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Review / Przegląd

Trends in the development of propellants regarding the demands of future firearms *Kierunki rozwoju miotających materiałów wybuchowych w aspekcie wymagań przyszłościowej broni palnej*

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Abstract: Progress in the development of solid propellants and knowledge determining the possibility of increasingly detailed analysis of phenomena occurring during the process of propelling projectiles are the main factors in the development of powders and gun propellant systems. The growth of potential ammunition and powder propellant systems is focused on improving the energetic, ballistic and operational characteristics of currently used powders and on searching for new propellants with a more environmentally friendly chemical composition (so-called green propellants).

This paper presents an analysis of the possibilities in propellant systems development in the 21st century, from the internal ballistics perspective. At present, the most promising, from the tactical and technical point of view, are the propellant systems with layered powders (for a classic propellant system solution) and ETC (Electrothermo-Chemical gun) systems.

Streszczenie: Postęp w rozwoju stałych miotających materiałów wybuchowych oraz wiedzy warunkującej możliwość coraz bardziej szczegółowej analizy zjawisk zachodzących podczas procesu miotania pocisku to główne czynniki rozwoju prochowych, lufowych układów miotających. Rozwój przyszłościowej amunicji oraz prochowych układów miotających jest ukierunkowany na poprawę charakterystyk energetyczno-balistyczno-użytkowych obecnie stosowanych prochów oraz na poszukiwanie nowych miotających materiałów wybuchowych o składzie chemicznym bardziej przyjaznym dla środowiska (tzw. Green propellants).

Wprezentowanym artykule zostanie zaprezentowana analiza możliwości rozwojowych układów miotających w XXI w. z punktu widzenia balistyki wewnętrznej. W chwili obecnej najbardziej perspektywicznymi, z taktycznego i technicznego punktu widzenia, wydają się być układy miotające z prochem warstwowym (dla klasycznego rozwiązania układu miotającego) oraz układy typu ETC (Electrothermo-Chemical gun).

Keywords: new propellants, future gun propellant systems

Słowa kluczowe: nowe materiały miotające, przyszłościowe prochowe układy miotające

1. Introduction

The development of armaments, military equipment and war means arises from the needs of the armed

forces of a given country to counteract emerging threats. Focusing on the development of powder systems, it should be remembered that until the end of the first half of the 19th century, black powder was the only known explosive material, and black powder guns were the dominant propelling devices used by all armies during this period.

The discovery of nitrocellulose and nitroglycerine in the first half of the 19th century, resulted in the development of a new class of powders in 1884-1888, which exhibited more than three times better energetic properties compared to black powder, and the geometric shapes of the powder grains, as well as knowledge of the nature of their burning, created the possibility of calculated regulation of the intensity of the supply of propelling gases in the gun barrel.

In addition, the discovery of new explosives sensitive to mechanical stimuli (initiating explosives) at the beginning of the 19th century, followed by the construction of an integrated cartridge, created the foundations for the construction of automatic shooting and artillery firing weapons.

The current work includes a presentation of the analysis of the possibilities in propellant systems development in the 21st century, from the internal ballistics perspective. Promising solutions for future propellants are presented, with an emphasis on the development trends in the field of new propellants.

2. Development trends in the field of new explosives

Nitrocellulose (NC), nitroglycerine (NG) or dinitrodiglycol (DNDG) and nitroguanidine (NQ) have been the basic components of smokeless powders for several decades. This does not mean, however, that the propellants have not changed during this time. For example, by partially or completely replacing nitroglycerine with other plasticisers, the combustion temperature was lowered and the susceptibility of the powders to accidental combustion or explosion was reduced. Initially, nitroglycerine was replaced by other less energy-rich and less sensitive polyalcohol nitrates, e.g. trimethylol ethane trinitrate (TMETN), triethyleneglycol dinitrate (TEGDN) or butantriol trinitrate (BTTN). Bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF) have also found widespread use as plasticisers. Usually, a BDNPA-BDNPF equilibrium mixture is utilised, as this composition has the lowest melting point [1]. The family of nitroxyethylnitroamine (NENAs) plasticisers with a general formula $RN(NO_2)CH_2CH_2ONO_2$, where R is a methyl, ethyl, propyl or butyl group, have similar applications. NENAs contain both the $-ONO_2$ (found in NC) and $-NNO_2$ (found in hexogen (RDX) and octogen (HMX)) functional groups in their structure. Because of this, they plasticise compositions containing these substances, even when the mass share of RDX or HMX exceeds 70%. They are still used, often in mixtures with structurally related 1,5-diazid-3-nitroazapentane (DANPE), in LOVA powders and rocket fuels. A typical composition of such a powder is: 76% RDX or HMX, 19.6% BuNENA/DANPE, 4% NC and 0.4% centralite I. Propellants containing NENAs/DANPE and RDX/HMX are characterised by excellent energy properties (high powder value, low average molecular weight of combustion products, relatively low combustion temperature) and are simultaneously resistant to accidental mechanical and thermal effects. An important disadvantage of NENAs (particularly those with the lowest molecular weight) is their excessive volatility.

The development of potential ammunition and powder propellant systems is focused on improving the energetic, ballistic and operational characteristics of currently used powders and on searching for new propellants with a more environmentally friendly chemical composition (the so-called *green propellants*), which would allow for:

- a) an increase in muzzle velocity, especially in the classic design of the propellant system;
- b) a reduction in the wear of the inner surface of the barrel, which contributes to increasing its service life, as well as improving accuracy;
- c) a reduction in the sensitivity of ammunition to mechanical and thermal stimuli (during transport, storage and operation);
- d) an increase in the stability of the ballistic characteristics when subjected to wide-ranging environmental temperature changes.

These expectations can be met through the use of powders containing energetic polymers and new high-nitrogen explosives. The individual distribution of such polymers is an exothermic process due to the presence of azido ($-N_3$), nitro ($-NO_2$) or nitrate ($-ONO_2$) groups in their structures. The azido functionality deserves special

attention as its decomposition is associated with the release of large amounts of energy (approx. $355 \text{ kJ}\cdot\text{mol}^{-1}$), with the only combustion product being molecular nitrogen. The natural consequence of these observations was the idea of using polymers with azido groups, which may contain much more nitrogen. The first polymer of this type was the poly(glycidyl azide) polymer (GAP). GAP is a polyether(polyethylene oxide) functionalised with azidomethyl groups $-\text{CH}_2\text{N}_3$ (Figure 1). GAP polymers have a low glass transition temperature (-45°C for the linear polymer and -55°C for the branched polymer); however, after crosslinking and at negative temperatures, they are excessively hard and brittle.

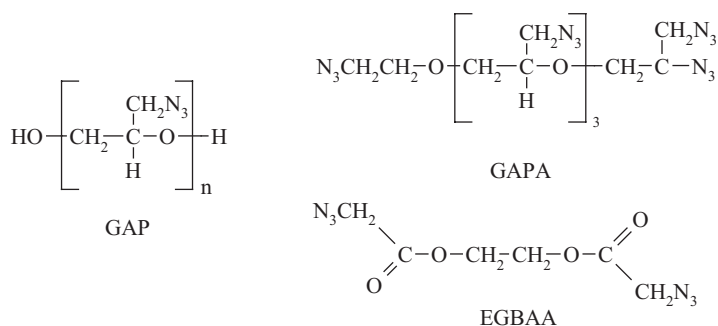


Figure 1. Structure of poly(glycidyl azide) and compatible plasticisers

This shortcoming can be eliminated by incorporating plasticisers into the composition of the mixture. The best effects were obtained using oligomers (*e.g.* trimers) of glycidyl azide. To prevent their reaction with isocyanates, the hydroxyl groups of these compounds are substituted with azido groups (GAPA) (Figure 1). Polyalcohol nitrates (*e.g.* BTTN, TMETN) or recently obtained polyalcohol esters and azidoacetic acid (EGBAA) may also be used as the plasticisers of GAP.

Energetic polyoxetanes were synthesised by Manser [1] from 3-nitroxymethyl-3-methyloxetane (NIMMO), 3,3-bis(azidomethyl)oxetane (BAMO) and 3-azidomethyl-3-methyloxetane (AMMO) (Figure 2).

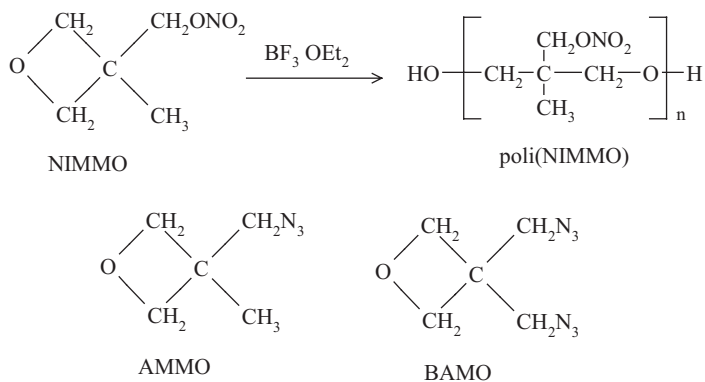


Figure 2. Oxetane structures used for the synthesis of energetic polymers

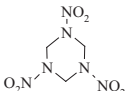
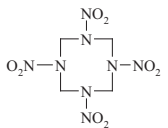
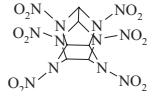
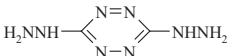
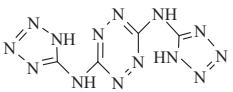
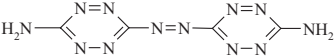
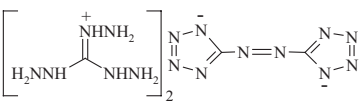
BAMO has a symmetrical structure and is a solid with a melting point of approx. 80°C . It forms polymers with a high degree of crystallinity. Its copolymers with asymmetrical AMMO have thermoplastic properties (called *Thermo Plastic Elastomers, TPE*).

Unsymmetrical oxetane polymers, *e.g.* poly(NIMMO), have low glass transition temperatures, mix unlimitedly with structurally similar plasticisers (usually corresponding oxetane or NENA oligomers), and can be cross-linked with isocyanates at increased temperatures (similarly to GAP). Poly(NIMMO) is classified as a non-

explosive substance, although it has a relatively high positive enthalpy of formation, approx. $820 \text{ kJ}\cdot\text{kg}^{-1}$ [1]. Studies conducted so far have clearly confirmed the advantage of LOVA-type powders containing TPE over previously developed compositions, e.g. RDX (76%)/NC-BuNENA-DANPE (24%). Simple replacement of the NC/BuNENA/DANPE binder with the BAMO-AMMO copolymer leads to an increase in power of approx. 3% and a reduction in combustion temperature of over $200 \text{ }^\circ\text{C}$ (up to approx. 2830 K). If the more energy-rich CL-20 (HNIW, hexanitrohexaazaisowurtzitane) is used instead of RDX, energy increases from $1180 \text{ J}\cdot\text{g}^{-1}$ to $1290 \text{ J}\cdot\text{g}^{-1}$. The adiabatic combustion temperature of such powder is then approx. 3380 K [2]. In the longer term, a wider use of high-nitrogen compounds should be expected. Some of them do not contain nitro groups in their structures at all, yet are capable of self-sustaining explosive transformations. This is a result of the high positive enthalpies of formation of such compounds. Their advantages include low average molecular weight of combustion products and low sensitivity to mechanical stimuli, including shock waves.

Table 1 shows the comparison of the structures and properties of current and future high energy components of the propellants. This summary is a good illustration of the currently dominant concept of the development of energetic materials, *i.e.* the accumulation of energy in the structure of nitrogen-rich compounds (increasing enthalpy of formation), rather than obtaining it from the reaction of carbon and hydrogen oxidation (decreasing oxygen balance).

Tab. 1. Struktury i właściwości obecnych i przyszłych składników materiałów miotających

| Compound | | Enthalpy of formation [kJ·mol ⁻¹] | Oxygen balance [%] | Nitrogen content [%] |
|--------------|---|---|--------------------|----------------------|
| Abbreviation | Chemical formula | | | |
| AP | NH_4ClO_4 | -298 | +35 | 11 |
| ADN | $\text{NH}_4\text{N}(\text{NO}_2)_2$ | -151 | +26 | 45 |
| HNF | $\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$ | -71 | +13 | 38 |
| RDX |  | +67 | -22 | 38 |
| HMX |  | +75 | -22 | 38 |
| CL-20 |  | +420 | -11 | 38 |
| DHTz |  | +536 | -79 | 79 |
| BTATz |  | +883 | -65 | 79 |
| DAAT |  | +1035 | -73 | 76 |
| TAGAT |  | +1067 | -73 | 82 |

BTATz and DHTz charges burn without a visible flame, undergoing complete gasification. The linear combustion speed u is extremely high; however, at the same time it only lightly depends on the pressure [3]. The benefits

of using the TPE energy from the group of polyoxetanes and the unique characteristics of the combustion process of compounds built mostly from nitrogen, allows the assumption that their importance as components of future high-energy and low-sensitivity propellants and explosives will increase systematically.

3. Development trends in new propelling systems

Research on improving the energetic and ballistic characteristics of conventional powders, as well as the search for new propellants and other energy sources, allows for the further development of propellant systems which meet the expectations of the modern battlefield. For example, meeting the needs of the American Army's Future Combat System program [4] requires a reduction in the calibre of in-service tank barrels (120 mm) with a simultaneously expected increase in the energy of fired missiles of 25%. It is assumed that the use of the new propellants will not increase the internal wear of the barrel.

In the powder propelling system, the factor determining the energy and muzzle velocity of a projectile in a specific propelling system is the work of the propelling gases, which depend on the nature of the pressure changes $p(t)$ of these gases in the barrel during the shot. In the case of powder propellant systems using conventional nitrocellulose and nitroglycerine powders, the size of tactical and operational capabilities was enormous, requiring multi-man operated cannons from World War II. The characteristic feature of these was the large consumption of powder charge mass for each shot, and this is still valid when constructing classic propellant systems using conventional nitrocellulose and nitroglycerine powders.

The structural solution analysed in the 70s and 80s of the 20th century which allowed an increase in the projectile's muzzle velocity was a propellant system with an additional powder charge, the so-called travelling charge (*Travelling Charge System*, TCS) [5, 6]. The main element distinguishing this from the classic propelling system was the additional travelling charge powder (mechanically associated with the projectile), whose task was to shape a different qualitative-quantitative distribution of the gas pressure in the barrel as a result of its combustion, causing the projectile velocity to increase.

Work on the powders for the purpose of travelling charges focused at that time around materials called VHBR (*Very High Burning Rate propellants*), in which the main oxidising component was a friable explosive (e.g. HMX), decahydrodeboric acid borate was the fuel, while nitrocellulose with polyethylene glycol was the main component of the binder.

A typical comparative picture of changes (over time) of powder gas pressure in the barrel confines for a classic propelling system (straight line) and for a propelling system with a travelling charge (dashed line) is presented in Fig. 3. Such a trend of pressure changes in the barrel allows an increase in muzzle velocity of the projectile as a consequence of increasing the powder gas pressure impulse (larger area under the pressure curve $p(t)$).

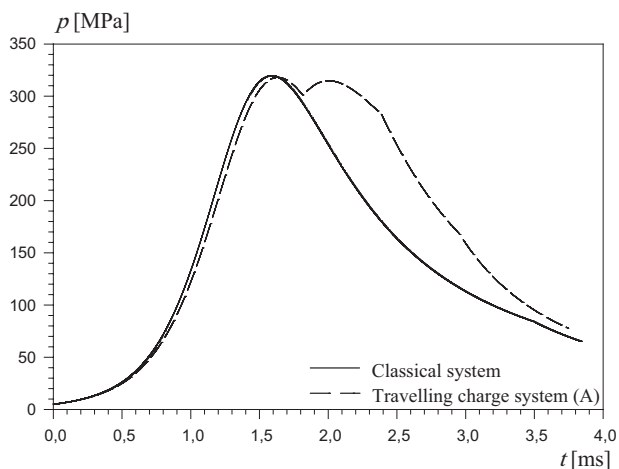


Figure 3. Charts showing $p(t)$ of powder gases in the barrel of the TCS [6]

Similar effects can be obtained in the propellant system with a mobile powder chamber (*Serial Chamber Gun System, SCS*) [5]. In this system (Fig. 4), as in the case of a system with a travelling charge, the combustion of an additional powder charge (also of the VHBR type) is initiated when the projectile, together with the powder chamber moving with it (the space between piston 3 and projectile 4), is located in a specific place in the barrel.

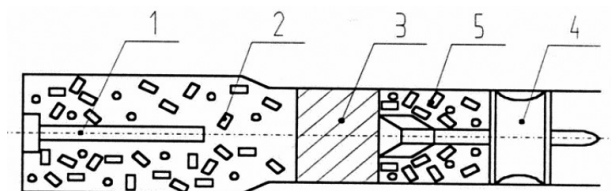


Figure 4. Propellant system with wandering powder chamber (schematic diagram): 1) ignition element; 2) basic propelling charge; 3) movable piston; 4) missile; 5) additional powder propellant charge

The energy of the gas arising from the combustion of an additional powder charge accelerates the projectile already moving in the barrel at a given speed. However, both ideas of the propellant systems presented above do not go beyond research models and theoretical analysis, mainly due to the need for accurate synchronisation of the ignition process of the travelling charge.

The new CL-20 explosive mentioned in section 2 and other next-generation explosives (*e.g.* DHTz, BTATz, DAAT, TAGAT) with the addition of a thermoplastic binder may create a new generation of propellants, the so-called layered powders (Fig. 5).

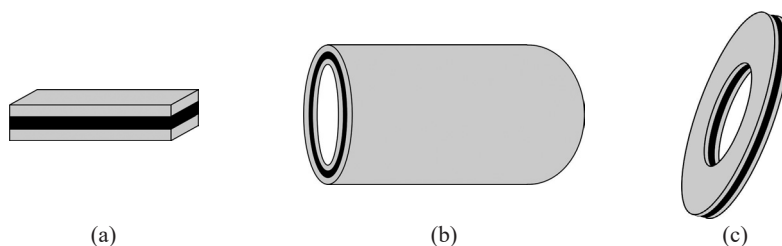


Figure 5. Examples of the structures of layered powders: (a) layer arrangement in layered powder: an outer layer (grey) – with a low burning rate; an inner layer (black) – with a high burning rate; (b) layered tube; (c) layered disc

Layered powders, regardless of the shape of the powder grain, are distinguished by the existence of layers (inner and outer) consisting of powders with different burning rates (Fig. 5). The *slow burning rate outer layer* is characterised by a much slower burning rate compared to the *fast burning rate inner layer*.

The use of layered powders enables a different quality (in comparison to the use of conventional powder) of the pressure distribution of the propelling gases in the barrel, to be obtained. This distribution is qualitatively identical to the picture of the pressure changes in the TCS system (Fig. 3) and allows the muzzle velocity of the projectiles to increase in a classic propellant system. Unlike the TSC system, the use of layered powder does not entail any changes in the structure of the ammunition or the propellant system.

The increase in muzzle velocity resulting from the increase in the value of the gas pressure pulse in the barrel, is not just due to the improvement of energetic and ballistic characteristics of propellants. It is also a result of the modification of the ignition method. This process is reflected in the ETC propellant systems (*Electrothermal-Chemical gun system*).

In this system (Fig. 6), the ignition of the propellant charge is initiated *via* a plasma generator, and the propellant material is catalysed by both plasma and typical heat transfer processes (conduction, convection, radiation).

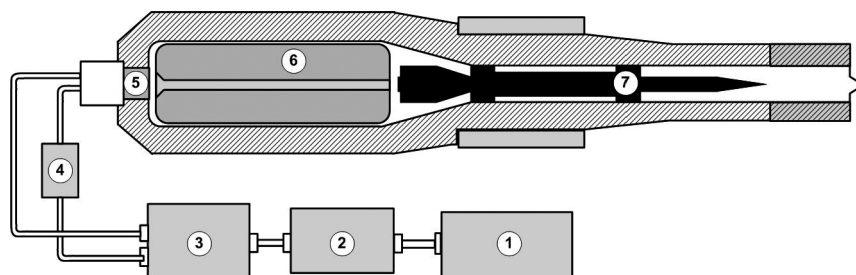


Figure 6. The ideological concept of the ETC propellant system: 1) primary storage; 2) secondary storage; 3) pulse forming network; 4) firing switch; 5) plasma ignition cartridge; 6) propellant; 7) penetrator and sabot

The ETC systems arose from the concept of an electrothermal propellant system (*ElectroThermal gun, ET*) developed in the 1980s by the USA, Germany and France. Although these systems achieved high muzzle energies, they required delivery of much larger amounts of energy. For example, launching a projectile weighing 2 kg with a 105 mm calibre at a muzzle velocity of approx. 2400 ms^{-1} (an energy value of 5.4 MJ) required approx. 30 MJ of electrical energy [7].

The ETC systems do not require such large amounts of electrical energy. Launching an 8.4 kg projectile with a 120 mm calibre and a muzzle velocity of over $1800 \text{ m}\cdot\text{s}^{-1}$ (an energy value of 14.1 MJ) requires approximately 100 kJ of electrical energy. In the case of utilising the ammunition with reduced sensitivity propellant (LOVA), the use of plasma ignition not only allows for a more effective initiation of the ignition process of this propellant [8], but also contributes to obtaining a higher muzzle velocity of the projectiles, by approx. $50\text{-}100 \text{ m}\cdot\text{s}^{-1}$, compared to the ignition of this propellant using black powder.

Problems with storing the electrical energy necessary to power the plasma generator led to improving the performance of capacitors (while minimising their volume and mass) or to replacing the electrically powered plasma generators with generators powered by energy resulting from an explosion. The production of a high-temperature plasma in such a generator is the result of the ionisation of liquid helium by a blast wave from low-mass explosives. Subsequent analysis showed that ETC propellant systems may create a new generation of tank and field artillery in the near future.

4. Conclusions

At the present, the most promising, from the tactical and technical points of view, are propellant systems with layered powder (for a classic propellant system solution) and the ETC systems (*Electrothermo-Chemical gun*). In parallel with the development of solid propellants and powder propellant systems, studies on propellant systems are underway in which a solid powder charge is only used to give initial velocity to the projectile in the barrel, and its further acceleration is due to other forms of energy. Such systems include the gas and powder (RAM Accelerator) and the electromagnetic systems EMC (*ElectroMagnetic-Chemical Gun*) [9-11].

Although a clear progress in the development of both the explosive propellants and the powder propellant systems has been made, the speed of the physical projectiles fired from these systems is far from the maximum speed, which is the speed of light.

Emitting weapons, namely directed energy weapon systems including, among others, laser technologies, offer such possibilities [12]. Does this mean that the use of powder propellant systems will come to an end? Probably not. As long as a systematic progress in the development of the chemical energy sources continues, it will also be possible to make advances in the powder propellant systems, and their compilation with the emitting weapons may bring very interesting design solutions in the future.

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