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Research paper / Praca doświadczalna

# Theoretical analysis of the use of glycidyl polyazide and polynitratomethylmethyloxetane in high-performance reduced-smoke rocket propellants Poliazydek glicydylu i poliazotanometylometyloksyetan w wysokowydajnych paliwach rakietowych o zmniejszonym

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Abstract: Conducting preliminary calculations of the ballistic effectiveness and smoke generation of new rocket propellant compositions is beneficial due to the high cost of tests. In this work, the combustion temperature  $(T_{comb.})$  and specific impulse  $(I_{sp})$  for rocket propellants were determined using the Air Force Specific Impulse Program. The effect of replacing the non-energetic binder hydroxyl terminated polybutadiene (HTPB) with binders containing explosophoric groups with glycidyl polyazide (GAP) or polynitratomethylmethyloxetane (polyNIMMO), and replacing ammonium perchlorate (AP) with ammonium dinitramide (ADN) are discussed. The highest  $T_{comb}$ . and the highest  $I_{sp}$  were obtained for a system containing 20% GAP, 60% ADN and 20% Al. Another important aspect of modern rocket propellants is smoke intensity, so smoke classifications were determined for the proposed compositions in accordance to the classification given in a report by the Advisory Group for Aerospace Research & Development (AGARD).

The use of the new components - GAP, polyNIMMO and ADN - is beneficial because it enables a higher  $I_{sp}$  and reduced smoke. The maximum  $I_{sp}$  of these propellants is obtained for compositions containing higher amounts of binder, which facilitates the manufacturing process. The use of computer calculations in the first phase of research into new rocket propellants makes it possible to estimate the improvement in performance of the new propellant and to learn about the impact of composition changes on performance.

Streszczenie: Przeprowadzenie wstępnych obliczeń efektywności balistycznej oraz dymności nowych składów paliw rakietowych jest korzystne ze względu na wysokie koszty badań gotowych wyrobów. W pracy, przy wykorzystaniu programu Air Force Specific Impulse Program wyznaczono temperaturę palenia (T<sub>comb.</sub>) i impuls właściwy (I<sub>sp</sub>) układów trójskładnikowych zawierających jako utleniacz:

chloran(VII) amonu (AP), sól amonową dinitroaminy (ADN), jak lepiszcze: polibutadien zakończony grupami hydroksylowymi (HTPB), poliazydek glicydylu (GAP), poliazotanometylometyloksyetan (NIMMO) oraz glin (Al). Omówiono wpływ zastąpienia nieenergetycznego lepiszcza HTPB, lepiszczami zawierającymi grupy eksplozoforowe oraz zastąpienie AP ADN. Opisano również wpływ Al na temperaturę i I<sub>sp</sub> omawianych paliw. Najwyższą T<sub>comb</sub>, oraz najwyższy I<sub>sp</sub> uzyskano dla układu GAP-ADN-Al. Kolejnym istotnym aspektem nowoczesnych paliw rakietowych jest intensywność dymienia. Określono klasy dymienia według klasyfikacji AGARD zaproponowanych składów. Zastosowanie nowych składników GAP, NIMMO i ADN jest korzystne, ponieważ: pozwala na uzyskanie większego I<sub>sp</sub> oraz zmniejszonego dymienia. Maksimum I<sub>sp</sub> tych paliw jest uzyskiwane dla składów zawierających większe ilości lepiszcza, co ułatwia proces wytwarzania. Wykorzystanie obliczeń komputerowych w pierwszym etapie badań nad nowymi paliwami rakietowymi pozwala na oszacowanie poprawy parametrów użytkowych nowego paliwa oraz poznanie wpływu zmian składu na parametry użytkowe.

**Keywords:** solid rocket propellants, specific impulse, combustion temperature, HTPB, GAP, polyNIMMO, ammonium dinitramide, ammonium perchlorate

*Słowa kluczowe:* stałe paliwa rakietowe, impuls właściwy, temperatura palenia, HTPB, GAP, NIMMO, sól amonowa dinitroaminy, chloran(VII) amonu

## 1. Introduction

The range and load of a rocket depends on the design of the rocket motor and the rocket propellant [1]. The use of a rocket propellant with a higher ballistic efficiency, using the same engine design, yields increased rocket performance characteristics. The use of a rocket propellant with a specific impulse  $(I_{sp})$  of 260 instead of 255 s increases its lift capacity by 10% [2]. New, more energetic components are being sought to increase the ballistic efficiency of rocket propellants. Due to rocket propellant tests being very expensive, preliminary calculations of the ballistic effectiveness of new rocket propellant compositions are often conducted. The above approach is presented a paper by Lempert et al. [3], which contains a comparative analysis of the ballistic effectiveness of heterogeneous rocket propellants containing metallic additives such as aluminium (Al), zirconium (Zr) or zirconium hydride ( $ZrH_2$ ) as components increasing the energetics of a system. The calculations were performed for two types of binder (non-energetic - hydrocarbon with the formula  $C_{73,17}H_{120,9}$ ; and active – polyvinyltetrazole plasticised with nitroglycerine and 2,4-dinitrodiazapentane  $C_{18.96}H_{34.64}N_{19.16}O_{29.32}$ ) and several oxidants. The calculations showed that, for most oxidisers, the use of Zr and its hydride increases the ballistic effectiveness of rocket propellants. Only when octogen was added did the use of Zr and its hydride reduce the ballistic efficiency of the propellant. In modern heterogeneous rocket propellants, 3 main components can be distinguished: oxidiser – compounds devoid of halogen atoms are preferred; high-energy binder; and energetic filler [4]. Ammonium perchlorate (AP) is commonly used as an oxidiser, while ammonium dinitroamide (ADN) constitutes a promising, environmentally friendly compound which could replace it [5]. The main disadvantage of AP is the formation of large amounts of hydrogen chloride during the combustion of a propellant containing it. Hydrogen chloride has a devastating effect on the environment and produces a plume behind a flying rocket. Currently, polymers which do not contain explosive groups are used as binders, e.g. polybutadiene with hydroxyl end groups (HTPB), BKN [6, 7]. Application studies are being conducted on new high-energy binders such as:

- glycidyl polyazide (GAP): H-[-OCH<sub>2</sub>CH(CH<sub>2</sub>N<sub>3</sub>)-]<sub>n</sub>-OH, and

- polynitratomethylmethyloxetane (polyNIMMO): HO-[-CH<sub>2</sub>-C(CH<sub>3</sub>)(CH<sub>2</sub>ONO<sub>2</sub>)-CH<sub>2</sub>-O-]<sub>n</sub>-H.

The use of energetic binders improves performance and physical properties of rocket propellants [8, 9]. Solid heterogeneous rocket propellants with polyNIMMO were found to have high efficiency and low susceptibility to damage [10]. The use of GAP produces an increase in  $I_{sp}$  of 4-10% compared with propellants based on HTPB [11]. Propellants with GAP and ADN present a higher  $I_{sp}$  compared with those

composed of HTPB, AP and AI [12]. The use of different additives, e.g. CL-20 for propellants with GAP, increases the combustion rate [13]. Propellants containing AN and GAP are described in literature as having low sensitivity, smokeless combustion and high efficiency [14] The use of GAP and high-energy fillers, e.g. hexogen, leads to a reduction in the propellant's AP content and, consequently, a reduction in smoke [15]. This paper discusses the impact of replacing the non-energetic HTPB binder in rocket propellants with binders containing GAP and polyNIMMO explosophoric groups. Smoke classes were also assigned in accordance with the Advisory Group for Aerospace Research & Development (AGARD) classification [16].

## 2. Results

#### 2.1. Combustion temperature (T<sub>comb.</sub>) and I<sub>sp</sub>

The  $I_{sp}$  calculations were conducted on three-component systems: binder, oxidiser and Al as a component raising the energy of the system. It was decided that the amount of binder would range from 10 to 30 wt.%. Calculations were performed for systems containing 0, 10 and 20% Al. AP and ADN were taken as the oxidiser. To determine  $T_{comb.}$  and  $I_{sp}$  the Air Force Specific Impulse Program was used [17]. An engine chamber pressure of 70 atm and gas expansion to 1 atm, were assumed. Oxygen balance (OB) was also used in the mixture analysis. OB is a parameter characterising the amount of oxygen required to oxidise a mixture of combustible compounds and, for oxidisers, describes the amount of oxygen given off during their decomposition. It is expressed in grams per 100 g of compound. OB of a compound or mixture of compounds with an overall molecular formula  $C_aH_bN_cO_dCl_eY_f$ , is calculated using the following equation:

$$BO = \frac{-1600 \cdot \left(2a + \frac{b}{2} + \frac{n \cdot f}{2} - \frac{e}{2} - d\right)}{M}$$
(1)

where: n – valence of metal Y, M – molar mass calculated from the molecular formula. Figure 1 shows the relationship between  $T_{\text{comb.}}$  and the composition of the binder-oxidiser-Al system. GAP, HTPB or polyNIMMO was used as the binder, while AP or ADN as the oxidiser.



Figure 1. Relationship between  $T_{\text{comb.}}$  and the composition of the binder-oxidiser-Al system with GAP, HTPB or polyNIMMO as the binder and AP or ADN as the oxidiser, and Al as the energy-increasing additive

#### 2.1.1. AP-HTPB

In the AP-HTPB system, as the binder content increases from 10 to 30%, the OB of the propellant decreases from -2% to -73%. This results in a reduction of the  $T_{\text{comb.}}$  from  $\sim3000$  to  $\sim1400$  °C, i.e. by 1600 °C. When increasing binder content from 10% to 12.5%, the change in  $T_{\text{comb.}}$  is relatively small. A further increase in binder content results in a further steady reduction in  $T_{\text{comb.}}$ .

#### 2.1.2. AP-HTPB 10% AI

In this system, as binder content increases from 10% to 30%, the OB of the propellant decreases from -14% to -85%. For the composition 80% AP; 10% HTPB and 10% AI, the calculated  $T_{\text{comb.}}$  is  $\sim3400 \,^{\circ}\text{C}$ , which is 400 °C higher than in the case of 10% HTPB, 90% AP. This difference increases to 700 °C when the HTPB content in the system is 30% ( $T_{\text{comb.}} = 2100 \,^{\circ}\text{C}$ ). The combustion temperature results show that, in the concentration range of 10% to 25% HTPB, AI makes a consistent contribution in increasing the combustion temperature. For changes in the HTPB content ranging from 25% to 30%, despite a reduction in OB from -67% to -85%,  $T_{\text{comb.}}$ , is slightly reduced. This may be associated with phase transformations of the combustion products or the appearance of new compounds in the combustion products. This aspect will be discussed later in the paper.

#### 2.1.3. AP-HTPB 20% AI

In the AP-HTPB-Al system, as the binder content increases from 10% to 30%, the OB of the propellant decreases from -26% to -97%. The combustion temperature of propellant with the lowest binder content is  $\sim$ 3700 °C, which is 300 °C higher than for 10% Al and 700 °C higher than for 0% Al. For propellant with 30% binder content,  $T_{comb.}$  equals 2400 °C. The temperature values for the 10% and Al-free systems are 300 and 1000 °C, respectively. With changes in HTPB content from 10% to 20%, there is a relatively steep reduction in temperature from 3700 to 2500 °C which is associated with the worsening OB. With changes in HTPB content from 20% to 30%, there is a slight reduction in temperature associated, as in the AP, HTPB 10% Al system, with the appearance of condensed HTPB combustion products and the reaching of the Al<sub>2</sub>O<sub>3</sub> melting point. One of the combustion products of a propellant with a negative OB, is soot. Figure 2 shows the relationship between the amount of soot in the combustion products and the propellant composition.



Figure 2. Relationship between the amount of soot in the combustion products and the composition of the AP-HTPB-Al three-component mixture

A reduction in the OB of the propellant results in a decrease in the amount of energy released from its combustion and the formation of an increasing amount of condensed combustion products (soot). For the system containing 10% Al, soot in the combustion products is formed at a 25% HTPB content, which coincides with the onset of inhibition of the combustion temperature decrease. For a system containing 20% Al, soot as a combustion product, is formed at a binder content of ~17% while the combustion temperature drop was inhibited at a binder content of ~20%. Condensed combustion products require the supply of less energy compared to gaseous products to raise the temperature by the same amount. Therefore, despite increasing the binder content from 25% to 30% in a mixture containing 10% Al or from 20% to 30% in a mixture containing 20% Al and decreasing the amount of heat release, the combustion temperature value is only reduced slightly.

#### 2.1.4. AP-GAP system

In the AP-GAP system, as the binder content increases from 10% to 30%, the OB of the propellant decreases from 19% to -13%. The mixture 78% AP, 22% GAP has a zero OB. The  $T_{comb.}$  of the propellant increases with the increasing content of GAP, from 2500 C (10% GAP) to 3000 C (30% GAP), reaching a maximum at 26% binder content.

## 2.1.5. AP-GAP-10% AI

In the AP-GAP-Al system, as binder content increases from 10% to 30%, the OB of the propellant decreases from 6 to -25%. The mixture 76% AP, 14% GAP, 10% Al has a zero OB. For the GAP 10%, Al 10% and 80% AP system, the combustion temperature is 3400 °C. It is 900 °C higher than that calculated for the analogous system without Al. Such a large increase in combustion temperature is related to the introduction of Al and a more favourable OB of +6%, compared with +19% for the GAP 20%, 80% AP system. Despite the large changes in OB for different binder content, the combustion temperature varies little from 3400 °C for 10% binder with a maximum of 3500 °C (14% binder) to 3300 °C at 30% binder. Maximum combustion temperature occurs at zero OB.

## 2.1.6. AP-GAP-20% AI

In the AP-GAP-Al system, with increasing binder content, the OB of propellant AP-GAP-Al (20%) decreases from -16% to -37%. For a GAP 10%, Al 20% and 70% AP system, the combustion temperature is 3900 C, which is 500 C higher than that calculated for an analogous system containing 10% Al. A relatively greater decrease in  $T_{\text{comb.}}$  with increasing GAP content is visible, indicating the effect of a worsening OB.

## 2.1.7. AP-polyNIMMO and AP-polyNIMMO-AI

The waveform of combustion temperature changes in these systems is comparable respectively to those of AP-GAP and AP-GAP-Al. However, these temperatures are correspondingly lower by about 50 °C. The results indicate that the influence of oxygen atoms of the polyNIMMO molecules on the oxidation reaction is less favourable than the breakdown of the azide groups in GAP.

## 2.1.8. Systems containing ADN

Changes in  $T_{\text{comb.}}$  in systems containing ADN, depending on the quantities of individual components, are similar to changes in  $T_{\text{comb.}}$  in systems containing AP, although the maximum combustion temperature values are shifted towards a lower binder content due to the poorer OB of ADN compared to AP. It is only for the ADN-HTPB-AI system that some differences in combustion temperature change waveforms are observed. This may be related to the formation of the new compound aluminium nitride in the combustion products. Figure 3 shows the relationship between the amount of soot and aluminium nitride in the combustion products and the propellant composition.



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Figure 3. The relationship between the amount of soot (a) and aluminium nitride (b) in the combustion products on the composition of the three-component rocket propellant ADN-HTPB-Al

As expected, the inflection of the combustion temperature-binder content curve for the ADN-HTPB-20%Al system occurring at 16% binder, is related to the formation of aluminium nitride. The inhibition of the temperature drop for systems containing 10% and 20% Al at a binder content of around 22-24% is related to the formation of soot in the combustion products.

For all the systems, the effect of Al addition on the combustion temperature is evident. The higher the Al content of the propellant, the higher the combustion temperatures, with two exceptions. For the HTPB-AP-Al system, a reduction in the combustion temperature of rocket propellant composed of ~20% HTPB and ~20% Al compared to a system composed of ~20% HTPB and ~10% Al, is observed. For the HTPB-ADN-Al system, similar combustion temperatures for mixtures with compositions ~17% HTPB; ~20% Al and ~17% HTPB; ~10% Al, are observed.

Calculated results of systems containing GAP or polyNIMMO modified with Al additives indicate that, depending on the prices of these components, suitable rocket propellant compositions can be created in which this modification will always increase  $T_{\text{comb.}}$  in a beneficial manner. Rocket propellant  $I_{\text{sp}}$  depends on the temperature of the combustion products in the chamber  $(T_1)$  and the mean molecular weight of the combustion products (M) as follows:

$$I_{sp} \sim \sqrt{\frac{T_1}{M}} \tag{1}$$

The highest rocket propellant  $I_{sp}$  is a compromise between the highest combustion temperature and the lowest possible average molar mass of the combustion products. The highest combustion temperature is obtained at zero OB, the resulting combustion products being at the highest oxidation state: CO<sub>2</sub>, H<sub>2</sub>O. A low mean molar mass of combustion products is obtained for a composition which allows complete combustion of the propellant, obtaining gaseous products at the lowest oxidation state: CO, H<sub>2</sub>. Figure 4 shows the relationship between the  $I_{sp}$  of three-component mixtures and their composition.



**Figure 4.** Relationship between *I*<sub>sp</sub> and compositions of binder-oxidant-Al mixtures with GAP, HTPB or polyNIMMO as a binder and AP or ADN as an oxidiser, and Al as an energy-increasing additive

Calculations of the  $I_{sp}$  values of the systems tested indicate that these values depend significantly on the composition of the propellants. Data for the individual propellants tested are as follows.

#### 2.1.9. AP-HTPB-AI

In the AP-HTPB system, increasing the HTPB content from 10 to 30% results in a systematic decrease in  $I_{sp}$  from 253 to 204 s. The addition of 10% Al to the AP-HTPB system significantly increases the  $I_{sp}$  values. The highest  $I_{sp}$  of 262 s is for the system containing 10% HTPB. Increasing the HTPB content to 30% reduces the  $I_{sp}$  to 230 s. For the AP-HTPB-20% Al system, even higher  $I_{sp}$  values are obtained and, as for the two previous examples, these are obtained with lower binder content. A maximum  $I_{sp}$  of 265 s was reached at a binder content of 14%. For this system, the maximum  $I_{sp}$  is achieved at low binder content, which can be troublesome during propellant casting.

#### 2.1.10. AP-GAP-AI

In the AP-GAP system, increasing the binder content from 10 to 30% increases the  $I_{sp}$  from 212 to 252 s. For this system, a maximum  $I_{sp}$  of 256 s at 24% binder content, is observed. Adding 10% Al to the AP-GAP system increases  $I_{sp}$  values considerably. The highest  $I_{sp}$  of 264 s is for the system containing 26% binder. A system containing 16% to 30% binder has a  $I_{sp}$  of 260-264 s. For the AP-GAP-20% Al system, even higher  $I_{sp}$  values are obtained, but the effect of the additional 10% Al is small. At 10% binder content, a  $I_{sp}$  of 257 s is achieved – an increase of 6 s compared with the system containing 10% Al. At a binder content of 30%, a  $I_{sp}$  of 267 s is obtained – an increase of 4 s. For the AP-GAP-20% Al system, a high  $I_{sp}$  of 263-267 s is achieved for systems containing between 14% and 30% binder. Large changes in binder content result in small changes in  $I_{sp}$  whereas maximum  $I_{sp}$  is obtained at high binder content, which can facilitate the casting of propellants containing AP-GAP-Al.

#### 2.1.11. AP-polyNIMMO-AI

 $I_{sp}$  calculations for all the AP-polyNIMMO-Al systems tested showed analogous changes in their values compared to the AP-GAP-Al systems. The maximum  $I_{sp}$  values calculated for propellants containing polyNIMMO are as follows:

- AP-polyNIMMO: 254 s,
- AP-polyNIMMO-10%Al: 262 s,
- AP-polyNIMMO-20%Al: 266 s,

and are smaller by 1-2 s compared to analogous systems containing GAP as a binder.

Replacing AP with AD eliminates chlorine compounds from the combustion products. If a comparable combustion temperature is achieved, the reduction in mean molecular weight of the combustion products should lead to an increase in the  $I_{sp}$  of the systems in question. The relationships between the calculated  $I_{sp}$  values and the composition of a given propellant are as follows.

## 2.1.12. ADN-HTPB-AI

In the ADN-HTPB system, increasing the HTPB content from 10% to 30% results in a systematic decrease in the  $I_{sp}$  from 262 to 211 s. The addition of 10% Al to the ADN-HTPB system significantly increases the  $I_{sp}$  values. The highest  $I_{sp}$  of 272 s is for the system containing 10% HTPB. Increasing the HTPB content to 30% reduces the  $I_{sp}$  to 237 s. For the ADN-HTPB-20% Al system, even higher  $I_{sp}$  values are obtained and, as in the two previous examples, higher  $I_{sp}$  values are obtained with lower binder content. A mixture containing 10% HTPB has a  $I_{sp}$  of 276 s. At 30% binder content, the  $I_{sp}$  drops to 248 s. The ADN-HTPB-20% Al system containing 10 to 14% binder has a  $I_{sp}$  of 272-276 s. For this system, the maximum  $I_{sp}$  is reached at low binder content and over a small range of binder content changes, which can cause difficulties in propellant casting.

## 2.1.13. ADN-GAP-AI and ADN-polyNIMMO-AI

 $I_{sp}$  calculations for all ADN-GAP-Al and ADN-polyNIMMO-Al systems tested showed analogous changes in their values compared to the AP-GAP-Al and AP-polyNIMMO-Al systems. The maximum  $I_{sp}$  values calculated for propellants containing ADN and GAP are as follows:

- ADN-GAP: 266 s,
- ADN-GAP-10%Al: 274 s,
- ADN-GAP-20%Al: 276 s,

and are greater by 9-10 s compared to analogous systems containing AP as the oxidiser. The maximum  $I_{sp}$  values calculated for propellants containing ADN and polyNIMMO are as follows:

- ADN-polyNIMMO: 264 s,
- ADN-polyNIMMO-10%Al: 272 s,
- ADN-polyNIMMO-20%Al: 274 s,

and are smaller by 8-10 s compared to analogous systems containing GAP as a binder.

The relationship between  $I_{sp}$  and composition indicates that propellants containing AP achieve lower  $I_{sp}$  than those containing ADN. The presence of chlorine, atomic mass 35.5 g/mol, in AP results in correspondingly higher molar masses of combustion products than ADN, which is made up of nitrogen, hydrogen and oxygen atoms only. The results obtained allow an indication of the ranges of tested propellant compositions in which certain  $I_{sp}$  values are obtained and the ranges where the addition of Al increases the  $I_{sp}$  to their maximum values. These data enable the selection of propellant compositions containing AP, ADN, HTPB, GAP, polyNIMMO and Al for the required rocket engine performance, to be made. Table 1 shows the compositions of individual propellants achieving the highest  $I_{sp}$ .

System	Binder content [%]	I <sub>sp</sub> [s]
HTPB-AP-Al	14	265.2
HTPB-ADN-Al	10	275.8
GAP-AP-Al	26	267.5
GAP-ADN-A1	20	276.3
polyNIMMO-AP-Al	30	265.8
polyNIMMO-ADN-Al	20	274.3
HTPB-AP	30	204.3
HTPB-ADN	28	213.6
HTPB-ADN	14	252.4
GAP-AP		252.3
GAP-ADN	20	257.3
polyNIMMO-AP		251.3
polvNIMMO-ADN		256.7

**Table 1.** Maximum  $I_{sp}$  of two-component binder-oxidiser and three-component binder-oxidiser-Alpropellants containing AP or ADN as the oxidiser, HTPB, GAP or polyNIMMO as the binder and20% Al

The graphs show that the use of energetic binders, such as GAP and polyNIMMO instead of HTPB in rocket propellants, allows for an increase in ballistic parameters, which will translate directly into an increase in the range and lift capacity of the rockets in which such propellants will be used. In addition, the use of ADN instead of AP in rocket propellants also allows the propellant's ballistic parameters to be improved. Optimised systems containing HTPB as a binder, provide the highest  $I_{sp}$  with small amounts of binder (10-14%), making it difficult to cast such propellants. The use of energetic binders enable the highest  $I_{sp}$  to be achieved with larger amounts of polymers in the mixture. Therefore, propellants containing energetic binders should be easier to form. The calculations also showed that adding more than 10% Al does not significantly increase the  $I_{sp}$  of propellants containing an energetic binder. The elimination of Al from the HTPB- and AP-based propellant compositions results in a significant decrease in  $I_{sp}$ . In contrast, simply replacing an inert polymer with an energetic polymer allows suitable  $I_{sp}$  values to be achieved in Al-free propellants.

## 2.2. Smoke generation of selected rocket propellant compositions

A number of calculations were carried out based on the AGARD guidelines – Chapter 2 – Propellant Smoke Classification, determining the smoke classes of the individual solid rocket propellants listed in Table 1. The primary and secondary smoke classes of the selected propellants were determined. The primary class results from the condensation of compounds such as metals, metal oxides or soot in the flue gas. The secondary class results from the condensation of water vapour or acids produced during the combustion of the propellant [18]. Based on the exhaust gas compositions data, calculations are made in accordance with the methodology given in AGARD Chapter 2. Section 3 of the latter indicates the methodology for calculating the value of the primary smoke class. An AGARD index below 0.35 classifies the primary smoke as A, between 0.35 and 0.9 it classifies it as B, and above 0.9 as C. When it comes to secondary smoke, the content of HCl, water or HF in the exhaust gas determines the A, B or C classification. The result of the calculation and the relative humidity value are plotted on the graphs presented in the document and determine the secondary smoke classification. The results of the primary and secondary smoke classification, determined using the AGARD methodology, are shown in Table 2.

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System	Binder content [%]	Primary smoke	Secondary smoke	
HTPB-AP-A1	14		С	
HTPB-ADN-Al	10		А	
GAP-AP-Al	26	С		
GAP-ADN-Al	20		А	
polyNIMMO-AP-Al	30		С	
polyNIMMO-ADN-Al	20		А	
HTPB-AP	30	A	С	
HTPB-AND	28		А	
GAP-AP	30		С	
GAP-AND	30		А	
polyNIMMO-AP	30		С	
polyNIMMO-ADN	30		A	

 

 Table 2.
 Primary and secondary smoke classification of two-component binder-oxidiser and threecomponent binder-oxidiser-Al propellants containing AP or ADN as the oxidiser, HTPB, GAP or polyNIMMO as the binder and 20% Al

When it comes to primary smoke, the content of metallic compounds of lead, Zr, Al, copper or iron in the rocket propellant composition is important. For propellants containing more than  $1.5 \text{ wt.}\% \text{ Al}_2\text{O}_3$  in the combustion products, the propellant is classified as B. A content of 20 wt.% Al results in a classification of C. When it comes to secondary smoke, combustion products such as H<sub>2</sub>O, HCl or HF are taken into account. The content of these compounds in combustion products determines the secondary smoke class of a solid rocket propellant. In the case of propellants containing ADN, these achieve Class A, i.e. they are reduced-smoke propellants. No HCl is present in the combustion products of such propellants. Propellants containing AP are propellants with increased smoke. Smoke class depends on the HCl content of combustion products. Obviously, propellants based solely on AP are classified as C. Changing the type of oxidiser or partially substituting AP with other oxidisers, can reduce the smoke generation of a rocket propellant and hence, reduce the class to B or A.

## 3. Summary

- This work investigated the dependence of combustion temperature and I<sub>sp</sub> on the composition of three-component binder-oxidiser-Al systems containing AP (or ADN as the oxidiser, HTPB, GAP or polyNIMMO as the binder, and the addition of a metallic fuel Al. The highest combustion temperature (3913 K) and the highest I<sub>sp</sub> (276.3 s) were achieved for the GAP-ADN-Al rocket propellant. The use of energetic GAP and polyNIMMO binders instead of HTPB is beneficial because it enables a higher I<sub>sp</sub> and a maximum I<sub>sp</sub> to be obtained for compositions containing higher amounts of binder, thereby achieving a reduction in smoke generated by the propellant. The possibility of using more binder enables the fragmentation of the solid propellant components to be reduced. Using ADN instead of AP as an oxidiser also enables the I<sub>sp</sub> of a rocket propellant to be increased and for the propellant's smoke generation to be reduced. Two-component ADN-binder systems are propellants with the lowest primary and secondary smoke, classified in accordance with AGARD as Class A A.
- Given the calculations presented, the criterion for seeking an optimum composition is not necessarily obtaining the maximum  $I_{sp}$ . In some circumstances, especially civilian ones, the criterion driving the search for new rocket propellant compositions may be the availability of raw materials and the absence of an adverse environmental impact. In military applications, the criterion may be, in addition to achieving a maximum  $I_{sp}$ , a low plume of the rocket propellants, which can also be obtained by calculation.

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