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Directions of studies into high energy materials
Kierunki badań materiałów wysokoenergetycznych

Martyna Wijata

Łukasiewicz Research Network, Institute of Industrial Organic Chemistry, 6 Annopol Street,
03-236 Warsaw, Poland
** E-mail:* martyna.wijata@ipo.lukasiewicz.gov.pl

ORCID Information:
Wijata M.: 0009-0004-6171-4346

Abstract: *This paper is a review of the current direction of research into high energy materials. Chemical compounds and compositions which have potential in increasing the safety of people and the environment are presented. The possibility of using 3D printed explosives and rocket propellants is described. Smart energetic materials and rocket propellants with controlled combustion processes are included.*

Streszczenie: *W pracy dokonano przeglądu aktualnych kierunków rozwoju materiałów wysokoenergetycznych. Przedstawiono związki chemiczne oraz kompozycje perspektywiczne w zastosowaniu pod kątem zwiększenia bezpieczeństwa ludzi oraz środowiska. Opisano możliwości zastosowania różnych technik druku 3D do otrzymywania materiałów wybuchowych, a także paliw rakietowych. Następnie omówiono inteligentne materiały energetyczne oraz stałe paliwa rakietowe z kontrolowanym procesem spalania.*

Keywords: *safety, low-sensitivity compositions, 3D printing, smart energetic materials*
Słowa kluczowe: *bezpieczeństwo, mało wrażliwe mieszaniny, druk 3D, inteligentne materiały energetyczne*

1. Introduction

The first known explosive was black powder, probably invented in China in the 9th century. It was produced by mixing sulphur, charcoal and potassium nitrate. For many centuries, black powder, also known as smoke powder due to its high content of gas combustion products, had universal applications as a propellant, blasting agent and initiating explosive. As a result of technological advances, the 19th century was a turning point in terms of the use of new mixtures and explosive compounds. Black powder was replaced in many applications and, in military use, by smokeless nitrocellulose and nitroglycerine powders. These changes increased accuracy and parameters such as weapon range and striking power. In 1867, dynamite and ammonium(V) nitrate were patented and found application in the mining industry, while at the turn of the 19th and 20th centuries, a mixture called dynamone, consisting of ammonium nitrate, wood flour and other combustible ingredients, began to be used. The second half of the 20th century was characterised by significant advances in the field of mining explosives. ANFOs and slurry and emulsion explosives were developed, showing low sensitivity to mechanical stimuli, making it possible to load them mechanically into blasting holes. Currently, ANFOs and emulsion explosives are the primary blasting agents used in open-pit mining [1, 2]. Further important steps in the history of explosives included the discovery of the phenomenon of shaped charge and the development of plastic bonded explosives which in addition to being less sensitive to mechanical stimuli than traditional high explosives e.g. TNT, are also characterised by high detonation parameters (Table 1).

Table 1. Comparison of the properties of TNT and C4 composition [3]

Explosive	Density [g/cm^3]	Detonation velocity [m/s]	Friction sensitivity [N]	Impact sensitivity [J]
TNT	1.60	6900	>353	15
C4	1.61	8055	214	21.1

Currently, there is a growing emphasis on environmental protection, not only in households, but also in industrial applications. Therefore, new chemical compounds are being sought as alternatives to those containing toxic substances or substances which emit large quantities of gaseous products, currently used in both civil and military industries. Furthermore, to increase the safety of ammunition during use, research is being conducted into materials which are less sensitive to explosive and mechanical stimuli than those currently in use.

3D printing technology allows for faster production of certain components, such as shells. In addition, it ensures mobility, as the printers can be transported from place to place due to their small size, ensuring that the necessary components are delivered to the battlefield. Intelligent energy materials, on the other hand, could usher in an era of completely new design possibilities for the defence industry.

2. Explosives and pyrotechnic materials with safer composition in terms of toxicity of components and substances released into the environment

The M67 hand grenade is a fragmentation grenade manufactured since the late 1960s. Grenades of this type are primarily designed to target live-armed targets with fragments. When the firing pin strikes the primer, a delay mixture is initiated, which then ignites the initiating charge. This initiating charge enables the detonation of the main charge within the grenade. A team of scientists from Innovative Materials and Processes (IMP) and DEVCOM-AC developed a complete fuze for the M67 hand grenade, eliminating harmful substances such as chlorates(VII) and hexavalent chromium compounds, which are currently used in delay mixtures, as well as lead compounds used in primers. New delay mixtures (W/MnO_2 and $SrMoO_4$/Al/Si) and two types of lead-free primers (DBX-1 and MIC, a mixture based on nanothermites) were proposed [4-6]. The drawing (Figure. 1) shows the structure of both the classic and the newly developed fuze.

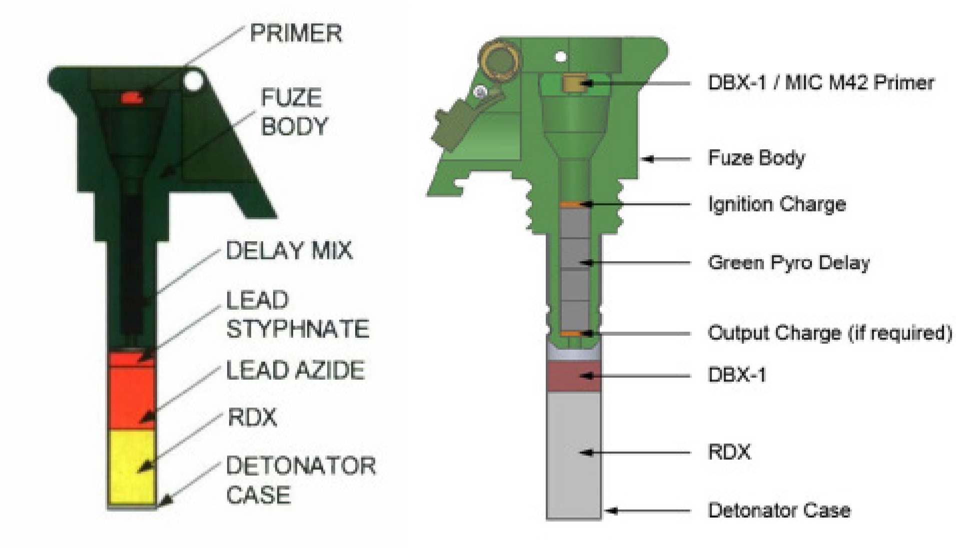


Figure 1. Construction of fuzes (from left) of the classic M213 and the newly developed one [5, 6]

In terms of replacing lead azide and lead trinitroresorcinate, high-nitrogen compounds appear promising, as their energy efficiency is due to their high heat of formation. This group includes transition metal salts and high-nitrogen heterocyclic compounds, as well as high energy coordination compounds. Among others, triazoles, tetrazoles, triazines and tetrazines are being studied, whose salts are successfully used as explosives. This is the case with DBX-1, or copper(I) 5-nitrotetazolate, a crystalline substance with a maroon colour. This compound turned out to be a very good and, importantly, non-toxic substitute for lead azide in primer applications. Due to difficulties encountered in the industrial production of this compound, as well as the high costs of the process and the lack of industrial production capabilities, DBX-1 is not widely used. Furthermore, it was found that the traditional method does not result in a pure product. Figure 2 shows the synthesis of DBX-1. Current methods mainly use 5-aminotetrazole as the substrate. Due to its unprotected amino group, it decomposes in the Sandmeyer reaction with the release of a nitrogen and carbon molecule. The released carbon atoms lead to a dangerous phenomenon known as micro-detonations. Scientists from the USA decided to tackle these problems and developed and optimised a new synthesis method in which there is no risk of micro-detonations, thanks to the use of a compound called *Procten* (a derivative of 5-amionotetrazole with a protected amino group). The new method features fewer steps (no need to inoculate the mixture to precipitate the product), which shortens the process time. The amount of material obtainable in a single synthesis process is 600 g. In addition, the new method is characterised by lower costs compared to the traditional method of synthesis and is safer for those involved in its production [7-9].

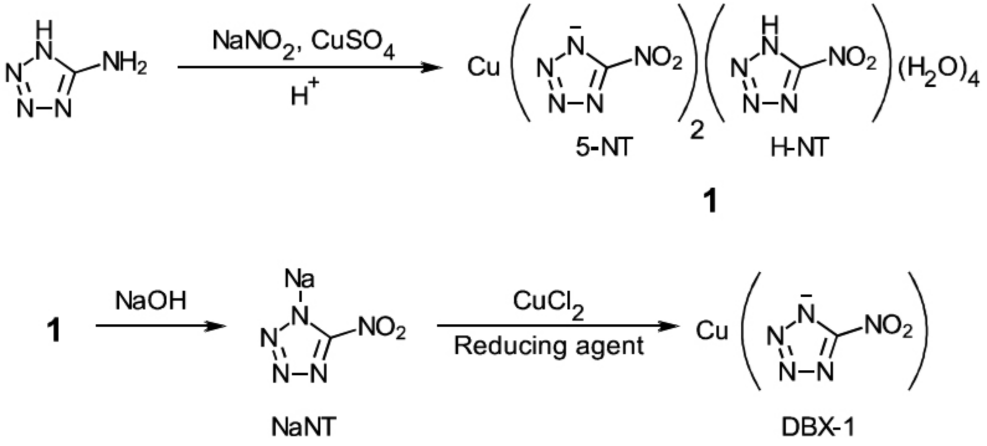
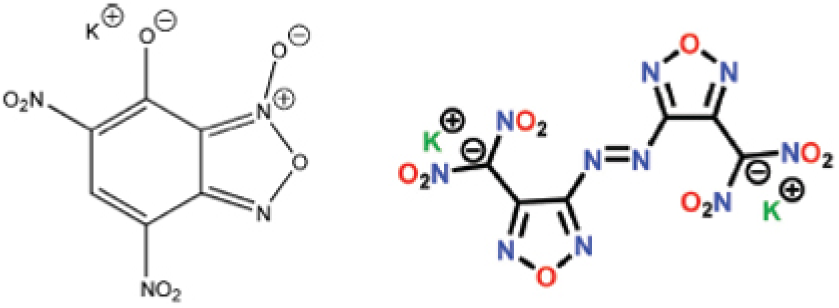


Figure 2. DBX-1 synthesis [9]

Another competitive compound already implemented by the United States Army is KDNP, or potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide (Figure 3a). By replacing lead cations with potassium cations, these compounds are safer for the environment. Furthermore, the introduction of potassium cations causes decomposition temperatures, which are usually low for high-nitrogen compounds, to exceed 200 °C [10, 11]. In recent years, many other potassium salts have been investigated as potential substitutes for the lead compounds used currently. The compound shown in Figure 3b is promising in this regard. Its undoubted advantages include friction sensitivity, which is approximately 20 N, and a decomposition temperature of 229 °C. An attempt to increase the oxygen content in a molecule by connecting furazan rings with oxygen atoms leads to an increase in the heat of formation of this compound but also makes it more sensitive to mechanical stimuli [12].



a) b)

Figure 3. KDNP (a) and potassium 4,4’-bis(dinitromethyl)-3,3’-azofurazanate (b) [10, 11]

Sparklers are a popular feature at parties. However, they may have a negative impact on health due to the toxic effect of one of the commercial ingredients – barium nitrate, which is as an oxidizer. Sparklers contain the following ingredients:

- an oxidizer, which is the source of oxygen,

– iron filings, which are responsible for the formation of sparks,
– binder,
– Al or Mg powder, which accelerate the combustion reaction.

A team in Germany has developed sparklers in which barium nitrate has been replaced by strontium nitrate, which is less harmful to health and the environment. The lethal dose (LD_{50} rat, oral) for barium nitrate is 355 mg/kg, while for strontium nitrate it is 2750 mg/kg. Table 2 presents the compositions of sparklers characterized by green and purple flame colours [13, 14].

Table 2. Compositions of selected sparklers [14]

Composition	**Component [%]**						
	$Sr(NO_3)_2$	**Fe**	**Al**	**Starch**	**CuBr**	**B_4C**	**5-At***
P1	27	31	15	16	11	-	-
P2	26.5	33	15	14.6	11	-	-
G5	49	37	-	8	-	16	-
G6	55	17	-	6	-	16	6

*5-At – 5-aminotetrazole

3. Low-sensitivity ammunition

One of the most widely used materials for filling shells is TNT (which has low sensitivity to mechanical stimuli) and compositions based on it, particularly composition B. Nowadays, these do not meet the increased safety requirements of STANAG 4439, as they detonate when penetrated by a shaped charge. There have been incidents involving the explosion of ammunition containing TNT. One such incident occurred because of a fire on the aircraft carrier USS Forrestal in 1967 [15, 16].

Compositions IMX-101 and IMX-104 have been successfully implemented in the US Army (Table 3), replacing the previously used composition B in 120 and 150 mm calibre artillery ammunition, as well as in 60 and 81 mm calibre mortar ammunition. These compositions are based on 2,4-dinitroanisole (DNAN) and are characterised by reduced sensitivity to all stimuli. Despite the development of less sensitive mixtures, TNT and composition B are still widely used due to their numerous advantages. These include low price, high availability and relatively high detonation parameters. Currently, research is still ongoing to find a cast-melt composition which could be a good alternative to TNT [17-19].

Table 3. Composition of low-sensitivity IMX-1 and IMX-4 compositions [18, 19]

Composition	**Component [%]**			
	DNAN	**NQ**	**NTO**	**RDX**
IMX-1	43.5	36.8	19.7	–
IMX-4	32	–	53	15

At the Military University of Technology, compositions consisting of 40% DNAN or TNT, 20% RDX, and 40% NTO were prepared and tested. The composition and parameters of these are presented in Table 4. They are characterized by reasonable impact sensitivity and a detonation velocity higher than that of cast TNT (approximately 6700 m/s) [20].

Table 4. Composition and parameters of compositions containing DNAN, NTO, RDX and TNT [20]

Composition	**Density [g/cm^3]**	**Detonation velocity [m/s]**	**Impact sensitivity [J]**
TNT/RDX/NTO	1.66	7500±100	14
DNAN/RDX/NTO	1.64	7200±200	25

Nitroguanidine derivatives appear to be a promising component for compositions which are insensitive to elaboration by melt-casting. The most promising is its n-propyl derivative (n-propyl-nitroguanidine, n-PrNQ), which is obtained by transamination (Figure 4). It is a simple and inexpensive process which results in a high-purity product. Due to its advantages, it appears to be a promising replacement for TNT [21-23].

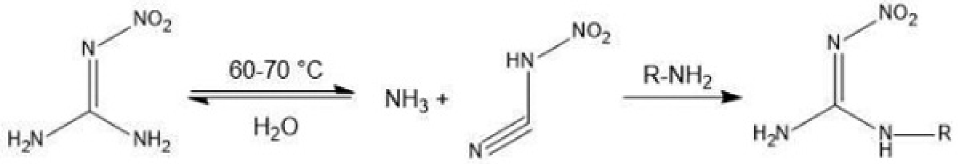


Figure 4. The transamination reaction mechanism according to Davis [20]

In China, the effect of the length of the alkyl substituent chain on the stability of nitroguanidine derivatives and their melting point, was investigated. It was found that by increasing the length of the alkyl chain, the melting points of the derivatives decrease significantly (Figure 5).

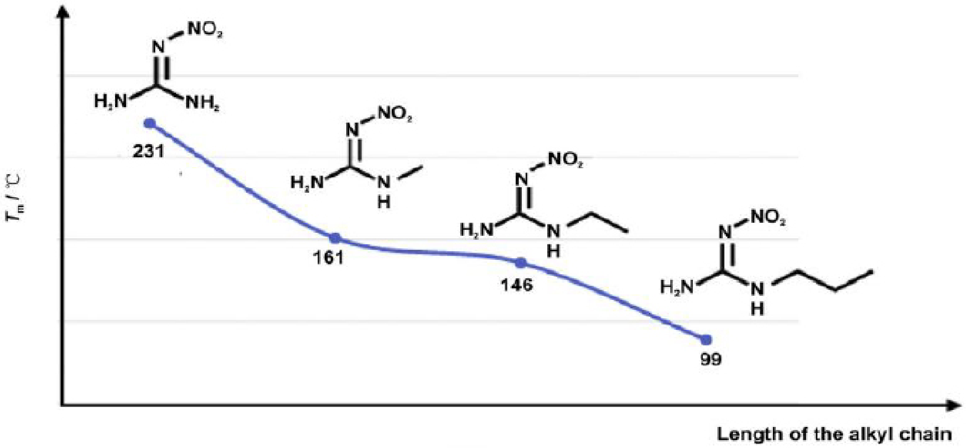


Figure 5. Relationship between melting point and the length of the alkyl chain in properties nitroguanidine derivates [24]

Properties such as a relatively low melting point and low sensitivity to mechanical stimuli, i.e. friction sensitivity >360 N and impact sensitivity >40 J, make n-propyl-nitroguanidine a favourable component in low-melting composite mixtures, from a technological point of view [23]. A team from the Military University of Technology has developed the PRX-1M composition, consisting of 65% RS-RDX, 30% n-PrNQ, 4.95% carnauba wax and 0.05% lecithin, which achieves parameters such as detonation velocity and pressure higher than those of TNT, but lower than those of composition B. The lower impact sensitivity limit for this composition is 23 J, which is similar to that of TNT, while the lower friction sensitivity limit is higher than 360 N. Furthermore, the PRX-1M composite mixture does not contain high vapour pressure nitroarenes, which are toxic and can be dangerous to ammunition factory workers [25].

4. Additive techniques in manufacturing processes

Using conventional methods of forming explosive charges, such as pressing or melt-casting method, it is difficult to obtain complex shapes due to the need to use appropriate molds. Various additive techniques have been developed for this purpose. Additive manufacturing involves forming a product by adding successive layers using automation. This requires CAD software and a suitable printer. 3D printing technology has become widely used in many fields such as modelling, aviation, the automotive industry and even medicine, thanks to its ability to produce many complex shapes in a short time. Currently, 3D printers are also gaining importance in the arms industry [26]. The first attempts at printing high-energy materials were based on depositing molten material, which was TNT. However, it turned out that using the vat hotopolymerisation (VP) method produces prints with much better resolution. The VP method, which uses photopolymerisation to cure liquid material layer by layer in a vat, is described in [27, 28].

A team of scientists from Japan has conducted research into the production of gas generators using 3D printing with the VP method. The gas generator contained nitroguanidine, strontium nitrate and basic copper(II) nitrate, while a soybean oil based resin was used as a hardener. It was found that gas generators containing between 20% and 30% of solid components in a mixture used for 3D printing can be successfully prepared with particle sizes ranging from 75 to 150 μm while maintaining a layer height of 0.1 mm. If the size of the particles used is greater than the height of the layer, structural defects such as cavities and cracks appear [29]. The team also conducted research in which they used the same technique to produce printable mixtures based on potassium perchlorate. It turned out that in this case, the solid particle content could be increased to 70% without the need to add any dispersing agent. The printouts were of very good quality, with no blank spaces or cracks. However, their burning speed at a manometric pressure of 10 MPa is approximately 40 mm/s [30].

A team of scientists from the Netherlands has developed a mixture based on bimodal hexogen, which they used for 3D printing using the VP method. The discs were printed, placed in cartridges, and then used for demonstration purposes in a 30 mm calibre American Gau-8 cannon, which is used to perform impact tests on projectiles or fragments. The witness plate was shot through (Figure 6).

Figure 6. Cartridge filled with printed discs and a witness plate after firing [27]

Another promising method is Drop On Demand (DOD), which is a type of inkjet printing. The print is produced by dispensing an appropriate amount of droplets. This method allows for a high degree of control over the density, surface and shape of the print. Scientists have investigated its potential for use in the preparation of hexogen based prints. It is difficult to use in DOD printing because it has two crystal phases, α and β. However, prints prepared based on this material have good homogeneity and consist predominantly of the α phase with a small admixture of the β phase [26, 31].

Additionally, scientists from the United States conducted research involving the printing of nanothermite based on aluminium nanoparticles and copper(II) nanoxide, with positive results. Figure 7 shows the ignition of 5-layer samples prepared by the RIP (reactive inkjet printing) method with a single nozzle [32].

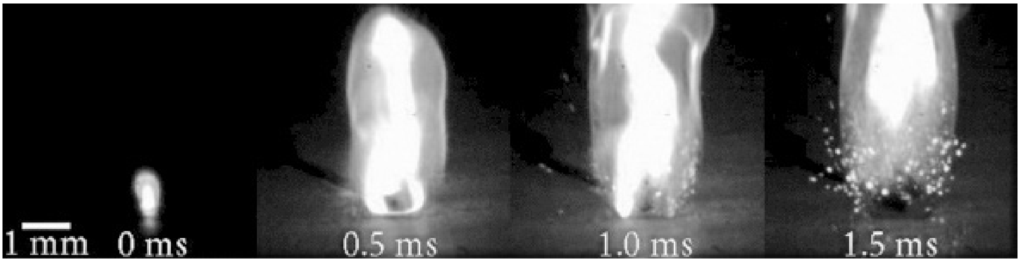


Figure 7. Ignition of 5-layer samples of nanothermite prepared using the RIP method [32]

In the Direct Ink Writing (DIW) method, energetic ink is continuously and evenly extruded under pressure from a nozzle. This technique is inexpensive and is characterised by high accuracy and a wide range of raw materials. Furthermore, the printing process can be carried out at room temperature [33].

A team from China has developed a binder consisting of polyvinyl alcohol, a solution of Viton A in ethyl acetate, sodium dodecyl sulphate and Tween-80. This was mixed with 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) to produce an energetic ink. Using the DIW method, an explosive composition based on this material was printed. The process of preparing the composition is shown in Figure 8. The measured average detonation velocity for this composition is 8079 m/s. Furthermore, its sensitivity to impact is lower than that of CL-20 itself, and its critical diameter is 0.17 mm [34]. When selecting an appropriate additive technique for a given project, the limitations and disadvantages of the individual methods presented in Table 5 should be taken into account.

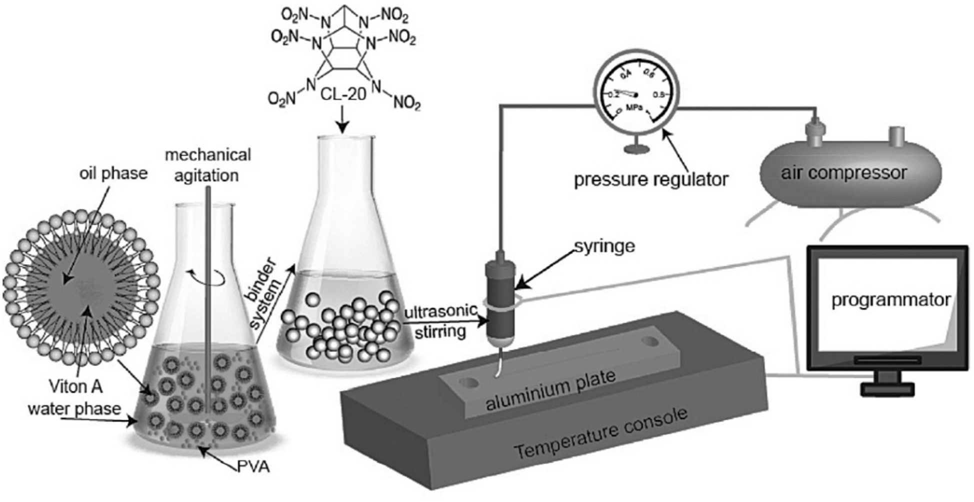


Figure 8. The process of energy preparation of the binder and printing of the composition based on CL-20 [34]

Table 5. Disadvantages of individual additive techniques [35-38]

Additive technique			
VP	**DOD**	**RIP**	**DIW**
High operating costs	High operating costs	Complex design of print heads	Lower resolution compared to VP
Need for print processing (UV curing)	Long printing time for larger models	The necessity of working with potentially hazardous substances	Limited layering capability
Limited model size	Material restrictions (liquids only)	Material restrictions	Material restrictions (appropriate ink rheology)
Lower mechanical resistance of models than in the case of prints made from PLA	Environmental requirements (suitable temperature and humidity)	–	Additional steps, such as drying

5. Smart energy materials

Smart energy materials are materials whose principle of operation is based on two mechanisms. The first is adaptation to changing environmental parameters such as temperature or pressure. The second one involves adapting the material to external forces, such as a magnetic field (Figure 9).

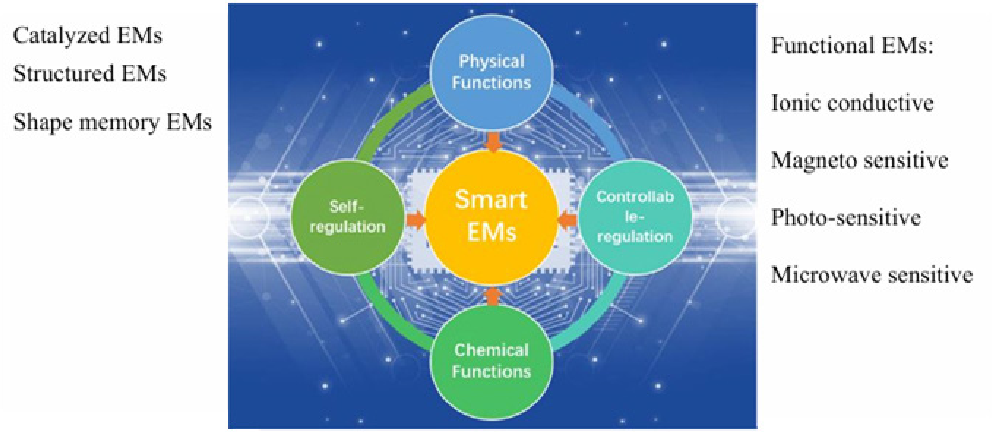


Figure 9. The potential of smart energy materials [39]

Smart energy materials can be obtained by introducing appropriate functional groups, specific compounds or creating appropriate material structures which can respond to physical stimuli. The use of polymers modified by appropriate chemical compounds, e.g. glutaraldehyde, as smart binders in the production of rocket propellants, would enable the design of propellants in which ignition and even combustion kinetics could be controlled by light, microwaves or magnetic fields [39].

Currently, a team of scientists from China is working on smart energy materials whose ignition and combustion would be controlled by microwaves, but this technology still requires refinement and further research [40]. Scientists from Japan have developed a solid propellant micro-engine capable of stopping the combustion process, which is initiated by an 808 nm wavelength laser beam. The combustion process is active only when the propellant surface is heated. The propellant, consisting of HTPB, AP and carbon, is placed in a PMMA or PC casing. By moving the laser beam, the casing in which the propellant is held is heated [41]. Figure 10 shows a schematic diagram of the structure of this micro-engine.

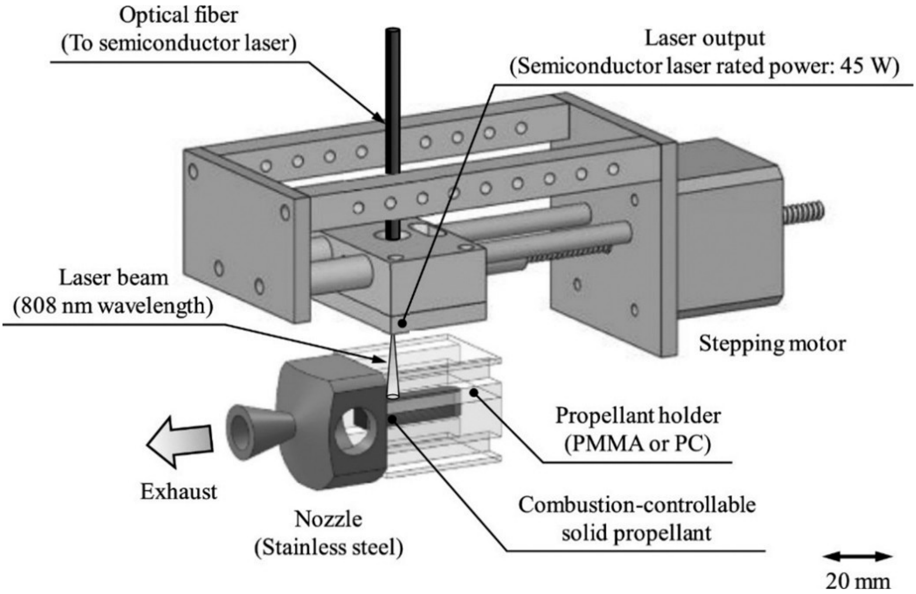


Figure 10. Schematic diagram of a solid propellant micro-engine initiated by a laser beam [41]

Electrically controlled solid propellants (ECSP) are another innovative solution with a wide range of applications. Hydroxyl ammonium nitrate (HAN) is mainly used as an oxidiser in fuels of this type [42]. A team from has China prepared a propellant consisting of 72.2% HAN, 3.8% ammonium nitrate(V), 2% 5-ATZ, 20% poly(vinyl alcohol) and 2% boric acid. It was found that adding aluminium powder with a particle size of 5 and 100 µm to the above composition improves the combustion efficiency of these propellants, while the addition of multi-walled carbon nanotubes leads to an increase in propellant conductivity [43, 44]. The ECSP preparation process is shown in Figure 11.

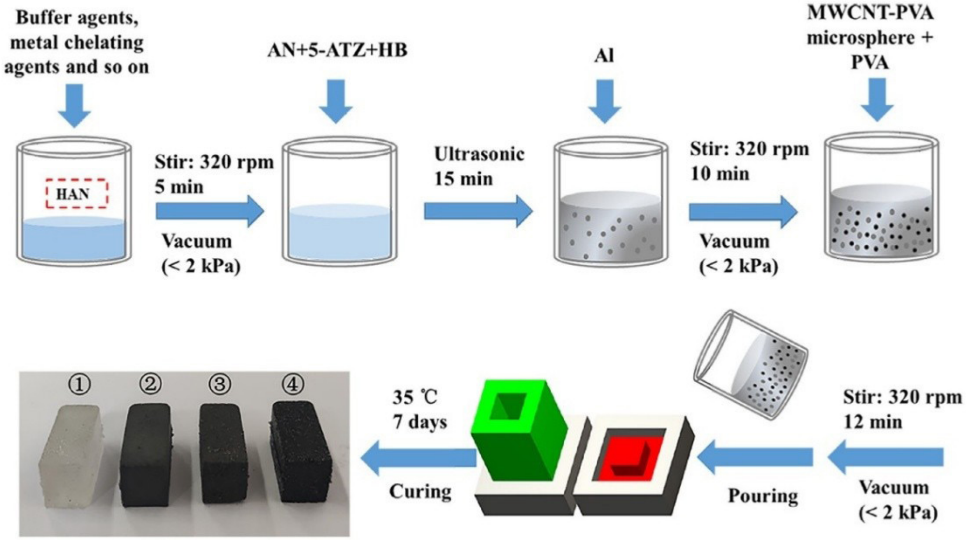


Figure 11. ECSP preparation diagram [43]

Further research on ECSP has shown that electrolysis plays an important role in their controlled combustion process. Furthermore, when the power supply to the system is disconnected, the propellant shuts off [43]. However, the technologies discussed in this chapter are not yet sufficiently developed and require further research.

6. Conclusions

- Currently, it is very important to develop mixtures which could replace those used so far, but which have a negative impact on human health and safety, as well as the environment. Methods are being developed and optimized for the industrial-scale production of substances which previously could only be produced on a laboratory scale or posed a risk to production line workers. 3D printing is becoming increasingly important in the production of explosives and propellants, as it is less time-consuming and cheaper than the melt-casting method. In addition, it allows for the creation of shapes which are more complex than those achieved with previously used methods.
- Smart energetic materials can usher in a whole new era for high-energy materials thanks to properties such as self-regulation or regulation controlled by external factors like optical radiation. The possibility of producing propellants with a controlled combustion process (which can be stopped at any time) is likely to impact the design of ammunition and its performance. Furthermore, the use of propellants which adjust the combustion rate depending on the pressure in the shell casing, could improve the ammunition. However, materials of this type still require a lot of research and are an issue for the future.

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