Review

Advances in science and technology of modern energetic materials: An overview

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Abstract

Energetic materials such as explosives, propellants and pyrotechnics are widely used for both civilian and military explosives applications. The present review focuses briefly on the synthesis aspects and some of the physico-chemical properties of energetic materials of the class: (a) aminopyridine-*N*-oxides, (b) energetic azides, (c) high nitrogen content energetic materials, (d) imidazoles, (e) insensitive energetic materials, (f) oxidizers, (g) nitramines, (h) nitrate esters and (i) thermally stable explosives. A brief comment is also made on the emerging nitration concepts. This paper also reviews work done on primary explosives of current and futuristic interest based on energetic co-ordination compounds. Lead-free co-ordination compounds are the candidates of tomorrow's choice in view of their additional advantage of being eco-friendly. Another desirable attribute of lead free class of energetic compounds is the presence of almost equivalent quantity of fuel and oxidizer moieties. These compounds may find wide spectrum of futuristic applications in the area of energetic materials. The over all aim of the high energy materials research community is to develop the more powerful energetic materials/explosive formulations/propellant formulations in comparison to currently known benchmark materials/compositions. Therefore, an attempt is also made to highlight the important contributions made by the various researchers in the frontier areas energetic ballistic modifiers, energetic binders and energetic plasticizers.
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Contents

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1. Introduction

Energetic materials are generally organic compounds containing nitro, azide and hydrazino groups in the molecules [1]. When explosive materials undergo decomposition, they produce energy by a process called oxidation. During the oxidation reaction, an explosive is detonated with sudden release of energy or a fuel is burnt. The oxidation reaction produces heat because the internal energy of reactant molecule is higher than that of the end product. The difference between the internal energies of reactant and product of a reaction is called heat of reaction. When an explosive material detonates to form gaseous products, the heat of reaction is called heat of explosion. Most of the explosives consist of elements of carbon, hydrogen, oxygen and nitrogen. The highest oxidation state of carbon, when burnt in oxygen, is CO_2 and that of hydrogen is H_2O. The molecular nitrogen is at a lower state of internal energy than the oxides of nitrogen (NO, NO_2, N_2O_3, etc.). Therefore, any nitrogen in the reactant is given out as N_2 gas in the end. The $-NO_2$ and $-ONO_2$ groups are the major source of oxygen in the energetic molecules, which contribute significantly to the detonation or combustion processes.

The search for the promising high-energy materials during the last one decade has led to the discovery of a vast number of energetic oxidizers, fuels and explosives for their possible use as an energetic ingredient in propellants/explosives formulations. Exploitation of structure property relationships, coupled with the use of computer codes to predict the energetic properties from molecular structure, has led to the development of new energetic materials with increased performance, reduced sensitivity to external stimuli and or enhanced chemical and thermal stability.

The other important properties which decide the fate of newly synthesized energetic material for its application in propellant and explosive formulations are its chemical compatibility with other ingredients in the formulation, less toxicity, stable physical form and ease of its handling. All these mentioned properties are compared with the properties of known benchmark energetic materials which are currently in use in propellant or explosive formulations. High energy materials (HEMs) research area received less attention from the energetic materials chemists/technologists/scientists in the past. This may be attributed to the risks and hazards associated with the research investigations.

There has been reasonable progress in the synthesis and development of new energetic compounds in recent years.These compounds include nitro compounds based on nitrate esters,

nitramines, azido compounds, azido nitrates, azido nitramines, difluoro nitramines, polycyclic compounds, furazans (1,2,5-oxadiazoles) and furoxans (1,2,5-oxadiazole-*N*-oxides). The other category of nitro compounds emerging as key ingredients for propellant and explosive formulations are tetrazoles, triazines, tetrazines, co-ordination compounds of metallic salts of hydrazines, carbohydrazines and polymeric binders containing azo, nitro, nitroxy groups in the backbones. More recently attention has been paid to replace hydroxyl terminated polybutadiene with nitrated hydroxyl terminated polybutadiene (NHTPB) to achieve higher energetics. New requirements such as reduction of the vulnerability of combat platforms, stealth characteristics, and increased demand to achieve higher energetics in terms of specific impulse and performance coupled with environmental issues have forced the researchers to produce novel energetic materials [2–6]. To develop a new energetic material, it is essential to consider the factors such as indigenous availability of starting materials, ease of its preparation, purity of energetic material and its cost effectiveness. In the following pages a brief account on the specific class of energetic materials is given.

2. Aminonitro heterocyclic *N*-oxides: promising high energy materials

The amino/aminonitro heterocycles may be effectively used as precursors for the synthesis of new energetic material/s. Several heterocyclic compounds bearing nitro, amino and *N*-oxide substituents have been studied as possible replacement for the insensitive explosives, viz., trinitrotriaminobenzenes (TATB) and nitrotriazolone (NTO). The potential use of nitro derivatives of pyridines, pyrimidines, pyrazines and their bicyclic analogues has been reported [7] for the synthesis of novel insensitive explosives.

2,5-Diamino-3,6-dinitropyrazine (ANPZ-i) has been synthesized by the nitration of 2,5-diethoxypyrazine using nitronium tetrafluoroborate in sulfolane and subsequent amination under autoclave conditions. The theoretically predicated performance of 2,5-diamino-3,6-dinitropyrazine is in par with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The performance and insensitivity characteristic properties of ANPZ-i indicates its potential use in futuristic insensitive explosive formulations [8].

Ritter and Licht [9] reported the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) by the nitration of 2,6-diamino-3,5-dinitropyridine (ANPy) followed by oxidation using acetic acid and 30% H_2O_2. It is reported that, 2,6-diamino-3,5-dinitropyridine-1-oxide exhibits a density of 1.878 g/ml with melting point of >340 °C. The extensive performance

Table 1
Properties of some nitropyridine and their N-oxides and their comparison with 2,4,6-trinitrobenzene

Compound	TNPy (I)	TNPyOx (II)	DazNPyOx (III)	TNB
O.B. (%)	−37.4	−27.8	−57.6	−56.3
VOD (m/s)	8161	8369	8532	7277
Impact sensitivity (Nm)	4.5–6.5	1.5–3.0	<1.5	7.5
Friction sensitivity (kp)	>36	16	10	>36

TNPy: 2,4,6-trinitropyridine; TNPyOx: 2,4,6-trinitropyridine-N-oxide; DazN-PyOX: 2,6-diazido-4-nitro-pyridine-N-oxide; TNB: 2,4,6-trinitrobenzene.

evaluation needs to be carried out on ANPyO to prove its usefulness in explosive applications. Hollins et al. reported [10,11] the synthesis of 2,4,6-triamino-3,5-dinitropyridine-N-oxide by the amination of 2,6-diamino-3,5-dinitropyridine-1-oxide with hydroxylamine in aqueous potassium hydroxide. Pagoria et al. [12] reported the synthesis of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) by reacting 2,6-dichloropyrazine with sodium methoxide followed by nitration and oxidation [13]. The compound LLM-105 exhibits a density of 1.918 g/ml [14] and decomposition temperature of 354 °C.

Liu et al. [15] reported the synthesis of 3,5-dinitro-2-picrylaminopyridine by condensing one mole of picryl chloride with 2,6-diaminopyridine followed by nitration using fuming nitric acid. Wang et al. [16,17] reported the studies on 2,6-bis(picrylamino)-3,5-dinitro pyridine (PYX). It is reported that PYX may be used as potential heat resistant explosive in drilling oil wells and in plastic bonded explosive formulations. Some of the energetic properties of nitropyridine derivatives (I–III) in comparison to 2,4,6-trinitrobenzene are given in Table 1.

(I)   (II)   (III)
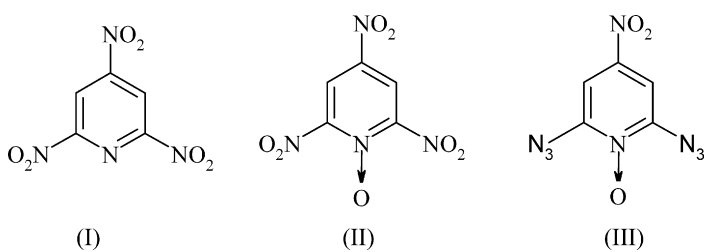
It is reported [18] that 2,4,6-trinitropyridine shows a very good thermal stability, satisfying chemical stability, favorable oxygen balance and very good density. The insertion of picryl moiety in the pyridine ring may enhance the thermal stability and performance of the parent compound and the introduction of the alternate amino and nitro group in the pyridine ring or in aromatic ring system may also increases the insensitivity of the parent molecule. It is also reported that the incorporation of nitro group/s on phenyl substituent increases density, thermal stability and the energetic performance of the parent heterocyclic moiety. Further increase in density and the thermal stability of the parent compound could be achieved by converting the tertiary amines into their corresponding N-oxide functionality. The N−O bond of a tertiary N-oxide possesses significant double bond character due to π bond formation. The formation of a heterocyclic N-oxide also changes the charge distribution of the heterocyclic ring. This may further increases in the aromaticity (over all sta-

bility) of the heterocyclic ring system [19]. The introduction of N-oxide functionality also increases the oxygen balance and allows better crystal packing.

3. Azides: potential energetic materials

The use of energetic additives in the propellant formulations in place of conventional non-energetic additives certainly enhances the performance level of solid propellant and gun propellant formulations [20]. In this aspect organic azides are attracting researcher's attention more recently. The possible use of energetic azides in propellant formulations reduces the amount of flame and smoke in the exhaust gases, thus making the propellant formulations more eco-friendly. During the past two decades a large number of organic azides have been reported in the literature. Compounds from this category include azidopolyethers, azidonitramines, azidonitro compounds, azidoalkanes and azidoesters. Most of the currently used solid-rocket fuels are still based on mixtures of ammonium perchlorate, aluminium and epoxy resins, which produces hydrochloric acid (HCl) and aluminium oxides during combustion. Therefore ammonium perchlorate based propellant formulations are not considered as green propellants.

3.1. Explosive properties of azide containing energetic materials

In the view of the explosive and toxic nature of hydrazoic acid and its derivatives it is pertinent to discuss the hazards associated in handling azides. It is well known that azides easily undergo decomposition in presence of heat, mechanical shock or exposure to certain chemical reagents. The decomposition process of azides normally accompanied by the release of large amounts of energy release with the formation nitrogen molecule. The highly sensitive azides are prepared in situ in the solvent and are utilized immediately for their use in the synthesis of high energy materials. In this context it has been suggested that a threshold value is given by the ratio of (C + O)/N and that a violent decomposition of azide may occur when this ratio is lower than 3:1. Organic azides have been extensively investigated for primary and secondary explosive applications. The extensive care must be exercised while handling the low molecular weight azide compounds. The low molecular weight azide compounds are highly treacherous and the explosions may occur for unknown reasons during handling.

The substitution of hydrogen by energetic azido (–N$_3$) group in organic molecules results in the formation of energetic azido plasticizers and polymers. Organic azides possesses high density, high positive heat of formation, good thermal and hydrolytic stability, lower impact sensitivity, high burning rate and gives reduced flash. Some of the potential azido compounds of high energy materials interest are bis(azidomethyl)oxetane, azidomethyl methyl oxetane, 1,3-diazido-2-nitrazapropane (DANP), 1,5-diazido-2,4-dinitrazapentane (DADZP), 1,7-diazido-2,4,6-trinitrazaheptane (DATH) [21–29]. Table 2 summarizes the properties of some of the potential azido compounds.

Table 2
Properties of azides compounds

Compound	Melting point ($^\circ$C)	ρ (g/cm^3)	Oxygen balance (%)	Energy (J/g)
DANP	−8	1.43	−37.2	6670
DADZP	80	1.70	−32.5	6412
DATH	136	1.71	−30.0	5873
Pr NENEA	−2	1.26	−87	3672

DANP: 1,3-diazido-2-nitrazapropane; DADZP: 1,5-diazido-2,4-dinitrazapentane; DATH: 1,7-diazido-2,4,6 trinitrazaheptane; Pr NENEA: *n*-propyl azidoethyl nitramine.

4. High nitrogen content high energy materials: potential green additives for rocket propellants

The synthesis of high nitrogen content high energetic materials has been in the focus for the last two decades [30–35]. High nitrogen content (HNC) materials form a unique class of novel energetic materials, deriving most of their energy from their very high positive heat of formation rather than from the oxidation of the carbon backbone as is the case with conventional energetic materials. Polynitrogen compounds is another upcoming area for the high performance high density green energetic materials. Recently, Talawar et al. [36] have extensively reviewed on the possibilities and opportunities exist in the area of synthesis of polynitrogen compounds for their potential high energy materials applications.

The high nitrogen content in the molecule enhances the density and leads to generation of large quantity of gas per gram. One of the unique, reported energetic materials of this series is diamino azobis tetrazine (DAAT) having highest positive heat of formation (about +800 kJ/mol) among the reported high nitrogen content energetic materials. This compound also shows remarkable insensitivity towards external stimuli with the theoretical performance level exceeding that of the currently used powerful military explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).

Sivalaban et al. [37] have reported the synthesis, characterization and thermolysis studies of a series of azotetrazolate salts, viz., ammonium/guanidinium/triaminoguanidinium [azotetrazolate]. Thermal analysis studies on these compounds indicate the highest heat release (2804 J/g) for guanidinium azotetrazolate salt during its exothermic decomposition. The sensitivity data reported by the authors suggests low vulnerability of ammonium and guanidinium salts. Triaminoguanidinium azotetrazolate (TAGAZ) was incorporated into solid propellant formulations in order to establish the compatibility of this class of compounds. The burning rate data obtained indicated that triaminoguanidinium azotetrazolate acts as an efficient energetic additive in composite modified double base (CMDB) propellant formulations in high-pressure region.

5. Imidazole based high energy materials

Imidazole derivatives with more than two nitro groups are expected to be potential energetic ingredients for insensitive explosive formulations. 2,4-Dinitroimidazole (DNI) is much less sensitive than hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and it is reported that 2,4-dinitroimidazole may be more energetic than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The cost of production of 2,4-dinitroimidazole appears to be less expensive.

Various nitroimidazole derivatives (IV–VIII) including 2,4-dinitroimidazole [38] 4,5-dinitroimidazole [39] 2,4,5-trinitroimidazole [40,41] and 4,4′,5,5′-tetranitro-2,2′-benziimidazole [42] have been investigated. One of the problems associated with these molecules is their chemical stability. The hydrogen attached to first position, of the ring is known to be quite acidic [43] and may interfere with some of the other generally used ingredients in the explosive or propellant formulations. The nitration of first position in imidazole gives 1,4-dinitroimidazole which undergoes isomerization on heating to form 2,4-dinitroimidazole [44,45].

1H-imidazole   4-Nitro-1H-imidazole   2,4-dinitro-imidazole   4,5dinitroimidazole   2,4,5-trinitroimidazole

(IV)   **(V)**   **(VI)**   **(VII)**   **(VIII)**
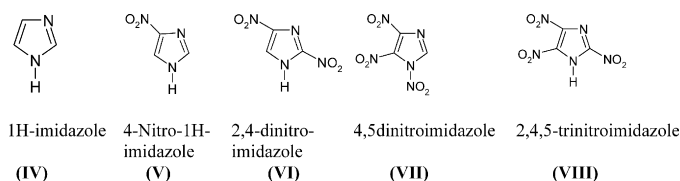
Bulusu et al. [46] reported the synthesis of 2,4-dinitroimidazole (2,4-DNI) and found it highly promising for high energy materials application. The exhaustive literature survey indicates that *N*-methyl, *N*-esters and *N*-picryl derivatives of the 2,4,5-trinitroimidazole for energetic materials application. It is well known that the insertion of picryl group in an organic compound increases the density while incorporation of hydrocarbon chain increases the thermal stability. Table 3 illustrates the properties of some potential polynitroimidazole derivatives for high energy materials applications.

6. Insensitive high explosives (IHEs)

One of the approaches used to synthesize insensitive high explosives is to basically incorporate maximum possible percentage of nitrogen into energetic materials. The insensitivity is achieved basically (i) use of nitrogen rich heterocycle/s or its *N*-oxide as key synthons for the synthesis of IHE's. (ii) Introduction of nitro and amino groups in the ring *ortho* to each other. The formation of hydrogen bond formation between two groups increases the stability of the molecule. There are also reports that insertion of picryl moiety in the ring not only increases the insensitivity as well as thermal stability of the molecule.

An ideal explosive is one, having high performance, but insensitive enough to handle during its use, storage and transport. Most common explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are used as key energetic ingredients for different weapons applications. The current and futuristic research on high energy materials focuses mainly on the development of new energetic ingredients and energetic formulations, which are better than the above mentioned conventional energetic materials [47].

Table 3
Properties of some polynitroimidazole derivatives

Compound	Molecular formula	Density (g/cm^3)	Oxygen balance (%)	Detonation velocity (km/s)	Detonation pressure (GPa)
MTNI	$C_4H_3N_5O_6$	1.78	−25.76	8.80	34.66
CTNII	$C_7H_7N_5O_8$	1.63	−58.28	7.61	23.78
PTNI	$C_9H_2N_8O_{12}$	1.91	−27.05	8.41	33.91

MTNI: 1-methyl-2,4,5-trinitroimidazole; CTNII: 1-carboxy-2,4,5-trinitroiodoimidazole; PTNI: 1-picryl-2,4,6-trinitroimidazole.

The development of these classes of explosives have led to the reduction of quantity distances between storage sites, decrease the battle field vulnerability of armoured vehicles, personnel and increased capacity to carry a large quantity of ordnance. A series of new explosives have been developed with promising blend of insensitivity and performance and thermal stability [48]. 2,4,6-Triamino-1,3,5-trinitrobenzene (TATB) is the most important insensitive high explosive of this series which may be used in modern warheads. Its attributes are greater thermal, physical and shock stability, which are greater than that of any other known material of comparable energy [49]. The development of TATB is one of the most remarkable contributions of scientist/technologists working in the field of energetic materials. The TATB based insensitive high explosive formulations significantly improve the safety and survivability of munitions, weapons, and personnel in the vicinity.

MATB (IX)   **DATB (X)**   **TATB (XI)**
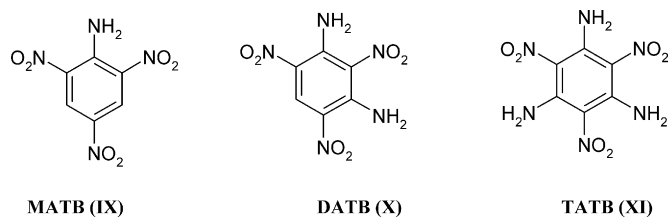
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was first reported in 1888 by Jackson and Wing [50]. TATB can be readily synthesized from aniline and has qualified as a heat resistant insensitive explosive. The unique structure of 1,3,5-triamino-2,4,6-trinitrobenzene confirms its properties, which include high density and extreme insensitiveness to impact and shock. The introduction of the amino group in these molecules adds sufficient energy to the crystal lattice and increases the melting point. The initial decomposition mechanism of 1-amino-2,4,6-trinitrobenzene (MATB) and 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) below 500 °C is more complicated, since a –NH$_2$ group *ortho* to –NO$_2$, in the ring, may undergo cyclization on heating to form furazan and furoxan derivatives.

The explosive sensitivity is found to be in the order: MATB > DATB > TATB. However, the desensitizing influence of –NH$_2$ group is due to its electron donating and/or hydrogen bonding characteristics. Recently the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene from picramide or 1,3,5-trinitrobenzene was claimed by Mitchell et al. [51–53] at Lawrence Livermore National Laboratory which may significantly reduce the further cost of 2,4,6-trinitro-1,3,5-triaminobenzene manufacturing.
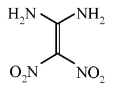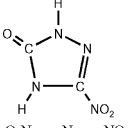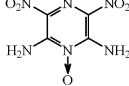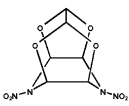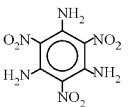
Recently, Swedish Research Laboratory has developed another potential insensitive high explosive, viz., 1,1-diamino-2,2-dinitroethylene (DADNE or FOX-7), which attracted substantial attention because of its insensitivity towards external stimuli and [54] and its performance comparable with the performance of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [55]. Politzer et al. [56] have reported that 1,1-diamino-2,2-dinitroethylene (FOX-7) has the same molecular stoichiometric as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), which are among the most powerful currently used for explosives and monopropellants applications. The complete decomposition of FOX-7 gives CO, N$_2$ and H$_2$O. The decomposition of FOX-7 also gives the same amount of gaseous product per gram of compound in comparison to RDX. It is interesting to note that the reported activation energy ($E_a = 58$ kcal/mol for temperature interval 210–250) [57] for 1,1-diamino-2,2-dinitroethylene (DADNE) is higher than that of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) ($E_a = \sim 40$ kcal/mol) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) ($E_a = \sim 35$ kcal/mol), which favors DADNE as potential insensitive explosive [58]. The reported energetic properties of FOX-7 indicate its use as energetic filler in insensitive munitions [58]. Efforts are on to produce 1,1-diamino-2,2-dinitroethylene in multigram quantity for its use in insensitive applications [59].

Pagoria et al. [60] reported the synthesis of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) from 2,6-diamino-3,5-dinitropyrazine (ANPZ). 2,6-Diamino-3,5-dinitropyrazine-1-oxide was first reported from USA [61]. LLM-105 exhibits density $\rho = 1.91$ g/cm^3, impact insensitivity $h_{50\%} = 117$ cm and also possesses excellent physical properties, good safety characteristics properties. The energetic performance is anticipated to be more than 20% of the 1,3,5-triamino-2,4,6-trinitrobenzene. The overall properties of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) makes it more attractive insensitive high explosive for futuristic applications. Physico-chemical properties of the promising energetic materials have been presented in Table 4.

7. Energetic oxidizers

An oxidizer is one having high oxidation potential and high electro negative atom or functional group. The periodic classification of the elements can be used to distinguish the oxidizer (high electro negativity) and the fuel (high electropositivity). In other words, the atoms on the right side of the periodic table are anticipated to show oxidizers

Table 4
Physico-chemical properties of potential insensitive high explosives (IHEs)

HEM	Structure	Mol. wt.	O.B. (%)	Density (g/cm^3)	ΔH_f (kcal/mol)	mp (°C)	VOD (m/s)	CJ pressure (GPa)	Impact sensitivity ($h_{50\%}$, cm)	Friction insensitivity (>kg)
FOX-7		148	−21.6	1.885	−32	254	9090	36.6	126	36
NTO		130	−24.6	1.93	−28	270	8564	31.2	93	36
LLM-105		216	−37	1.91	−3	354	8560	35.0	117	36
TEX		262	−42.7	1.99	−106	299	8560	31.4	>177	36
TATB		258	−55.7	1.94	−33	330	8108	31.1	>177	36

FOX-7: 1,1-diamino-2,2-dinitroethlyene; NTO: nitrotriazolone; LLM-105: 2,6-diamino-3,5-dinitropyrazine-1-oxide; TEX: tetraoxa-explosive; TATB: 2,4,6-trinitro-1,3,5-triaminobenzene.

properties while those on the left are expected to show fuel characteristic properties. Thus, fluorine is the best oxidizer and F$_2$/H$_2$ propellant system gives maximum specific impulse among chemical propulsion system. The oxidation potential of the oxidizing group varies in the order [62] F$^-$ > OF$^-$ > NF$_2$$^-$ > ClF$_4$$^-$ > O$^-$ > NO$_3$$^-$ > ClO$_4$$^-$ > NO$_2$$^-$ > ClO$_3$$^-$.

The first rocket (developed in 1232) propelled using black powder using (KNO$_3$) and NaNO$_3$ as oxidizers. Then the scientists started in search for high performance oxidizers. Sodium perchlorate (NaClO$_4$), potassium perchlorate (KClO$_4$), lithium perchlorate (LiClO$_4$), nitronium perchlorate, etc. are the results of the search for new high-energy oxidizers [61,63–77]. Some of the physico-chemical properties of the oxidizers is given in Table 5. Sodium perchlorate and lithium perchlorate possesses positive oxygen balance and substantially large positive heat of formation compared to ammonium perchlorate. Ammonium dinitramide (ADN) is less sensitive to impact and exhibits low melting point (90 °C), where as hydrazinium nitroformate

(HNF) shows higher melting point but less hygroscopic in comparison to ADN.

Ammonium dinitramide (ADN) is prepared from aliphatic monoisocyanate using stoichiometric quantities of nitronium tetrafluoborate and nitric acid in acetonitrile as the nitrating medium followed by ammonia treatment. The NH$_4$$^+$or K$^+$ salts of dinitramide are more stable compared to dinitramines. Ammonium dinitramide combines the low sensitivity of ammonium salts with the high burning rates of nitramines. It has low melting point and is slightly hygroscopic and hence needs special process conditions. The use of ammonium dinitramide in place of ammonium perchlorate certainly increases the energy of the propellant formulation and the burning rate of propellants. According to the literature reports, the space shuttle can lift 8% more mass into orbit by using ammonium dinitramide in comparison to ammonium perchlorate.
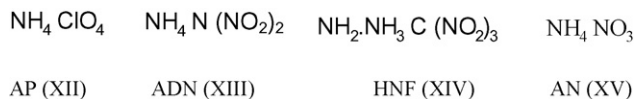
NH$_4$ ClO$_4$ NH$_4$ N (NO$_2$)$_2$ NH$_2$.NH$_3$ C (NO$_2$)$_3$ NH$_4$ NO$_3$

AP (XII)   ADN (XIII)   HNF (XIV)   AN (XV)

Another potential energetic oxidizer, hydrazinium nitroformate has been synthesized by the reaction of anhydrous hydrazine with trinitromethane in ethylene dichloride. The purity of the hydrazinium nitroformate produced plays a major role in its stability. The work on the new energetic oxidizers has opened up new avenues and challenges for the high energy materials research community. Energetic eco-friendly oxidizers-ammonium dinitramide (ADN) [78] and hydrazinium nitroformate (HNF) [79] have entered in the domain of advanced propellant systems. These materials have dual advantage over the workhorse oxidizer, viz., ammonium perchlorate (AP) in

Table 5
Physico-chemical properties of oxidizers

Oxidizer	Heat of formation (ΔH_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

AP: ammonium perchlorate; ADN: ammonium dinitramide; HNF: hydrazinium nitroformate; RDX: hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; CL-20: hexanitrohexaazaisowurtizitane.

terms of clean combustion and superior heat of formation (−71 and −151 kJ/mol). The energetic performance of the propellant formulations based on ADN and HNF exceeding 260 s. Moreover, hydrazinium nitroformate and ammonium dinitramide undergo highly exothermic combustion reactions.

Ammonium dinitramide was first synthesized in Zelinsky Institute of Russia in 1970 and subsequently ammonium dinitramide based propellants were productionized in Russia. Ammonium dinitramide based propellants may have found application in TOPOL-M intercontinental missile. However, research work carried out at Thiokol, USA suggests that smooth development of large scale propellants based on ADN is hampered due to its severe hygroscopicity as well as low melting point (∼90 °C) and decomposition temperature (123 °C). Researchers also observed degradation of ammonium dinitramide in formulations. Efforts are on to produce prilled ammonium dinitramide to realize improved stability characteristics.

Work on hydrazinium nitroformate was carried out mainly at TNO, The Netherlands and is manufactured by Aerospace Propulsion Products (APP), The Netherlands at the scale of 300 kg/annum. Hydrazinium nitroformate has advantage over ammonium dinitramide in terms of its higher melting point and higher decomposition temperature, which are relevant from the application point of view. Moreover, hydrazinium nitroformate is non-hygroscopic. However, major concern is its high friction sensitivity. Phlegmatization of hydrazinium nitroformate by special gels is being attempted to tackle sensitivity problems. The preparation methods of hydrazinium nitroformate have bearing on its stability and sensitivity, while the recrystallization process decides the size and length/diameter ratio of the crystals, which in turn influence the processibility of the propellant formulations. In addition to the problems associated with purity and crystal structure, utilization of hydrazinium nitroformate in practical formulations suffers from the drawback of its incompatibility with the workhorse binder (Hydroxy terminated polybutadiene). Glycidyl azide polymer (GAP) [80] and poly-3-nitratomethyl-3-methyl oxetene (PNIMMO) [81] have emerged as possible energetic binders suitable for hydrazinium nitroformate based propellants.

8. Nitramines: potential energetic materials

Nitramines are potentially high energy density materials (HEDMs) and are among the types of substances that have been targeted for synthesis. It has been found from the database that amino groups in nitramines are rather flexible. The nitramines are the most recently introduced class of organic nitrate explosives. The most prominent member of this class is RDX (research department explosive; hexahydro-1,3,5-trinitro-1,3,5-triazine, which is also known as cyclonite, XVI), HMX (high melting explosive; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, XVII), nitroguanidine and tetryl. Hexahydro-1,3,5-trinitro-1,3,5-triazine received great importance during World War II; it is used in combination with 2,4,6-trinitrotoluene, wax, etc. to facilitate ease of handling and to reduce sensitivity.

(XVI) RDX   (XVII) HMX
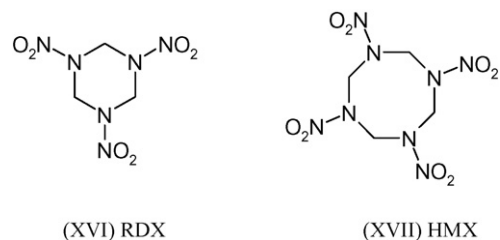
8.1. HMX [octogen; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine]

Molecular structure of HMX (XVII) is similar to RDX (XVI), with advantages of higher melting point, density and velocity of detonation. However, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine is relatively costly and sensitive in comparison to hexahydro-1,3,5-trinitro-1,3,5-triazine. Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine exists in four polymorphic forms, the β form being the most stable and the least sensitive. The α and γ forms exist at room temperature but above 160 °C all forms transform to the δ polymorph.

Henning first prepared hexahydro-1,3,5-trinitro-1,3,5-triazine in 1898, followed by Herz (2) in 1921, who patented its use as an explosive and by Hale in 1925. Two main processes of manufacture of hexahydro-1,3,5-trinitro-1,3,5-triazine are known. The Woolwich, or direct nitrolysis process, is based on reaction of hexamethylene-tetramine (hexamine) with a large excess (11 parts by weight) of 99% nitric acid (below 25 °C). In the Bachmann or combination process, the reaction mixture contains nitric acid, ammonium nitrate, acetic anhydride and acetic acid. The product obtained by Bachmann process also contains 10% HMX and therefore the process requires additional purification procedures.

8.2. 1,3,3-Trinitroazetidine (TNAZ)

TNAZ (XVIII) is a highly nitrated four member nitrogen heterocyclic ring with increased performance in comparison to conventional melt castable explosive trinitrotoluene. The additional contribution of energy is expected from the strained ring system [82–86]. There are more than 16 methods reported for the synthesis of 1,3,3-trinitroazetidine [87]. Most of the reported methods of synthesis of 1,3,3-trinitroazetidine offer low yields. Therefore efforts are on to improve upon the yields of final product (TNAZ) by reducing the number of steps in the synthesis. 1,3,3-Trinitroazetidine is more powerful than the widely used conventional melt castable explosive (2,4,6-trinitrotoluene) (Table 6). The low melting point of 1,3,3-trinitroazetidine (101 °C) compared to the melting point of 205 °C for hexahydro-1,3,5-trinitro-1,3,5-triazine, would enable processing of formulations on modified production lines. 1,3,3-Trinitroazetidine can safely sustain twice the energy of impact compared to octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine without detonation. Successful formulations development would enable a more powerful general purpose explosive. Efforts are also on to reduce the volatility of 1,3,3-trinitroazetidine by adding certain other ingredients to the 1,3,3-trinitroazetidine energetic formulations.

Table 6
Physico-chemical properties of nitramines

| Properties	TNAZ	RDX	HMX	CL-20
Molecular formula	$C_3H_4N_4O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$
mp (°C)	101	205	276–286	228
Density (g/cm^3)	1.84	1.806	1.95	α (1.97), β (1.99), γ (1.92), ε (2.04)
ΔH_f (kJ/mol)	+2	+63	+76	+454
Oxygen balance (%)	−17	−21.61	−21.61	−11
Detonation pressure (GPa)	35.68	33.92	38.39	46.65
DTA [Exo] (°C)	233	215	278	228
VOD (m/s)	8600	8600	8900	9580
Impact sensitivity, $h_{50\%}$ (cm)	22	71	65	16–20

TNAZ: trinitroazetidine; RDX: hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; CL-20: hexanitrohexaazaisowurtzitane.

Baum and coworkers [88] reported the synthesis of 1,1,3,3-tetranitro cyclobutane (TNCB) (XX), by the nitration of 1,3-dinitrocyclobutane with AgNO$_3$ and NaNO$_2$. Recently, Tartakovskii and coworkers [89] reported the synthesis of *trans*-1,2,3-tris(nitramino)cyclopropane (NACP) (XXI) using cyclopropyl triamine and Ac$_2$O/HNO$_3$ or trifluoroacetic acid/HNO$_3$.

Efforts are also on to form binary eutectic compositions with a variety of structurally similar energetic molecules like 1,3-dinitro-1′,3′-dinitroazetidine-3′-yl azetidine (TNDAZ, XIX).

TNAZ (XVIII)   TNDAZ (XIX)   TNCB (XX)   NACP (XXI)
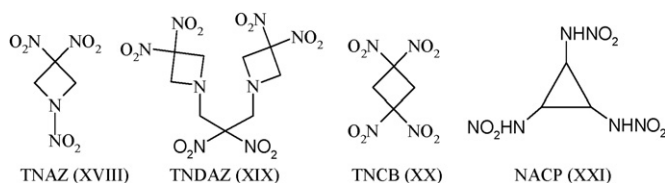
A series of new nitramines arranged in cyclobutane ring system with different confirmers have been reported. The strain energy of cyclobutane ring is 26 kcal/mol. The strain energy of the cyclobutane ring also contributes to the energetics of the system.

(XXII)   (XXIII)   (XXIV)
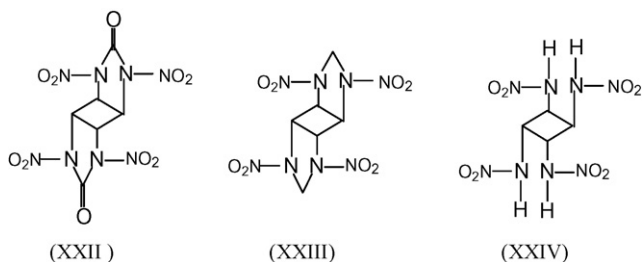
Dimidazole derivative of (compound-XXII) is soluble in polar organic solvents such as dimethyl formamide and dimethyl sulfoxide. Compound (XXII) may be possible replacement for pentaerythritol tetranitrate (PETN) for applications such as exploding bridge wire detonators.

8.3. CL-20/HNIW

CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HN-IW)] is another new nitramine explosive with 20% more energy than octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine. The dis-

covery of hexanitrohexaazaisowurtzitane was a breakthrough in energetic materials with higher performance, minimum signature, and reduced hazard characteristics. The studies carried out on CL-20 (hexanitrohexaazaisowurtzitane) indicated that it has numerous military and commercial applications. The method of synthesis of CL-20 involves the preparation of hexabenzyl isowurtizitane followed by debenzylation, acetylation and nitration. The one of the steps involved in the CL-20 synthesis requires the use of expensive palladium catalyst. Efforts are on all over the world to reduce the cost of CL-20 using less expensive catalytic materials. Hexanitrohexaazaisowurtzitane reported to exists in four crystalline forms. HNIW exhibits density (>2 g/cm^3) and velocity of detonation (9400 m/s). The studies on hexanitrohexaazaisowurtzitane has also been reported by Geetha et al. [90]

9. Octanitrocubane

Octanitrocubane is another emerging high explosive of interest to HEMs community. Recently, the synthesis of octanitrocubane is reported by Philip Eaton's group of United States of America. Octanitrocubane (ONC) [91] can outstrip the performance level of even today's most powerful molecule hexanitrohexaazaisowurtzitane. It has density more than 2 g/cm^3 and heat of formation exceeding +400 kJ/mol, velocity of detonation of the order 10,450–11,800 m/s. The material is likely to revolutionize the high energy materials research in the future. The cost involved in the synthesis of octanitrocubane appears to be the constraint for the energetic materials community for its actual application in the high energy materials formulations.

10. Nitrate esters

Organic nitrate esters such as nitrocellulose (NC, XXV), nitroglycerine (NG, XXVI), penerythritol tetranitrate (PETN, XXVII) and isosorbide dinitrate (IDN, XXVIII) possess explosive properties and as such have been widely used by the military for many years in shell and demolition charges. These organic nitrate esters have been also used in the treatment of angina for a hundred years [92]. Nitrocellulose is formed by the esterification/*O*-nitration of cellulose using mixture of HNO$_3$ and H$_2$SO$_4$. In propellant grade nitrocellulose, the

nitrogen content lies between 12.2 and 13.4%. Nitrocellulose is pulped, washed thoroughly and stabilized by the addition of a suitable stabilizer before use. It is a white amorphous, fibrous/powdery solid with a density of $1.66 \, g/cm^3$. The heat of explosion, volume of gases evolved and the temperature of explosion vary depending upon the nitrogen content of the nitrocellulose. Nitroglycerine (glycerol) is the nitrate ester of glycerol. Nitroglycerine is highly sensitive and is a powerful energetic material. It is an oily colorless and transparent liquid with a specific gravity of 1.6 at $15\,°C$. NG starts boiling at $180\,°C$, with exothermic decomposition and explodes at $215–218\,°C$.

NC (XXV)　　　NG (XXVI)　　　PETN (XXVII)　　　IDN (XXVIII)
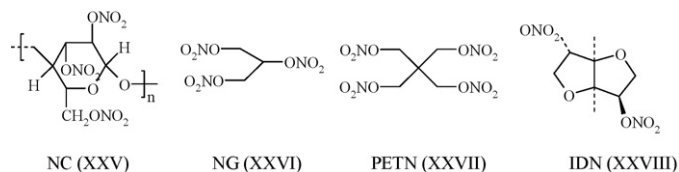
11. Thermally stable explosives

Researchers from United States of America have reported several thermally stable energetic materials. The first compound prepared under this program was 2,4,6-tris(picrylamino)-s-triazine or N,N-nitropicrylmelamine (TPM, XXIX). The compound 2,4,6-tris(picrylamino)-s-triazine is reported to exhibit moderate thermal stability, with a performance slightly better than that of trinitrotoluene. Subsequently, the heterocyclic nitrogen atoms of N,N-nitropicrylmelamine were systematically replaced with the C-nitro function to give nitro substituted tris(picrylamino)pyrimidine (XXX), pyridine (XXXI), and benzene (XXXII). XXX is more thermally stable than TPM (XXIX). However, the thermal stability decreased with further substitution of C-nitro for heterocyclic nitrogen to give XXXI and XXXII in spite of the increased resonance stabilization of the parent ring systems.

Thermal stability is an important characteristic of the energetic materials. Improved thermal stability ensures safer production, increased shelf life of munitions and low vulnerability to accidental initiations. Moreover, specific missions demand special class of high energy materials having decomposition temperatures superior to that of high performance explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and cyclotetramethylene tetranitramine (HMX) ($>220\,°C$). Nitro compounds namely 2,4,6-tripicryl-s-triazine (TPT), 2,2′,4,4′,6,6′-hexanitrostilbene (HNS), 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl (DIPAM) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) having decomposition temperatures in the range of 290–350 °C have received attention for applications in supersonic missiles encountering high temperatures [93–95]. Tetranitrodibenzotetraazapentalene (TACOT) [96,97] having decomposition temperature of 400 °C also belongs to this class.

Owing to more favorable elemental composition, heteroaromatic nitro compounds represent class of explosives capable of delivering higher performance compared to analogous aromatic

system [98,99]. The preparation of the energetic pyridines with higher energy potential implies the introduction of more than three nitro groups into the rings. However, it may lead to unstable vicinal dinitro groups. Another approach may be nitration of amino groups of aminopyridines resulting in primary and secondary nitraminopyridines.

Coburn and Singleton [100] have described the explosive properties of the nitropyridine derivatives namely, 2,4,6-trinitropyridine (TNPy), 2,4,6-trinitropyridine-1-oxide (TNPyOx), and 2,6-diazido-4-nitropyridine-1-oxide (DazN-PyOx). However, analogous nitro compounds of the series of N-heterocyclic aromatics (pyridine, diazine, triazine) have not become popular. 3,5-Dinitro-2,6-bispicrylamino pyridine (PYX) [101] is also reported as an attractive thermally stable high explosive with decomposition temperature 460 °C. It can offer higher velocity of detonation (7497 m/s) and detonation pressure (308 kbar) compared to tetranitrodibenzotetraazapentalene. Extraordinary thermal stability and insensitivity to mechanical stimuli has paved way for applications of 3,5-dinitro-2,6-bispicrylamino pyridine in the area of sheet explosives as well as civil applications such as oil-well perforation [102,103].

Trudell et al. [104] reported the synthesis of pyridine based tetranitrodibenzotetraazapentalene analogues namely, 2,4,8,10-tetranitro-5H-pyrido[3″,4″:4′,5′][1,2,3]-triazolo [5,4-b]-pyridin-6-ium inner salt and 2,4,8,10-tetranitro-5H-pyrido[3″,2″:4′5′][1,2,3]-triazolo [1′,2′:1,2][1,2,3]-triazolo [5,4-b]-pyridine-6-ium inner salt, having decomposition temperatures of 340 and 396 °C. The compounds having crystal density of $1.88 \, g/cm^3$ are significantly more energetic than tetranitrodibenzotetraazapentalene. Recently, Badgujar et al. [105] reported synthesis, characterization, thermal stability and explosive behavior some new explosives based on 1,2-[bis-(2,4,6-trinitro) phenyl hydrazine]. The further work on these materials is underway in the author's laboratory for their applications in explosive formulations. Tables 7 and 8 describe the physico-chemical properties and explosive properties of some of the thermally stable explosives.
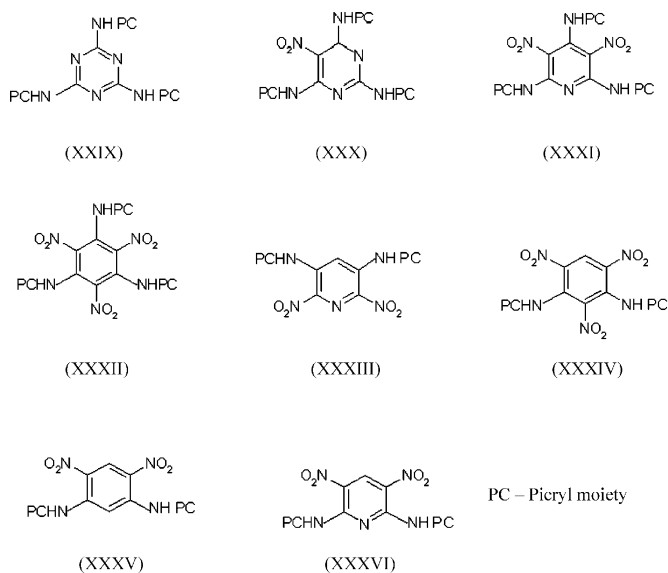

(XXIX)　　　(XXX)　　　(XXXI)

(XXXII)　　　(XXXIII)　　　(XXXIV)

(XXXV)　　　(XXXVI)　　　PC – Picryl moiety

Table 7
Physico-chemical properties of TPM, AFX-511 and AFX-521

Properties	TPM	AFX-511	AFX-521
Molecular formula	$C_{21}H_9N_{15}O_{18}$	$C_{17}H_7N_{11}O_{16}$	$C_{17}H_7N_{11}O_{16}$
Crystal density (g/cm^3)	1.74	1.75	1.75
Melting points (°C)	316	460	460
Differential thermal analysis (°C)	Stable up to 290	Stable up to 350	Stable up to 350

TPM: *N,N*-nitropicrylmelamine; AFX-511: 2,4,6-tris(picrylamino)-*s*-triazine (95%) + 5% Kel-F 800; AFX-521: PYX (95%) + Kel-F 800 (5%).

12. Emerging nitration concepts

Nitration reactions and synthesis of nitro compounds have an immense importance in the synthetic organic chemistry [106]. Nitro compounds are widely used as chemical feedstock and also for synthesis of medicines, dyes, perfumes, anti-cancerous drugs, fertilizers, plastics and explosives [107,108]. Therefore, nitration of aromatic compounds has received great attention more recently, due to unsolved problems such as regioselectivity, over nitration and competitive oxidation of substrates. Explosions may occur in many of the procedures in the preparation of aromatic nitro compounds, and it is therefore necessary to adopt safer methodologies, which involve low cost, eco-friendly [109] and easily available reagents while preparing nitro compounds. Traditional nitration with a mixture of nitric acid and sulfuric acid is notoriously unselective for nitration of substituted compounds and disposal of spent liquors presents a serious environmental concern. Although this process is still in use in industries, nitrations are generally hazardous processes, generating nitrogen oxide (NOx) fumes and large quantities of waste acids. Nitration of aromatic compounds using solid supported reagents [110,111] has also received attention more recently. The use of solid acid catalyst is potentially attractive because of the ease of removal and recycling of the catalyst and the possibility that solid support might influence the selectivity. An inorganic solid offer significant benefits by providing effective catalysis and enhances the selectivity of the reaction. Application of inorganic nitrates such as bismuth nitrate [112,113] [Bi(NiO$_3$)$_3$], cerium ammonium nitrate [114] (CAN), sodium nitrite [115] (NaNO$_2$) and potassium nitrate (KNO$_3$) as nitrating agent were found to be more useful for nitration of aromatic compounds using silica gel as a solid support. Badgujar et al. [116] recently reported the environmentally benign synthesis of aromatic nitro compounds using silica supported inorganic nitrates. This is an important step towards eco-friendly nitration process. Dinitrogen pentoxide is another emerging versatile green nitrating agent for the synthesis of high energy materials. Recently, Talwar et al. [117] have reported synthesis of world's most powerful non-nuclear explosive, viz., hexanitrohexaaza-isowurtzitane using dinitrogen pentoxide as nitrating agent. Research group from High Energy Materials Research laboratory also have also reported [117] the brief review on dinitrogen pentoxide.

13. Primary explosives

During the past eight decades the most prominent primary explosives which found entry into military applications are mercury fulminate, lead azide, lead styphnate and tetracene. Now with the exception of mercury fulminate, all the detonator chemistry revolves around the rest of the three in spite of their limitations. The poor thermal stability of mercury fulminate leads to its replacement by lead styphnate in percussion primers and lead azide in detonators. Many efforts had to be devoted with the electrostatic hazards of lead styphnate and it was necessary to supplement its use by a sensitizer (tetracene) which introduced a substance of poor thermal stability. Lead azide has considerable advantage in detonative efficiency, but brought in the safety problems associated with sensitive metal azides and its hydrolysis adjacent to copper components could and did give rise to serious accidents.

There have been continuing efforts throughout the ordnance community to improve on detonator technology, particularly safety aspects. There are a large number of high energy materials which could be prepared from nitro phenols, tetrazoles, triazoles, diazo, nitrobenzofuraxons, co-ordination compounds, etc., and represented by a varieties of metals as single or double salts which has been reported as potential initiatories. Sandia National Laboratories (NSL) and Pacific Scientific Energy Dynamics Division have been investigating a series of cobalt based energetic co-ordination compounds as deflagration to detonation transition (DDT) explosives for use in detonator applications. In addition to exhibiting acceptable performance characteristic for detonator use, these are superior with regard to safety/handling in comparison to detonants such as lead azide. Also cobalt is considered less objectionable than lead regarding toxicity and contamination concerns. Recently High Energy Materials Research Laboratory, India, reported the investigations in this direction with a possible use of such complex compounds in detonators or in pyrotechnic compositions. In this part of the review an attempt is made to present some important selected works in this relatively new emerged field of co-ordination compounds with its prospects as safe primary explosives.

Chemical structure of co-ordination compounds (CC) of the common formula of [MLn](OX)m, where M is the central ion, L is ammonia or organic base (ligand) and OX is an anion, makes it possible to create substances capable of explosion.

Table 8
Explosive properties of thermally stable explosives

Explosive properties	XXIX	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI
mp (°C)	316	334	276	234	460	250	245	311
Thermal stability (DTA)	300	330	260	185	350	235	245	300
Impact sensitivity (cm)	200	201	–	60	63	66	68	92
Crystal density (g/cm^3)	1.74	1.88	1.80	1.82	1.75	1.79	1.78	1.77
CJ pressure (kbar)	238	286	263	272	242	262	254	242
Detonation velocity (mm/μs)	7.42	7.88	78.65	7.73	7.45	7.63	7.56	7.45

(XXIX): *N,N′,N″*-tris picryl melamine; (XXX): 5-nitro-2,4,6-tris(picryl amino) pyrimidine; (XXXI): 2,4,6-tris(picryl amino)-3,5-dinitro pyridine; (XXXII): 1,3,5-tris(picryl amino)-2,4,6-trinitrobenzene; (XXXIII): 3,5-dinitro-2,6-bis(picryl amino) pyridine; (XXXIV): 2,6-bis(picryl amino)-2,4,6-trinitrobenzene; (XXXV): 1,3-dinitro-4,6-bis(picryl amino) benzene; (XXXVI): 3,5-dinitro-2,6-bis(picryl amino) pyridine.

Co-ordination compounds of this sort may be considered as energetic compositions, in which metal atom, fuel and oxidizer are mixed at a molecular level. Some of the metals, particularly transition metals are the "working horses" of co-ordination chemistry. Salts of the bivalent metals form stable complexes with various organic compounds. The valence of central metal atom define a sum of oxidizing group, whereas the co-ordination number of metal controls the fuel content in the molecule. These co-ordination compounds are known for more than 70 years and also some of them have found specific applications as primary explosives or igniters. The possibility of significant variations in nature of co-ordination compounds along with the presence of metal atom, which acts as a burning catalyst suggests a wide range of conceivable burning rates of co-ordination compounds. The combustion parameters, in turn, have been shown for high and primary explosives to be responsible for such explosive property as deflagration to detonation transition (DDT) length [118,119]. A lucid presentation has been given by Sinditskii et al. [120] for design and combustion behavior of explosive co-ordination compounds. Since the burning rate of an explosive compound is thought to be an important characteristic determining deflagration to detonation transition and initiating efficiency which depends upon the nature of oxidizers and nature of control atoms, change of nitrate ion to perchlorate one usually raises burning rates. Metal atom included in complexes can serve not only as a matrix, which ties up ligand fuel and anion oxidizer, also as a catalyst of redox reactions occurring during combustion and each anion has its own set of metals that possess a catalytic activity. Such complexes enable to carry out a chemical tailoring of the molecule such that various chemical groups which for complexation to occur and result in optimum explosive sensitivity and which can be introduced into the molecule by a proper choice of the ligand. Tetrazoles offer interesting possibilities as ligands since various energetic derivatives can be synthesized.

In the following pages we have discussed some of the reported important co-ordination compounds, viz., 2-(5-cyanotetrazolato) pentaamminecobalt(III) perchlorate (CP) [121,122] and its analogs, tetraamine *cis*-bis(5-nitro-2*H*-tetrazolato-N2)cobalt(III) perchlorate (BNCP), and some similar high energy co-ordination compounds. Several researchers extensively studied the detonation behavior of 2-(5-cyanotetrazolato) pentaamminecobalt(III) perchlorate for different applications [123–125]. The compound 2-(5-cyanotetrazolato) pentaamminecobalt(III) perchlorate was developed to provide a relatively safe explosive material for low voltage, hot wire detonators. Researchers have reported the use of CP for different applications in the area of energetic materials.

Another notable in the series is BNCP [126–130] other than CP. In addition to exhibiting acceptable performance characteristics for its use in detonators, BNCP is superior with to safety/handling in comparison to detonant lead azide. CP based detonators have been in production since 1979, it has been demonstrated that BNCP possess superior performance properties. In 1986 Bates of Royal Armament Research and Development Establishment (RARDE), reported a 2-(5-cyanotetrazolato) pentaamminecobalt(III) perchlorate related compound, as a possible replacement for lead azide and for other priming materials. It was found to undergo deflagration to detonation transition in smaller and less confining configurations than required for CP and exhibited a higher explosive yield than CP as indicated by witness block testing. The applications of BNCP in detonators have been discussed by several researchers [131,132].

Patil and co-workers [133] reported transition metal complexes of nitrate/azide/perchlorate and proposed their application as initiators. The preparation of nickel hydrazinium nitrate (NHN) as initiatory compound has been recently reported by Shunguan et al. [134]. Hariharnath et al. [135] evaluated potential use of NHN as component of squib composition. High Energy Materials Research laboratory (HEMRL) also embarked on the development of energetic co-ordination compounds for initiator applications [136].

Zang et al. studied the molecular structure, physico-chemical properties and characteristics of cadmium carbohydrazide perchlorate (GTG) [137]. The primary explosive was low sensitive to mechanical action and insensitive to heat and static electricity and suggested for its possibility for its use in various detonators. Similarly Lu synthesized a novel initiatory compound for explosives with cobalt as central atom and carbohydrazide [138] as ligand. The co-ordination number of the central atom cobalt was six and the coordinate polyhedron was a distorted octahedron. The compound was found to have excellent initiating ability which can be used as primary explosive in various detonators. Talawar et al. [139] have reported the carbohydrazide complexes of cobalt and nickel perchlorates for initiator applications. Some of the important properties of initiator compounds are listed in Tables 9 and 10.

Table 9
Comparative properties of important initiatory compounds

S. no.	Property	Service lead azide (SLA)	Lead styphnate (LS)	Tetracene	Mercury fulminate (MF)
1.	Bulk density (g/cm^3)	1.75	1.5–1.6	0.6	1.35–1.75
2.	Explosion temperature (0 °C)	325	250	154	210
3.	Impact sensitivity (F of I)	20	18	10	10
4.	Friction sensitivity, $E_{50\%}$ (g)	50	300	650	150
5.	Flame sensitivity	Less	Sensitive	Sensitive	Sensitive
6.	Compatibility with copper and brass	Not compatible	Compatible	–	Not compatible
7.	Thermal stability	Stable	Stable	Less stable	Less stable
8.	Volatile matter (%)	0.1	–	0.15	–
9.	Stability in presence of moisture	Less stable	Stable	Less stable	Less stable

Table 10
Comparative properties of co-ordination initiatory compounds

Initiator	NCP	CCP	BNCP	NiHN
Nature	Free flowing	Free flowing	Acicular	Free flowing
Bulk density (g/cm^3)	0.85–0.90	0.85–0.90	0.3	0.8–0.9
Thermal stability (°C)	290	300	250	180
Ignition temperature (°C)	332	322	260	210
Impact sensitivity, $h_{50\%}E$ (cm)	55–60	55–60	30	85
Friction sensitivity (kg)	1.0	1.0	3.0	1.0
Spark sensitivity (J)	–	–	5	5
VOD (m/s)	–	–	5700	3750

NCP: nickelcarbohydrazide perchlorate; CCP: cobaltcarbohydrazide perchlorate; BNCP: tetraamine *cis*-bis(5-nitro-2*H*-tetrazolato-N2)cobalt(III) perchlorate; NiHN: nickel hydrazinium nitrate.

14. Energetic ballistics modifiers

A solid rocket propellant is a heterogeneous mixture of metallic fuel, oxidizer, binder cum fuel, ballistic modifier and other additives. Oxidizer and fuel interaction produces the energy while ballistic modifiers alter the combustion behavior to obtain desired burning rate characteristics. Generally, composite propellants comprise of ammonium perchlorate (AP)—an oxidizer, aluminium (Al)—a metal fuel and hydroxy terminated polybutadiene (HTPB)—binder cum fuel. The burning rate of AP-composite propellants is routinely adjusted by the addition of small amounts of combustion catalysts to the propellant formulation. Kishore and Sunitha [140] carried out comprehensive literature survey on the combustion catalysts spanning roughly two decades up to late 1970.

A large number of publications have appeared since then on the role and site of action of catalysts. Inorganic transition metal oxides (TMOs) are generally used as ballistic modifiers in composite solid rocket propellants. Fe_2O_3 is widely used as a ballistic modifier in composite propellants due to its reactive centers in the flame [141]. Copper chromite (CC) is another conventional ballistic modifier used in composite propellants and is reported to catalyze both condensed and gas phase combustion reactions [142]. However, incorporation of Fe_2O_3 and copper chromite as ballistic modifier beyond 2–3% level causes undesirable penalty on the energetics of the propellant system due to their inert nature as because of being solid, their incorporation is at the cost of AP/Al. Ferrocene based compounds are relatively new to join the class of ballistic modifiers for composite propellants and are claimed to be more effective [143]. Due to their liquid nature, they have processing advantage and enable higher solid loading of AP and Al. However, commonly used non-bonded ferrocene derivative—*n*-butyl ferrocene tends to migrate to surface, if used in quantity more than 2–3% and undergoes oxidation during storage yielding sensitive products [144]. Moreover, even if such drawbacks are mitigated by various approaches (grafting/bonding on polymer), they also impair energetics like Fe_2O_3 and CC. Russian researchers also reported the potential of energetic co-ordination compounds for ballistic modifiers application [145,146].

15. Energetic binders

Emergence of novel propellants having unique combination of high energy and low vulnerability has led to development of energetic polymers [147–151]. Prepolymers having exothermically decomposing azido groups or oxygen-rich facile nitro/nitrato groups offer formulations with superior performance potential at relatively lower solid loading. Synthesis routes and the properties of potential azido polymers namely, glycidyl azide polymer (GAP) and poly bis azidomethyl oxetane (P-BAMO), poly azidomethyl methyl oxetane (PAMMO) as well as nitrato polymers namely, polyglycidyl nitrate (PGN) and nitratomethyl methyl oxetane (NIMMO) are widely reported. Energetic copolymers have also evinced considerable interest. Some of the interesting physico-chemical properties of energetic binders are given in Table 11.

Table 11
Physico-chemical properties of binders

Energetic binder	Heat of formation (kJ/mol)	Density (g/cm^3)	Oxygen balance (%)	Glass transition temperature (°C)
GAP	+117	1.30	−121	−45
Poly-BAMO	+413	1.30	−124	−45
Poly-AMMO	+179	1.06	−170	−35
Poly-NIMMO	−335	1.26	−114	−25
PGN	−285	1.39	−61	−35
HTPB	−52	0.92	−324	−65
BAMO-THF copolymer	+189	1.18	−125	−56

GAP: glycidyl azide polymer; HTPB: hydroxy terminated polybutadiene; PGN: polyglycidyl nitrate; NIMMO: nitratomethyl methyl oxetane; BAMO: bis azidomethyl oxetane; AMMO: azidomethyl methyl oxetane; THF: tetrahydrofuran.

16. Plasticizers

The plasticizers need to be added to the binder to realize the desired possibility. Conventional plasticizers used with hydroxy terminated polybutadiene (HTPB) namely, phthalates like dioctyl adipate (DOA), and isodecyl pelargonate (IDP) find applications with energetic binders also. From the point of view of augmenting the energetics, a large number of compounds containing nitro, azido, nitrato group are emerging as potential plasticizer candidates [152,153] (Table 12).

Table 12
Selected energetic plasticizers and their properties

Name	Structure	mp/bp (°C)	ρ (g/cm^3)	ΔH_f (kcal/mol)	Energy of comb. (cal/mol)	O.B. (%)
TEGDN		−23	1.3	−149	823	−67
BTTN		−6	1.5	−99	523	−17
TMETN		15.7/182	1.49	−99.6	674	−34.5
Ethyl NENA	Et—N(NO$_2$)—CH$_2$—CH$_2$—ONO$_2$	5	1.3	−34	3549	−67
Propyl NENA	Pr—N(NO$_2$)—CH$_2$—CH$_2$—ONO$_2$	–	–	−37	4132	−87
Bu NENA	Bu—N(NO$_2$)—CH$_2$—CH$_2$—ONO$_2$	−9	1.2	−40	4630	–
Mixture of BDPF and BDPA	CH$_3$CH [OCH$_2$C(NO$_2$)$_2$CH$_3$]$_2$ CH$_2$ [OCH$_2$C(NO$_2$)$_2$CH$_3$]$_2$	−18	1.39	484	–	−51
DEGBAA		–	1	−329	–	−100
TMNMTAA		–	1.4	−230	–	−72
PETAA	C—(CH$_2$OCOCH$_2$N$_3$)$_4$	–	1.4	−215	–	−89
DAFP	FC (NO$_2$)$_2$ CH$_2$ O CH$_2$ CH (N$_3$) CH	–	1.4	57	–	–
AFFO	FC (NO$_2$)$_2$ CH$_2$ O CH$_2$ O CH (CH$_2$	–	–	23	–	–

TEGDN: triethylene glycol dinitrate; BTTN: 1,2,4 butane triol trinitrate; TMETN: metriol trinitrate; NENA: nitroethyl nitramine; BDPF and BDPA: bis 2,2 dinitro propyl formal and bis 2,2 dinitro propyl acetal; DEGBAA: diethylene glychol bis (azido acetate); TMNMTAA: trimethylol nitromethane triazido acetate; PETAA: pentaerythritol tetrakis azido acetate; DAFP: 1,2 diazido 3 fluro dinitro ethoxy propane; AFFO: 1,3 diazido isopropyl fluro dinitroethyl formal.

17. Conclusions

This review describes in brief about the synthesis and the performance characteristic properties of some of the energetic materials of current and futuristic interest. Authors strongly feel that, the review will be of great help to high energy materials researchers/scientists/technologist/engineers for their futuristic research and development work. Authors also have covered some of the interesting and recently published frontline research papers in the field of high energy materials from openly available literature. Over all the review has focused on oxidizers, powerful explosives, energetic ballistic modifiers, energetic co-ordination compounds, energetic polymers and energetic plasticizers. The research and development activities have taken momentum in many high energy materials schools to produce more powerful high energetic materials using eco-friendly synthesis route/s. High energy materials technologists and engineers are also focusing more on producing the safe (insensitive) and powerful energetic materials in comparison to conventional energetic materials. The future in the energetic materials research area appears to be bright and authors hope that, more and more new powerful and strategic energetic materials may appear in literature in the future.

Acknowledgement

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