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High energy materials (HEMs) – innovations with regard to the environment
Materiały wysokoenergetyczne (MW) – Innowacje w aspektach środowiska przyrodniczego

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Abstract: *The study presents the direction of research being undertaken into high-energy materials in respect of environmental sustainability and the increasing requirements of national and international legislation.*
Streszczenie*: W pracy przedstawiono kierunki badań nad materiałami wysokoenergetycznymi (MW) w świetle zasad zrównoważonego środowiska przyrodniczego i konieczności spełnienia rosnących wymagań określonych przez krajowe i międzynarodowe akty legislacyjne.*

Keywords*: high-energy materials, HEMs, ecological issues, new research directions*
Słowa kluczowe*: materiały wysokoenergetyczne, problemy ekologiczne, nowe kierunki badań*

1. Foreword

Striving to meet the requirements determined by sustainable development principles means that the issue of recycling high-energy/explosive materials (HEMs) has been the focus of attention for the last decade. The amount of expired or decommissioned blasting explosives, powders and rocket propellants withdrawn from military stores is estimated at thousands of tonnes annually [1-6]. In 2005, the amount of HEMs in Ukraine was estimated at several hundred thousand tonnes [7], whereas in Albania the amount is so huge that its disposal will require international support [8]. In all locations where redundant HEMs are stored, there is a hazard of uncontrolled activation and detonation. Between 1950-2013, 26 unexpected detonations were reported in Albania [9] as a result of external stimuli (*e.g.* mechanical, thermal, electrical or chemical – *e.g.* autocatalytic decomposition) acting on the HEM [2, 3, 5, 10-27].

The components of HEMs used in the mining industry are not only hazardous due to the risk of high-energy processes but also pose a health and life hazard due to their irritating, carcinogenic and/or toxic properties [28-30]. The effect of HEM explosion products on the environment is also a serious issue [3-5, 10, 31-33].

In the recovery of HEMs from decommissioned ammunition, elimination by detonation and combustion in open areas or storage in underground burial sites are currently the conventional methods. The practice shows that these methods have no prospect for future use, are not cost-effective and are hazardous, as can be seen by the example of an accident in an underground burial site in Switzerland [34].

The need to meet the increasingly strict requirements of legal regulation and IT systems used in HEM management for production, recycling and disposal of warfare agents [35], economic and security considerations, mean that action is taken to limit the total cost of obtaining HEMs. This consists of seeking new, more efficient, cost-effective, safer, more stable and feasible large-scale HEM synthesis methods [36-38]. Studies are carried out to develop new, effective and non-toxic alternatives to currently used HEM components, including solid composite rocket propellants with no ammonium perchlorate (AP) content [39]. Such technical progress requires new types of propellant [40]. New methods are also being developed to dispose of HEMs, involving the most effective recovery of the energy stored in the chemical bonds [2, 4, 11, 41-44] by:

a) using HEMs from decommissioned munitions for producing blasting explosives [45-48],
b) recovery of valuable HEMs from decommissioned munitions, including nitramines (hexogen (RDX), octogen (HMX)) [49-53], cheap and difficult to dispose of substances including AP [54] or recyclable substances including trinitrotoluene [55],
c) reformulation of HEMs for military [56] and civil [57] applications,
d) using components of decommissioned products in new solutions [58].

An alternative solution is to replace currently used HEMs with new, more effective products [59].

2. The concept of sustainable development

A generally accepted solution to the ecological issues, is the concept of sustainable development presented in the UN report “Our Common Future” published in 1987 [60-63]. In a monograph published in 1998 [1], Anastas and Warner presented the concept of sustainable development and the main directions of implementation, included in the twelve principles of green chemistry:

1) **Prevention** - prioritize the prevention of waste, rather than neutralize, recycle or dispose.
2) **Atom Economy** – incorporate the feedstock used in the synthesis into the final product.
3) **Less Hazardous Chemical Syntheses** – use the safest possible solvents and auxiliaries with the lowest toxicity on people and the environment.
4) **Designing Safer Chemicals** – minimise use of solvents and auxiliaries.
5) **Safer Solvents and Auxiliaries** – ensure safety of the product which should not be toxic to human and environment.
6) **Design for Energy Efficiency** – minimize the process energy expenditure.
7) **Use of Renewable Feedstocks** – use only renewable feedstocks in the synthesis.
8) **Reduce Derivatives** – minimize the use of derivatives to reduce the number of reaction steps.
9) **Catalysis** – use catalytic and biochemical processes to help increase efficiency and selectivity, and reduce energy demand.
10) **Design for Degradation** – select feedstocks and auxiliaries safe for people and environment.
11) **Real-time analysis for Pollution Prevention** – monitor the process in real-time.
12) **Inherently Safer Chemistry for Accident Prevention** – ensure process safety.

The relevance of ecological issues in relation to HEMs was validated by the awarding of the 2016 Nobel Prize in technology, to the “green biochemistry” promoter – professor Frances H. Arnold from the California Institute of Technology (Caltech). The implemented technology used a newly developed enzyme converting the renewable material – plant sugars to isobutanol used as a jet propellant and rocket propellant [64]. A result of this approach on the development of HEMs is referred to as Green Energetic Materials (GEMs) [65].

One of the key tools of the environmental management system (EMS) based on ISO 14000 series standards related to a specific product, is the Life Cycle Assessment (LCA). One of the basic assumptions is to analyse the environmental aspects and potential effects of the product on the environment in its entire life cycle “from cradle to grave", *i.e.* from obtaining raw materials through production and use, until it becomes a waste product [66-68]. The LCA includes the following four phases:

- determining the purpose and scope of the analysis,
- analysing the LCI (Life Cycle Inventory) inputs and outputs,
- Life Cycle Impact Assessment,
- interpretation of the obtained data.

In relation to the LCA, the interests of the research institutes are focused on the process of HEM disposal, fabrication of emulsion explosives and determining the effect of small-calibre ammunition on the environment [69-71]. The LCA of a specific product is an example of using mathematical modelling in environmental protection, to analyse the waste management system used. The developed models can be used to optimise the waste management techniques. One of them is IWM-Pl – Integrated Waste Management – the first application available in Polish for developing a waste management system and estimating its effect on the environment [41]. One of the first documented operations using LCA were tests on methods of the efficient utilisation of energy. LCA techniques are in common current use, and a comprehensive view of the HEM life cycle can be shown both in relation to the HEMs used in mining [72], pyrotechnics [73], ammunition [74, 75], as well as blasting and propellant explosives [76]; and in the economic aspect, *e.g.* country-specific analyses [77-79].

3. Chemical substances used in multi-component explosive compositions

HEMs are individual chemical compounds or compositions characterized by high energy density. Apart from chemical compounds with explosive properties, multi-component explosive compositions may include different additives improving their performance, facilitating processing or added for detection and identification purposes. The markers are added as carriers of information of the presence and type of HEM in a specific location and its origin, to reduce the risk of terrorist attacks and criminal acts using HEMs. Volatile additives, *e.g.* 2,3-dimethyl-2,3-dinitrobutane are added to plastic HEMs and marker strings are incorporated in detonating fuses. Fine multi-layer plates, scattered in an explosion, can also be used as markers [80]. Not all substances can be used in all types of multi-component HEMs, often due to high implementation costs.

HEMs used for military purposes are characterized by very high standards regarding the components used, since they are designed to last for decades. Finally, the decision on applying a specific component in HEMs for military applications, is determined by the cost of achieving a specific purpose, for example destroying munition or enemy personnel. Sometimes, changing the solution used in non-explosive modules is preferred over modification of the HEM or replacing the explosive module with one not containing HEMs. The examples include:

a) shaped charges, in which the effects of the detonation process form a cumulative stream able to puncture a thick steel armour plate, are obtained by shaping and forming metal components (cumulative inserts) and not by the introduction of new HEMs. Using explosively formed projectile (EFP) charges and multi-layer cumulative inserts [81] is more promising than using new HEMs with improved performance, but also more expensive, although, similar solutions are also being considered, including the utilisation of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexsaazatetracyclo$[5,5,0,0^{3,11}0^{5,9}]$dodecane (CL-20, HNIW) or 1,2,3,4,5,6,7,8-octanitrocubane.
b) Exploding Bridge Wire detonators (EBWs) and Exploding Foil Initiators (EFIs). These are utilised mainly in low-vulnerability ammunition, since their initiation is due to the effect of a shock wave resulting from an electro-explosion of an electric conductor, eliminating the use of standard primers in the fuse, and to significantly increase their resistance to external factors [82].

The conventional organic components with explosive properties can be classified into one of three groups of nitro compounds [83]:

a) O-nitrocompounds: cellulose nitrate (nitrocellulose, guncotton, NC, pyroxilin), glycerol trinitrate, (nitroglycerin, NG) and ethylene glycol dinitrate (nitroglycol), pentaerythritol tetranitrate (penthrite, nitropenta, ten, PETN),

b) C-nitrocompounds: 2,4,6-trinitrotoluene (trotyl, TNT), 1-hydroxy-2,4,6-nitrobenzene (picric acid, melinite, ammonium picrate, TNF), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1,1′-diamino-2,2′-dinitroetene (FOX-7), 3-nitro-1,2,4-triazol-5-one (NTO),

c) N-nitrocompounds: 1,3,5-trinitro-1,3,5-triazycyclohexane (hexogen, Hx, RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazycyclooctane (octogen, HMX), CL-20 or ammonium dinitramide (ADN).

Apart from high-energy components, key components of explosive compositions for use in military applications, include binders and plasticizers:

a) Currently used binders include polyurethanes, rubbers and fluoroelastomers. They include polymerized liquid rubbers with different functional groups, *e.g.* polybutadiene acrylonitrile (PBAN) copolymer, carboxyl-terminated polybutadiene (CTPB), hydroxyl-terminated polybutadiene (HTPB) which, in modern rocket propellants, are used both as a binder and a propellant [2, 3, 11, 84, 85], and are also used in plastic explosives as binders. In plastic HEMs, fluoroelastomers including trifluorochloroethylene and vinylidene chloride copolymer (Exon), polychlorotrifluoroethylene (KelF) or hexafluoropropylene and vinylidene fluoride copolymer (Viton) are used as binders [83]. Addition of those compounds allows plastic bonded explosives (PBXs) with a maximum concentration of blasting explosives, to be obtained.

b) Common plasticizers include esters: dioctyl phthalate, dibutyl phthalate, dioctyl adipate or dibutyl sebacate.

Inorganic components include the following:

a) AP or AN (ammonium nitrate) type inorganic oxidizers used in solid composite rocket propellants added in a modified form which does not undergo crystallographic transformation at 32 ºC [86]. Pyrotechnic compositions usually use potassium chlorate and potassium perchlorates ($KClO_3$ and $KClO_4$, respectively), metal oxides (Fe_3O_4, MnO_2, BaO_2, PbO_2, Pb_3O_4), sodium (Na), potassium (K) and barium (Ba) nitrates.

b) Metallic and semi-metallic powders in different forms including nano-powders used as flammable agents and modifiers [2, 3, 5, 20, 87-92] to modify:
   - HEM structure, *e.g.* aluminium (Al), magnesium (Mg), boron (B), beryllium (Be),
   - HEM combustion rate, *e.g.* aluminium (Al), lead (Pb), titanium (Ti), boron (B),
   - qualitative and quantitative composition of detonation, deflagration or combustion products.

A specific group of substances used in military products and mining blasters are initiating explosives including mercury(II) fulminate ($Hg(CNO)_2$) which decomposes to carbon monoxide (CO), nitrogen(II) oxide (NO) and metallic mercury vapours (Hg), and lead(II) azide ($Pb(N_3)_2$) which decomposes to elemental nitrogen (N_2) and lead vapours (Pb) or lead trinitroresorcinate [2, 3, 10, 11]. They are used in igniferous and disruptive detonators.

HEMs used in mining usually include an oxidizer/component system. These are characterized by a lifetime of up to 12 months, after which no further applicability tests are carried out. Introduction of new components to HEMs for blasting applications is limited by price and availability. Ammonium nitrate, not used in military blasting explosives, except for the war period and special applications [93], is a key component of HEMs for mining purposes. It is cheap to manufacture, has several other applications (mainly agriculture) and is easily accessible – although currently limited due to terrorist threat – in amounts significantly exceeding HEM market requirements. The explosives used in mining can be classified into 10 groups (**SI** to **SX**) of components with similar chemical constitution [94]:

SI – Inorganic oxo-acid salts (*e.g.* nitrates, perchlorates).
SII – Inorganic hydracid salts, non-explosive.
SIII – Inorganic components, non-explosive other than included in group **SI** and **SII**, (*e.g.* sulfates, phosphates, chromates, carbonates, oxalates, metal oxides, glass microspheres, water).
SIV – Organic metal salts, non-explosives (*e.g.* zinc and calcium stearate).
SV – Elemental components – elements (*e.g.* aluminium as aluminium powder and carbon as soot or graphite).
SVI – Components containing explosophores ($–C–NO_2$ and $–C–O–NO_2$ compounds).
SVII – Organic components, non-explosive – hydrocarbons other than included in group **SIX** (*e.g.* oils, paraffins, waxes, slack waxes).
SVIII – Organic components, non-explosive – natural, other than included in group **SVII** (*e.g.* charcoal, guar gum powder, wood flour, cellulose derivatives).

SIX – High-molecular organic components, non-explosive – (synthetic polymers, plastics including hydrocarbon plastics, *e.g.* polystyrene).

SX – Low-molecular organic components, non-explosive – not containing explosophores – other than those included in groups **SIV**, **SVII** and **SVIII**.

4. HEM degradation products

Detonation, deflagration or combustion of HEM leads to degradation with a simultaneous release of significant amounts of [3, 10, 11, 42]:

a) heat energy,
b) radiant energy,
c) mixture of hot gases (quality and volume determine the type and ratio of atoms in a specific HEM) at high velocity.

HEM degradation products usually include the following atoms [3, 11]:

a) carbon (C) as a grey or black smoke (soot, graphite or diamond), carbon monoxide (CO) and carbon dioxide (CO_2),
b) hydrogen (H) as elemental hydrogen (H_2) and water (H_2O),
c) nitrogen (N) as elemental nitrogen (N_2), nitrogen (II) and nitrogen(IV) oxides,
d) chlorine (Cl) as HCl.

A key factor, from the point of view of HEM application safety and environmental protection, is the quality and quantity of the products of high-energy decomposition of toxic components. The main factor determining chemical composition of the products is the oxygen balance (OB_{MW}) [42]:

$$OB_{\mathrm{MW}} = \frac{(\mathrm{a}-\mathrm{b})M_{\mathrm{O}}}{M_{\mathrm{MW}}}100\% \tag{1}$$

where:

- *a,* the number of oxygen atoms required for complete oxidation of combustible components present in the material,
- *b*, the number of oxygen atoms in the material,
- *(a – b)*, the difference showing excess (+) or deficit (–) of oxygen atoms (O) required for complete oxidation of combustible components present in the HEM,
- M_{O}, oxygen (O) atomic mass,
- M_{MW}, HEM molecular weight.

OB_{MW} is the relation between the mass of combustible elements (C and H) and the oxygen (O) in the HEM's unit weight (100 g) expressed as a percentage of mass. It is a key indicator, since it determines both the quality and the volume of HEM decomposition products. The difference between the actual and stoichiometric number of oxygen atoms in the mixture and the amount required for complete oxidation of the components is designated as (0), (+) or (–). If the value is [3, 11, 42]:

- zero, $OB_{\mathrm{MW}} = 0\%$, the number of oxygen atoms in the material corresponds to the stoichiometric amount required to oxidize all material components to their higher oxidation state (C to CO_2). The example compound with $OB_{\mathrm{MW}} = 0\%$ is nitroglycol ($CH_2(ONO_2)_2$),
- positive, $OB_{\mathrm{MW}} > 0\%$, the number of oxygen atoms is higher than required for complete oxidation of all material components to the products in form of gas, mainly carbon to CO_2 and hydrogen to H_2O, *e.g.* nitroglycerine ($C_3H_5(ONO_2)_3$): $OB_{\mathrm{MW}} = +3.52\%$,
- negative, $OB_{\mathrm{MW}} < 0\%$, the number of oxygen atoms is lower than required for complete oxidation of HEM components, *e.g.* trinitrotoluene ($(NO_2)_3C_6H_2CH_3$): $OB_{\mathrm{MW}} = -78\%$.

The materials characterized by positive *OB* may include nitrogen oxides (NOx) as their decomposition products [42].

Introducing aluminium (Al) as flakes or dust, reduces the volume of gaseous products of HEM decomposition. Aluminium content reduces the critical diameter of detonation of charges made of selected calcium ammonium nitrates and increases the amount of heat released and the effectiveness of HEMs [3, 11, 91, 92].

5. The effects of HEM decomposition products on the environment

The products of HEM decomposition usually include carbon monoxide and dioxide (CO, CO_2); nitrogen(II) and nitrogen(IV) oxides (NO, NO_2) – hazardous both to health and environment, contributing to the greenhouse effect (CO, CO_2, HC, soot particles), ozone depletion (NO, NO_2, HCl) and acid precipitation (HCl) [3, 4, 11, 20, 63, 66, 95, 96]. The inorganic substances listed in item 3 are the source of toxic heavy metals (Hg, Pb, Fe, Mn, Ti, Mo, Zn), carbon monoxide and dioxide (CO, CO_2), nitrogen oxides (NOx), methane (CH_4), chlorine atoms (Cl●) (HCl) and sulfur oxides (SOx) [62, 63].

Literature includes a growing number of publications which discuss the hazards resulting from the effects of HEMs and the products of detonation or combustion released into the environment at testing grounds, shooting-ranges and their surroundings. Test results carried out in all biospherical elements (air, soil, plants, surface and ground water) show that HEMs:

a) disturb species biodiversity [97],
b) contaminate air, soil, surface and groundwater with decomposition products, including heavy metals (Pb, Cu, Zn) [63, 98],
c) contaminate soil (particularly decomposition products of rocket propellants and ammunitions *etc.*) [99-102].

The high chemical reactivity of AP means, that when used as an oxidizer in rocket propellant, the service life of the propellant is significantly lower than for the composite propellants (NC and NG-based), which means a increased frequency of testing to determine further applicability of the product for military purposes and hence higher operational costs [20, 103]. Hydrochloride (HCl) and the product of its decomposition in troposphere – a highly reactive chlorine free radical (Cl●), released as a product of AP decomposition is a serious ecological concern [63, 95, 96].

Gas products formed during the detonation of HEMs for civil and mining applications may contain carbon oxide (CO), nitrogen oxides (NOx), other gases, vapours and solids in quantities which will not affect health. A significant accomplishment in the area of blasting explosives for mining purposes was the introduction of emulsion HEMs without explosive components such as nitroglycerine or TNT. The emulsion HEMs may be O/W type emulsions, with water (W) as a continuous phase, and W/O type emulsions with oil (O) as a continuous phase. These explosives are more environmentally friendly and safer to use (showing no sensitivity to friction and impact) [3, 86, 104-106].

6. Overview of HEM disposal methods

The following disposal methods of decommissioned HEMs are usually suggested [4, 107]:

a) Chemical conversion, *e.g.* hydrolysis [4, 108].
b) Storage in underground stores; a palliative solution, since the released decomposition products are a potential source of groundwater contamination [4, 109]. After the Second World War, significant amounts of HEMs and chemical weapons were disposed of in the seas and oceans, including the Baltic Sea.
c) Controlled physical and chemical HEM decomposition by:
    - water (H_2O) in supercritical condition (*i.e.* in the fourth state of matter), in which high reactivity results in decomposition leading to HEM mineralization in the final phase [4, 110],
    - hydrogen peroxide (H_2O_2) introduced to water contaminated with HEMs (high-explosives, rocket propellants *etc.*) and the decomposition process initiated by UV radiation; a relatively expensive method [4, 111],
    - catalytic photo-degradation leading to complete HEM mineralization; the method demonstrated using 3-nitro-1,2,4-triazol-5-one (NTO), where the nitrous group ($–NO_2$) is reduced as a result of UV radiation

($\lambda > 290$ nm), and the presence of titanium dioxide (TiO_2) causes the specimen to mineralize [4, 112].

d) Direct incineration or detonation in open areas; these are currently the most common disposal methods, however, from the practical point of view, should be abandoned due to economic reasons (loss of energy) and the adverse effects of high-energy reaction products on health and the environment [4, 113].
e) Biological decomposition using various microorganisms; the method allows the elimination of HEM in the soil and water environment; the products of multi-stage decomposition include gases: dinitrogen (N_2) and carbon dioxide (CO_2), and solids: sludge; the example of trinitrotoluene shows that in some cases, compositions exhibiting toxic and/or mutagenic properties can be present in the decomposition products [114].
f) Recycling or reuse of military HEMs, the best example of which is melting trinitrotoluene from the warheads and using it in blasting explosives for mining purposes; the practice shows that it is an economically viable and eco-friendly method [4, 115].

7. Directions of HEM research

Analysis of monographs, available publications and patent applications regarding HEMs shows that the current directions of research focus on:

1. Improving the synthesis methods of currently used explosives to improve their performance; by selecting the optimum synthesis procedure, feedstocks and/or reaction medium.
   a) Using new feedstocks to fabricate LLM-105 (2,6-diamino-3,5-dinitropyrazine-l-oxide) enables [116]:
      - increased efficiency of the final product (up to 43.4%),
      - higher purity product,
      - increased production safety,
      - reduced production costs,
      - product use without recrystallization.
   b) Developing new synthesis methods of 4,4’,5,5’-tetranitro-2,2’-bi-1*H*-imidazole (TNBI) to improve its energy properties [14].
   c) Proposals of new, safe and effective oxidant/high-energy filler compositions for solid composite rocket propellants, providing new benefits discussed in a review study with many examples [20].
2. Developing new, safer, more effective synthesis methods at reduced costs, at a scale corresponding to demand.
   a) Using a sol-gel method to synthesise high-energy components of CL-20 and binders enables end products with improved performance in the nanoscale, to be obtained [117].
   b) Using different methods of ADN synthesis, in 2015 resulted in developing the safest method of obtaining a final product on a large scale [17], however, it took several years in Poland (the research has been ongoing since 2011 [118]).
   c) Four new methods of TNBI synthesis were proposed, indicating possible performance improvements [14].
3. Seeking new effective and non-toxic alternatives to currently used HEMs.
   a) 1-[(2*E*)-3-(1*H*-tetrazol-5-yl)triaz-2-en-1-ylidene]methanediamine) (MTX-1) was proposed as a potential alternative to (1-(5-tetrazolyl)-3-guanyl tetrazene hydrate) (tetrazene). MTX-1 shows good thermal stability, higher efficiency and is much safer as an initiating charge [119].
   b) ADN was proposed as an alternative to AP in solid rocket propellants; it is considered eco-friendly due to more benign combustion products [17].
   c) Commonly used oxidizers, including AN and AP are replaced with lithium perchlorate ($LiClO_4$) [20, 120].
   d) In the last decade, due to the need to develop new alternatives for rocket propellant components, research has mainly focused on: ADN, RDX, CL-20 also referred to as HNIW, HNF $[(N_2H_5)^+(C(NO_2)_3^-]$, glycidyl polyazide (GAP) [121-125].
4. A key method of increasing the energy performance of solid and liquid explosives is a partial substitution of oxygen atoms (O) with fluoride atoms (F); the best effects were achieved by partially substituting $-NO_2$

functional groups with $–NF_2$ groups in oxidizers and other components. An increase in energy performance was observed with an increase in gradual substitution of $–NO_2$ groups with $–NF_2$ groups [126].

5. Introduction of new HEMs in practical applications:
   a) Allowed new inorganic coordinate bonds to be obtained, characterized by high energy efficiency and sensitivity in HEMs use as initiating charges, including:
      - alkaline-earth carbohydrazide perchlorates with a generalized formula $[Me^{II}(CHZ)_3](ClO_4)_2]$, where: Me^{II} = Be, Ca, Mg, Sr, and Ba, CHZ – nitrogen-rich ligand – carbohydrazide $NH_2NHCONHNH_2$ [127],
      - iron(II) carbohydrazide perchlorate, $[Fe^{II}(CHZ)_3](ClO_4)_2]$ also referred to as FeCP, characterized by higher sensitivity and energy density compared to other presented coordinate bonds [26].
   b) Research on aminonitronaphthalenes as a new class of high energy materials following a discovery of potentially high energy density of FOX-7 [3-5, 10, 27].
   c) Research on compositions of ionic salts, *e.g.* eco-friendly ADN showing a great potential of practical applications [128].
6. New solutions and research methods aimed at introducing new HEMs in practical applications are being proposed:
   a) Octanitrocubane (ONC), $C_8(NO_2)_8$ with the highest known energy density and great potential of practical applications; its synthesis is a complex and costly multi-stage process [129-131].
   b) ADN, HNF and HAN (hydroxylammonium nitrate) are considered as potential future components of propellant explosives [27].
   c) A new transferred arc plasma reactor (TAPR) was developed for obtaining nano aluminium powder (NAP) [132].

The need to meet the requirements of sustainable development and legal requirements means that:

a) Research is carried out to increase the effectiveness of currently used and effective newly developed HEM management methods, in particular, in utilizing the energy stored in chemical bonds and to meet [2, 5, 11, 12, 107, 133]:
   - relevant regulations,
   - safety requirements,
   - economic considerations.

b) The methods of managing HEMs are constantly improving and, over the last decade, remain a focus due to the need to observe the limitations resulting from relevant national and international legislation. This was discussed in item 2 on the example of LCA.

8. Summary

The analysis of available materials, including original studies, monographs, reports from scientific conferences and patent applications relating to high energy materials, has allowed following conclusions to be reached:

♦) Currently, the focus of researchers' attention is on the improvement of known HEMs showing high energy density, and involves increasing their efficiency and limiting their sensitivity to thermal and mechanical stimuli.

♦) New HEMs are usually obtained by modification of currently used HEM particles by adding new or modifying existing substituents to improve performance.

♦) There is a need to step up the research on new methods or improve the effectiveness of currently used HEM management methods, particularly those aimed at utilizing the energy stored in chemical bonds conforming to:
   - relevant regulations,
   - safety requirements,
   - economic considerations.

- ♦) A special focus should be on the comprehensive analysis of the effects of quality and quantity of high-energy additives obtained from disposal, to optimize those in existence and designing new HEMs for mining purposes.
- ♦) The 12 principles of "green chemistry" should be observed when developing new HEMs, including the latest developments in organic synthesis to minimize derivatization, and thus the negative effect of the fabrication processes on the environment.
- ♦) HEM detonation and combustion processes should not cause ecological hazard.
- ♦) The effects of specific products, including HEMs on the environment should be analysed using the LCIA concept.
- ♦) The disposal of decommissioned explosives bringing economic gain and conforming to the environmental protection requirements should include the re-processing of all components.

References

[1] Anastas T.P., Warner C.J. *Green Chemistry, Theory and Practice*. New York: Oxford University Press, **1998**.

[2] Agrawal P.J. *High Energy Materials: Propellants, Explosives and Pyrotechnics.* Weinheim: Willey-VCH, **2010**.

[3] Maranda A. *Industrial Explosives.* (in Polish) Warsaw: Wyd. Wojskowa Akademia Techniczna **2010**; ISBN 978-83-61486-61-9.

[4] Lipińska K., Lipiński M., Maranda A. Disposal of Waste High Energy Materials. [in:] *Waste and Packaging – New Legal Regulations and Obligations.* (in Polish) Wachowski L. Ed., Poznań: Wyd. Forum, **2009**.

[5] Olah G.A., Squire D.R. *Chemistry of Energetic Materials.* New York: Academic Press. Inc., **1991**.

[6] Nienartowicz M. Progress of the Disposal Program for Decommissioned Warfare Agents in the National Defense Department. (in Polish) *Problemy Techniki Uzbrojenia* **2006**, *98*: 25-30.

[7] Polyakov L. *Aging Stocks of Ammunition and SALW in Ukraine: Risks and Challenges.* Bonn International Center for Conversion, Bonn, **2005**, Paper 41.

[8] Boulay R., Kotobelli A. *The Demilitarization of Small Arms and Light Weapons Ammunition in Albania – A NATO PFP Trust Fund Project*, NAMSA, **2006**.

[9] Sałaciński T. Sources of Data on Accidents and near-to-Accident Events Connected with Explosives. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2014**, *6*: 64-71.

[10] Urbański T. *Chemistry of Technology of Explosives.* Vol. 4, Oxford: Pergamon Press, **1984**.

[11] Klapotke M.T. *Chemistry of High-Energy Materials*. Berlin: Walter de Gruyter, **2012**.

[12] Sikder A.K., Sikder N.A. A Review of Advanced High Performance, Intensitive and Thermal Stable Energetic Materials Emerging for Military and Space Applications. *J. Hazard. Mater.,* A **2004**, *112*: 1-15.

[13] Wu J.-T., Zhang J.-G., Zhang T.-L., Yang L. Energetic Nitrogen-rich Salt. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(3): 417-437.

[14] Szala M., Lewczuk R. New Synthetic Methods for 4,4',5,5'-Tetranitro-2,2'-bi-1*H*-imidazole (TNBI). *Cent. Eur. J. Energ. Mater.* **2015**, *12*(2): 261-270.

[15] Sabate Miro C., Delalu H. 2-Tetrazene Derivatives as New Energetic Materials; Synthesis, Characterization and Energetic Properties. *Cent. Eur. J. Energ. Mater.* **2014**, *11*(4): 515-537.

[16] Bayat Y., Zarandi M., Khadiv-Parsi P., Salimi Beni A. Statistical Optimization of the Preparation HNIW Nanoparticles *via* Oil-in-Water Microemulsions. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(3): 459-472.

[17] Gołofit T., Maksimowski P., Kotlewski A. Safety of Ammonium Dinitramide. Synthesis *vs*. Size of a Commercial Production Scale. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(4): 817-830.

[18] Pang. S.P., Yu Y.Z., Zhao X.Q. A Novel Synthetic Route to Hexanitroheksaisowurtzitane. *Propellants Explos. Pyrotech.* **2005**, *30*(6): 442-444.

[19] Lempert D., Nechiporenko G., Manelis G. Influence of Heat Release Value and Gaseous Combustion

Products Content on Energetic Parameters of Solid Composite Propellants. *Theory Pract. Energ. Mater.* **2009**, *8*: 234-243.

[20] Dey A., Sikder A.K., Talawar B.M., Chottopadhyay S. Towards New Directions in Oxidizers/Energetic Fillers for Composite Propellants: an Overview. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(2): 377-399.

[21] Manelis G.B., Nazin G.M., Rubtsov Y.I., Strunin V.A. *Thermal Decomposition and Combustion of Explosives and Propellants.* New York: Taylor & Francis Inc., **2003**.

[22] Trzciński W.A., Cudziło S., Paszula J. Studies of Free Field and Confined Explosions of Aluminium Enriched RDX Compositions. *Propellants Explos. Pyrotech.* **2007**, *32*(6): 502-508.

[23] Trzciński W.A., Cudziło S., Paszula J. Study of the Effect of Additive Particle Size on Non-ideal Explosive Performance. *Propellants Explos. Pyrotech.* **2008**, *33*(3): 227-235.

[24] Srinivasan P., Kumaradhas P. Crystal Density Prediction, Charge Density Distribution and the Explosive Properties of Highly Energetic Molecule 2-Methyl-5-nitramino-tetrazole: and DFT and AIM Study. *Cent. Eur. J. Energ. Mater.* **2013**, *10*(1): 53-68.

[25] Cubero E., Orozco A.I., Luque F.J. Theoretical Study of Azidotetrazole Isomerism; Effect of Solvent and Substituents and Mechanism of Isomerization. *J. Am. Chem. Soc.* **1998**, *120*: 4723-4731.

[26] Liu R., Zou Z., Qi S., Yang L., Wu B., Huang H., Zhang T. Synthesis, Crystal Structure, and Properties of a Novel, Highly Sensitive Energetic, Coordination Compound: Iron(II) Carbohydrazide Perchlorate. *Cent. Eur. J. Energ. Mater.* **2013**, *10*(1): 17-36.

[27] Śliwa W. *Selected Chemistry Fields for the Students of the Faculty of Mining*. (in Polish) Wrocław: Wyd. Politechniki Wrocławskiej, **1977**, pp. 235-246.

[28] Wojewódka A. Toxicity of Dinitrotoluene and Trinitrotoluene. (in Polish) *Research Studies of the Central Mining Institute, Conference Series – Materials from the Blasting Works Safety Conference in Mining Industry* **1999**, *28*: 239-245.

[29] Lewis T.A., Newcombe D.A., Crawford R.L. Bioremediation of Soils Contaminated with Explosives. *J. Environ. Manage.* **2004**, *70*(4): 291-307.

[30] Kuczyńska B., Maranda A. Toxicity of Selected Explosives on Living Organisms. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2011**, *3*: 90-99.

[31] Maranda A., Gołąbek B., Kasperski J. *Emulsion Explosives.* (in Polish) Warsaw: WNT, **2008**; ISBN 978-83-204-3427-9.

[32] Maranda A., Kuczyńska B. Environmental Management of Explosives. [in:] *High-Energy Materials.* Maranda A., Sałaciński T., Lewandowska A. Eds., Vol. 2., Warsaw: Institute of Industrial Organic Chemistry, **2010**.

[33] Velsko C.A., Watkins B.E., Pruneda C.O., Stephens J.R., Lipkin J. *Emissions Characterization in the Contained Underground Demilitarization Laboratory at the Nevada Test Site.* UCRL-JC-126887, LLNL USA, **1999**.

[34] *Explosion inside an Underground Storage of Explosives 2 November 1992. „Steingletscher", Swiss Alps Switzerland.* French Ministry for Sustainable Development – DGPR/SRT/BARPI, ARIA No 37776.

[35] Figurski J. IT System for Warfare Agent Recycling and Disposal Process Management. *Problemy Techniki Uzbrojenia* **2006**, *98*: 31-42.

[36] Bayat Y., Hajighasemali F. Synthesis of CL-20 by a Greener Method Using Nitroguanidine/HNO_3. *Propellants Explos. Pyrotech.* **2016**, *41*(1): 20-23.

[37] Badgujar M.D., Talawar B.M., Mahulikar P.P. Review on Greener and Safer Synthesis of Nitro Compounds. *Propellants Explos. Pyrotech.* **2016**, *41*(1): 24-34.

[38] Szala M., Sałaciński T. 2,4,6-Trinitrotoluene as a Source of Modern Explosives. Review. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2015**, *7*: 125-143.

[39] Florczak B. Solid Rocket Propellants – Current State and Future Perspectives. (in Polish) [in:] *Explosives. Research – Applications – Safety.* Maranda A., Sałaciński T., Waszkiewicz I. Eds., Vol. I. Warsaw: Institute of Industrial Organic Chemistry, **2006**.

[40] Leciejewski K.Z., Cudziło S. Trends in Development of Propellants in Aspects of Requirements of Future

Gun Propellant System. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2011**, *3*: 64-71.

[41] *Evaluation of Waste Management System. Part 2. Practical Applications.* Kraszewski A., Pietrzyk-Sokulska E. Eds., Kraków: Wyd. IGSMiE PAN, **2011**.

[42] Politzer P., Murray S.J. The Role of Products Composition in Determining Detonation Velocity and Detonation Overpressure. *Cent. Eur. J. Energ. Mater.* **2014**, *11*(4): 459-474.

[43] Clark P.R., Grens B.W., Machacek O., Eck R.G. *Beneficial Use of Energy-Containing Waste.* Patent US 5612507, **1997**.

[44] Wieciński W. Disposal in View of Changes in Management of Decommissioned Ammunition Stores. *Problemy Techniki Uzbrojenia* **2010**, *115*: 85-90.

[45] Rez J., Kouba M.. Utilization of Demilitarized Energy Materials (DEM) as One of the Raw Materials for Production of Industrial Explosives. *Proc. Conf. Blasting Techniques 2008*, Stara Lesna, Slovakia, **2008**.

[46] Lipińska K., Lipiński M., Maranda A., Sobala J., Badura E. Analysis of Possible Applications of Decommissioned Composite Solid Rocket Propellants in Mining Blasting Materials. (in Polish) *Research Studies of the Central Mining Institute, Conference Series – Materials from the Blasting Works Safety Conference in Mining Industry* **2002**, *43*: 185-189.

[47] Lipińska K., Lipiński M., Maranda A. Demilitarized Double Base Propellants as Ingredients of Commercial Explosives. *Cent. Eur. J. Energ. Mat.* **2005**, *2*(1): 69-78.

[48] Wendong W., Jianhong L., Zhibin Z. Study and Application of Emulsion Explosive and Water Gel Explosives Containing Waste Propellant. *Explos. Mater.* **2003**, *5*(32): 13-16.

[49] Cao Z., Kovenklioglu S., Kalyon D.M., Yazici R. Dissolution Study of BAMO/AMMO Thermoplastic Elastomers for the Recycling and Recovery of Energetic Materials. *J. Energ. Mater.* **1997**, *15*: 73-107.

[50] Spencer F.A., Hartline F.D. *Recovery of Secondary Explosives from Explosive Compositions.* Patent US 5977354, **1999**.

[51] Phillips S.R., Cain W.A., Schilling T.J., Miks M. *Recovering Nitramines and Reformulation of By-products.* Patent US 6653506, **2003**.

[52] Cannizzo L., Huntsmann L. *Extraction and Recovery of Nitramines from Propellants, Explosives, and Pyrotechnics.* Patent US 6414143, **2002**.

[53] Warner F.K., Cannizzo F.L., Hajik M.R. *Method for Recovery of Nitramines from Aluminized Energetic Materials.* Patent US 6610156, **2003**.

[54] Melvin S.W., Graham F.J. *Method to Demilitarize Extract, and Recover Ammonium Perchlorate from Composite Propellants Using Liquid Ammonia.* Patent US 4854982, **1989**.

[55] Borkowski A.J., Borkowski J.P., Bielecki M., Maranda A., Borkowski J., Danielewicz D., Warchoł R. Laboratory and Firing Ground Examinations of TNT Hydrojetting Washing out from Artillery Shells. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2011**, *3*: 40-56.

[56] Lee E.K. *Reformulation of Composition C-4 Explosive.* Patent US 6887324, **2005**.

[57] Mcnicol A.M. *Broken-emulsion and Process for Recycling Emulsion Explosives.* Patent US 5700970, **1997**.

[58] Sapija D., Śliwiński J., Wojciechowski A., Ludas M., Madej W., Czubaty Ł., Krysiak P., Strzałkowski D. Using the Decommissioned Antipersonnel Mines in Development of Land Mine Alternatives. (in Polish) *Problems of Mechatronics: Armament, Aviation, Safety Engineering* **2014**, *5*(1): 81-90.

[59] Chyłek Z., Szala M. The Review of Potential High-energetic Components for Modern Plastic Bonded Explosives. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2015**, *7*: 144-155.

[60] Wachowski L., Domka F. Green Chemistry in the Sustainable Development of the Environment. [in:] *Waste and Packaging – New Legal Regulations and Obligations.* (in Polish) Kubera H. Ed., Poznań: Wyd. Forum, **2007**, Ch. 2/1.1., pp. 1-29.

[61] Wachowski L., Kirszensztejn P. DDT and Its Derivatives. [in:] Waste and packaging – New Legal Regulations and Obligations. (in Polish) Urbaniak Wł. Ed., Poznań: Forum, **2003**, Ch. 3/3.10, pp. 1-23.

[62] O'Neill P. *Environmental Chemistry.* (in Polish) 1st ed., Warsaw/Wrocław: PWN, **1997**.

[63] vanLoon W.G., Duffy J.S. *Environmental Chemistry.* (in Polish) Warsaw: PWN, **2007**.

[64] *Enzyme Engineering for Fuels and Chemicals*. Project realised by the Arnold F.H. research group CaliTech, USA.

[65] Talwar B.M., Sivabalan R., Mukundan T., Muthurajan H., Sikder K.A., Gandhe R.B., Subhananda Rao A. Environmentally Compatible Next Generation Green Energetic Materials (GEMs). *J. Hazard Mater.* **2009**, 161: 589-607.

[66] Foltynowicz Z., Wachowski L. Commodity Science and Ecological Aspects of Marketing CFC and HCFC Alternatives. (in Polish) Poznań: Wyd. Uniwersytetu Ekonomicznego w Poznaniu, **2009**.

[67] Kaim A. *Computer Simulation of Technological Processes using CHMCAD.* (in Polish) Practical classes materials from the Learning Laboratory of the Chemistry Technology at the Warsaw University Faculty of Chemistry.

[68] Spahlinger G. *Recent Advances in High Nitrogen Energetic Materials.* http://findpdf.top/advances/recent-advances-in-high-nitrogen-energetic-materials.html [retrieved 12.12.**2016**].

[69] Ferreira C., Ribeiro J., Freire F. Life-Cycle Assessment Applied to Military Systems: Overview of the Work Developed in the ERM Project. *Greener and Safer Energetic and Ballistic Systems Conf.,* Bucharest, **2015**.

[70] Amirhossein M., Arunprakash T.K. Environmental Life Cycle Assessment of New Energetic Materials. *12th AIChE Annual Meeting*, Pittsburgh, USA, **2012**, 174e.

[71] Amirhossein M., Arunprakash T.K. Energetic Ionic Materials: How Green are They? A Comparative Life Cycle Assessment Study. *ACS Sustainable Chem. Eng.* **2013**, *1*(4): 448-455.

[72] Kuczyńska B., Maranda A. Life Cycle Inventory of Production Processes Selected Mining Explosives. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2011**, *3*: 122-135.

[73] a) Red, white and plasticized phosphorus. (Vol. 2); b) Cichowicz J.J., HC Smoke (Vol. 4), [both in:] *Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants.* Report ARCSL-EA-83004, **1983**.

[74] Alverbro K., Björklund A., Finnveden G., Hochschorner E., Hägvall J. A Life Cycle Assessment of Destruction of Ammunition. *J. Hazard. Mater.* **2009**, *170*(2-3): 1101-1109.

[75] Figurski J., Fonrobert P., Mazur I., Ignaciuk A. Ammunition Lifecycle. (in Polish) *Problemy Techniki Uzbrojenia* **2013**, *128*: 87-97.

[76] Hoffman D.M., Hawkins T.W., Lindsay, G.A., Wardle R.B., Manserd G.D. Clean, Agile Alternative Binders, Additives and Plasticizers for Propellant and Explosive Formulations. *Conf. Life Cycles of Energetic Materials,* Del Mar, CA, **1994**.

[77] Figurski J, Kostrow R., Milewski E. Determining Costs in the Lifecycle of Armament Systems and Military Equipment. (in Polish) *Problemy Techniki Uzbrojenia* **2008**, *108*: 29-40.

[78] Milewski E., Figurski J. Economic Indemnity of the Lifecycle of Armament Systems and Military Equipment. (in Polish) *Problemy Techniki Uzbrojenia* **2010**, *115*: 91-97.

[79] Morawa R., Barański K. Cost Analysis of Blasting Agents at Various Methods of Initiation for Shooting Long Holes Method. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2013**, *5*: 45-58.

[80] *Taggants in Explosives*. NTIS PB80-192719, 04.**1980**.

[81] Zygmunt B., Wilk Z., Koślik P. Metallic Sintered Inserts for EFP Charges – Technology Concept. (in Polish) *Problems of Mechatronics: Armament, Aviation, Safety Engineering* **2014**, *5*(2): 63-76.

[82] Bazela R., Krysiński B., Nita M., Warchoł R. Characteristic Features of Low-vulnerability Ammunition Fuses. (in Polish) *Problems of Mechatronics: Armament, Aviation, Safety Engineering* **2015**, *6*(4): 83-94.

[83] Cudziło S., Maranda A., Nowaczewski J., Trębiński R., Trzciński W.A. *Military Explosives*. (in Polish) Częstochowa: Wyd. Wydziału Metalurgii i Inżynierii Materiałowej Politechniki Częstochowskiej, **2000**.

[84] Florczak B., Bogusz R., Skupiński W., Chmielarek M., Dzik A. Study of the Effect of Nitrated Hydroxyl-terminated Polybutadiene (NHTPB) on the Properties of Heterogenous Rocket Propellants. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(4): 841-854.

[85] *Solid Composite Rocket Propellants Based on HTPB Synthetic Rubbers.* (in Polish) Florczak B. Ed., Warsaw: Instytut Przemysłu Organicznego, **2016**; ISBN 978-83-914922-4-6.

[86] Zygmunt B., Maranda A., Buczkowski D. *Third Generation Explosives.* (in Polish) Warsaw: Wyd. Wojskowa Akademia Techniczna, **2010**.

[87] Zygmunt B. Detonation Parameters of Mixtures Containing Ammonium Nitrate and Aluminium. *Cent. Eur. J. Energ. Mater.* **2009**, *6*(1): 57-66.

[88] Xu H., Pang W., Guo H., Zhao F., Wang. Y., Sun Z. Combustion Characteristics and Mechanism of Boron-based, Fuel Rich Propellants with Agglomerated Boron Powder. *Cent. Eur. J. Energ. Mater.* **2014**, *11*(4): 575-587.

[89] Vadhe P.P., Pawar R.B., Sinha R.K., Asthana S.N., Subhamanda Rao A. Cast Aluminized Explosives (Review). *Combust. Explos. Shock Waves* **2008**, *44*: 461-467.

[90] Sazaki T., Date S., Satoh J.-i. Study on the Effects of Addition of Boron Particles to RDX-based PBX Regarding Prevention of Neumann Effect. *Mater. Sci. Forum* **2004**, *465-466*: 195-200.

[91] Babar Z.-ud-d., Malik A.Q. Thermal Decomposition, Ignition and Kinetic Evaluation of Magnesium and Aluminum Fuelled Pyrotechnic Compositions. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(3): 579-592.

[92] Zohari N., Keshavarz M.H., Seyedsajadi S.A. The Advantages and Shortcomings of Using Nano-sized Energetic Materials. *Cent. Eur. J. Energ. Mater.* **2013**, *10*(1): 135-147.

[93] Florczak B. Ammonium Nitrate – Prospective Oxidizer for High Energy Density Materials. (in Polish) *Przem. Chem.* **2011**, *90*(4): 597-601.

[94] Sałaciński T. A New Method of Description of Composition of Explosives. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2014**, *6*: 72-77.

[95] Wachowski L. Chemical Environmental Hazards. [in:] *Ecology Science Compendium.* (in Polish) Strzałko J., Mossor-Pieraszewska T. Eds., Warsaw: PWN, **2009**; ISBN 83-01-13589-1.

[96] Manaham S.E. *Environmental Chemistry*. Chelsea: Lewis Publishers, Inc., **1991**.

[97] Warren D.S., Holbrook W.S., Dale A.D., Whelan L.N., Elyn M., Grimm W., Jentsch A. Biodiversity and Heterogeneous Disturbance Regime on Military Training Lands. *Restor. Ecol.* **2007**, *15*(4): 606-612.

[98] Martel R., Mailloux M., Gabriel U., Lefebvre R., Thiboutot S., Ampleman G. Behavior of Energetic Materials in Ground Water at an Anti-Tank Range. *J. Environ. Qual.* **2009**, *38*: 75-92.

[99] Walsh M.R., Walsh M.E, Amplenam G., Thiboutot S., Brochu S., Jenkins T.F. Munitions Propellants Residue Deposition Rates on Military Training Ranges. *Propellants Explos. Pyrotech.* **2012**, *37*(4): 393-406.

[100] Walsh M.R., Walsh M.E, Hevitt A.D. Energetic Residue from Field Disposal of Gun Propellants. *J. Hazard. Mater.* **2010**, *173:* 115-122.

[101] Sanderson P., Naidu R., Bolan N. Ecotoxicity of Chemically Stabilised Metal(loid)s in Shooting Range Soils. *Ecotox. Environ. Safe.* **2014**, *100*: 201-208.

[102] Petre R., Rotariu T., Zecheru T., Petrea N., Bajenaru S. Environmental Long Term Impact on a Romanian Military Testing Range. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 3-19

[103] Ariz A., Ali W.K.W. Effect of Oxidizer-Fuel Mixture Ratio to the Pressure Exponent of Ammonium Perchlorate Based Composite Propellant. *Appl. Mech. Mat.* **2011**, *1380-1386*: 110-116.

[104] Szastok M. The Effect of High Temperature on Selected Parameters of Emulsion Explosives. (in Polish) *Mater. Wysokoenerg.* (*High Energy Mater.*) **2015**, *7*: 106-109.

[105] Papliński A., Maranda A. Investigation of the Influence of Cooling Salts upon the Explosive Performance of Emulsion Explosives. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(3): 523-535.

[106] Maranda A. Methods for Testing Sensitivity of Explosives to External Stimuli in the View of ADR Regulations, Polish and European Standards. (in Polish) *Górnictwo i Geoinżynieria* **2004**, *28*(3/1): 349-360.

[107] Mathieu J., Stucki H. Military High Explosives. *Chimia* **2004**, *58*(6): 383-389.

[108] Heilman H.M., Wiessman U., Stenstrom M.K. Kinetics of the Alkaline Hydrolysis of High Explosives RDX and HMX Solutions and Adsorbed to Activated Carbon. *Environ. Sci. Technol.* **1996**, *30*(5): 1485-1492.

[109] *Regulation of the Minister of Economy of 16 July 2015 on the Acceptance of Waste for Depositing*

in a Landfill. (in Polish) J. of Laws (Dz. U.) **2015**, item 1277.

[110] Kritzer P. Corrosion in High-temperature and Supercritical Water and Aqueous Solutions: a Review. *J. Supercrit. Fluids* **2004**, *29*(1-2): 1-29.

[111] Munter R. Advanced Oxidation Processes – Current Status and Prospects. *Proc. Estonian Acad. Sci. Chem*. **2001**, *50*(2): 59-80.

[112] Bulusu S.N. *Chemistry of Energetic Materials.* Kluwer Academic Publishers, **1990**, pp. 21-49.

[113] Smoleński D., Heger L. Combustion and Detonation. [in:] *General Issues in Modern Technology*. (in Polish) Vol. 9, Warsaw: PWN, **1964**.

[114] Panikov N.S., Sizova M.V., Ros D., Christodoulatos C.J., Balas W., Nicolich S. Biodegradation Kinetics of the Nitramine Explosive CL-20 in Soil and Microbial Cultures*. J. Biodegr.* **2007**, *18*(3): 317-332.

[115] Lewis D.H., Wong E.Y., English W.D. *Utilization of Alternate Propellants to Reduce Stratospheric Ozone Depletion.* Space and Missile Systems Center El Segundo, California, **1994**.

[116] Jing S., Liu Y., Liu D., Guo J. Research on a New Synthesis of LLM-105 Using *N*-Nitroso-bis(cyanomethyl) amine. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 21-33.

[117] Wardle R.B., Hinshaw J.C., Braithwaite P., Rose M., Johnston G., Jones R., Poush K. Synthesis of the Caged Nitramine HNIW (CL-20). *Proc. 27th Int. Ann. Conf. ICT*, Karlsruhe, Germany, **1996**, V27:1-10.

[118] Gołofit T., Książczak A. Using DSC and DTA Methods to Estimate Safety Parameters of High Energy Materials using Ammonium Dinitramine as an Example. (in Polish) *Problems of Mechatronics: Armament, Aviation, Safety Engineering* **2011**, *2*(3): 31-42.

[119] Fronabarger W.J., Williams D.M., Stern G.A., Parrish A.D. MTX-1 – A Potential Replacement for Tetrazene in Primers. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 33-52.

[120] Ross M.H., Edward H.M. *Solid Composite Propellant Containing Lithium Perchlorate and Polyamide Polymers.* Patent US 3094444, **1958**.

[121] Li J., Brill T.B. Nanostructural Energetic Composites of CL-20 and Binders Synthesized by Sol-Gel Methods. *Propellants Explos. Pyrotech.* **2006**, *31*(1): 61-69.

[122] Badgujar D.M., Talawar M.B., Asthama S.N., Mashulikar P.P. Advances in Science and Technology of Modern Energetic Materials, An Overview. *J. Hazard Mater.* **2008**, *151*: 295-305.

[123] Nagamachi M.Y., Oliveira J.I.S, Kawamoto A.M. AND – The New Oxidizer Around the Corner for an Environmentally Friendly Smokeless Propellant. *J. Aeroesp. Technol. Manage.* **2009**, *1*(2): 153-160.

[124] Frankel M.B., Grant L.R., Flanagan J.E. Historical Development of Glicydyl Amine Polymer. *J. Propuls. Power* **1992**, *8*: 560-563.

[125] Murali Mohan Y., Padmanabha Raju M., Mohana Raju K. Synthesis, Spectral and DSC Analysis of Glicydyl Azide Polymers Containing Different Initiating Diol Units. *J. Appl. Polym. Sci.* **2004**, *93*(5): 2157-2163.

[126] Lempert B.D., Dorofeenko M.E. Quantitative Variations Resulting from the Gradual Replacement of NO_2 with NF_2-Fragments in Energetic Materials. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(1): 35-46.

[127] Liu Y., Zhang R., Feng C.-G., Yang L., Zhang T.-L. Predicted Crystals Structures, Analysis, Impact Sensitivities and Morphology of Solid High-energy Complexes: Alkaline-earth Carbohydrazide Perchlorates. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(2): 229-248.

[128] Singh R.P., Verma R.D., Meshri D.T., Shreeve J.M. Nitrogen-Rich Salts for Ionic Liquids. *Angew. Chem., Int. Ed.* **2006**, *45*(22): 3584-3601.

[129] Eaton P.E.. Zhang M.X., Gilardi R. Octanitrocubane: a New Nitrocarbon. *Propellants Explos. Pyrotech.* **2002**, *27*(1): 1-6.

[130] Griffin G.W., Marchand A.P. Synthesis and Chemistry of Cubanes. *Chem. Rev.* **1989**, *89*(5): 997-1010.

[131] Marchand A.P. Synthesis of New High Energy/High Density Monomers and Polymers. Synthesis of D3-Hexa-nitro-tris-homocubane. *Proc. Naval Workshop on Energetic Crystalline Material*s, Publication Office of Naval Research, Maryland, **1989**.

[132] Pant A., Seth T., Raut B.V., Gajbhiye V.P., Newale S.P., Nandi A.K., Prasanth H., Pandey R.K. Preparation of Nano Aluminium Powder (NAP) Using a Thermal Plasma: Process Development and Characterization.

Cent. Eur. J. Energ. Mater. **2016**, *13*(1): 53-71.
[133] Murawski J.R., Ball W.D. Aminonitronaphtalenes as Possible High Energy Density Materials. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(1): 3-12.

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