Review

Environmentally compatible next generation green energetic materials (GEMs)☆

M.B. Talawar, R. Sivabalan*, T. Mukundan*, H. Muthurajan, A.K. Sikder, B.R. Gandhe, A. Subhananda Rao

High Energy Materials Research Laboratory, Pune 411021, India

A R T I C L E I N F O

A B S T R A C T

This paper briefly reviews the literature work reported on the environmentally compatible green energetic materials (GEMs) for defence and space applications. Currently, great emphasis is laid in the field of high-energy materials (HEMs) to increase the environmental stewardship along with the deliverance of improved performance. This emphasis is especially strong in the areas of energetic materials, weapon development, processing, and disposal operations. Therefore, efforts are on to develop energetic materials systems under the broad concept of green energetic materials (GEMs) in different schools all over the globe. The GEMs program initiated globally by different schools addresses these challenges and establishes the framework for advances in energetic materials processing and production that promote compliance with environmental regulations. This review also briefs the principles of green chemistry pertaining to HEMs, followed by the work carried out globally on environmentally compatible green energetic materials and allied ingredients.

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1. Introduction

Green chemistry is a topic of interest that is receiving significant attention in recent years due to the importance of environmental issues and has an important goal of making synthesis methods more environmentally benign. Researchers in the field of chemistry have to practice sustainable development, industrial ecology, cleaner synthesis processes, and life-cycle analysis in addition to the new approaches. According to Sheldon [1] green chemistry is all about 'efficiently using (preferably renewable) raw materials, eliminating waste and avoiding the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products'.

1.1. Principles of green chemistry

The importance of use of green processes in any chemical industry greatly contributes [2] effectively in the (a) prevention of waste formation, (b) increased consumption of reactants, (c) utilization of less toxic reactants and solvents, (d) enhancement of atom economy in the reaction, (e) use of ambient reaction conditions (ambient pressure and temperature), (f) recycling of raw material and (g) in avoiding the formation of hazardous materials and minimization of hazards and risks. These green principles will help the chemists to carry out their work in a safer and cleaner way. Further, green chemistry has been extended to help the process chemists, chemical engineers/technologists/scientists, to make a process more eco-friendly [3,4]. The green chemistry principles basically concerned more about the process operations; identification and quantification of products, conversions, selectivity and productivities, mass balance for processes, catalyst and solvent losses in air and aqueous effluent, thermochemistry, heat and mass transfer limitations, development and application of sustainability measures, incompatibility of safety and waste minimization, monitoring and reporting laboratory waste emitted [5,6]. Sikdar and Howell recently reported [7], some of the engineering approaches for cleaner nitration reaction in the chemical process. According to authors, the reaction could be made more eco-friendly and green by devising a method of purifying waste acid and using state of the art engineering techniques to batch nitration by optimizing agitation speed, temperature, and water removal.

The important factors/goals green chemists need to consider in the area of energetic materials/processes are (i) to minimize life-cycle waste generation during manufacture, testing, proofing, and storage (ii) minimize polluting combustion products generated during the utilization of the ammunitions. About 40% of waste production is generated during manufacture. The strategy adopted to achieve these goals is multi-pronged: (i) assess the environmental issues associated with HEMs to identify major areas of concern, (ii) adopt a paradigm shift in the selection of binders for propellants and explosives by replacing the cast-curable polymers by thermoplastic elastomers, which exhibit good recover, recycle and reuse (R^3) characteristics, (iii) use HEMs which are inherently non-polluting, like the high nitrogen containing compounds and those devoid of elements like chlorine, (iv) use solvent less methods of manufacture of gun propellants, (v) demonstrate technologies that utilize liquid or supercritical CO_2 and enzymes for the synthesis of HEMs and (vi) bio-degradation of HEMs to alleviate the problem of water and soil contamination by HEMs and the decomposition products.

The advent of advanced explosive and propellant technology has laid emphasis on the use of ingredients that impart enhanced performance and reduced vulnerability. Improved mechanical properties, decreased signature, extended shelf-life as well as reduced environmental impact in manufacture, use and disposal

are other important design considerations for such systems. To enhance the performance of the formulation, it is desirable to use all energetic ingredients in the formulation. This allows partitioning of the energy contributions, and thus not necessitating the concentration of only solid components (oxidizer and metal fuels) in the formulations, which may affect adversely other critical parameters such as processibility and mechanical properties. Increasing the density of the HEM would also increase the vehicle capability (payload and range). One way to achieve higher energy and density is to alter the chemical structure of materials so as to introduce cage like geometry or chemical groupings that have more and more of nitrogen, oxygen or fluorine. In the area of oxidizer/explosive compounds, cage structures are becoming the preferred option while in the field of binders and plasticizers the range of compounds that contain such functional groups as the azido ($-N_3$), nitro/nitrato, nitramino ($N-NO_2$) or the less common geminal difluoroamino are gaining prominence.
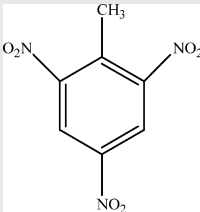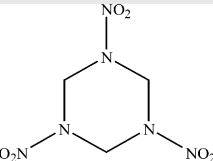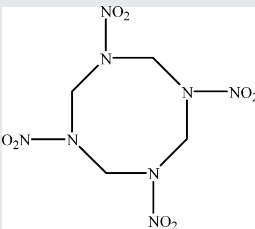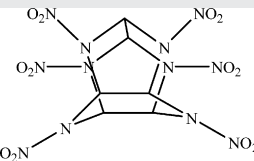
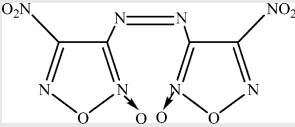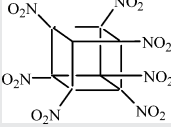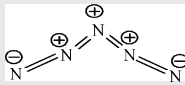## 2. High-energy density materials (HEDMs)

These classes of materials have attracted the attention of the chemists all over the world in recent times. HEDMs can be realized either with the help of conventional chemistry, or with novel chemistry dealing polynitrogen compounds or by exotic physics (e.g., metallic hydrogen). Potential HEDM can find applications both in explosives as well as in propulsion system. The decomposition of a HEDMs releases maximum energy and gives eco-friendly gaseous products (non-toxic in nature). In order to achieve the above requirements, a HEDM should not possess any metal atom in its structure.

The performance of the material depends on the stoichiometry, i.e., a good oxidizer/fuel balance and high negative heats of formation of the combustion products, density, amounts of gas or working fluid generated, the burning rates, and, very importantly, the heat of formation of the HEDM. The energy release is given by the difference between the heats of formation of the HEDM compound and of the combustion products and, therefore, increases with increasing endo-thermicity of the HEDM [8].

The continued current thrust for search of more powerful HEDMs is also focusing attention on the environmental issues. HEMs scientist /technologist needs to address certain issues before embarking on the synthesis of new HEDMs of futuristic interest. Some of the specific issues needs attention by the HEMs researchers in order to construct or synthesis an ideal explosive is (a) highest possible velocity of detonation, detonation pressure, density, acceptable level of sensitivity parameters in comparison to benchmark explosives, (b) the another important concern is also the detonation end products or combustion end products have to be environmentally compatible and (c) preferably metal free HEM target compounds are more acceptable. Some of the most sought after energetic materials of current and futuristic interest are given (Table 1).

Hydrazinium azide is one of the reported compounds of HEDM category. The velocity of detonation (VOD) of hydrazinium azide reported is greater than that of bench-mark energetic materials, viz., RDX [9]. However, hydrazinium azide is reported to be hygroscopic and volatile [10]. Hence, it is not much useful as an energetic material. However, an interesting material namely hydrazinium azide hydrazinate is prepared from hydrazinium azide [11] for its application as HEDM. The important features reported for hydrazinium azide hydrazinate are its insensitivity towards external stimuli. Hydrazinium azide hydrazinate is less hygroscopic and less volatile than hydrazinium azide, though its melting point is lower. The decomposition of the hydrazinium azide hydrazi-

Table 1
Performance of most important energetic materials with performance properties

HEDM	TNT	RDX	HMX	CL-20
Structure				
Density (g/cm^3)	1.78	1.82	1.91	2.04
ΔH_f (kcal/mol)	−16.03	+16	+18	+100
O.B. (%)	−73.96	−21.6	−21.6	−11
VOD (m/s)	6800	8750	9100	9400
P_{CJ} (GPa)	19	34	39	42
Impact sensitivity (cm)	>170	46	36	24
Friction sensitivity (kg)	>36	16	12	8

HEDM	DNAF	ONC	N_5^+
Structure			
Density (g/cm^3)	1.91	2.1	1.85
ΔH_f (kcal/mol)	159	144	350
O.B. (%)	0	0	–
VOD (m/s)	10,000	9800	12,501
P_{CJ} (GPa)	50	50	73.95
Impact sensitivity (cm)	–	–	–
Friction sensitivity (kg)	–	–	–

nate gives more amount of ammonia than hydrazinium azide [11]. The reported synthesis of hydrazinium azide hydrazinate is given below.

$$[NH_2-NH_3]^+[N_3]^- + NH_2-NH_2 \rightarrow [NH_2-NH_3]^+[N_3]^- \cdot NH_2-NH_2$$

$$[NH_2-NH_3]^+[N_3]^- \cdot NH_2-NH_2 \rightarrow 2.63N_2 + 1.91H_2 + 1.73NH_3$$
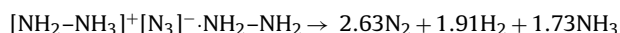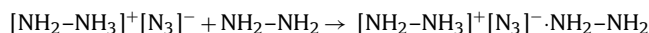
3. High nitrogen content high-energy materials (HNC-HEMs)

High nitrogen energetic materials are becoming the center of attention of research in the area of advanced HEMs aimed at futuristic defence and space sector needs. The high-energy content of HNC-HEMs stems from the presence of adjacent nitrogen atoms poised to form nitrogen (N≡N). Such transformations are accompanied with an enormous energy release due to the wide difference in the average bond energies of N–N (160 kJ/mol) and N=N (418 kJ/mol) compared to that of N≡N (954 kJ/mol). As a natural consequence of their chemical structure, HNC-HEMs also generate large volume of gas (N$_2$) per gram of HEM projecting them as a choice material for clean burning gas generators. Generation of nitrogen gas as decomposition product of a propellant or explosive formulation is desired in order to avoid environmental pollution, health risk as well as untraceable signatures [12].

High nitrogen content materials have a large number of N–N and C–N bonds and therefore possess large positive heats of formation. The low percentage of carbon and hydrogen in these compounds has triple positive effects: (i) enhances the density of the compounds, (ii) allows a good oxygen balance to achieve easily and (iii) produces more number of moles of gaseous products per gram of the high-energy materials. Since nitrogen is the major decomposition product, the products are inherently cooler [13].

Hydrazines and azides are typical examples of nitrogen compounds used as energetic materials. The high nitrogen materials can show remarkable insensitivity towards electrostatic discharge, friction and impact. Triazoles, tetrazines and triazines are the nitrogen rich organic compounds currently in use for energetic applications. The linking of several nitrogen atoms in a row (N-catenation), however, is usually unstable and is typically very sensitive to impact. The one method that could stabilize nitrogen catenation is through cyclic conjugation, where the energy of the N–N bond is increased by alteration of N atoms with different electro negativity.

3.1. Tetrazine compounds

The tetrazine derivatives for a long time, have occupied an important place among other N-heterocycles as, prospective component of high energetic material, used as explosives, rocket propellants, photographic dyes and additives to photographic layers, reducing agents, inhibitors of steel corrosion, fuel additives, pesticides, pharmaceuticals, and in the gas generating compositions. Compounds fulfilling these requirements could be regarded as a new generation of HEDMs which might be used as propellants, explosives or especially as gas generators. One of the major disadvantages of common gas generators such as guanidinium derivatives, sodium azide, etc. is the liberation of toxic gases, e.g., NH$_3$, HCN, and HN$_3$. Apart from the environmental issues gas generating compositions with high gas yield (preferably N$_2$) are more attractive.

Heterocyclic compounds such as tetrazole and 1,2,4,5-tetrazine are explored as potential synthons for nitrogen rich energetic materials. Recently, there has been considerable attention has been

paid in the study of [14–18] tetrazine compounds. Tetrazine moiety displayed unique and interesting characteristic properties and has been utilized for the preparation of several energetic materials [19]. Furthermore, tetrazines also possess high positive heats of formation and crystal densities, properties important in energetic materials applications [20].

Among tetrazines, 3,3′-azobis (6-amino-1,2,4,5-tetrazine) (DAAT) [15,21], 3,6-dihydrazino-1,2,4,5-tetrazine (DHTz) [22], 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) [23] and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112) [12] have received major attention due to their high positive heat of formation. DAAT and LAX-112 may find wide spectrum applications as an energetic ingredient in rocket propellants and IHE formulations. DHTz has been reported as an energetic eco-friendly smoke ingredient for pyrotechnic applications [22]. Some of the important HNC-HEMs with properties are presented in Table 2.

Synthesis and characterization of bis-tetrazolylaminotetrazine (BTATz) has been reported recently [24]. The salient features of BTATz are impact insensitive, non-explosive, non-pyrotechnic, and an inflammable solid that decomposes rapidly without flame and produces nitrogen as the main combustion product. BTATz is a solid compound that decomposes primarily to nitrogen gas once initiated by heat and the decomposition is rapid, self-sustained, flameless, and occurs readily at most pressures. The nitrogen gas produced from BTATz at a high degree serves to displace oxygen, thus extinguishing a fire. Because of these qualities, BTATz has been identified as a composition highly suitable for fire suppression applications [25]. BTATz is also can be used as a gas generating ingredient in automobile airbags. BTATz burns very rapidly to form 0.7 l of nitrogen gas per gram of solid. Because of its low carbon content, it burns cleanly, without smoke, leaving a minimal residue. Propellant formulations incorporating BTATz structurally similar to the 5-aminotetrazole (5-AT) appear to provide increased means for reducing propellant combustion temperature [24].

Research and development efforts on BTATz as a fire suppressant shown better performance with the existing suppressant of choice Halon-1301(bromotrifluoromethane) [26]. Halon is a compound having halogens, which are polluting the environment and destroys the ozone layer and the suppressant is stored in bottle, which adds additional load to the air craft. The results of BTATz based compositions make it as an alternative to Halon [25]. Another important compound namely GZT, it burns at a lower temperature than carbon-rich compounds of similar molecular weight.

Walsh et al. investigated various high nitrogen energetic materials viz., triaminoguanidinium azotetrazolate (TAGAT), triaminoguanidinium azotetrazolate (GAT or GZT), bistetrazolylamino tetrazine (BTATz), dihydrazino tetrazine (HzTz or DHTz) and diamino azobistetrazine N-oxide (DAAT-N-Ox) as additive in gun propellant formulation to reduce the barrel erosion [27]. The RDX from the control composition (RDX: 76%; CAB: 12%; NC: 4%; BDNPF/A: 7.6% and ethyl centralite: 0.4%) was partially replaced with the promising HNC compounds. It was inferred that all the ingredients reduced the flame temperature of the gun propellant considerably and minimum was achieved with GAT (Fig. 1). The force constant also decreased with all HNC ingredients, particularly minimum observed with GAT whereas HzTz showed the maximum force constant among them (Fig. 2). A combination effect of high nitrogen to carbon monoxide ratio in the combustion products and the reduced flame temperature, work together and reduces the gun barrel erosion.

The performance evaluation of TAGAT in CMDB propellant formulations is reported recently. The burning rate studies have indicated that TAGAT acts as an efficient energetic additive at higher pressure (>6.9 MPa) as revealed by 25% increase in burn-
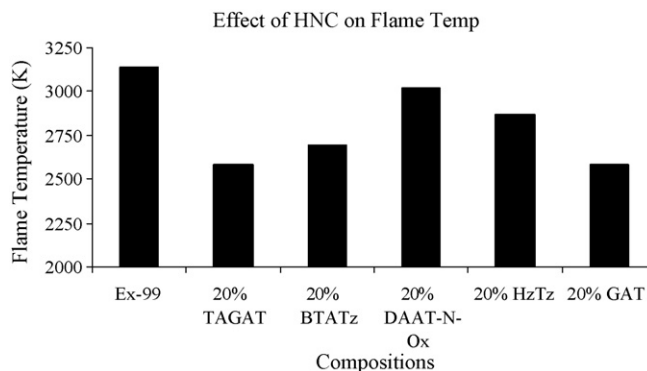
ing rate ($11–23\,\mathrm{mm\,s^{-1}}$) in comparison to control formulation ($11–17\,\mathrm{mm\,s^{-1}}$) in the pressure region of 3–7 MPa [28]. Certain non-azide gas generating compositions are based on the use of fuel with high nitrogen substances such as aminotetrazole and diammonium-5,5-tetrazole with metallic oxidizers such as strontium nitrate/potassium nitrate have been reported. These formulations provide moderate burning rates but relatively low gas yield with excess amount of solid combustion products. TAGAT-based gas generating composition is capable of generating large amount of nitrogen gas while overcoming various problems associated with conventional gas generating compositions.

The German researchers recently developed high nitrogen content explosive, viz., diazyl tetrazolate that is 25% more powerful than HMX and once exploded, only leaves nitrogen in the air. However, it is currently 100 times more expensive than HMX, but the research group believes the costs could be brought down dramatically [29]. Energetic salts offer more advantages over conventional energetic compounds. Nitrogen containing anions and cationic species contributes to high heats of formations and high densities. A good oxygen balance is achieved with their low carbon and hydrogen content and decomposes predominantly to gaseous nitrogen molecule, which makes them very promising candidates for highly energetic materials applications [30]. Some of the recently reported potential energetic nitroformate salts are given in Fig. 3.

3.2. Polymeric nitrogen

Homoleptic polynitrogen compounds are the real contenders [31] as an eco-friendly HEMs of this class. Storage of the maximum amount of energy in a polynitrogen molecule would mean having the largest number of single N–N bonds in its molecular structure. To obtain isolable and manageable homoleptic polynitrogens,

Fig. 1. Effect of HNC compounds on flame temperature o gun propellant.
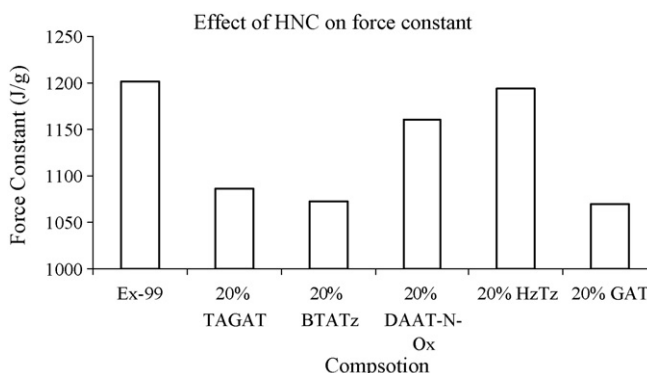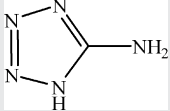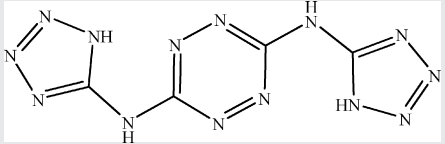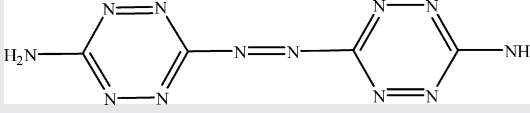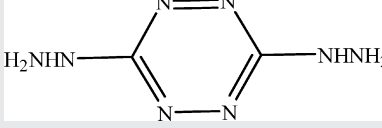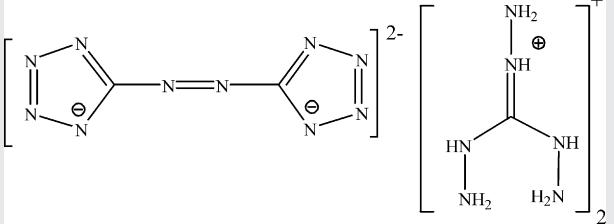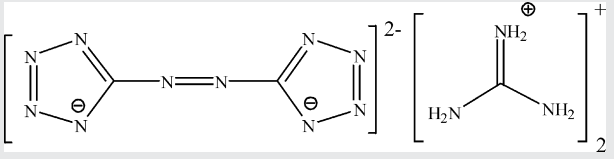
Fig. 2. Effect of HNC compounds on force constant of gun propellant.

Table 2
Potential high nitrogen ENERGETIC materials

HEM	Structure	Density (g/cm^3)	ΔH_f (kcal/mol)	N$_2$ (%)	Impact sensitivity (cm)	Friction sensitivity (kg)	O.B. (%)
Aminotetrazole		1.65	50	82	–	–	−65.83
3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATZ)		1.76	211	79	71	>36	−64.47
3,3′-Azobis (6-amino-1,2,4,5-tetrazine) (DAAT)		1.76	206	76.4	70	>36	−72.6
3,6-Dihydrazino-1,2,4,5-tetrazine (DHTz)		1.69	128	78.8	37	>36	−78.8
Triaminoguanidinium azotetrazolate (TAGAT)		1.6	255	82.3	51	16	−72.66
Guanidinium azotetrazolate (GAT)		1.54	98	78.3	170	>36	−78.8

$$[Cat]^+[C(NO_2)_3]^-$$
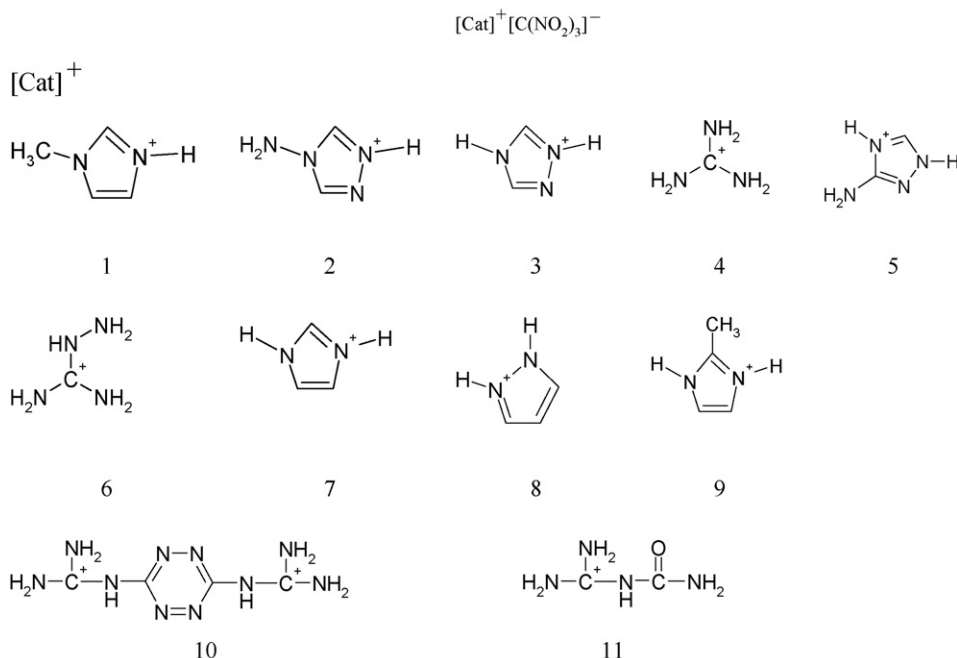
Fig. 3. Potential energetic nitroformate salts.

the compound needs to possess a sufficiently high-energy barrier to decomposition. Researchers at U.S. Air Force Office of Scientific Research (AFOSR) have explored unusual polynitrogen molecules [32] with the aim of finding new rocket fuels, which could surpass cryogenic systems based on hydrogen and liquid oxygen. Efforts are on in many laboratories to explore the possibilities of synthesis of different poly nitrogen green energetic materials [33,34].

The discovery of N_5^+ has opened up new vistas [32] in research and development activities on polynitrogen compounds. The imagination-driven route [35] for N_{60} synthesis may come to reality in the near future. Such a molecule confined to a specific geometrical shape is the prime candidate to fuel supersonic transport vehicles. Because of the nature of nitrogen bonding, the explosive power of these unusual compounds will be stunning. If it is possible to realize polynitrogens in large amounts, they can drastically change the technologies of high-energy rocket propellants and explosives. Some of the conseptualized and realized polynitrogen molecules are presented in Table 3. Despite the proven worth of advanced HEMs, AP and HMX-based systems still dominate. Compatibility problems of novel HEMs with other propellant components need to be tackled. Ultrahigh power materials are conceptualized to meet future demands. However, novel technologies need to be mastered to bring such polynitrogen green materials into realm. A major technological breakthrough is needed to economically justify obtaining of new HEMs.

Table 3
Performance characteristics of polynitrogen compounds

| HEM	Density (g/cm^3)	Heat of formation (kcal/mol)	Detonation velocity (km/s)	Detonation pressure (GPa)
N_4	1.75	268.7	13.24	77.02
N_5^+	1.85	350	12.51	73.95
N_6	1.97	345.58	14.04	93.32
N_8	2.15	406.69	14.86	108.39
N_{10}	2.21	473.42	12.08	58.05
N_{12}	2.28	579.82	12.53	64.07
N_{60}	2.67	546	17.31	196

3.3. Novel uranium–nitrogen compounds

William and co-workers recently reported the first molecular uranium compounds containing bimetallic nitride linkages [36]. The compounds are made up of uranium metallocene groups joined together by nitride (N_3^-) ligands, and these units are in turn coupled together by azide (N_3^-) groups. A sequence of four of these UR_2–N–UR_2–NNN moieties (where R = cyclopentadienyl) forms the edges of a 24-membered uranium–nitrogen "molecular square." Uranium nitrides are generally obtained by reduction of a nitrogen-containing substrate, such as N_2 or NH_3, with uranium reducing agents at high temperatures and pressures [37]. Several 24-membered uranium nitrogen rings ($UNUN_3$)$_4$ have been synthesized by reduction of sodium azide with organometallic metallocene derivatives. In a related development, Margaret-Jane et al reported the synthesis and characterization of an ammonium salt of a uranium polyazide, $U(N_3)_7^{3-}$ [38]. This polyazide is the first structurally characterized heptaazide compound for any element, and it is the first known example of a binary actinide azide compound containing only an actinide metal and azide groups. These uranium–nitrogen compounds eventually could be important as precursors to a sought-after uranium nitride nuclear reactor fuel or perhaps as high explosives.

4. High performance explosives

Dinitrodiazenofuroxan—a new super-power explosive [39] was developed (zero hydrogen explosive) by the Russian researchers from 4-amino-3-furoxancarboxylic acid azide. The final nitro functionality was introduced into the compound by the oxidation of amino group. The final step of the reaction appears to be more eco-friendly. Furazans and furoxans [40] are likely to enjoy the prime place in the area of high-energy materials. Highly nitrated cubanes are predicted to be shock-insensitive, very dense, high-energy compounds with great potential as explosives and propellants [41]. Application of the Kamlett ± Jacobs equations [42] to octanitrocubane using predicted values for density (1.9 ± 2.2 g/cm^3) [43]

Table 4
Promising CL-20-based HE formulations

Composition	CL-20 (%)	Other ingredient (%)	VOD (km/s)
LX-19	95.8	Estane: 4.2	8.8
PAX-29	77	BDNPF/A: 4.8; Al: 15 and CAB: 3.2	8.8 (increase: 42% in total energy and 28% in expansion energy)
Aluminized PAX-11	79	BDNPF/A: 3.6; Al: 15 and CAB: 2.4	8.92
Russian composition (CL-20И)	79	Inert binder: 2	9.19
Russian composition (CL-20A)	79	Active binder: 2	9.35
DLE-C038	90	HTPB/plasticizer: 10	8.73 (increase: 32% in P_{CJ} and 22% in expansion energy)
Melt pour composition	70	TNAZ and 4-amino-3-nitrobenzotrifluoride: 30	VoD: 8.68 km/s
PATHX-1	92	Estane: 8	8.9
PATHX-2	95	Estane: 5	9.12
PBXC-19	95	EVA: 5	9.08

and ΔH_f (81 ± 144 kcal/mol) [44] leads to calculated detonation velocities and pressures much higher than that of the classic C-nitro explosive TNT, 15 ± 30% greater than that of the N-nitro compound HMX, presently the most energetic of standard military explosives, and perhaps even better than that of the experimental polycyclic nitramine CL-20, arguably the most powerful non-nuclear explosive known [45]. Zhang et al. have reported [46] the successful synthesis of one of the most powerful energetic materials —octanitrocubane. The nitration methodology used in the last step of the synthesis utilizes in situ generation of eco-friendly nitrating agent dinitrogen pentoxide.

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane [47,48] popularly known as CL-20 is a polycyclic nitramine possessing a cage like structure. CL-20 can release energy at a much higher level than current benchmark high explosives, RDX and HMX. The strain introduced due to the cage like structure and the presence of six N–NO$_2$ groups render CL-20 a rich source of energy. The cage like structure of the molecule also results in close packing of constituent atoms, leading to high density ($\rho > 2.04$ g/cm^3). CL-20 is well entrenched as the most powerful explosive of today and outperforms RDX and HMX not only as an explosive but also as a clean, combustion-efficient oxidizer for futuristic propellants. CL-20 is currently commercially manufactured in 50–100 kg batches. Efforts are also on to produce CL-20 using eco-friendly approaches. It has good chemical and thermal stability and is compatible with most binder and plasticizer systems. CL-20 has all the characteristics required for application in explosive, propellant and pyrotechnic composition.

CL-20 in explosive formulations results in a 10–15% performance increase compared to HMX based compositions [45]. CL-20 combined with an energetic binder in solid rocket propellant formulations results in a reduced smoke composition that approaches the performance of conventional HTPB/AP propellants. The favorable oxygen balance of CL-20 is particularly advantageous in terms of unwanted signature. The high pressure exponent must be reduced through the addition of burn rate modifiers with CL-20. As a result of its high energetic content and favorable oxygen balance, CL-20 is also applicable as a component of propellant ingredient. The challenges ahead with CL-20 are its high cost and sensitivity. The synthesis requires hazardous steps like hydrogenation and cost intensive nitrating agents to avoid collapse of the precursor. Some of the reported density and VOD of selected CL-20 based explosive formulations are given in Table 4.

5. Eco-friendly oxidizers

Oxidizer is a chemical substance with high oxygen content in its chemical structure. A potential oxidizer should possess a high positive oxygen balance (+O.B.) The important function of an oxidizer in a propellant composition is to provide oxygen for the combustion of the fuel elements (C & H) present in the composition into gaseous products. In addition to positive oxygen balance, oxidizers should possess superior heat of formation, density and thermal stability. Oxidizer is an important ingredient in any of the rocket propellant/pyrotechnic compositions. The key oxidizers used as well as proposed for military used are given in Table 5.

The upper stage space craft engine normally uses dinitrogen tetroxide (N$_2$O$_4$) and hydrazine (NH$_2$–NH$_2$)/monomethyl hydrazine (CH$_3$–NH–NH$_2$) as fuel ingredients. Both these ingredients are toxic and cause harmful effect to human beings and environment. Research activities are underway to replace dinitrogen tetroxide and monomethyl hydrazine for upper stage space engines [49]. The combustion reaction between dinitrogen tetraoxide and monomethyl hydrazine can be expressed as follows:

$$2N_2H_4 + N_2O_4 \rightarrow 4H_2O + 3N_2$$

$$CH_3-NH-NH_2 + N_2O_4 \rightarrow 3H_2O + CO + 2N_2$$
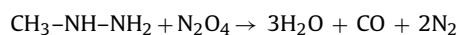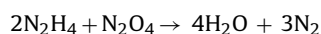
The combination of dinitrogen tetraoxide and hydrazine/monomethyl hydrazine may be replaced with eco-friendly systems like hydrogen peroxide (H$_2$O$_2$) as an oxidizer and hydrocarbons (HC) as fuel in near future [49]. The combustion chemistry involved in this system presented below:

$$N_2H_4 + 2H_2O_2 \rightarrow 4H_2O + N_2$$

$$CH_3-NH-NH_2 + 4H_2O_2 \rightarrow 7H_2O + CO + N_2$$

$$HC's + H_2O_2 \rightarrow H_2O + CO_2$$
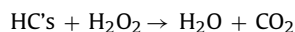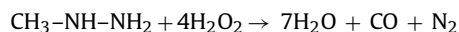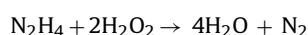
Ding and Inagaki proposed [50] green HEDM, which should satisfy four conditions: (i) material/s should have high-energy densities; (ii) material/s should have considerable kinetic stability; (iii) predominant products of the reactions should be green compounds, i.e., species benign to human health and environment, especially ones, e.g., N$_2$, H$_2$O, silica, etc., which exist in nature; and (iv) the possibility to actually synthesize them for practical use should be high. They reported N$_2$H$_2$O isomers [50] and silanes/oxygen/water [51] systems are green HEDMs. The energy densities of these systems are higher than or comparable to the conventional H$_2$/O$_2$ and N$_2$H$_4$/O$_2$

Table 5
Some of the physicochemical properties of energetic oxidizer candidates

Oxidizer	Heat of formation (Δ_f) (kJ/mol)	Oxygen balance (%)	Density (g/cm^3)
AP	−298	35	1.9
ADN	−151	26	1.8
HNF	−71	13	1.9
RDX	63	−22	1.8
HMX	76	−22	1.9
CL-20	454	−11	2.1

systems. The Si/H ratio together with ring strain is important for the HEDM power of silanes.

Ammonium perchlorate (AP) is the work-horse oxidizer used in modern rocket propulsion systems. The most widely used solid rocket propellant for space applications consists of ammonium perchlorate (70%), aluminium (16%) and binder (14%). AP-based propellant system produces chlorine rich combustion products, posing environmental hazards such as ozone depletion and acid rain. Further, the main combustion products of aluminized AP based propellants are hydrochloric acid (HCl), aluminum oxide (Al_2O_3), carbon dioxide (CO_2) and water. Moreover, the compounds of aluminium are toxic and are harmful to human beings, animals and plants. Research activities have been undertaken for the search of superior and eco-friendly oxidizer for futuristic solid rocket propellants. Ammonium dinitramide (ADN), hydrazinium nitroformate (HNF) and its derivatives [50] are the recent entrants in this class.

Synthesis of metal dinitramide is achieved and numerous research publications have appeared [52–54] with a mixed acid nitration of a sulphamic acids salt followed by neutralization with the corresponding base. During the nitration and neutralization process, the intermediate product dinitramidic acid [$NH(NO_2)_2$] decomposes since it is unstable in acidic condition [55]. Hence, the yield of dinitramide is low [56]. In order to improve the yield of the process, recently a new approach is reported [57]. The dinitramidic acid formed during nitration is treated with N-guanylurea sulphate, results in water insoluble N-guanylurea dinitramide (GUDN) as a precipitate. GUDN can be removed by filtration, which is stable as well as insensitive to mechanical stimuli. GUDN can be transformed to ADN in two separate ion exchange reaction: GUDN is first converted to potassium dinitramide (KDN) using potassium hydroxide and converted into ADN in an ion exchange reaction with ammonium sulphate. ADN is separated by filtration. The use of GUDN for making ADN is an environmentally acceptable process. GUDN is a very stable salt of dinitramide and thermally stable upto 205 °C. GUDN is projected as insensitive gun propellant ingredients with low flame temperature [57]. Further, GUDN is a novel energetic material with low sensitivity and good potential for use as a propellant or insensitive munitions (IM) explosive [57].

Another main problem associated with ADN is its incompatible nature with other ingredients. ADN is incompatible with isocyanates, which are commonly used as curing agents in the binder while formulating a rocket propellant composition. ADN is compatible with prepolymers, but requires a specialized curing agent. More research is required to solve the problems related to ADN compatibility [58].

Further, GUDN incorporated gas generating formulations produces high gas yield makes it excellent as a gas generant for automotive safety devices. Use of GUDN based composition in automotive air bags is the first commercial application for dinitramides. The high oxygen balance in GUDN is a great advantage since only small amounts of inorganic oxidizer are needed to achieve an emission free from the poisonous carbon monoxide. GUDN burns with a moderate rate at a pressure coefficient approximately 0.5–0.7.

HNF has certain advantages over ADN such as its simple method of synthesis, non-hygroscopic nature, higher density and melting point [59,60]. ADN has a low melting point (<100 °C). On the other hand, HNF is non-hygroscopic in nature and has a melting point above 100 °C. But the major disadvantage of HNF is its sensitivity towards friction [61].

The task of developing environment-friendly high-energy propellants is assuming top priority. Hydrazinium nitroformate (HNF) and ammonium dinitramide (ADN) propellants are poised to replace modern AP based composite and composite modified double base (CMDB) propellants in vogue, in the coming decades. These materials have superior heat of formation (−151 and −71 kJ/mol,

respectively) than that of AP (−290.3 kJ/mol), and thereby they are capable of offering propellants with performance level exceeding 280 s despite their lower oxygen balance. Moreover, they undergo highly exothermic combustion reactions near the surface unlike nitramines, leading to efficient heat feed back to the deflagrating surface enhancing the burning rates. It is reported in the literature that, researchers from Russia have mastered the technology of production of ADN and ADN based propellants. Theoretical estimates suggest that ADN can increase the lift capacity of space vehicles by ~8%. HNF based propellants are expected to increase the payload capacity of the current ARIANE vehicle by thousands of kg.

These clean energetic oxidizers like hydrazinium nitroformate (HNF) and ammonium dinitramine (ADN) combined with new energetic binders like glycidyl azide polymer (GAP), polyglycidyl nitrate (PGN), polynitromethyloxetane (PLN) and 3,3-bis(azydomethyl)oxetane (BAMO) may yield enhanced propellant performance in terms of specific impulse as well as produce clean environmentally acceptable combustion products.

6. Green preparation methods of high explosives

6.1. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)

An innovative environmentally driven approach was developed at Lawrence Livermore National Laboratory to synthesize 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) through the use of vicarious nucleophilic substitution (VNS) chemistry. TATB is manufactured by nitration of 1,3,5-trichlorobenzene (TCB) to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), which is then aminated to yield TATB [62]. The new VNS method developed at Lawrence Livermore National Laboratory for the synthesis of TATB has many 'environmentally friendly' advantages over the current method of synthesis of TATB.

Most significantly, it allows the elimination of chlorinated species from the synthesis of insensitive energetic materials. The new synthesis of TATB uses unsymmetrical dimethylhydrazine (UDMH), a surplus propellant from the former Soviet Union, and ammonium picrate (explosive D), a high explosive [63], as starting materials in lieu of the chlorinated species, trichlorobenzene (TCB). Several million pounds of Explosive D are targeted for disposal in the United States; 30,000 metric tons of UDMH also await disposal in a safe and environmentally responsible manner. The use of these surplus energetic materials as feed stocks in the new VNS method of synthesizing TATB allows an improved method of demilitarization of conventional munitions that also should offer significant savings in production, thereby making this IHE more accessible for civilian applications. The VNS process (Scheme 1) is more environmentally friendly than the current synthesis [64]. It employs mild reaction conditions and eliminates the need for chlorinated starting materials [65].

6.2. 2,4,6-Trinitrotoluene

There are concerns over the environmental effects of manufacturing processes currently available to make TNT (trinitrotoluene). The first step in the preparation of TNT (toluene to mononitrotoluenes (MNTs)) is currently carried out by a non-selective process using mixed acid (nitric and sulphuric acids) which results in the formation of ~4% of *meta*-nitrotoluene (*m*-NT). In subsequent nitration steps the *m*-NT impurity, which cannot be separated from the main products (*ortho*- and *para*-nitrotoluenes), gives rise to unsymmetrical trinitrotoluene isomers, present in levels of 3.5–4%, which contaminate the TNT rendering it unfit for military use. Present purification methods use a sulfiting process which removes the
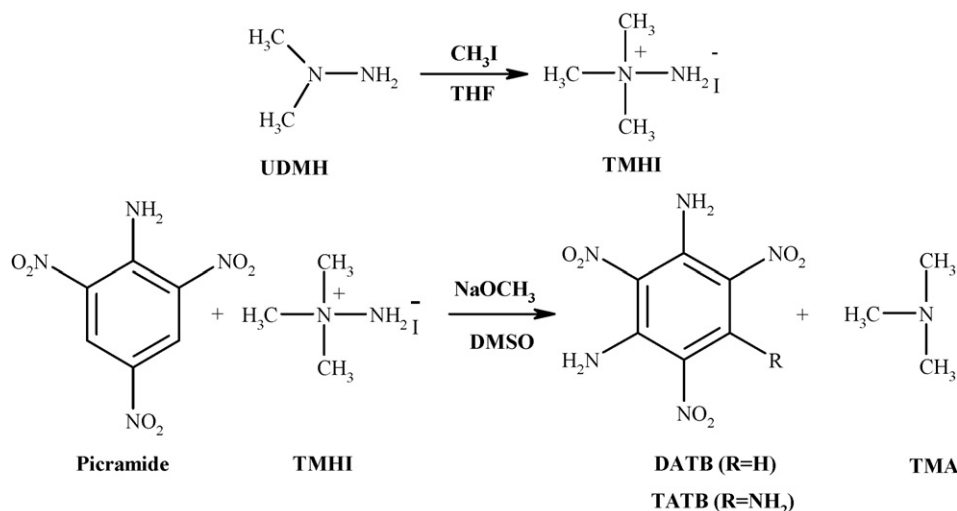
Scheme 1. Synthesis of TATB via VNS method.

unsymmetrical trinitrotoluene isomers, but also produces a waste stream called red water, which is environmentally unfriendly and costly to dispose off. Miller et al from UK have worked on the regioselective nitration of toluene (formation of *m*-NTs is suppressed) using eco-friendly nitrating agent dinitrogen pentoxide in dichloromethane (DCM) instead of nitric-sulphuric acid mixture [66]. Recently, a US patent disclosed another method for the preparation of TNT in an eco-friendly manner [67].

7. Energetic polymers

Path-breaking research on energetic materials has led to the emergence of novel propellants having unique combination of high energy and low vulnerability. Introduction of exothermically decomposing azido groups or oxygen-rich facile nitro/nitrato groups in prepolymers results in realization of formulations with superior performance. Energetic polymers are polymers, which generally contain energetic groups like the nitro, nitrato, azido, etc.; and their combustion products contain significant amount of nitrogen gas. They give out high energy during combustion and thereby increase the performance of the systems that contain them significantly, and because they contain less of carbon compared to conventional hydrocarbon elastomer binders, they are relatively environment friendly.

Prominent among the energetic groups is the azido group which contributes a heat release close to 355 kJ/N_3 unit. Feasibility of the use of low molecular weight azido compounds such as 1,7-diazido-2,4,6-trinitrazaheptane and 1,3-diazido-2-nitrazapropane in solid propellants widened the scope of application of azide compounds beyond the class of initiatory category [68].

It was quite logical to extend the scope of azide containing molecules further to the area of polymers. The first polymer to be developed in this category was glycidyl azide polymer (GAP), which came into prominence during early 1990s. Subsequently, a series of poly azidooxetanes emerged on the scenario [69].

Innovations culminating in the introduction of NC–NG combination as binder for composite modified double base (CMDB) class of propellants are clearly indicative of the advantage of –NO_2 groups in binder matrix. However, poor strain capability of these nitrate esters due to their high glass transition temperature proved a hindrance to their universal binder applications. This catapulted research on open chain nitro/nitrato polymers. PVN finds mention as an explosive (VOD 6560 m/s at 1.5 g/cm^3) as well as low flame temperature propellant ingredient. However, PVN being a solid with melting point 30–45 °C, does not fulfill the requirement of a polymer system capable to take up minimum 80% loading of solid particulates. Subsequent research led to the emergence of polyglycidyl nitrate (PGN) and nitrato methyl-methyl oxetane (NIMMO) as promising compounds. Their potential is evident from the relative Isp values which are much superior to those of current composite and CMDB systems (∼260 s) [70].

Azido polymers, particularly glycidyl azide polymer (GAP) [71] (Table 6) and co-polymers of bisazidomethyloxetane (BAMO) [72] have entered the domain of advanced propulsion systems in a big way. Replacement of the current workhorse binder—hydroxyl terminated polybutadiene (HTPB) by these energetic materials will act as a force multiplier. Poly-3-nitrato methyl-3-methyl oxetane (PNIMMO) [73] and polyglycidyl nitrate (PGN) [74] have also made foray in the area of advanced systems. However, their stability problems need to be tackled. BAMO and nitrato methyl methyloxetane (NIMMO) copolymer are fast emerging as energetic thermoplastic elastomers for wide applications in the area of extruded composite rocket propellants as well as pressed/sheet explosives. Recently the thermal decomposition studies on cured energetic polymer systems (GAP and BAMO-THF) has been reported by Nair et al. [75].

7.1. Energetic thermoplastic elastomers (ETPE) as binders

Binder (polymer matrix) for explosives and propellant systems is changing from the irreversibly cross-linked thermoset polymers to reversible, physically cross linked thermoplastic elastomers

Table 6
Performance of pseudo-propellants containing GAP and modern HEMs

Basic formulation (binder/plasticizer/oxidizer/fuel)	Specific impulse (s)	Density impulse (s g cm^{-3})
HTPB/AP/Al	264.5	464
GAP/AP/Al	–	492
GAP/AN/Al	261.5	463
GAP/AN/CL-20/Al	263.7	475
GAP/ CL-20/Al	273	521
GAP/AND/Al	274.2	491
GAP/HNF/Al	272.6	492
GAP/TMETN/BTTN/RDX (63%)	283.5	405
GAP/TMETN/BTTN/RDX (60%)	242	411
GAP/TMETN/BTTN/CL-20 (63%)	252	452
HTPB reduced smoke	247	421

Table 7
Performance levels of BAMO-AMMO thermoplastic elastomer

Composition	Impetus (J/g)	Density (g/cm^3)	Flame temperature (K)
M30	1081	1.674	3006
BAMO-AMMO – 24%, TAGN – 24%, CL20 – 52%	1166	1.65	2794
BAMO-AMMO – 24%, TAGN – 24%, RDX – 52%	1089	1.57	2493

Table 8
ETC gun propellants

Composition	Impetus (J/g)	Flame temperature (K)
Cellulose binder – 24%, RDX – 76%	1157	3042
BAMO-AMMO – 24%, RDX – 76%	1182	2827
BAMO-AMMO – 24%, CL20 – 76%	1291	3378
BAMO-AMMO – 24%, CL20 – 56%, ANF – 24%	1247	3217

(TPE) [76]. A TPE polymer would enable the recovery and reuse of the ingredients of a system, and could preferentially lower the life-cycle wastes. At operational temperatures, thermoplastic elastomers are solid, behaving much like the polymers we use today. At higher temperature they melt. Once melted, the ingredients, which were bound together in the TPE, can be separated, recovered, and saved for future use. They can be repeatedly melted and used to manufacture new products [76]. This results in the cost savings and environment friendly demilitarization and disposal. To facilitate this, TPE polymers, which melt/soften at a safe processing temperature range of 85–100 °C are desirable.

Typically, such polymers contain a hard (crystalline) block and a soft (non-crystalline) block. They have reversible spherulitic (polymers crystallized from melt show circular birefringent regions called spherulites) crosslinks. These crosslinks disappear above the melting point of the crystalline hard blocks. The physical crosslinks reform upon cooling. Some of the non-energetic TPEs are Estane, Hytrel, EVA and Kraton, while the energetic thermoplastic elastomers include BAMO-AMMO copolymer, BAMO-NIMMO copolymer, and GAP based TPEs. The performance levels of BAMO-AMMO thermoplastic elastomers are given in Table 7. The some of the reported gun propellant formulations based on BAMO-AMMO TPE's are also given in Table 8.

The GEM rocket propellant R^3 concept was demonstrated on a lab scale that resulted in a recovery of 98.9% of the ammonium perchlorate. TPE binder was recovered almost quantitatively with only 19.42 ppm of the solid oxidizer as a contaminant, and with little or no change in the number average molecular weight (Mn) or weight average molecular weight (Mw) of the BAMO-AMMO copolymer TPE [77]. The ammonium perchlorate removal process was done first to reduce the hazards associated with an energetic binder filled with an oxidizer. After the AP was removed, the remaining material was less sensitive and safer to process. Likewise, a TPE based gun propellant was separated by non-chlorinated solvent process to recover 99% of the nitramine and 98% of the TPE binder [78]. Similarly, a TPE based high explosive composition ingredients were separated with 99% recovery of pure CL-20 and 95% recovery of TPE binder.

A TPE energetic formulation does not always have to be separated into its various components in order to be reused. On the ETC gun propellant program, for example, 300 pounds of seven-perforation gun propellant were remelted and formed into rolled sheet propellant without removing or adding any components to the original formulations. No change in laboratory safety characteristics, propellant density, or mechanical properties was observed as a result of the re-processing. The burn rate decreased slightly during the first three cycles then increased approximately 3% higher than the average for the first three iterations. Full-scale gun firing of reprocessed gun propellant has been performed [79]. A flow diagram for the recycle of TPE-based rocket propellant is given in Fig. 4.

Thermoplastic elastomers based on tri-block oxetane copolymers containing azido functional groups offer an improved binding material for solid, high-energy formulations. Current technology uses chemically cross-linked energetic prepolymer mixes that intro-duce the problems of thermally labile chemical linkages, high end-of-mix viscosities, and vulnerability to premature detonation. These materials are also non-recyclable and generate large amounts of pollution during disposal.

The use of energetic thermoplastic elastomers eliminates [80] the need for chemical cross-linking agents, makes processing easier due to their low melt viscosities, and eliminates the need for solvents during casting. Their superior processing qualities and the ease of recycling make these materials a much more environmentally sounds choice for energetic binders. However, their synthesis still involves the use of large quantities of toxic chemicals, such as methylene chloride, as solvents.
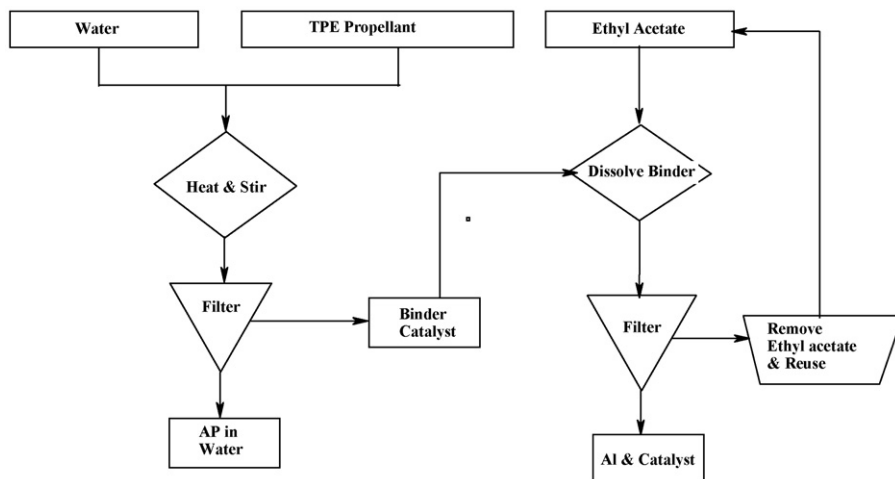
Fig. 4. Flow diagram of separation and recovery methods of ingredients in the TPE propellants.

Carbon dioxide has been proven to be a viable, environmentally responsible replacement solvent for many synthetic and processing applications. It is cheap, easily recyclable, and available from current sources. Research at the University of North Carolina has shown that carbon dioxide is a viable solvent for the polymerization of vinyl ether monomers. Furthermore, poly-oxetanes can be polymerized in carbon dioxide with molecular weight, molecular weight distribution, and functionality maintained. The University of North Carolina has demonstrated the synthesis of both non-energetic and energetic homo-polymers and random copolymers.

8. Dinitrogen pentoxide: versatile nitrating agent for HEMs

The nitrated products find broad spectrum of applications in the area of high-energy materials (HEMs) [81]. The selection of a nitrating agent for a particular nitration reaction is mainly dependent on the chemical nature of substrate molecule. The most commonly used nitrating agent is a relatively inexpensive mixture of concentrated nitric acid and sulphuric acid in different proportions. However, conventionally used nitrating agents pose serious pollution threat to the environment and meet with failure in case of deactivated substrates or selective nitration needs. Nitronium tetrafluoroborate and nitronium hexafluorophospahte are found effective nitrating agents for deactivated substrate molecules. Suzuki et al. [82] reported selective nitration of certain aromatics using $N_2O_4/O_3/O_2$ mixtures. $(CF_3CO)_2O/HNO_3$ can also be used for selective nitration of certain deactivated substrates. However, it is not recommended because of explosion hazards involved during its use for nitration reactions.

Although, dinitrogen pentoxide (DNPO or N_2O_5) has been known for almost 150 years, its very limited application has been made as a nitrating agent. None of the publications in open literature disclose the finer details of actual process for the synthesis of DNPO in a crystal clear form due to its strategic importance. The advantages of using DNPO in comparison to conventional nitrating agents are (a) high selectivity in position of attack with poly functional substrates, particularly when used in organic solvents, (b) feasibility towards the reaction in acidic medium to offer strong nitrating system, (c) simple isolation of the product, (d) ease of temperature control, (e) very high yields (80–90%) and (f) absence of spent acid for disposal.

The non-selective nitration by N_2O_5 in acidic medium can be exploited to nitrate deactivated precursors [83], while nitration by N_2O_5 dissolved in an organic solvent (especially chlorinated hydrocarbons) is an effective means for selective nitration of substrates where there is more than one possible nitration site in the molecule. This unique dichotomy of dinitrogen pentoxide chemistry may lead to a wide variety of products of interest to energetic materials community and has accelerated R&D efforts towards utilizing the potential of dinitrogen pentoxide as nitrating agent. The importance and potentiality of DNPO has been described in brief.

Dinitrogen pentoxide can be generated by adopting different approaches [84,85]. It can be prepared by electrochemical process along with nitric acid and can be isolated [86]. Preparation of N_2O_5 by reacting N_2O_4 with ozone is considered one of the most versatile methods to obtain high purity N_2O_5 in inert organic solvent at −20 to −30 °C [87]. A plant manufacturing N_2O_5 at 360 g/h by the gas phase oxidation of N_2O_4 with ozone is operative at Indian Head Division [88]. Synthesis of a variety of inorganic and organic compounds using N_2O_5 is reported in literature. The chemical, physical properties and various applications of N_2O_5 in synthesis of HEMs and allied materials are also reported [89].

Application of inorganic nitrates such as bismuth nitrate $[Bi(NiO_3)_3]$ [90,91], cerium ammonium nitrate [92], sodium nitrite $(NaNO_2)$ [93] and potassium nitrate (KNO_3) [94] as nitrating agent

were found to be more useful for nitration of aromatic compounds using silica gel as a solid support. These new nitrating systems will drastically reduce the use of acid in the nitration system, which will be an added advantage in terms of green and eco-friendly process. There is continued research input in this scientific field and the technological feasibility need to be studied for these nitrating systems.

Researchers from United Kingdom reported that the use of DNPO for nitration reactions is one of the important solutions to produce energetic materials with a significant reduction in waste acids. DNPO can reduce the acid waste and thereby reduces environmental pollution [95].

Liquid carbon dioxide (L-CO_2) replaced methylene chloride as the solvent in nitrations with dinitrogen pentoxide (N_2O_5) and anhydrous nitric acid. This new L-CO_2 nitration procedure overcame many of the drawbacks of conventional mixed acid (HNO_3/H_2SO_4) media when dealing with sensitive substrates. Both N_2O_5 and anhydrous nitric acid are soluble in L-CO_2 which is a major advantage because they can be added directly into the substrate being nitrated. The N_2O_5 was dissolved in L-CO_2, cooled, and added to L-CO_2 containing the material to be nitrated [96].

9. Supercritical fluid technology: possible green technology for the 21st century

Supercritical fluids (SCF) possess properties that are intermediate between liquids and gases. They act as very good solvent and differ from conventional solvents. The main difference between supercritical fluids and conventional solvents is their compressibility. Conventional solvents in the liquid phase require very large pressures to change the density, whereas for supercritical fluids very significant changes in density can be achieved with small pressure and/or temperature changes near their critical point. The main candidate in this class is supercritical carbon dioxide (SC-CO_2) is now well established as a solvent for use in extraction. This is for a number of reasons. It can generally penetrate a solid sample faster than liquid solvents because of its high diffusion rates, and can rapidly transport dissolved solutes from the sample matrix because of its low viscosity. There are also of course less solvent residues present in the products. Further, it is an attractive alternative against to the halogenated solvents, which pollutes the environment. A recent review on super critical CO_2 gives an overview of research performed in the preparation fine particles of energetic materials [97]. Supercritical fluid recycling would have both economic and environmental advantages over destructive open burning / open detonation processing. Unfortunately, the nitramine ingredients (RDX, HMX) found in many of military explosives and composite low vulnerability ammunition (LOVA) propellants have insufficient solubility in non-reactive supercritical fluids (e.g., CO_2). Search for alternate suitable supercritical solvent and suitable conditions for recovery of HEMs ingredients is underway.

10. Alternate techniques—green context

An expeditious and solvent-free approach for selective organic synthesis is described which involves simple exposure of neat reactants to microwave (MW) irradiation. The coupling of MW irradiation with the use of catalysts or mineral supported reagents, under solvent-free conditions, provides clean chemical processes with special attributes such as enhanced reaction rates, higher yields, greater selectivity and the ease of manipulation.

Our recent results on this eco-friendly approach utilizing recyclable inorganic oxides or supported reagents such as $Fe(NO_3)_3$–clay (clayfen), $Cu(NO_3)_2$–clay (claycop), NH_4NO_3–clay (clayan), NH_2OH–clay, $PhI(OAc)_2$–alumina, $NaIO_4$–silica,

CrO_3–alumina, MnO_2–silica, and $NaBH_4$–clay, etc. have been reported in MW-assisted deprotection, condensation, cyclization, oxidation and reduction reactions including the efficient one-pot assembly of heterocyclic molecules from in situ generated intermediates [98].

Supported reagents have gained considerable attention in the recent past for the development of green chemical process like nitration. These class of reagents possess many advantages over its conventional methods such as easy handling of reagents, reduced product contamination by having the reagent fully bound to the solid support, relatively safe handling owing to the full chemisorptions of the toxic chemicals, reduced environmental problems, allowing higher stirring rates, good dispersion of reactants for improvement in reaction selectivity, high yield and clean work-up. Laszlo et al. have introduced clay-supported iron(III) nitrate (clayfen) and clay-supported copper(II) nitrate (claycop) as potential source of nitrosonium ion (NO^+) mainly in the regioselective C-nitration of aromatic hydrocarbons [99,100]. Even though the utility of these "green" nitrating agents have been well established for aromatic C-nitration reactions, its capability for N-nitration is yet to be established. Another important insensitive energetic materials TEX was synthesized by using montmorillonite K10 clay supported iron(III) nitrate (clayfen) or montmorillonite K10 clay supported copper(II) nitrate (claycop) as nitrating agents in presence of acetic anhydride under Menke conditions [101].

The non-solvent reaction, experimental simplicity, and enhanced selectivity are the main attractive features of the approach. The use of water, the ultimate "green" solvent, in a chemical reaction greatly reduces the cost of the reaction and also provides a more environmentally benign chemistry. These techniques may find applications in the synthesis of HEMs.

The use of electrochemical reactions in the synthesis of HEMs is another attractive option to reduce environment pollution and to make the chemical process more eco-friendly. This new synthesis approach for the preparation of alkylnitro compounds is underway, which will reduce the environmental related issues and will avoid the usage of powerful oxidizing chemicals [102]. Electrochemical reactions are the cleanest process in chemical conversion.

11. Nano-energetic materials

With the rapid advances made in the realm of nanoscience and nanotechnology, the shape and size of nanostructures can be easily controlled and this in turn facilitates tuning the surface area of the engineered nanomaterials. When the surface area is high, it is comparatively easier to achieve higher interfacial contacts than with that of the corresponding bulk counterparts. Furthermore, homogeneous mixing of the oxidizer and the fuel is the key to achieving higher rates of energy release and combustion speeds. Tunable energetic materials [103–105] are attractive and promising and indeed the need of the hour. These materials are highly sensitive to electrostatic discharge (ESD), friction and impact. Therefore, it is important to desensitize them without losing their energetic performance. Efforts are underway to realize this. In short, it is possible to design nano-structured metastable intermolecular composites (MIC) materials with the combustion speeds ranging from few tens to 2500 m/s. MIC materials with very high burn rates are extremely sensitive to electrostatic discharge (ESD). For examples, the metal nanoparticles used in the MIC formulation are extremely sensitive to ESD and have ESD energy of 0.98 mJ. Energetic polymers are being used to coat the MIC materials to desensitize the MIC materials. The critical concern is to preserve the performance of MIC materials while decreasing their ESD sensitivity.

12. Lead-free ballistic modifiers: environmentally more compatible materials

Modern/futuristic missiles demand propulsion systems based on advanced high burning rate propellants to realize higher thrust and reduction in action time. Current solid rocket propellants have reached a plateau in terms of ballistics. Efforts are on all over the world to develop super burn rate (>40 mm/s at 7 MPa) propellants meeting challenging requirements of tomorrow. New ballistic modifiers are being synthesized for this purpose since lead-free compounds are found to be the preferred choice.

The transition metal oxides (TMOs) [106], like ferric oxide – Fe_2O_3 (FO) and copper chromite – $CuCr_2O_4$ (CC) are widely used as ballistic modifiers (BMs) in ammonium perchlorate (AP)-based composite propellants. A detailed literature survey on TMOs of composite propellants was carried out in the year 1970 [107].

The ferrocenes are relatively new entrants as BMs for this class of propellants and are claimed to be more effective. However, incorporation of these BMs at the cost of active ingredients, like AP beyond 3% level causes undesirable penalty on the energetics of the propellant due to their inherent non-energetic nature and tend to migrate to the propellant surface if incorporated beyond 3% level resulting in change in pre-programmed ballistic profile, and also form sensitive products on air-oxidation. An intensive search is on all over the globe for non-migrating energetic ballistic modifiers (EBMs) to realize desired combustion characteristics without much penalty on energetics even if higher percentages are need to be added to realize ultra high burning rates. The important compounds considered for development in the last decade are (i) ferrocene-based polymers like FPGO, (ii) carborane-based compounds like *n*-hexyl carborane, (iii) metal carbohydrazides like Cu, Ni and Co metal nitrates, (iv) energetic metal salts like NTO metal salts, (v) organometallic compounds and (vi) metal salts of nitro or azido group containing carboxylic acids.

The transition metal complexes (co-ordination compounds) having energetic heterocycle ligands and nitrate/perchlorate anions, are front runners as EBMs. The high nitrogen content tetrazoles and triazoles offer a wide range of high-energy heterocyclic eco-friendly ligands [108]. It is anticipated that HNC based compounds are the potential contenders for their use in composite propellants for different applications including burn rate modifiers. Talawar et al. [109] also utilized the aminotriazole ligand for the synthesis of energetic ballistic modifiers for propellant applications. The metal nitrate complexes derived using aminotriazoles and aminotetrazoles are envisaged to be eco-friendly ballistic modifiers. Energetic metal salts are emerging as attractive alternatives in view of their potential to ballistically modify the combustion pattern of propellants without much adverse effect on energetics. Metal salts of 3-nitro-1,2,4-triazol-5-one have also been recommended as potential energetic ballistic modifiers (EBMs) for solid propellants [110]. Limited studies have been carried out on the salts of trinitroanilino benzoic acid (TABA) in HEMRL as ballistic modifier in double base systems [111,112]. Study on the synthesis and performance evaluation of various EBMs like Li and K [113] and transition metal salts [114] of TABA and NTO as an alternate new ballistic modifiers for ammonium perchlorate (AP)–hydroxyl terminated polybutadiene (HTPB) composite propellant is reported.

The application of lead salts to render burning rates of double-base rocket propellants independent of chamber pressure has been investigated by a number of research workers [115]. Double base propellant processing utilizing lead based compounds poses a hazard to the environment and to personnel in the workplace. The precursor to propellant is a water-wet paste which is partially dried and plasticized into a colloidal sheet by rolling between heated calendars. It is likely that some amount of the lead compound is lost in
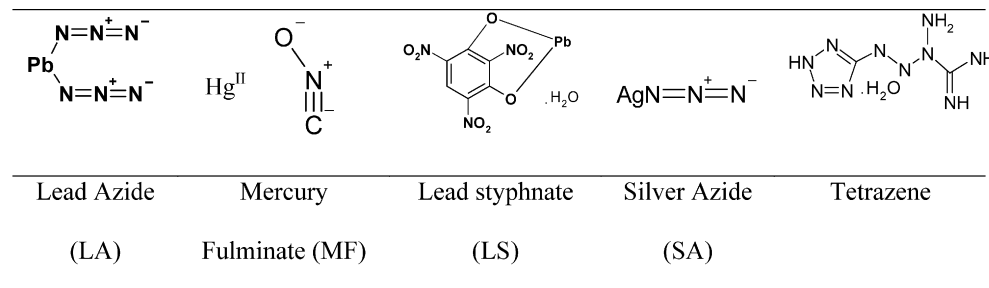
the excess water during the rolling process and subsequently carried into the waste stream. While collection and treatment methods can help clean the wastewater and are in place for any foreign material that may enter the waste stream, the best approach is to replace the problematic compound. The use of lead salts also leads to health hazards caused by lead oxides in the exhaust gases.

Nitramines like RDX and HMX have acquired prominence as energetic component of eco-friendly propellants by virtue of their positive heat of formation (+58.5 and +75 kJ mol^{-1}, respectively), superior chemical and thermal stability as well as presence of reduced pollutants in combustion products and non-smoky exhaust similar to that of double base propellants However, the major drawback of these formulations is high-pressure index (n) values [116]. The potential of diaminoglyoxime (DAG) [117] and diaminofurazan (DAF) [118] as a ballistic modifier for RDX incorporated double base propellant formulations was evaluated by determining strand-burning rates experimentally. The effect of DAG and DAF on sensitivity, compatibility and mechanical properties of propellant formulations was also investigated [117,118].

Two bismuth compounds, bismuth salicylate and bismuth citrate, have been evaluated as lead alternatives in a propellant formulation similar in theoretical performance properties of currently fielded propulsion systems. Industrially, bismuth is considered less toxic of the heavy metals. Double base propellants having a mixture of bismuth and copper salts of hydroxy-substituted benzoic acids added as burning rate (ballistic) modifiers [119]. Minimum signature propellants based on ammonium nitrate have been reported as eco-friendly propellant formulations [120].

13. Eco-friendly (lead-free) primary explosives

The conventionally reported initiatory compounds are viz., mercury fulminate, lead azide, lead styphnate and tetrazene.

and explosive properties whereas; Sinditski and Serushkin [125] have co-related design and combustion behaviors of explosive co-ordination compounds. Although these coordination compounds [126] are known since long, they have recently [127] evinced interest as primary explosives.

Patil et al. [128] reported transition metal complexes of nitrate/azide/perchlorate and proposed their application as initiators. The preparation of nickel hydrazinium nitrate (NHN) has been recently reported by Shunguan et al. [129]. NHN is an initiatory compound in fine granular pink colour free from gritty particles. The preparation involves the treatment of nickel nitrate solution with hydrazine hydrate at 65–70 °C.

$$Ni(NO_3)_2 \cdot 6H_2O + NH_2 - NH_2 \cdot H_2O \xrightarrow{\Delta} Ni(N_2H_4)_3(NO_3)_2$$
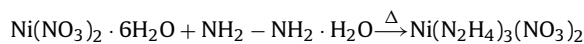
Hariharanath et al. [130] evaluated potential use of NHN as component of squib composition. Nickel hydrazinium nitrate (NHN) is a lead-free, safe initiatory compound that has attracted great attention [131] of the researchers in the primary explosives field. This material has the potential to replace the conventional lead containing compounds like the lead azide for a range of initiatory applications. This material has been extensively evaluated in tubular detonators replacing conventional ones containing ASA composition [132], and as detonants for demolition charges. Globally, researchers from China are exploring the possibility of its use as a replacement for lead azide in conventional detonators. The performance levels of characteristics of NHN are given in Table 9 with lead based primary explosives.

Other important lead-free initiatory compounds are silver azide and tetraammine-cis-bis (5-nitro-2H tetrazolato-N^2) Cobalt(III) perchlorate (BNCP). Silver azide is prepared by adding silver nitrate solution to a mixed solution of sodium azide and barium acetate in presence of a crystal habit modifier [133]. The product obtained was

Lead Azide	Mercury	Lead styphnate	Silver Azide	Tetrazene
(LA)	Fulminate (MF)	(LS)	(SA)	

Mercury fulminate [121] and lead azide [122] are the foremost primary explosives, which has gained prominence in the military ammunitions as well as civil applications. Despite being an excellent detonating agent, it suffers from certain inherent drawbacks, such as hydrolytic instability, incompatibility with copper or its alloys (commonly used for encapsulation of primary explosive formulations) and high friction sensitivity. Moreover, its high thermal stability (up to 330 °C) is undesirable from the point of view of its initiation by thermal stimuli. Search is on for the potential primary explosives with figure of insensitivity (F of I) >20 which are less prone to initiation from eventual mechanical shock during storage, transport or handling of the finished ammunitions and are stable as well as compatible. Lead- and mercury free co-ordination compounds are the choice of tomorrow in view of their additional advantage of being eco-friendly. Another desirable attribute of this class of compounds is the presence of almost stoichiometric fuel and oxidizer moieties. These compounds may enter in all the spectrum of explosives. Tomlinson et al. [123] and Joyner [124] have reported relationship between co-ordination structure

having purity 99% and bulk density of 1.25 g/cm^3. BNCP is another energetic lead-free initiator [134]. It is very safe to handle, thermally stable (264 °C) and high velocity of detonation (5700 m/s) at loading density of 0.6 g/cm^3. The synthesis of BNCP was achieved by reacting the precursors tetraammine carbonato cobalt(III) nitrate, CTCN [135] and sodium 5-nitrotetrazolate dihydrate [136] in HC1O$_4$ at 80–90 °C for about 2 h [137] (Scheme 2).

Carbohydrazide is another interesting azotic ligand with non-bonded lone pair of electrons on the nitrogen of amino group and oxygen of the carbonyl group. It is well reported [138] that carbohydrazide coordinates with many metal ions as bidentate ligand. Chunhua et al. [139] from Beijing Institute of Technology, China, have recently reported the synthesis, molecular structures and explosive properties of [M(CHZ)$_3$](ClO$_4$)$_2$ (M = Cd, Ni, Zn, Mn; CHZ = carbohydrazide). The synthesis and characterization of the transition metal nitrates as well as perchlorates have been reported by Sinditskii et al. [140]. Thermodynamics of coordination compounds of Co, Ni, Zn and Cd nitrates and perchlorates with carbohydrazide have been reported by Kon'kov et al. [141]. Zhang et al.

Table 9
Comparative properties of some of the more environment compactable in comparison to lead based primary explosives

Property	SA	MNT	NHN	BNCP	NiCP	CoCP	BLA
Nature	Free flowing	Free flowing	Free flowing	Fluffy	Free flowing	Free flowing	Free flowing
Bulk density (g/cm^3)	1.4	1.3	1.2	0.65	0.9	0.9	2.0
Thermal stability (°C)	260	220	180	264	290	300	200
Ignition temperature (°C)	228	318	210	260	332	322	>350
Impact sensitivity, $h_{50\%}E$ (cm)	118	54	85	30	55	55	>150
Friction sensitivity (kg)	0.005	0.50	1.0	3.0	1.0	1.0	0.3
Spark sensitivity (J)	0.007	–	5.0	5.0	–	–	0.009
Performance evaluation, lead plate test, diameter of puncture (mm)	Efficient as LA, 9	More efficient, 9	Efficient, capable alone to replace ASA, 8–9	Could not be initiated	Efficient as LA, 9	Efficient as LA, 9	Efficient as LA, 8–9

SA: silver azide; MNT: mercuric-5-nitrotetrazole; NHN: nickel hydrazine nitrate; BNCP: bis-(5-nitro-2H-tetrazolato-N^2)tetramiane cobalt(III) perchlorate; NiCP: nickel tris(carbohydrazide) perchlorate; CoCP: cobalt tris(carbohydrazide)perchlorate; BLA: basic lead azide.

[142] studied the molecular structure and physicochemical properties of cadmium carbohydrazide perchlorate—a potential primary explosive. Recently, HEMRL, India reported the work on the energetic co-ordination compounds [143].

Another interesting primary explosive candidate, known as TNTA [144], consists of a series of N$_3$ and NO$_2$ groups attached to a ring of carbon atoms. Like other nitrogen-based explosives, part of its energy release comes from single or double bonds between nitrogen atoms that break apart and re-form as more stable triple bonds. When mixed with an oxygen-rich material such as ammonium nitrate, TNTA explodes to produce harmless molecules of nitrogen and carbon dioxide. The compound is undergoing commercial tests, and German researchers hopes that it will be on the market in 2–5 years.

Recently, another organic compound has been reported as potential organic primary explosive viz., 1,4-diformyl-2,3,5,6-tetranitratopiperazine [145]. The 1, 4-diformyl-2,3,5,6-tetranitra topiperazine turned out to be a powerful highly energetic compound. Its physical and chemical properties were investigated by theoretical as well as experimental methods. The detonation energy of 1,4-diformyl-2,3,5,6-tetranitratopiperazine was determined to 5376 kJ/kg or 93% compared to HMX [145].

Development of environmentally friendly primary explosives or green primary explosives continued to be thrust area of research in the current as well as future context. The most sought after candidates are energetic co-ordination compounds, high nitrogen content compounds and organic azide-based compounds.

Huynh and co-workers at Los Alamos National Laboratory recently ended this long-standing search with her discovery of four series of green primaries from commercially available iron salts with energetic nitrotetrazole ligands. Unlike the conventional initiatory, these green primaries have controlled explosive sensitivities that prevent unexpected accidents and do not produce toxic by-products during detonation, which lead to environment related issues. The performance of promising lead-free primary explosives Cobalt(III)ammine coordination complexes (e.g., BNCP) can be increased with the number of perchlorate groups. But, it is proven that perchlorate is a possible teratogen and has adverse effects on thyroid functions [146]. Other health problems such as dermatitis, asthma, dyspnea, respiratory hypersensitivity, and diffuse nodular fibrosis are potential symptoms from overexposure of cobalt metal [146].

13.1. Green primary explosives

Huynh et al. [147,148] recently reported green primary explosives based on 5-Nitrotetrazolato-N^2-ferrate hierarchies. They reported novel environmentally friendly primary explosives viz., cat[Fe^{II}(NT)$_3$(H$_2$O)$_3$], cat$_2$[Fe^{II}(NT)$_4$(H$_2$O)$_2$], cat$_3$[Fe^{II}(NT)$_5$ (H$_2$O)], and cat$_4$[Fe^{II}(NT)$_6$] with available cations such as Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$, hydrazonium (Hyzm), nitrosocyanaminium (NCAm), 5-amino-1-nitroso-1,2,3,4-tetrazolium (ANTm), 1,5-diamino-4-nitroso-1,2,3,4-tetrazolium, and 1,2,5-triamino-1,2,3-triazolium (TATm) and 5-nitrotetrazole ligand as anion counterpart (Fig. 5).
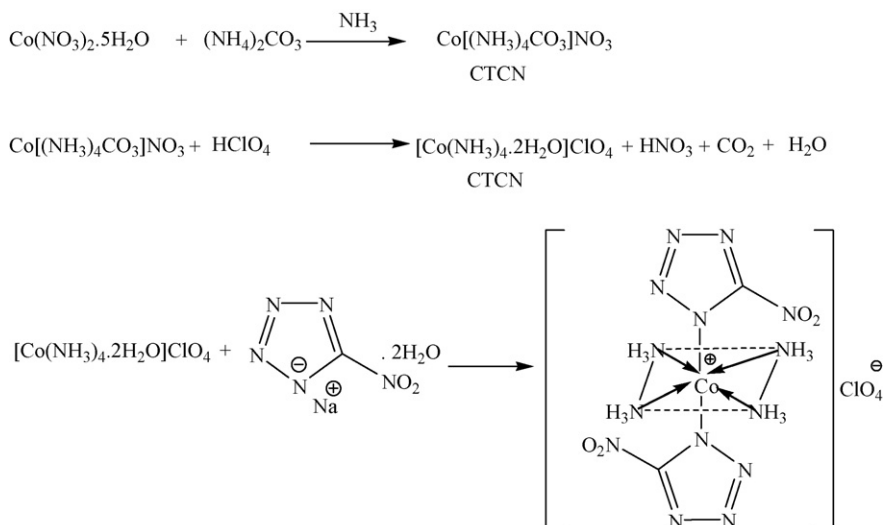
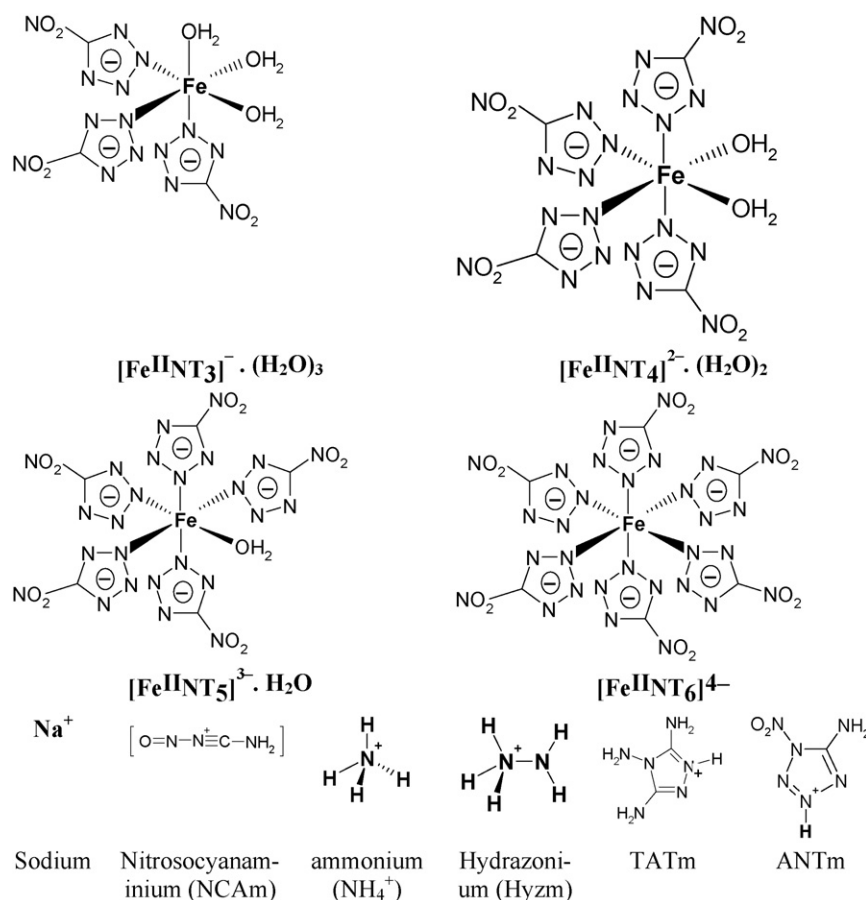**Scheme 2.** Synthesis approach for BNCP.

Fig. 5. Inorganic green primary explosives.

These compounds hold great promise for replacing not only toxic lead primaries but also thermally unstable primaries and poisonous agents. Strategies are also described for the systematic preparation of coordination complex green primaries based on appropriate selection of ligands, metals, and synthetic procedures. These strategies allow for maximum versatility in initiating sensitivity and explosive performance while retaining properties required for green primaries [147,148]. Further, it satisfies all the requirements of modern primary explosives including insensitivity to light, sufficient sensitivity to give reliable detonation, thermal stability, and chemical stability.

According to Huynh et al. the oxygen-rich NT ligands contribute sensitivity and explosive energy to the coordination complex anions; thus, the green primaries with the greater number of NT ligands are more sensitive and have better explosive performance [148]. The work on green primaries done by Huynh et al. was recognized as one of the best R&D in 2006. Some of the physical, sensitivity, and explosive performance properties of lead and lead-free primary explosives are represented in Table 10.

In an alternate approach, various high explosives were attempted for the use as an energetic in co-ordinations complexes since they possess oxygen-rich sensitive functional groups in their molecular structure. Variety of energetic materials considered for the above purpose under the following categories (i) strained ring with nitro groups, (ii) aliphatic N-based nitro compounds, (iii) complexes with oxygenic bidentate ligands and (iv) heterocylic nitro compounds. Among the above categories, heterocyclic compounds are the best choice for energetic co-ordinating anions (Fig. 6).
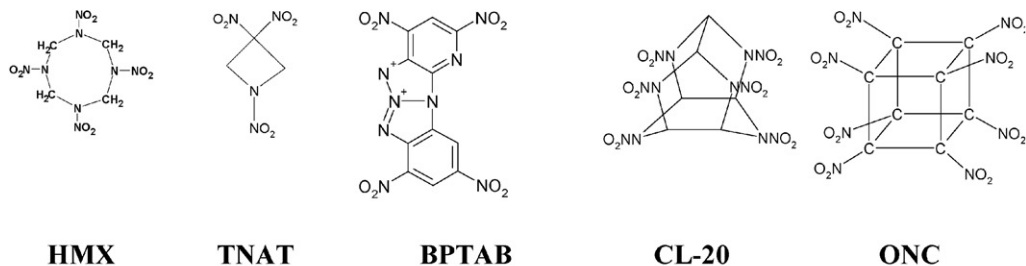
14. Biodegradation of HEMs

Biodegradation of HEMs is becoming an important aspect in the field [149,150]. This is because; the HEMs are increasingly becoming a common soil and ground water contaminant. The release of HEMs to environment occurs from various commercial and military activities including manufacturing, waste discharge, testing and training, ordnance demilitarization and open burning/detonation. RDX is a major contaminant because RDX is currently widely used,

Table 10
Properties of green primary explosives in comparison with conventional primary explosives

Primary Explosive	NH_4FeNT	NaFeNT	NH_4CuNT	NaCuNT	LA	LS	NHN
Density (g/cm^3)	2.2	2.2	2.0	2.1	4.8	3.0	1.2
Thermal stability (°C)	255	250	265	259	315	282	180
Impact sensitivity (cm)	12	12	12	12	10	14	85
Friction sensitivity (kg)	2.8	0.02	0.5	0.04	0.006	0.04	0.001
Spark sensitivity (J)	>0.36	>0.36	>0.36	>0.36	0.0047	0.0002	5
VOD (m/s)	7.7	NA	7.4	NA	5.5	5.2	4.5

Strained ring with nitro groups
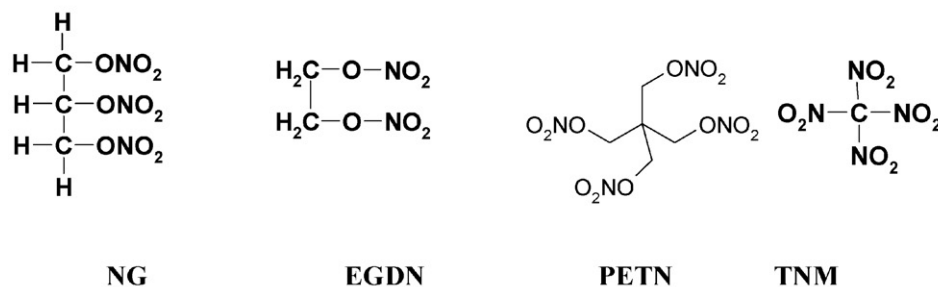
| HMX | TNAT | BPTAB | CL-20 | ONC |

Aliphatic N-based nitro compounds

| NG | EGDN | PETN | TNM |

Complexes with oxygenic bidentate ligands

5,5'-dinitro-3,3'-azo-1,2,4-triazolate

(DNAT) based primaries

4,4',5,5'-tetranitro-2,2'-biimmidazolate

(N4BIM) based primaries

Heterocylic nitro compounds.

| DNT | ANTz | NaNT |
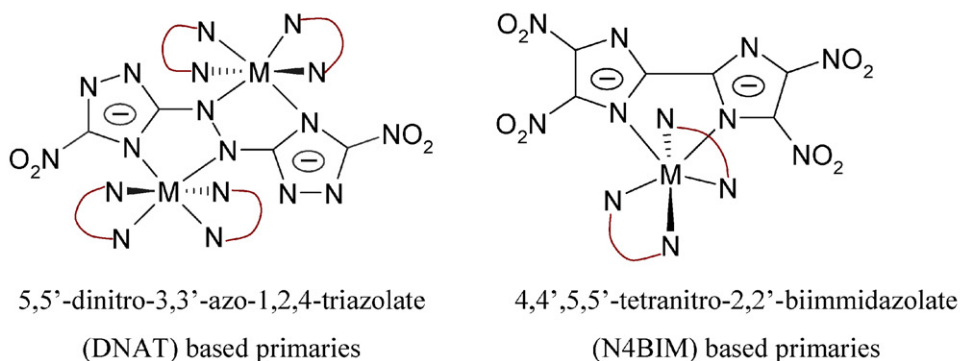
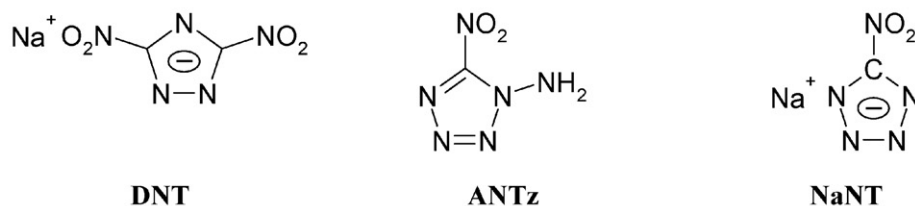**Fig. 6.** Prospective organic explosives for ligand consideration towards the synthesis of inorganic green primary explosives.

as it is more powerful and less toxic than TNT. This contamination necessitates cost effective technology such as bioremediation. Research has been centered on the biodegradation and metabolic pathways. A few investigations conducted under aerobic conditions present mixed results. Extent of degradation varies from 0 to 76%. Anaerobic conditions are preferred. Clostridium acetobutyllicum has been used. RDX has been converted through nitroso, hydroxylamino, and nitrosohydroxylamino to triamino compound. This is followed by ring cleavage to small molecules. Previous reports on the biodegradation and biotransformation of RDX and HMX by a variety of microorganisms (aerobic, anaerobic, and facultative anaerobes) and enzymes have shown that initial N-denitration can lead to ring cleavage and decomposition [151,152].

15. Conclusions

Materials listed in the foregoing sections not only improve the performance by leaps and bounds, but also comply with the evolving, soon-to-be mandatory concepts of green energetic materials (GEM), insensitive munitions (IM) and non-destructive demilitarization. As part of a global initiative on these lines, which includes total replacement/ban of environmentally polluting HEMs like ammonium perchlorate in future, every developing and developed nation would have to follow them strictly. The fact that these materials are generally not traded would put enormous constraint not just on the advancements in the field in any country, but the continuation of the existing, albeit outdated technology too. Therefore,

the development of these materials, and establishing an indigenous source for the same, pave the solid foundations for harnessing the much-needed strategic initiative. Thus, the development of these materials has direct relevance and has enormous impact on the environment. Currently green energetic materials are 100 times more expensive to produce than conventional ones. However, authors are hopeful the research and development activities will continue in the area of GEMs all over the world irrespective of cost.

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