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Review

Modern Highly Energetic Materials for the Production of Gun Powders and Rocket Propellants in Poland

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Abstract: Polish technology for the production of propellants uses methods which have been known for many years. The continuously developing market requires producers to enhance the parameters of their munitions in order to keep up with demands. Therefore, it is necessary to research and constantly implement new types of gun powders and rocket propellants. In the present work, highly energetic compounds were characterized as constituents of current propellants. Their advantages and disadvantages are described. The requirements for new materials, concerning toxicity, environmental impact, and safety are presented. It is shown that by using modern energetic compounds it is possible to obtain low-vulnerability or insensitive ammunitions. Finally, the situation in the Polish market is briefly described.

Keywords: gun powders, rocket propellants, highly energetic materials

Nomenclature

ADN	Ammonium dinitramide
AN	Ammonium nitrate, NH_4NO_3

AP	Ammonium perchlorate, NH_4ClO_4
BTTN	1,2,4-Butanetriol trinitrate
BuNENA	N-Butyl-2-nitratoethylnitramine
CI	*N*,*N′*-Diethyl-*N*,*N′*-diphenylurea (Centralite I)
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurzitane
CMDB	Composite modified DB
DB	Double-base
DBP	Dibutyl phtalate
DEP	Diethyl phthalate
DNDA-5	2,4-Dinitro-2,4-diazapentane
DNDG	Diethylene glycol dinitrate
DNT	2,4-Dinitrotoluene
DOP	Dioctyl phthalate
DPA	Diphenylamine
DOA	Dioctyl adipate
FOX-7	1,1-Diamino-2,2-dinitroethene
FOX-12	Guanylurea dinitramide
GAP	Glycidyl azide polymer
HEDO	High energy density oxidizers
HNF	Hydrazinium nitroformate
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (octogen)
HTPB	Hydroxyl-terminated polybutadiene
IM	Insensitive munition
LOVA	Low-vulnerability amunition
MB	Multi-base
NC	Nitrocellulose
NG	Glyceryl trinitrate (Nitroglycerin)
NQ	Nitroguanidine
polyNIMMO	Poly[(3-nitratomethyl)-3-methyloxetane]
polyBAMO	Poly[3,3-bis(azidomethyl)oxetane]
polyGLYN	Poly(glycidyl nitrate
RDX	1,3,5-Trinitro-1,3,5-triazinane (hexogen)
SB	Single-base
SHRP	Solid heterogeneous rocket propellants
TB	Triple-base
TMETN	Trimethylolethane trinitrate

1 Introduction

Domestic production of gun powders and rocket propellants has not changed much during recent decades. Many artillery systems are based on obsolete technologies. Modern armaments are imported. Changes in the Polish military industry are proceeding in the right direction, but slowly. Our army uses many types of weaponry, therefore the need for a variety of propellants is very obvious. A lot should be improved in the areas of single, double-, and multi-base powders, and solid rocket propellants. Progress can be achieved by:
– enhancing the energy content and specific impulse of propellants,
– lowering the emission of solid particles and toxic products of combustion,
– replacing composition ingredients with less toxic ones,
– lowering the mechanical sensitivity of the products.

Positive effects can be achieved if the classical components are replaced with modern alternatives. For many years, continuous efforts have been made to improve the parameters of propellants by introducing new compounds into compositions. As a result, physicochemical and ballistic parameters, such as specific impulse and caloricity, should have been enhanced.

In the present work, the advantages and disadvantages of modern propellants, as well as the energetic compounds useful in production, are described. New trends in the development of gun powders and rocket propellants in relation to the requirements are discussed. For reference, evaluation of further progress in the Polish market at the present time is summarized.

2 Possibilities for Solid Heterogeneous Rocket Propellants

Solid heterogeneous rocket propellants (SHRP) have been used by the military for decades. Generally, they consist of a solid oxidizer (65-90%), commonly ammonium perchlorate (AP), a polymeric matrix (8-15%), and metal powder (*e.g.* aluminium) as a fuel (10-20%) [1]. The use of metal causes increases in the burning temperature and high thrust. In addition to the main ingredients, plasticizers, curing agents, antioxidants, and catalysts are included. Although these propellants are cheap and possess high parameters (burning rate 5-55 m/s and specific impulse 235-260 s) they have disadvantages [2]. Most often, they contaminate the environment, deplete the ozone layer, generate highly corrosive gaseous products, and are toxic (AP). Currently, the endeavour is focused on the elimination of the negative environmental impact, the improvement in the mechanical properties, performance, and lowering of the risk of accidental ignition. These effects can be achieved by the modification of the compositions with new, better materials [1, 3, 4].

Much work deals with the substitution of the hydroxyl-terminated polybutadiene (HTPB) binder and fuel with energetic polymers containing explosophoric groups, which can decompose without an oxidizer [5-7]. Many such compounds have been synthesized, but the most prominent are:

- glycidyl azide polymer (GAP),
- poly[(3-nitratomethyl)-3-methyloxetane] (polyNIMMO),
- poly[3,3-bis(azidomethyl)oxetane] (polyBAMO), and
- poly(glycidyl nitrate) (polyGLYN).

These new energetic binders should improve the specific impulse.

Another very important task is the elimination of AP and the introduction of an oxidizer without the disadvantages of the previous one. The greatest rewards can be achieved by the lack of a vapour trail behind the rocket motor, which reveals the starting position, and a decrease in overall environmental contamination [8]. Ammonium nitrate (AN) is a good oxidizer which is cheap and is produced in Poland. It has both low toxicity and sensitivity. The main flaws of this salt are its hygroscopicity and physical instability; during heating to 32 °C there is a phase transition with a density change. This can be avoided when phase-stabilized AN is used [9]. Propellants with AN have relatively low burning rates 2-3 mm/s (with AP 7-9 mm/s), so additional catalysts for this process are needed.

A very promising group of oxidizers is formed by high energy density oxidizers (HEDO compounds). They generally have high heats of decomposition and do not emit hydrogen chloride, which is corrosive and causes vapour trails. Among these compounds can be found organic moieties with a positive oxygen balance, such as trinitromethyl derivatives, nitroformates, and dinitramides [8, 10]. In this group, a compromise between oxygen balance, specific impulse and favourable physicochemical properties (*e.g.* high thermal stability, no hygroscopicity) should be achieved. However, the cost and complexity of production, together with the general hazards are also significant factors.

According to many sources, ammonium dinitramide (ADN) is an excellent oxidizer in heterogeneous rocket propellants. ADN is a non-toxic, non-allergenic, and non-carcinogenic compound [11]. Initial information about its synthesis and properties was published in the 1990s, but ADN was used in rockets in the Soviet Union in the 1970s. It was reported that ADN-propellant was used in the Topol-M ballistic missile [12]. This time lag suggests that this compound was very important. It is hygroscopic and has a low melting point. It decomposes around 123 °C, which can complicate the production of propellants [13]. ADN can be used in a more suitable manner after granulation [12, 14]. Many researchers have studied propellants containing ADN and different binders, *e.g.*: GAP [15-17], HTPB [18], polyBAMO, polyNIMMO, polyGLYN [12], or paraffin [19]. Propellants with a GAP binder were characterized by very high thermal stability, high ballistic performance (burning rate 24 mm/s at 7 MPa, specific impulse 233 s), but on the other hand these materials need additives to improve their mechanical properties [20, 21].

Hydrazinium nitroformate (HNF) melts and decomposes at a higher temperature than ADN , which makes the technological processes safer [13]. Additionally, HNF is not hygroscopic. It is relatively sensitive to mechanical stimuli, but sensitivity characteristics generally do not result in any problems relating to processing of HNF in binder systems [22]. Moreover, purity and crystal morphology seem to have a negligible impact on the sensitivity. Athar *et al.* [23] successfully obtained a form of phlegmatized HNF with 7.5% of modifiers that resulted in reducing sensitivity to friction from 2.0 kg to 9.6 kg.

HNF forms needle-like crystals, therefore it should be recrystallized before incorporation into propellants. It is compatible with energetic binders like GAP, polyNIMMO, and polyGLYN [24]. The specific impulse of propellants containing HNF and these binders exceeds 300 s [12], while the addition of aluminium causes further increase to above 340 s [24]. HNF/Al/GAP composition is more sensitive to impact and friction than propellants containing ammonium perchlorate, but the values are still at an acceptable level [24].

HNF can be safely stored at room temperature for several years [25]. Unstabilized HNF is characterized by low thermal stability – lower than ADN, nitrocellulose containing 13.15% nitrogen, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurzitane (CL-20), hexogen (RDX), and octogen (HMX). Additionally, HNF decomposes via very reactive species, and probably these cannot be trapped fast enough by stabilizers added in the usual amounts. Taking into account the problems with stabilization, low thermal stability, and compatibility problems with some compounds used in propellants, it seems doubtful whether HNF can be safely used in military ammunition with high demands [25, 26]. Despite the facts that HNF is chlorine-free and burns cleanly without corrosive products, it cannot be fully considered as a green replacement for ammonium perchlorate because the synthesis of HNF involves using hydrazine, which is highly toxic and carcinogenic.

3 Modern Compositions of Double-base (DB) Rocket Propellants

DB propellants are the second type of rocket propelling agents. They are divided into homogenous and composite (CMDB, composite modified DB) propellants. They contain nitrocellulose (NC), nitroglycerin (NG), and additives for improving the mechanical and energetic properties. CMDB propellants contain a crystalline oxidizer or highly energetic compound, such as hexogen (RDX), and a metal powder [27-29]. The energetic parameters of DB propellants are lower than those of SHRPs. DB compositions exhibit specific impulses of 150-220 s and burning rates of 5-35 mm/s. The introduction of highly energetic compounds into CMDBs can increase the specific impulse to 230 s and keep the burning rate at a high level [30].

In the cases of the above mentioned highly energetic compounds, the oxidizer (oxygen in nitro groups) and the fuel (carbon backbone) are separated in distance by chemical bonds. In the compositions these substances undergo combustion. Nitramines (such as RDX) in solid propellants increase the parameters and lead to a lowering of the environmental impact. They should be characterized by a positive standard enthalpy of formation, high density, good oxygen balance, and high volume of gaseous decomposition products. For these reasons, in the search for new solid propellants, octogen (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurzitane (Cl-20) were investigated [31]. Another interesting compound is 1,1-diamino-2,2-dinitroethene (FOX-7) which has high energetic parameters and also low mechanical sensitivity. It is of interest as a low-vulnerability ammunition filler [32].

4 Issues with Nitrocellulose Powders

Gun powders are propelling agents used in ammunition to accelerate the projectiles. They also undergo controlled combustion without detonation. During this process a great volume of hot gas is produced. Nitrocellulose powders, known as smokeless powders, can be single-base (SB), DB, triple-base (TB), and multi-base (MB). They differ from each other in terms of type and amount of additives. However, the main ingredient is nitrocellulose, which is a cheap non-hygroscopic binder, and is itself energetic. It also has disadvantages. It can spontaneously decompose during storage, so stabilizers should be added. NC cannot be recycled, its production is not completely reproducible (different batches do not have exactly the same parameters), and it relies on natural sources [33].

SB powders contain more than 90% of highly nitrated NC (>13% nitrogen). Additives for enhancing the stability, elasticity, and energetic parameters comprise the balance. As additional ingredients there are often: stabilizers, *e.g.* urea and amine derivatives – N,N′-diethyl-N,N′-diphenylurea (centralite I, CI), diphenylamine (DPA); non-energetic plasticizers, *e.g.* diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), dioctyl adipate (DOA); energetic plasticizers, *e.g.* NG and diethylene glycol dinitrate (DNDG).

DB powders contain NC and NG (15-45%) as the main ingredients. In this type, NC with a nitrogen content of 12.5% is usually used. A third energetic component – nitroguanidine (NQ) – is present in triple-base powders. It decreases the flame temperature and prolongs the life of the barrel. Examples of compositions of classic powders are collected in Table 1 [33-35].

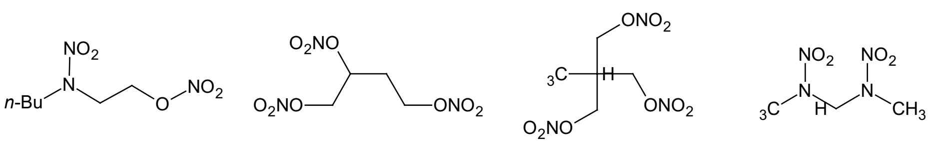
Table 1. Selected compositions (in %) of NC powders

Symbol of the composition	M1	M6	M5	M8	M30	HFP
Powder type	SB	SB	DB	DB	TB	MB
NC	85	87	81.95	52.15	28.0	29.3
NG	–	–	15.00	43.00	22.5	22.7
NQ	–	–	–	–	47.7	5.0
RDX	–	–	–	–	–	36.5
DOP	–	–	–	–	–	5.0
DEP	–	–	–	3.00	–	–
DBP	5	3	–	–	–	–
2,4-Dinitrotoluene (DNT)	10	10	–	–	–	–
CI	–	–	0.60	0.60	1.5	1.5
DPA	1	1	–	–	–	–
Cryolite	–	–	–	–	0.3	–
$Ba(NO_3)_2$	–	–	1.40	–	–	–
KNO_3	–	–	0.75	1.25	–	–
Graphite	–	–	0.30	–	–	–

Some of the chemicals used in the production of nitrocellulose powders have particularly negative health issues. Phthalates and diphenylamine are good examples. They are toxic and carcinogenic [36, 37]. Phthalates are controlled in the European Union due to REACH Regulations. The permissible quantity of DBP in plastic products was set to 0.1%, but in powders there is much more DBP. Diphenylamine can be replaced by other popular stabilizers like centralite I or acardite II [38-40]. Unfortunately, these stabilizers form carcinogenic nitrosamines in the reaction with nitrogen oxides and should be removed. New compounds with lower toxicity are needed instead. Prospective non-toxic plasticizers can be found in a group of citrates (triethyl or tributyl 2-acetylcitrate) [38]. As "eco-friendly" nitrocellulose stabilizers we can consider organic compounds such as: triphenylamine, derivatives of phenol, ionone, tocopherol [39-44] or inorganic components – zeolites [45]. Effective stabilizers should be non-toxic, compatible with the other ingredients, and highly reactive with nitrogen oxides [46-48].

5 Materials for Low-Vulnerability Ammunition (LOVA)

Apart from the environmental aspects, modern weaponry systems require explosives and propellants with high energetic parameters and with, what is equally or even more importantly, high resistance to accidental initiation during transport or storage. LOVA and insensitive munition (IM) meet these demands. Modern highly energetic compounds can be found in nitrocellulose powders of this type [49-51]. Amongst these can be placed RDX, HMX, Cl-20, as well as guanylurea dinitramide (FOX-12). For insensitive compositions the following plasticizers have been utilized: N-butyl-2-nitratoethylnitramine (BuNENA), trimethylolethane trinitrate (TMETN), 1,2,4-butanetriol trinitrate (BTTN), and 2,4-dinitro-2,4-diazapentane (DNDA-5). Müller and Langlotz [52] patented a powder for LOVA which contains NC, cellulose acetate butyrate, an energetic plasticizer (*e.g.* DNDA-5), and at least one energetic material (RDX, HMX, NQ, FOX-12, *etc.*). Müller also published results from a study of the properties of SB, DB, and TB propellants with DNDA-5. These compositions can be classified as insensitive. The powders were characterized as exhibiting long-term thermal stability and low burning temperatures [53]. The structural formulas of the described plasticizers are shown in Figure 1.



BuNENA BTTN TMETN DNDA-5

Figure 1. Plasticizers used in low-vulnerability ammunition

In the literature more papers can be found dealing with the properties of powders containing energetic plasticizers [49, 51, 54-56]. In the NENA group, the most interesting member mentioned is BuNENA. This causes a lowering of the flame temperature. Also, the average molar mass of the gaseous products is reduced. SB, DB, and TB propellants with BuNENA have better mechanical and energetic properties, lower flame temperatures, and similar stability and sensitivity in comparison to powders containing DOP [57, 58].

New energetic plasticizers will gradually displace NG from powders. NG is volatile and sensitive to impact, therefore technological operations are hazardous. Health aspects must also be taken into account because it is a potent vasodilator. Products with NG do not meet the requirements for LOVA.

LOVA and IM powders have been developed for many years. Presently, some global companies can offer such products. For example, EURENCO produces LOVA powders based on hexogen for cal. 40 and 57 mm [59]. They also make an insensitive powder with FOX-12 (UNIFLEX 2 IM), which has similar properties to single-base formulations but the burning temperature is decreased [60].

6 Characteristics of the Domestic Market

In Poland, mainly SB and DB multi-hole cylinder powders are produced. Their composition is similar to those in Table 1. In the manufacturing process various phthalates, NG, DNT, and centralite I are used. R&D work in scientific facilities concerns new propellants with NC, DNDG [61-63], and LOVA powders with more than 65% RDX [64-66]. Additionally, classical solid homogenous and heterogeneous rocket propellants are produced in ordnance factories. They are used as the main propelling charges in rocket engines.

In recent years, the demands of the Ministry of National Defence for modern armaments has been constantly growing. In 2020 2.1% of GDP was scheduled for weaponry, but in reality 2.37% of GDP was spent. Expenses for 2021 should be equal to 2.2% of GDP, that is 50 bln PLN [67]. This growing trend can be seen in future programs. In connection with the war in Ukraine, the Polish government plans to spend 2.2% GDP in 2022 on the army and its modernization; from 2023 these expenditures should equal 3.0% GDP or more [68]. Part of this amount will be destined for products from the Polish military industry. Resources put into the research and development sector dedicated to novel propellants will make our market more competitive and innovative. It will lead to cooperation with European and global companies from the defence industry. Supporting domestic production of energetic materials and weapon systems should remain the core principle in the process of strengthening our defensive abilities and becoming a self-reliant nation [69].

7 Summary

- ♦ The absence of modern gun powders and rocket propellants manufactured in Poland is a serious issue. To solve this problem significant funds should be allocated to research in the field of modern energetic materials for propulsion systems. Improvements can be introduced in a few areas.
- ♦ Solid heterogeneous rocket propellants with non-energetic binders are considered as one of them. Classic oxidizers could be replaced with compounds like ADN or HNF. Based on literature data, the technology of propellants containing ADN is more advanced than that of HNF-propellants, which still require further development. Also, part of the oxidizer and fuel can be substituted by highly energetic compounds, especially nitramines.
- ♦ NC powders await innovations. New less-toxic compounds could replace phthalates and NG, simultaneously decreasing erosivity, sensitivity to mechanical stimuli and improving the ballistic properties. Finally, new technology for CMDBs with reduced nitrocellulose content would be very beneficial. Therefore, new binders and modern energetic compounds ought to be implemented.
- ♦ Modified composite propellants with such compositions will be characterized by enhanced performance. As a result of the introduction of advanced energetic materials in the mentioned groups of propellants, improvements in physicochemical, ballistic, and energetic parameters, *e.g.* sensitivity to mechanical stimuli, specific impulse, and caloricity, can be expected.

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