the source propellant with three combustion modifiers: centralite I, DBP and rosin. The processes were carried out using three different modification methods.
- ♦ The study found that the geometry of the propellants did not change after modification. The method of carrying out the process affects the thickness of the modified combustible layer. The combustible layer, in the aqueous and suspension methods, was modified between 12% and 21%. Modification P6, carried out in ethanol, allowed the combustible layer to be modified by up to 24%.
- All the modifications resulted in a reduction in calorific value relative to the source material. Increasing the concentration of the modifier solution for processes P1 and P4 does not significantly alter the calorific value.
- P1 and P4 have a similar dynamic vivacity and progressivity coefficient. Modifications carried out from an aqueous suspension, reduce the dynamic vivacity relative to the source material in the initial stage of combustion.
- The P2 modification process increased the density relative to the source material. The other modifications did not result in a similar change in density.
- ♦ It is not possible to introduce rosin into the structure of the combustible layer of the grain in the modification process carried out by the water method. This method of modification causes the propellant grains to stick together, due to high intergrain adhesion. The effective introduction of rosin without inter-grain adhesion can be achieved using the alcohol method.

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