



## Review / Przegląd

# Development trends in artillery ammunition propellants *Analiza możliwości eliminacji nitrocelulozy z materiałów wybuchowych miotających*

Mateusz Szala

Chemistry Institute, Military University of Technology, 2 gen. S. Kaliskiego Street, 00 – 908 Warsaw, Poland

E-mail: mateusz.szala@wat.edu.pl

**Abstract:** A short history of nitrocellulose (NC) use in propellants is discussed. The advantages and disadvantages of NC as a semi-synthetic component of powders and rocket propellants are presented. Based on the conventional classification of propellants, the options of eliminating nitrocellulose in different types of powders and rocket propellants are discussed in detail. The analysis shows that in the foreseeable future, the elimination of NC in single-base and double-base propellants is highly unlikely. The observed trends in triple-base propellant development also does not show any tendencies in the elimination of NC, only the replacement of nitroguanidine with cyclic nitroamines. However, the elimination of NC in LOVA composite propellants is probable. Synthetic, rubber-based solid composite rocket propellants, with ammonium perchlorate as the oxidizer, are the only ones not dependent on NC.

**Streszczenie:** Przedstawiono krótki rys historyczny stosowania nitrocelulozy (NC) w materiałach miotających. Przedyskutowano wady i zalety NC jako półsyntetycznego składnika prochów i paliw raketowych. Następnie stosując klasyczny podział materiałów wybuchowych miotających szczegółowo przedyskutowano możliwości eliminacji nitrocelulozy z poszczególnych rodzajów prochów i paliw raketowych. Na podstawie przeprowadzonych analiz zauważono, że w perspektywie najbliższych lat eliminacja NC z prochów jedno- i dwubazowych jest bardzo mało prawdopodobna. Obserwowane tendencje w rozwoju prochów trójbazowych również nie wskazują na eliminację NC a jedynie na zastępowanie nitroguanidyny za pomocą cyklicznych nitroamin. Prawdopodobna jest eliminacja NC z prochów kompozytowych typu LOVA. Jedynie stałe heterogeniczne paliwa raketowe na bazie kauczuków syntetycznych oraz chloranu(VII) amonu, jako utleniacza, zostały niezależne od NC.

**Keyword:** nitrocellulose, energetic polymer, propellant, solid rocket propellant

**Słowa kluczowe:** nitroceluloza, polimer energetyczny, materiał miotający, stałe paliwo raketowe

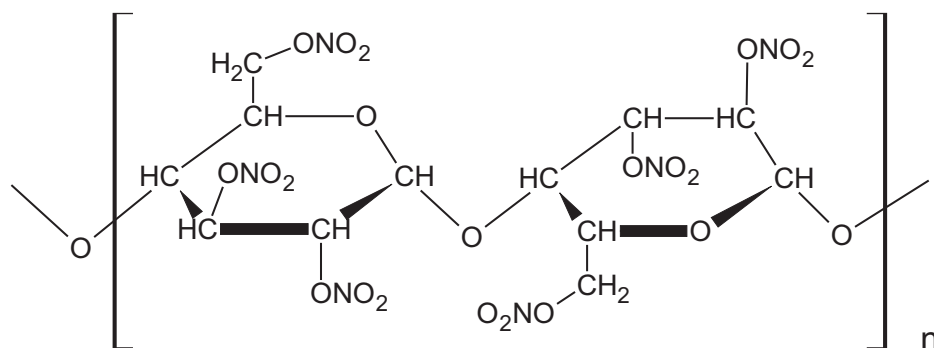
## 1. Introduction

For over 1000 years, up to the mid 19<sup>th</sup> century, black powder was the only known propelling and blasting material. In a relatively short time, it was replaced by nitrocellulose(NC)-based smokeless powders, which is still the case today. In some applications, NC-based compositions were replaced by energetic composites containing an inorganic oxidizer and a non-energetic polymeric binding agent. These are used almost exclusively

in different sized rocket motors. Due to the nature of the combustion process and other technological difficulties, they are not used as explosive. The propellants (powders) for guns, rifles, artillery and howitzers continue to be based on NC, with propellant charges in handguns containing over 90% NC. Due to the natural origins of cellulose used in NC manufacture, it can become a scarce material, particular in wartime. For this reason, studies have been carried out over many years to develop a synthetic replacement/alternative to NC, independent of natural sources.

## 2. History of nitrocellulose

The first documented cellulose esterification process was carried out in 1933 by H. Braconnot [1]. Figure 1 shows the monomeric unit of NC. Between 1846 and 1847, attempts were made by Schönbein and Pelouze to use NC instead of black powder for propelling projectiles. The first NC production plant was established by Lenk (von Wolfsburg) in 1855. The unstable burning of NC in the breech was overcome by Schultze in 1864 by manufacturing a propellant containing 50% NC.



**Figure 1.** Monomeric unit of a fully-esterified NC

The first NC-based smokeless powder in the modern sense was obtained by F. Volkmann in 1871 by the gelatinization of NC with ethanol and diethyl ether [2]. Paul Vieille [3-5] made a significant contribution to the development of smokeless powders by creating a strip powder which burnt in parallel layers through the use of high and low-nitrated NC. Vieille's powder was introduced into military applications in France in 1885 [6]. In 1890, D. Mendeleev modified Vieille's powder using NC soluble in an ethanol and diethyl ether solution. All the above powders are classified as single-base propellants. In 1888, A. Nobel used glyceryl trinitrate (nitroglycerin, NG) to gelatinize NC and thus obtained the first double-base propellant, known as ballistite. Introducing liquid nitrate esters to the NC-based powder improved its propelling properties but simultaneously increased the temperature of the gaseous combustion products and the barrel's susceptibility to erosion. To eliminate those disadvantages, during World War II, propellants started to be made using NC, liquid nitrate ester and nitroguanidine (NQ) to obtain triple-base powders, also known as Gudol powders. It is worth noting that pressed nitrocellulose was used as a blasting material (from 1868) until World War I, however, it was quickly replaced with 2,4,6-trinitrophenol (picric acid).

NC was the first polymer and the first semi-synthetic polymer to be used as a propellant. Although 175 years have passed (in 2020) since the very first attempts to use NC as a powder component and 135 years since its introduction into military service, it is still used in single-, double-, triple-base and composite propellants, igniters, varnishes *etc.* During those years, many explosives were introduced and abandoned (*e.g.* 2,4,6-trinitrophenol; *N*-methyl-*N*-nitro-2,4,6-tetranitroaniline), meanwhile the outlook for NC appears strong.

### 3. Advantages and disadvantages of nitrocellulose

The continuous use of nitrocellulose for over 135 years clearly shows that the advantages of this material outweigh its disadvantages:

a) **Key advantages:**

- well developed production technology of NC and NC-based propellants,
- simple control and scaling of the esterification process (nitration),
- relatively large raw material base (cellulose from trees, shrubs, cotton *etc.*),
- film-forming properties,
- flexibility and strength typical of polymer materials,
- plasticization and ability to form any shape,
- non-hygroscopic properties,
- low price.

b) **The most common disadvantages:**

- limited chemical stability due to autocatalytic decomposition,
- requires use of stabilizing agents and periodical inspection of NC-based products,
- limited repeatability, requires homogenization of large NC batches to ensure uniform properties,
- requires utilisation of product which fails acceptance tests,
- non-reusable material from decommissioned ammunition.

Currently, the advantages of NC outweigh its disadvantages, and it continues to be the main component of propellants. In the complex propelling systems of 105-120 mm calibre ammunition which include propellants with different geometries and composition, NC is still a key, though not a predominant, component. In military applications, a key element affecting the success of operations is the industrial base of the opposing forces. The first conflict in which victory was determined by industrial capability was World War I. This was proved by the outcome of World War II [7]. Based on its military experience, the US decided to conduct a long-term program of cutting off dependency on natural resources in military production. As per publicly available research data, the first fully synthetic energetic polymer was poly(glycidyl nitrate) (PGN) obtained in 1953 [8]. 23 years later, in 1976, poly(glycidyl azide) (GAP) was obtained [9]. Use of the azide group instead of the nitrate ester group present in NC shows a deliberate strategy by the manufacturers. GAP is not dependent on sources of wood cellulose and its manufacturing process does not require nitration/esterification which is hazardous and whose product is susceptible to hydrolysis.

### 4. Nitrocellulose elimination options

#### 4.1. Classification

The appeal of NC as a component of propellant compositions is it being both an energetic compound and a binding agent. Currently, this combination of properties can be found only in NC. Attempts to eliminate or partially replace NC with synthetic components resulted in the development of several propellant compositions detailed and discussed below.

The analysis of options to eliminate NC from different types of propellant compositions was based on the conventional classification of solid propellants [10]:

- single-base propellants (>90% NC),
- double-base propellant (NC + liquid nitrate ester),
- triple-base propellant (NC + liquid nitrate ester + NQ),
- composite (inorganic oxidizer + polymer) and LOVA,
- composite modified double-base (double-base + oxidizer and/or powdered metal).

## 4.2. Single-base propellants

### 4.2.1. Basic compositions

Single-base propellants contain a minimum of 90% NC. Two NC grades, with nitrogen contents of 12.6 to 13.2%, are usually used. There are many types of single-base propellants, with many different additives (phlegmatizing agents, modifiers) with potassium nitrate used in porous propellants. The combustion of NC-based propellants is a complex process, since NC with over 13% nitrogen content is practically insoluble in ethanol/ether solution, forming a matrix in which the combustion process depends on the direction of the NC fibres. Insoluble NC with high nitrogen content, has a different structure to NC, which is soluble and susceptible to plasticization. A typical single-base propellant burns in parallel layers in which the direction of flame propagation in the microscale is determined by the arrangement of NC fibres with high nitrogen content. This mechanism is difficult to replicate using synthetic polymers, and single-base propellants are still made using solely NC.

### 4.2.2. Oxygen- and nitrogen-containing polymers

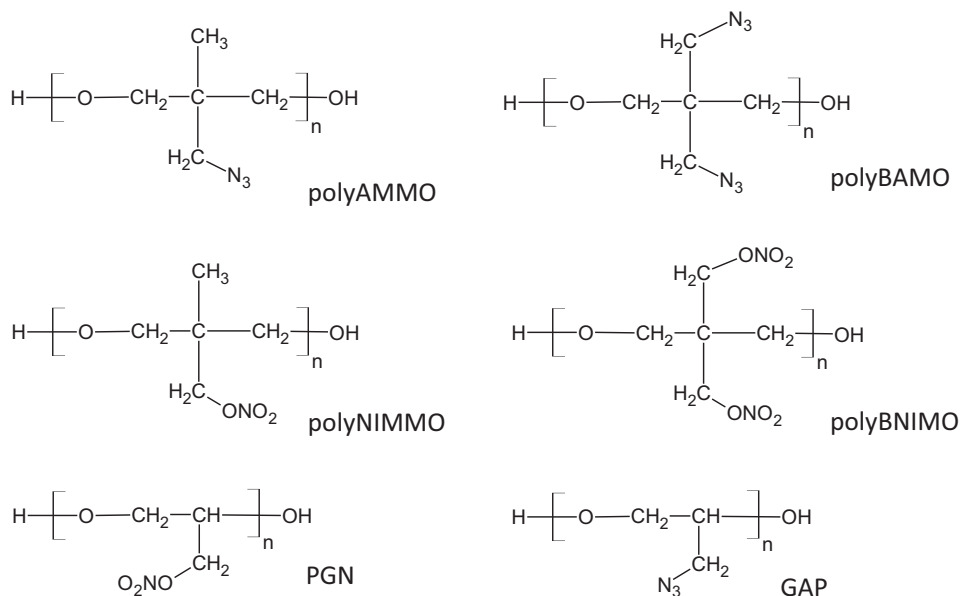
The first attempts to replace nitrocellulose with a fully synthetic material with similar properties, resulted in a series of polynitrates which are liquid under normal conditions; their conversion to solid requiring cross-linking. Fully synthetic nitrate esters most often referred to in literature include:

- poly(3-methyl-3-nitroxymethyl-oxetane) (polyNIMMO),
- poly(bis-3,3-nitroxymethyl-oxetane) (PBNMO),
- PGN.

A fully synthetic energetic polymer with a nitrate group is similar to nitrocellulose in its susceptibility to hydrolysis. Through the simple replacement of an explosophoric nitrate group, *e.g.* azide, the following polymers were obtained:

- poly(3-methyl-3-azidomethyl-oxetane) (poliAMMO),
- poly(bis-3,3-azidomethyl-oxetane) (poliBAMO),
- GAP.

Suitable copolymers including poly(BAMO-AMMO), poly(BAMO-NIMMO) are also known [11]. Figure 2 shows the their condensed structural formula.



**Figure 2.** Monomeric units of synthetic energetic polymers

Polymers with mixed functionality are also known, *e.g.* nitrate-acetylcellulose (CNA) [12-13]. Cellulose, a raw material for the synthesis, is esterified in two stages with nitric acid followed by acetic anhydride (or *vice versa*). The polymer can be processed in the same way as NC, *i.e.* pressed, rolled or extruded. The decomposition temperature, determined by thermal analysis (differential or scanning), is 181 °C which is almost identical to NC with the same nitrogen content.

Synthetic energetic polymers cannot replace NC in single-base propellants due to their different physical and energetic properties. They are good energetic binding agents which, in many forms including compositions of secondary explosives with polymer-based bonding agent (PBX), can easily replace NC. The polymers, liquid under normal conditions, are often good energetic plasticizers. The energetic polymers, solid under normal conditions, can be used to obtain energetic thermoplastic elastomers (ETPE) or used as binding agents in composite rocket propellants.

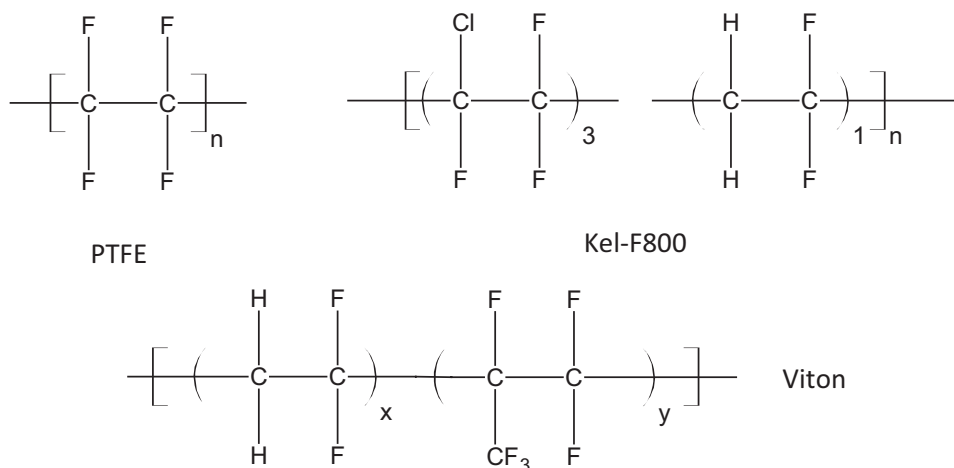
Cyclodextrin nitrates (CDNs) are an interesting alternative to NC. Their composition is similar to NC, but due to their supramolecular structure, various components can be introduced into their toroidal macromolecules. This allows for a unique homogenization of the components on a molecular level and an easy adjustment of the composite's properties [14-16]. Cyclodextrins are obtained by a controlled starch hydrolysis with enzymes. CDNs are a semi-synthetic polymer, however, their substrate is easier to isolate than cellulose from wood. CDNs may replace NC in single-base powders in the future, however, no relevant data is available at the moment.

#### 4.2.3. Fluorine- and chlorine-containing polymers

Oxygen is the element with the highest electronegativity in conventional energetic polymers. Oxygen-free oxidizing agents containing chlorine have been in use in pyrotechnics at least since World War II (*e.g.* C<sub>2</sub>Cl<sub>6</sub>, C<sub>6</sub>Cl<sub>6</sub>) [17]. A natural consequence is the use of the element with the highest electronegativity, *i.e.* fluorine. The most common polymeric binding agent containing fluorine is polytetrafluoroethylene (PTFE) also known as Teflon<sup>®</sup>. This polymer is used throughout industry for its low adhesion and high chemical resistance properties. PTFE in the presence of reducing agents, *e.g.* powdered metals, shows strong oxidizing properties. The most common pyrotechnic compositions containing PTFE are Magnesium-Teflon-Viton (MTV), used as IR emitting decoys for military planes and helicopters [18]. The autothermal combustion reaction of a stoichiometric mixture of aluminium-PTFE generates 21 GJ/m<sup>3</sup> of energy, whereas octogen (HMX) generates only 12 GJ/m<sup>3</sup> [19].

Viton can also be used as an energetic polymer, however, it is usually used for its mechanical properties and performance, including high flexibility, ductility, thermal and chemical stability. Viton is a copolymer of hexafluoropropylene (HFP) and 1,1-difluoroethene (vinylidene fluoride, VDF) and, like Teflon<sup>®</sup>, shows very good properties as a binding agent in pressed and extruded compositions [20].

Another interesting fluorocarbon polymer is a copolymer derived from the monomers chlorotrifluoroethylene (CTFE) and vinylidene fluoride (VDF), known as Kel-F800 [21]. It has a relatively low softening point (105 °C) and high density (2.12 g/cm<sup>3</sup>) [22], and is being intensively investigated as a binding agent for modern PBX type compositions. Figure 3 shows the condensed structural formula of these polymers.



**Figure 3.** Monomeric units of fluorocarbon polymers used in energetic compositions

Polyethers (also referred to as polyoxetanes), containing an energetic difluoramine group ( $-\text{NF}_2$ ), are also being investigated. Examples include structural analogs of polyBAMO with a nitrate ester group replaced by an  $-\text{NF}_2$  group; poly(difluoromethylamine)oxetane is a solid under normal conditions with a melting point of 158 °C and a decomposition temperature of 210 °C [23].

### 4.3. Double-base propellants

#### 4.3.1. Basic compositions

Double-base propellants include liquid NC-gelatinized nitrate esters. The nitrogen content of the NC is usually 12.4-12.6%N with the content of NC in the propellant being usually between 50 and 60%. Liquid nitrate esters (NG, ethylene glycol dinitrate) are added constitute 40 to 50% of the composition. Double-base propellants often include small amounts of other additives, including stabilizers, retardants *etc.* [24].

NC in a double-base propellant is an energetic compound susceptible to gelatinization, and a potential synthetic alternative must show similar properties or be susceptible to gelatinization by nitrate esters. To some degree, NC may be replaced by other cellulose esters (including non-energetic grades), however, this does not solve the general problem. An effective alternative to NC in double-base propellants has not been developed so far, and to improve the energetic properties of the propellant, a completely new type of propellant, known as composite modified double-base (CMDB), has been developed.

#### 4.3.2. Composite modified double-base propellants

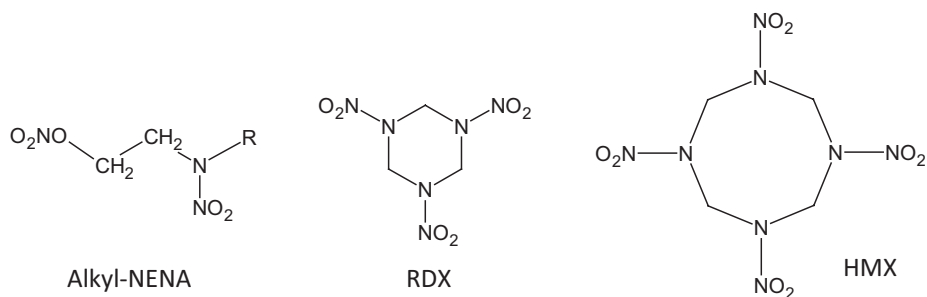
Some NC in a double-base propellant can be replaced with conventional secondary explosives, including hexogen (RDX) and HMX, without losing the ability of forming a composition using conventional methods for double-base propellants. This resulted in the first modifications of a basic double-base propellant for military purposes – JA-2 – [25]:

- 59.5% NC,
- 14.9% NG,
- 24.8% DEGDN,
- 0.8% additives

designated as PRD-20; RPDS-21; RPDS-22 *etc.* containing:

- 25.7-34.1% RDX, and
- 8.9-14.0% 2-(ethylnitroamino)ethyl nitrate (alkyl-NENA).

This allowed a reduction of approximately 50% in the amount of NC in the propellant. The complete elimination of NC from this type of propellant is impossible, as it also serves as a binding agent. Introducing other binding agents to CMDB compositions classifies them as composite propellants for low vulnerability ammunition (LOVA), described later in the study. Figure 4 shows the structural formula of some energetic nitroamines used in complex and composite propellants.



**Figure 4.** Energetic components used in composite powders and propellants

#### 4.4. Triple-base propellants

A conventional triple-base propellant includes:

- NC (20-30%),
- energetic plasticizer in form of nitrate esters (20-25%), and
- NQ (50-55%).

The complete elimination of NC is very difficult due to the structure-forming properties of NC against liquid nitrate esters. Hexogen or octogen in fine crystalline form (5-45  $\mu\text{m}$ ) can be used to replace part of NQ or NC. In STD compositions are added [26]:

- 20-28% NC,
- 20-22% NG,
- 28-55% NQ,
- 0-20% RDX, and
- 1.5-3.6% NC stabilizer.

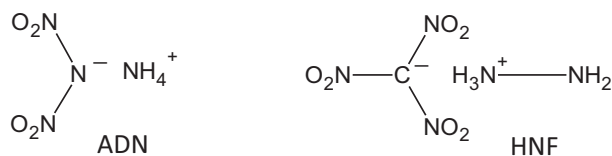
CLP-15 [27] and JAX [28] compositions include:

- 42-55% NC,
- 11-13% NG,
- 19-23 DEGDN,
- 10-21% RDX.

#### 4.5. Composite propellants

##### 4.5.1. Non-energetic binding agent - inorganic oxidizer

The simple replacement of nitrocellulose with non-energetic binding agents in propelling compositions causes a reduction in the oxygen balance and requires an oxygen-rich oxidizer. The oldest known synthetic non-energetic polymers used in similar compositions were probably polymeric organic polysulfides (thiorubbers, 1942-45) [29]. Later studies included polybutadienes, polyacrylates, polyacrylonitriles, polyurethanes, polystyrenes *etc.* Copolymers of those materials can be used as binding agents and fuels. Hydroxyl-terminated polybutadiene (HTPB) shows the most promise [29]. The oxidizers include ammonium, potassium and sodium perchlorates or nitrates, ammonium dinitramide (ADN) and hydrazine nitroformate (HNF), Figure 5. Compositions based on these components are not used as gun powders but are usually used in different sized rocket motors and are referred to as solid heterogeneous rocket propellants (SHRPs).



**Figure 5.** Molecular structure of advanced oxidizers used in solid propellants

Propelling compositions based on synthetic rubber (HTPB) and oxygen-rich oxidizers are currently used to propel rockets of different calibre and motor mass. The simplest composition includes ammonium perchlorate and cross-linked HTPB in the ratio of 70/30. In practice, compositions contain many dedicated additives, including antioxidants, combustion rate modifiers, plasticizers, powdered metals and blasting materials as energetic additives. These compositions were the first propellants not dependent on NC and in many forms can replace double- and triple-base propellants.

#### 4.5.2. Non-energetic binding agent – organic oxidizer

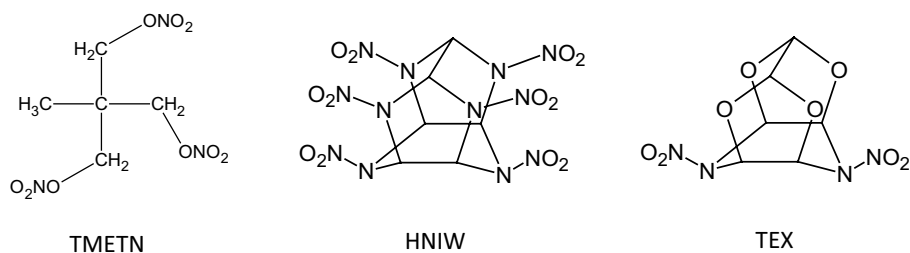
Non-energetic binding agents used in the compositions are often similar to those detailed in 4.5.1, however, non-energetic cellulose esters and ethers are used, including:

- methylcellulose (MC),
- ethylcellulose (EC),
- cellulose acetate (CA),
- cellulose acetate butyrate (CAB), and
- hydroxypropylcellulose (HPC).

The main organic compounds classified as oxidizers, usually include cyclic or caged polynitroamines, *e.g.* RDX, HMX, hexanitrohexaazaisowurtzitane (HNIW, CL20), Figure 6. Propellants containing non-energetic NC derivatives and RDX or HMX can be synthesized, however, they usually contain a small amount of NC. These compositions are referred to as LOVA propellants, with XM-39 being the most common example [30]. This material contains:

- 12-16% cellulose acetate,
- 0-4% NC (12.2%N),
- 76-80% RDX,
- 3.8-7.8 triacetin, and
- 0.2% stabilizer (usually centralite).

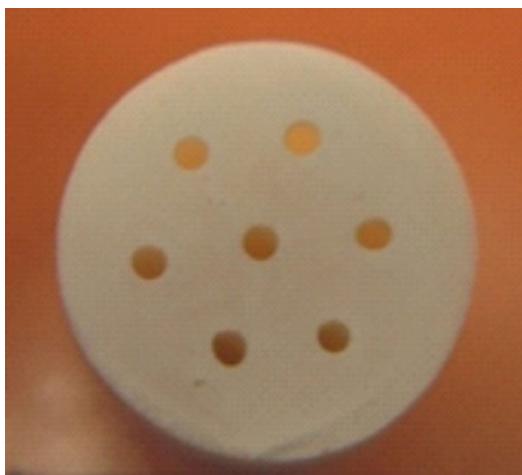
M43 propellant is a structural analog of the XM-39 composition using (bis-(dinitropropyl)acetal/methylal) as the energetic plasticizer [31]. A small amount of NC facilitates processing and slightly improves its energetic properties [30, 32, 33], however, it is not a key component. Experiments have shown that the size of RDX/HMX crystals used in LOVA compositions strongly affects their performance. A change in RDX crystal size in XM-39 from 4.5 to 32  $\mu\text{m}$ , reduces the propellant density from 1.65 to 1.45  $\text{g}/\text{cm}^3$ , increases the co-volume from 0.82 to 1.43 and increases the maximum burning rate from 9.5 to 46  $\text{cm}/\text{s}$  [34].



**Figure 6.** Molecular structures of TMETN, HNIW and TEX



Experimental propellant composition PAP-029 (for a 105 mm howitzer) uses cellulose acetate-nitrate (CAN), RDX (>5  $\mu\text{m}$ ), triethylene glycol dinitrate (TEGDN) and trimethylolethane trinitrate (TMETN) [13]. The composition, in the form of 7-multi-perforated grains shows reduced sensitivity compared to JA-2 propellant, except for the impact test using explosively propelled fragments [35]. Composite LOVA propellant grain, similar in shape to PAP-029, is shown in Figure 7.



**Figure 7.** Composite LOVA propellant grain [36]

XM-39 and similar compositions can be processed similarly to the nitrocellulose propellants, and can be used to form multi-perforated grains with different geometries and propelling charges for different rocket sizes and masses [35]. Compositions without NC are preferred in developing rocket motors, particularly those operating at lower pressures for longer times.

#### 4.5.3. Energetic polymer – organic oxidizer

The complete elimination of NC from a propellant requires the use of an alternative energetic binding agent. One of the solutions is to use synthetic polymers, including poliNIMMO, poliAMMO, poliGLYN or GAP. High-energetic nitramine, *e.g.* RDX, HMX, HNIW or TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>.0<sup>3,11</sup>]dodecane) is used as an oxidizer. As an example, propellants [31]:

- TGD-002 contains 78.0% HNIW, 14.3% BAMO and 7.7% AMMO,
- TGD-009 contains RDX/TEX/BAMO/AMMO (58.0/18.0/6.0/18.0), and
- TGD-019 contains 76.0% RDX, 6.0% BAMO and 18.0% GAP.

Compositions containing HMX as an oxidizer and polyBAMO/NIMMO as an energetic binding agent, were also analysed. These compositions included [37]:

- 23.6-25.0% binding agent,
- 70.8-75.0% HMX,
- 1.9-4.6% burning rate modifiers (organic copper, lead, iron or chromium compounds), and
- 0.5% carbon black.

Similar HMX based compositions, including GAP and polyBAMO binding agents, were also analysed [38].

Compositions including a binding agent as a multi-component mixture of NC/GAP/HTPB/cellulose acetate with RDX as an oxidizer, were also studied. The compositions included [39]:

- 70-80% RDX,
- 5-15% NC,
- 6% GAP,

- 4.5% cellulose acetate, and
- 4.5% HTPB.

These compositions show similar ballistic parameters, since the reduced amount of NC increased the amount of RDX in order to maintain the energetic properties of the system. With a decrease in NC content, the strength parameters of the propellant grains or charges were reduced.

## 5. Conclusions

Different options of eliminating NC in solid propellants were analysed. The analysis showed that for single-base propellants, with current knowledge, it is impossible to replace NC with any other energetic polymer, in the near future. Among the NC alternatives considered, the best known is GAP and it will probably be the first compound to replace NC in many applications. Despite the time from the discovery of a new compound until its military application becoming shorter, it is difficult to estimate a timeframe in which NC will be eliminated from single-base propellants.

The likelihood of eliminating NC in double-base propellants is also highly speculative, however, the amount of NC used can be reduced, replacing it with energetic nitramines. However, propellants obtained using nitramines are classified as composite modified double-base propellants (CMDBs). This also applies to triple-base propellants, with the current trend being the replacement of NQ with RDX and HMX. The structure-forming role of NC seems irreplaceable in the foreseeable future.

Composite propellants is the only group of special solid propellants which can be manufactured without NC, while maintaining their performance and properties. The critical task is to allocate the NC roles of binding agent and energetic component between other components of the propellant. The most promising are compositions based on high-energetic inorganic oxidizers and high-elastic organic polymers used as a fuel (reducer). These compositions are easily formed into large diameter rocket charges (approx. 5-10 cm). Propellant grains without NC for artillery, can be obtained using LOVA propellants and experimental compositions containing energetic thermoplastic elastomers (e.g. polyBAMO).

## Acknowledgements

The study was carried out with the support of the Ministry of National Defence as part of project no. UGB-22-761. The author would like to thank Prof. S. Cudziło for his material support and many valuable discussions.

## References

- [1] Braconnot H. De la transformation de plusieurs substances vegetales en un principe nouveaux (*xyloidine*). (in French) *Ann. Chim. Phys.* **1833**, 52: 290-294.
- [2] Chevalier B. Smokeless Powder. [in:] James C.R. Ed. *The ABCs of Reloading: The Definitive Guide for Novice to Expert*. 9<sup>th</sup> ed., Gun Digest Books, **2011**.
- [3] Moorehead W. Characterization of Smokeless Powders. [in:] Blackledge R.D. Ed. *Forensic Analysis on the Cutting Edge: New Methods for Trace Evidence Analysis*. John Wiley & Sons, Inc., **2007**, pp. 241-268.
- [4] Hopler R.B. The History, Development, and Characteristics of Explosives and Propellants. [in:] Beveridge A. Ed. *Forensic Investigation of Explosions*. London, Taylor & Francis Ltd., **1998**, pp. 1-12.
- [5] Medard L. The scientific work of Paul Vieille (1854-1934). *Revue d'Histoire des Sciences* **1994**, 47(3): 381-404.
- [6] Perrson P., Holmberg R., Lee J. *Rock Blasting and Explosives Engineering*. CRC Press, **1993**.
- [7] Gropman A. *The Big L: American Logistics in World War II*. National Defense University, Washington, **1997**.
- [8] Defence Technical Information Center (DTIC), Doc. AD 139462, **1957**.
- [9] Frankel M., Grant L., Flanagan J. Historical Development of GAP. *Proc. ASME, SAE and ASEE 25<sup>th</sup> Joint*

- Propulsion Conf.*, Monterey, California, **1989**.
- [10] Agrawal J.P. *High Energy Materials*. Wiley-VCH, Weinheim, **2010**.
- [11] Ang H., Pisharath S. *Energetic Polymers*. Wiley-VCH, Weinheim, **2012**.
- [12] Carignan Y.P., Bobinski J. *Cellulose Nitrate-Acetate Mixed Esters*. Technical Report no. 3105, Picatinny Arsenal, **1964**.
- [13] Manning T., Wyckoff J., Adam C., Rozumov E., Klingaman K., Panchal V., Laquidara J., Fair M., Bolognini J., Luhmann K., Velarde S., Knott C., Piraino S.M., Boyd K. Formulation Development and Characterization of Cellulose Acetate Nitrate Based Propellants for Improved Insensitive Munitions Properties. *Def. Technol.* **2014**, *10*(2): 92-100.
- [14] Maksimowski P., Grzegorzczak A., Cieślak K., Gołofit T., Chmielarek M., Tomaszewski W., Pawłowski W.  $\gamma$ -Cyclodextrin Nitrate/CL-20 Complex: Preparation and Properties. *Propellants Explos. Pyrotech.* **2019**, *44*(2) 207-216.
- [15] Maksimowski P., Rumiankowski T. Properties of the Gamma-Cyclodextrin/CL-20 System. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 217-229.
- [16] Consaga J., Gill R. Synthesis and Use of Cyclodextrin Nitrate. *Proc. 29<sup>th</sup> ICT Conf.*, Karlsruhe, **1998**, 5/1-5/5.
- [17] Ellern H. *Military and Civilian Pyrotechnics*. Chemical Publishing Company, New York, **1968**.
- [18] Christo F.C. *Thermochemistry and Kinetics Models for Magnesium/Teflon/Viton Pyrotechnic Compositions*. Report DSTO-TR-0938, Melbourne, Australia, **1999**
- [19] Yang Y., Wang S., Sun Z., Dlott D. Near-Infra Red Laser Ablation of PTFE Sensitized by Nanoenergetic Materials. *Appl. Phys. Lett.* **2004**, *85*(9): 1493-1495.
- [20] Brown G.W., Tencate J.N., Deluca R., Rae P.J., Todd S.N. Dynamic and Quasi-static Measurement of PBXN-5 and Comp B Explosives. *Proc. SEM Annual Conf.*, Albuquerque, New Mexico, USA, **2009**.
- [21] Dattelbaum D.M., Robbins D.L., Sheffield S.A., Orlor E.B., Gustavsen R.L., Alcon R.R., Lloyd J.M., Chavez P.J. Quasi-static and Shock Compressive Response of Fluorinated Polymers: Kel-F800. *APS Conf. Proc.* **2006**, *845*: 69-72.
- [22] DePiero S., Hoffman D. *Formulation and Characterization of LX-17-2 from New FK-800 Binder and WA, ATK, BAE TATBs*. Report LLNL-TR-416360, **2009**.
- [23] Archibald T., Manser G., Immoos J. *Difluoroamino Oxetanes and Polymers Formed there Form to Use in Energetic Formulations*. Patent US 5420311, **1995**.
- [24] Teipel U. *Energetic Materials, Particle Processing and Characterization*. Wiley-VCH, Weinheim, **2005**.
- [25] Brown L.G. *High Energy Gun Propellants*. Patent US 6241833, **2001**.
- [26] Sanghavi R.R., Khire V.H., Chakraborty T.K., Singh A. Studies of RDX Influence on Performance Increase of Triple Based Propellants. *Propellants Explos. Pyrotech.* **2006**, *31*(4): 318-322.
- [27] Shachar E., Gutman A., Goldberg M., Gali S., Welner S. Surveillance Tests of a New LOVA Gun Propellant. *Insensitive Munitions & Energetic Materials Technology Symp.*, Bristol, UK, **2006**.
- [28] Lieb R.J., Heimerl J.M. *Characteristics of JAX Gun Propellant*. ARL Technical Report ARL-TR-465, Aberdeen Proving Ground, USA, **1994**.
- [29] Hunley J.D. History of Solid Propellant Rocketry. What We Do and Do not Know. *Proc. 35<sup>th</sup> AIAA/SAE/ASME Joint Propulsion Conference and Exhibit*, Los Angeles, California. **1999**.
- [30] Pillai A.G.S., Joshi M.M., Barve A.M., Velapure S.P., Karir J.S. Cellulose Acetate Binder-Based LOVA Gun Propellant for Tank Guns. *Def. Sci. J.* **1999**, *49*(2): 141-149.
- [31] Leveritt C.S., Conroy P.J., Johnson A.W. Relative Erosivity of Nitramine Gun Propellants with Thermoplastic/Elastomer Binder Systems. *Proc. 10<sup>th</sup> U.S. Army Gun Dynamics Symposium*, ADP012470, Austin, USA, **2001**, pp. 258-263.
- [32] Vogelsanger B., Andres H., Schadel U., Huber A., Skriver A., Ryf K. Tomorrow's LOVA Propellants – Polymer-Bonded or Nitrocellulose-Based? *Proc. 35<sup>th</sup> ICT Conf.*, Karlsruhe, **2004**, 7/1-7/15.
- [33] Barrington L.M. *Full Scale Insensitive Munitions Testing of the RAN 5''/54 Cartridge Case*. Report DSTO-TR-0097, **1994**.

- [34] Pillai A.G.S., Sanghavi R.R., Dayanandan C.R., Joshi M.M., Velapure S.P., Singh A. Studies on RDX Particle Size in LOVA Gun Propellant Formulations. *Propellants Explos. Pyrotech.* **2001**, *26*: 226-228.
- [35] Petre C.F., Paquet F., Nicole C., Brochu S. Optimization of the Mechanical and Combustion Properties of a New Green and Insensitive Gun Propellant Using Design of Experiments. *Int. J. Energ. Mater. Chem. Propul.* **2011**, *10*: 437-453.
- [36] Hara M., Trzciński W.A., Cudziło S., Szala M., Chyłek Z., Surma Z. Thermochemical Properties, Ballistic Parameters and Sensitivity of New RDX-based Propellants. *Cent. Eur. J. Energ. Mater.* **2020**, *17*(2): 223-238.
- [37] Kimura E., Oyumi Y. Insensitive Munitions and Combustion Characteristics of BAMO/NMMO Propellants. *J. Energ. Mater.* **1996**, *14*: 201-215.
- [38] Kawamoto A.M., Diniz M.F., Lúcia Lourenço V., Takahashi M.F.K., Keicher T., Krause H., Menke K., Kempa P.B. Synthesis and Characterization of GAP/BAMO Copolymers Applied at High Energetic Composite Propellants. *J. Aerosp. Technol. Manag.* **2010**, *2*: 307-322.
- [39] Singh H., Khire V. Studies on Low Vulnerability Gun Propellants Based on Conventional Binders and Energetic Plasticizers. *Int. J. Energ. Mater. Chem. Propul.* **2008**, *7*: 187-192.

Received: June 05, 2020

Revised: November 4, 2020

Published first time online: November 25, 2020