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REVIEW PAPER

Advances in High Energy Materials

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ABSTRACT

Research and development efforts for realizing higher performance levels of high energy materials (HEMs) are continued unabated all over the globe. Of late, it is becoming increasingly necessary to ensure that such materials are also eco-friendly. This has provided thrust to research in the area of force multiplying HEMs and compounds free from pollution causing components. Enhancement of the performance necessitates introduction of strained structure or increase in oxygen balance to achieve near stoichiometry. The search for environment friendly molecules is focused on chlorine free propellant compositions and lead free primary explosives. Energetic polymers offer added advantage of partitioning of energy and thus not necessitating the concentration of only solid components (HEMs and metal fuels) in the formulations, to achieve higher performance, thereby leading to improvement in energetics without adversely affecting the processability and mechanical properties. During recent times, research in the area of insensitive explosives has received impetus particularly with the signature of STANAG. This paper gives a review of the all-round advances in the areas of HEMs encompassing oxidizers, high-energy dense materials, insensitive high-energy materials, polymers and plasticizers. Selected formulations based on these materials are also included.

Key words: HEMs, performance, insensitive, explosives, propellants, high energy materials, green energetic materials, trinitrotoluene, cyclotrimethylenetrinitramine

1. INTRODUCTION

In the area of rocket propellants, composite propellants comprising ammonium perchlorate - AP (oxidiser) and aluminium–*Al* (metal fuel) dispersed in hydroxyl terminated polybutadiene (HTPB) binder are widely used to propel missiles and space vehicles. They offer much superior performance level (I_{sp} 250-260 s) compared to conventional nitrocellulose (NC) and nitroglycerine (NG) containing double-base propellants (I_{sp} 220-230 s). Superior strain capability of composite propellants due to lower glass transition temperature of HTPB is another major advantage, particularly with respect to applications at subzero temperatures. Today, there is a wide production base of this class of propellants all over the globe. SNPE, Thiokol and Royal Ordnance are the major manufacturers of this class of propellants[1-5].

The resurgence of Ramjet and Scramjets has led to increase in importance of fuel rich propellants. Although, *Mg* based fuel-rich propellants are in vogue, boron-based solid propellants are the preferred choice among metallised fuel-rich systems due to their high energy potential. However, the problem associated with lack of efficient pyrolyzability of boron needs to be addressed. To improve the pyrolizability, inclusion of additives and energetic binders is being attempted. Liquid fuels are emerging as superior alternatives to metal fuels.

In the area of gun propellants, conventional triple-base propellants containing nitrocellulose (NC), nitroglycerine (NG), and picrite, i.e., nitrguanidine (NQ) as major ingredients, hold sway. They find wide applications in tank and field gun ammunition due to advantages of low flame temperature, flash less combustion, low barrel erosion, long shelf life, etc. However, demand for superior energy in terms of force constant *F* has led to attempts of replacement of NQ by energetic oxidisers and introducing energetic plasticizers to achieve $F > 1060$ J/g.

In the field of high explosives, weapon designers are facing the challenging task of realising shaped-charges with high jet velocity, fragment generating devices having high lethality and area destruction systems with high blast effect. To enhance the lethality of warheads/missiles, detonation pressure and velocity of detonation are the major criteria for selection of an explosive for application in projectiles/warheads[6]. Cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX) are the benchmark explosives used in conventional explosive compositions with melt castable trinitrotoluene (TNT) having VOD upto 8600 m/s.

2. GLOBAL SCENERIO

2.1 Green Energetic Materials (GEMs)

The concept of green energetic materials (GEMs)[7] for defence and space applications is acquiring importance. It may become mandatory requirement in near future. Xin[8] has reported green propellants, explosives, and related processing technologies.

2.1.1 Oxidizers

Ammonium dinitramide (ADN) and hydrazinium

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nitroformate (HNF) are emerging as potential ecofriendly replacement of AP[9-11]. Although, ADN and HNF have relatively less oxygen balance compared to AP, these have substantially higher heat of formation than AP leading to superior I_{sp}. Moreover, they undergo highly exothermic combustion reactions near the surface unlike nitramines, leading to efficient heat feedback to the deflagrating surface enhancing the burning rates. The ADN was synthesized in Zelinsky Institute of Russia during 1970s. EURENCO has commenced a pilot-scale production of crystalline, prilled, and coated ADN. Work on HNF was carried out mainly at TNO, The Netherlands, and, today it is productionised by Aerospace Propulsion Products (APP), The Netherlands.

Both the compounds have evinced interest all over the globe. However, severe hygroscopicity of ADN and higher sensitivity of HNF, particularly mechanical stimuli are cause of concern. These compounds are also beset with the problem of low melting temperature (92 °C and 123 °C). Various approaches are attempted to overcome these drawbacks. Prilled-ADN is reported in literature and phlegmatization is attempted for HNF. Change in particle morphology is also recommended by various researchers to improve the sensitivity problems. However, ADN propellants are productionised in Russia and are reported to be used in TOPOL-M intercontinental missile[12].

2.1.2 Primary Explosives

Presence of heavy metals like lead in most of the initiatory compositions poses the problem of toxicity/pollution during preparation and application. Initial work was aimed at development of basic lead azide (BLA)[13] to overcome the stability problem of service lead azide (SLA). However, the problem of toxicity remained unresolved for a long time.

During last one decade, lead free compounds like nickel hydrazine nitrate (NHN) and bis-5-nitro-2*H*-tetrazolato-tetrammine cobalt (III) perchlorate (BNCP) have emerged as ecofriendly alternative[14]. These have additional advantage of relatively lower impact, friction, and spark sensitivity.

2.2 Powerful HEMs

Although RDX and HMX are widely used in missile warheads and gun projectiles, hexanitro hexaazaisowurtzitane–HNIW, popularly known as CL-20 is fast emerging as powerful alternative[15-22]. Major attributes of CL-20 are its higher heat formation due to strained structure and superior oxygen balance than RDX and HMX. Cage structure of the molecule also results in close packing of constituent atoms leading to high density. The most powerful explosive of today is being manufactured in most of the countries. A CL-20 manufacturing facility (5000 lbs /year) has been established by Thiokol, USA. Although, several commercial and military products, based on CL-20, are reported, efforts are on to economize its production cost. Initially, 4, 10-dibenzyl-2, 6, 8, 12-tetraacetyl - 2, 4, 6, 8, 10, and 12 - hexaazaisowurtzitane (TADBIW) was considered the precursor for preparation of CL-20. However, synthesis of other precursors like 4,10-diamino – 2,6,8,12-tetraacetyl - 2,4,6,8,10,12-hexaazaisowurtzitae (TAIW) has led to reducing its production cost. The major cost reduction emanated from the change of nitrating agent to some extent.

Table 1. Physico-chemical properties of green oxidizers vis-à-vis AP

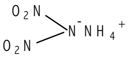
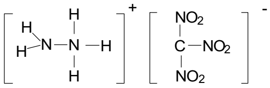
Oxidizer	Structure	ΔHf (kJ/mol)	Oxygen balance (%)	Density (g/cm^3)
AP	NH_4ClO_4	–298	35	1.9
ADN		–151	26	1.8
HNF		–71	13	1.9

Table 2. Comparative properties of SLA and BLA

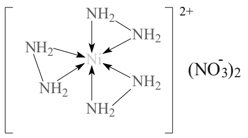
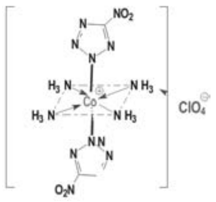
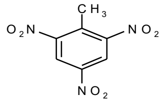
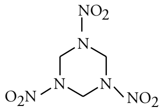
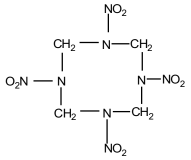
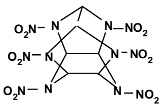
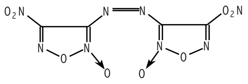
Property	SLA	BLA	NHN	BNCP
		$Pb(N_3)_2 . 2PbO$	 NHN	
Impact sensitivity (cm)	100	100	96	30
Spark insen.(J)	-	0.0008	5	5
Friction sensitivity	50 g	250 g	1 kg	3 kg
Thermal stability (°C)	325	350	210	260
VOD, m/s	4000		4500	5700

Table 3. Potential futuristic high explosives vis-a-vis today's benchmark explosives

Compound	Structure	*MP/Dc Temp. (°C)	Density (g/cm^3)	ΔH_f (kJ/mol)	OB (%)	VOD (m/s)	DETN *P* (GPa)
TNT		80.8	1.65	-63	-74	6950	18.9
RDX		204	1.82	61.78	-22	8700	34.3
HMX		286	1.91	75.30	-22	9100	39.5
CL-20		>220	2.04	419	-11	9400	41.9
DNAF		128	2.0	668	0	10000	-

* MP: Melting point; Dc: Decomposition temperature

Similarly, research work is being pursued on furazan/furoxan class of molecules. 4,4-dinitro-3, 3'-diazenofuroxan (DNAF) is reported by a research group at Zelinsky Institute of Organic Chemistry (ZIOC)[23], Russia as a HEM with density and VOD exceeding that of CL-20. The ZIOC team synthesized DNAF in three steps from a key synthon 3-azidocarbonyl-4-aminofuroxan (AzCAF). It involved the oxidative condensation of AzCAF with 3,3-bis (azidocarbonyl)-4,4'-diazenofuroxan (BAzCDF) followed by its Curtius rearrangement to 4,4'-diamino-3, 3'-diazenofuroxan (DADF). DADF on oxidation with hydrogen peroxide yielded DNAF. However, its applicability in explosive compositions requires address to the problem of its low decomposition temperature (127-128 °C), and high impact sensitivity.

Although a number of other molecules emerged, with the passage of time, these have been found less attractive. Some other molecules reported are 1,3,5,7-tetranitroadamantane (TNA), 1,3,4,6-tetranitroglycouril (TNGU), 1,4-dinitroglycouril (DNGU), 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6), 2,5,7,9-tetranitro-2,5,7,9- tetraazabicyclo(4.3.0)-nonane-8-ione (K-56), 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo(3.3.1)-nonane-3,7-dione (TNPDU),5,7-diamino-4,6-dinitro-benzofuroxan CL-14, etc[24].

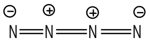
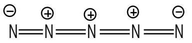
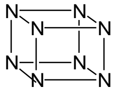
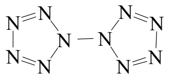
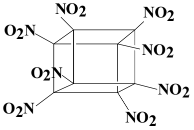
2.3 Futuristic HEMs

Octanitrocubane (ONC) is considered as the most powerful HEM of future for applications in explosives and propellants. Its synthesis is reported in the USA by adopting interfacial nitration. Search is on for cost-effective methods of its synthesis. However, a group of scientists is of the opinion that its high sensitivity will limit the scope of its application. Heptanitro cubane is being proposed as the molecule of interest[25-26].

A remarkable difference in the bond-energy of single-bonded and multiple-bonded nitrogens has led to the interest in polynitrogens with adjacent nitrogen atoms with intrinsic structural features leading to the formation of $N \equiv N$ accompanied with release of tremendous amount of energy (954 kJ/mol). A large number of polynitrogens are reported in literature as viable energetic molecules on the basis of theoretical quantum mechanical calculations.

N_5^+ is reported and its salt $N_5^+AsF_6^-$ has been isolated[27]. However, it is found to detonate violently. N_8 is considered a realisable polynitrogen by combining N_5^+ and N_3^- due to its corollary with ONC. It is suggested that N_5^- has transient existence and can interact with N_5^+ leading to formation of N_{10}. Manna[28] has reported that it may be possible to subject N_{10} molecules to ultra high pressure induced process leading to joining of six of its molecules into buckminster fullerene. Polynitrogens, if realised in large quantum, can drastically change the technology of high-energy rocket propellants and explosives.

Table 4. Polynitrogen compounds vs conventional HEMs

Compound	Molecular formula	Density (g/cm^3)	Heat of formation (kcal/mol)	VD (m/s)	Detonation pressure (GPa)
N$_4$	 $\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}$	1.752	268.7	13.24	77.02
N$_5$	 $\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\oplus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}$	1.85	350	12.51	73.95
N$_6$		1.974	345.58	14.04	93.32
N$_8$		2.15	406.69	14.86	108.39
N$_{10}$		2.21	473.4	12.08	58.05
N$_{12}$		2.28	579.8	12.53	64.07
N$_{60}$		2.67	546	17.31	196.0
ONC		2.1	111.0	10.1	50.0

Compounds like 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (BTATz), may be considered as forerunner of futuristic polynitrogen molecule sans oxygen. It has been synthesised and reported to have very fast burn-rate and may find application as a sensitive gas generator[29]. Other gas generating compounds reported of this class are 3,3′-azobis 6-Amino-1,2,4,5-Tetrazine (DAAT), triamino guanidinium azotetrazolate (TAGAT), triamino guanidinium azide (TAGAZ), etc.

2.4 Thermally stable explosives

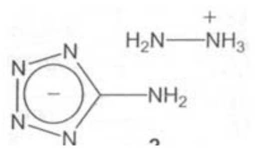
Thermal stability is a premier criterion for selection of HEMs for specific systems like supersonic missiles. Thermally stable explosives can also lead to safer production, longer shelf life and low vulnerable munitions. Generally, explosives with melting points and decomposition temperatures exceeding 300 °C are categorised as thermally stable explosives.

Triamino trinitrobenzene (TATB), first obtained in 1888 by Jackson and Wing[30], received major attraction despite its lower decomposition temperature compared to main contenders like hexanitrostilbene (HNS) and tetranitrodibenzotetraazapentalene (TACOT). This may be due to its relatively superior VOD. The structural features of TATB confer high density and extreme insensitiveness to impact and shock to this HEM. Introduction of amino groups in to this molecule is reported to confer such typical characteristics. TATB synthesis from picramide or 1,3,5-trinitrobenzene has recently been reported in three patents by Mitchell, *et al*[31-33] at the Lawrence Livermore National Laboratory, which may significantly reduce the cost of TATB. Currently, it is also being explored under Safe High Energy Explosive (SHEE) programme. In case of HNS, the extended conjugation is suggested to confer stability on the molecule. TACOT apparently owes its high thermal and chemical stability to planar structure and aromaticity. This class of HEMs also finds application in flexible linear shaped charge (FLSC) and sheet explosives in both civil and military sectors. 2,4,6-tripicryl-s-triazine (TPT) and 3,3'-diamino-2,2',4,4',6,6' hexanitrobiphenyl (DIPAM) are also some of the HEMs reported under the category of thermally stable explosives. However, their applications are limited[34-38].

2.5 Insensitive High Explosives (IHE)

The concept of insensitive munitions has led to impetus to apply some of the well known low vulnerable HEMs and also provided thrust to search new molecules less prone to unplanned stimuli. Such explosives are also referred as insensitive high explosives (IHE). The attempts are on to achieve immunity to almost all unplanned stimuli, namely, flame, sympathetic detonation, high velocity fragments, and explosive jet. A combination of design features of munitions hardware and low sensitivity of energetic materials need to be arrived at to achieve these effects. A widely reported IHE, 3-Nitro-1,2,4-triazol-5-one (NTO)[39] has found wide applications and reported to be inducted into Naval Ordnance. 1, 1-diamino-2, 2-dinitroethylene (DADNE or FOX-7) has emerged during recent times due to its superior performance almost comparable to that of RDX and insensitivity characteristics relatively superior to NTO. The sensitivity of FOX-7 to physical stresses such as impact, friction, heating, etc., has been extensively studied[40-42]. 2, 6-diamino-3,5-dinitropyrazine-1 oxide (LLM-105)[43-44] synthesised at the Lawrence Livermore National Laboratory (USA) is also of interest due to its reported high density and almost similar insensitivity characteristics. However, its VOD is relatively low than that of FOX-7. TEX is still superior to LLM- 105 in terms of density and insensitivity to impact stimuli with comparable VOD. However, its yield and purity are not fully established from production point of view. These compounds are widely explored for high explosives. FOX-12 is reported as potential HEM for gun propellant applications[45].

Various nitroimidazole derivatives including 4, 5-dinitroimidazole (DNI), 2, 4, 5-trinitroimidazole, and 4, 4', 5, 5'-tetranitro2, 2'-triimidazole[46-50] have been investigated as IHE. Out of these compounds, DNI is the most cost effective. 2, 4-Dinitroimidazole (DNI) of this category is much less sensitive than RDX and HMX. Recently, synthesized hydrazinium 5-aminotetrazolate acronymed as Hy-At and containing 83.72% nitrogen also belongs to this class of compounds. Researchers have computed its VOD as 9516 m/s using BKW code. However, the validation of the same experimentally could not be done as the compound could not be initiated even by PETN booster[51].



Hy-At

Insensitive/reduced sensitivity RDX (I/RS-RDX)[52-53] has evinced interest as low vulnerable RDX variant. Interestingly it has impact/friction sensitivity comparable to that of conventional RDX. However, it renders cast cured plastic-bonded explosive less vulnerable to shock stimuli. It is only characterised by higher floatation density compared to conventional RDX determined by STANAG-4566 method described for CL-20. Eurenco and SNPE have carried out extensive research work on RS-RDX.

2.7 Melt Cast Explosives

Although major work is aimed at replacement of RDX and HMX in explosive compositions, by more powerful and less vulnerable explosive compounds, attempts are also on to search replacement of TNT by melt cast alternatives. Trinitroazetidine (TNAZ)[6] has received attention during the last two decades. Its superior oxygen balance and heat of formation are responsible for its higher VOD than that of TNT. Its sensitivity levels are between that of TNT and RDX. Thus, TNAZ formulations can offer a culmination of more power and optimum vulnerability. However, there is a concern regarding its volatility.

Researchers at Weapons Systems Division of ARDEC have reported 2,4-dinitroanisole (DNAN), as a replacement of TNT[54]. Typical thermal properties of DNAN and its admixtures, sublimation/evaporation rate at various temperatures, solubility of RDX in molten DNAN have been determined. RDX can be loaded to high levels in a DNAN matrix. They have also described ARX and PAX compositions based on DNAN. Its processing has been established and considered viable using current pilot/ production plants due to viscosity comparable to that of TNT-based compositions and no variations because of the settling problems.

ARDEC has also reported 1-methyl-2,4,5-trinitroimidazole (MTNI)[55] as a promising candidate of new insensitive high explosives. Preliminary sensitivity tests revealed that it is almost as insensitive as TNT. The theoretically calculated explosive performances (detonation velocity and C-J pressure) are found to be comparable to that of RDX.

2.8 Nano HEMs

Increase in surface area by engineering a material to nano size has evinced interest in the field of HEMs technology. It is reported to have remarkable effect on energy delivering process. Nanomaterial can also influence overall sensitivity as well as mechanical properties of the formulations. A large number of researchers have reported nano Al in both propellant and explosive compositions. Sub micron size of the *Al* particles results in shift of the combustion region of *Al* particles near to the surface and efficient energy release during secondary reaction of blast producing explosive compositions. These features may be responsible for increase in burning rates or I_{sp} of the propellants and enhancement of VOD or blast effects of metallised explosives. Among nano energetic materials, both nano RDX and HMX have been attempted. However, nano RDX appears to be more viable as it is speculated that the conversion of â HMX to nano size may have bearing over its morphology. Nano CL-20 has also been studied by Chang[56] by applying DSC and TG-MS. Nano crystalline HNS is reported by Hao, *et al*[57]. Work is also being carried out on nano TATB as per reports in open domain.

2.9 Polymers (Binders/Plasticisers)

Among energetic polymers, glycidyl azide polymer GAP has the advantage of positive heat of formation (+117 kJ/mol) over HTPB (-62kJ/mol). But its incompatible nature with plasticizers and mechanical properties of GAP-based propellants need improvement. Other widely studied binders are poly bis- azido methyl oxetane (poly-BAMO), coplymers of BAMO and AMMO (azidomethyl methyl oxetane), polyglycidyl nitrate (PGN) and nitrato methyl-methyl oxetane (NMMO)[58-66]. Generally, GAP and PGN are explored in cast cure compositions, whereas BAMO-AMMO and BAMO-

Table 5. Properties of selected thermally stable/insensitive high explosives

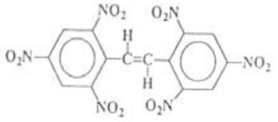
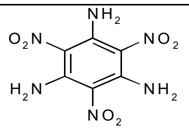
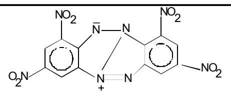
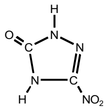
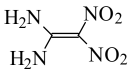
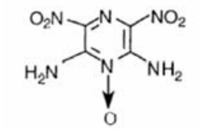
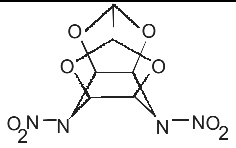
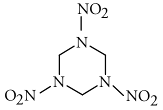
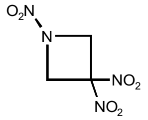
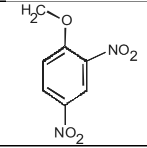
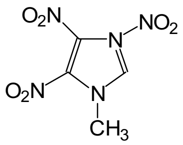
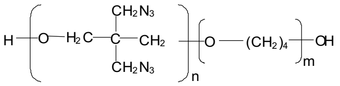
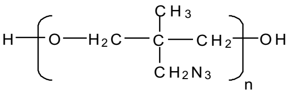
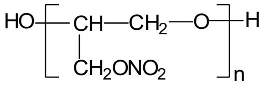
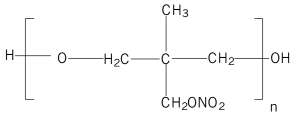
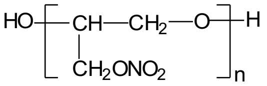
Compound	Structure	Decomposition temperature (°C)	Density (g/cm^3)	VOD (m/s)	Detonation pressure (GPa)	Impact sensitivity, (h_{50}, cm) for 2 kg fall weight	Friction sensitivity (Insensitive up to load, kg)
HNS		316	1.7	7000	26.2	80	16.8
TATB		350	1.86	8000	29.1	175	36
TACOT		410	1.85	7200	24.5	68	36
NTO		>252	1.91	8120	30.7	87	>36
FOX-7		254	1.88	8800	36	126	36
LLM-105		216.1	1.91	8560	35	117	36
TEX		262.1	1.99	8560	31	>177	36
RDX		204	1.81	8700	34.1	22	19
TNAZ		101	1.85	8500		45	36
DNAN		95	1.34	5344	9.5	>220	160N
MTNI		85		8800		100	36

Table 6. Physico-chemical properties of binders

Energetic binder	Structure	Heat of formation (kJ/mol)	Density (g/cm^3)	Oxygen balance (%)	Glass transition temp (^{0}C)
GAP		+117	1.30	- 121	- 50
Poly-BAMO		+ 413	1.30	- 124	- 39
Poly-AMMO		+ 18	1.06	- 170	- 35
Poly-NMMO		-335	1.26	- 114	- 25
PGN		- 285	1.39	- 61	- 35
HTPB		- 62	0.92	- 324	- 65

NMMO compositions are explored in pressed ones.

The most widely reported energetic plasticizers are, bis dinitro propyl formal/acetal (BDNPF/A), nitroxy ethyl nitramine (NENA), tri methylol ethane trinitrate (TMETN), tri ethylene glycol dinitrate (TEGDN), and 1, 2, 4 butane triol trinitrate (BTTN). The GAP with low molecular weight (about 500) can also be employed as energetic plasticizer. They have evinced great interest as safer energetic plasticizer components of propellants and explosives. Among these, BDNPF/A and TMETN/TEGDN are preferred for formulations[67].

A number of molecules are reported as energetic plasticizers by Cartwrght[68] and Ou, *et al*[69].

3. SELECTED COMPOSITIONS BASED ON NEW CLASS OF HEMS

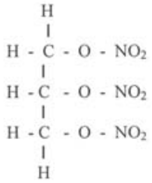
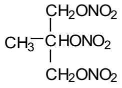
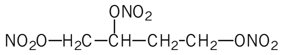
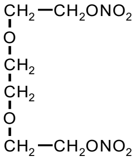
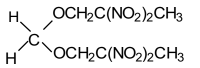
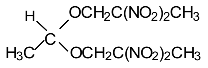
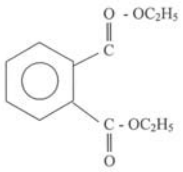
A brief discussion on potential of new class of HEMs is included in this section to bring out the significance of application of new class of HEMs for practical applications.

3.1 Rocket Propellants

In case of rocket propellants, composite propellants have acquired greater significance because of advantage of wide range of mechanical properties and superior strain capability compared to conventional propellants in addition to higher delivered I_{sp}. The NEPE propellants are considered as hybrid of double base and composite propellants and reported to offer improvement in I_{sp} by 2-5 s. RDX and HMX are also explored as component of both the classes of propellants for realizing smokeless exhaust[70]. A combination of AP and nitramines is also recommended to improve the I_{sp} marginally. Attempts towards realization of the superior performance level are directed towards replacement of HTPB binder by energetic polymer systems comprising of GAP and BAMO copolymers as polymer matrix in combination with TMETN/TEGDN/BTTN/BDNPF/A as plasticizers[71-72]. A typical AP-BAMO / NIMMO propellant is reported to have plateau burning unlike AP-HTPB system and I_{sp} potential of 265 s. Superior combustion characteristics are also observed for HMX propellant with BAMO – NIMMO binder. A 70/30 BAMO-NIMMO co-polymer is considered the preferred choice from the point of view of shock sensitivity.

CL-20 has also been investigated as a component of propellant despite its major potential as explosive. It is observed that CL-20 and GAP-based propellant with BDNPF/A as plasticizer have sensitivity comparable to that of HMX-based propellant. CL-20 and GAP formulations plasticized with the TMETN/BTTN system is reported to offer superior I_{sp} (251s) compared to RDX composition (241s) of the same class[3]. Although like CL-20, FOX-7 was synthesized as an explosive of interest. It has also been evaluated as a component of propellants. Most of the work on performance characteristics like I_{sp} is confined to theoretical computation. Floreszek[73-74] has reported the effect of replacement of AP by FOX-7 in slurry cast composition. They determined burning rate of the propellant in sub scale rocket motor and observed marginal decrease in it on replacement of AP by FOX-7. The computation based on ICT Thermodynamic code revealed that incorporation of FOX-7 as replacement of AP (15 to 29 %) results in 3-9s reduction in I_{sp} and 200-400 K reduction in chamber

Table 7. Physico-chemical properties of plasticisers.

Plasticizer	Structure	ΔH_f (kJ/mol)	Oxygen balance (%)	Density (g/cm^3)
NG		-349	+3.5	1.59
TMETN		-411	-34	1.48
BTTN		-91.42	-16.6	1.52
TEGDN		-601.8	-66	
BDNPF/A	 	-480	-51	1.39
DEP		-720	-194	1.12

temperature. These results can be attributed directly to remarkable decrease in oxygen balance of the composition. These authors have also carried out studies on HMX and FOX-7-based composition.

Basic composition comprised, AP/FOX-7: 79, *Al*: 5, Binder [Polybutadiene acrylonitrile (PBAN)/Epoxide/Dioctyl adipate (DOA)]: 16.

A marginal increase was observed in decomposition temperature in DTA on incorporation of FOX-7 in place of HMX and decrease in burning rate was from 1 mm/s to 0.85 mm/s at 10 kg/cm^2 whereas heat of combustion of these propellants was found comparable **(**4194 & 3900 kJ / kg respectively). They have also theoretically determined the heat of explosion, explosion temperature and volume of gases for these propellants.

Hy-At was also evaluated as a component of propellant in combination with ADN. A decrease in density of composition from 1.78-1.573 was observed on replacement of 30 %

Table 8. Burning rates of CL-20 incorporated rocket propellants[22,3]

Composition	Burning rate (mm/s)		*n*
60 % CL-20; 40 % PGA	11.5-23	(7-15 MPa)	0.92
60 % HMX; 40 % PGA	6-11	(7-15MPa)	0.89
60 % CL-20; 40 % GAP	13.4-27.2	(7-15 MPa)	0.94
60 % HMX; 40 % GAP	7.2-13.6	(7-15 MPa)	0.91
60 % CL-20; 40 % GAP (Ballistically modified)	20.0-32.4	(7-20 MPa)	0.48 (5-25 MPa)
60% RDX; 40 % GAP (Ballistically modified)	14.6-21.4	(7-20 MPa)	0.37(4-20 MPa)

Table 9. Theoretically computed properties of AP/FOX-7 rocket propellant compositions[74]

AP/FOX-7		Density (g/cm^3)	Specific impulse ($Ns.kg^{-1}$)	Vol. specific impulse ($Ns.dm^{-3}$)	Chamber temp (K)	OB (%)
AP:79		1.71	2432	4163	3053	-19.65
AP:64	FOX-7:15	1.7	2396	4082	2857	-28.00
AP:50	FOX-7:29	1.7	2343	3976	2645	-35.79

Basic composition: AP/FOX-7: 79, Al: 5, Binder [Polybutadiene acrylonitrile (PBAN) / epoxide / dioctyl adipate (DOA)]: 16

Table 10. Therotically calculated characteristics of AP/HMX/FOX-7 propellant formulations[73]

Properties	Propellants	
	HMX	FOX-7
Density (g/cm^3)	1.61	1.61
T_{onset} (K)	517.3	518.9
T_m (K)	517.6	519.3
Explosion temp (K)	2804	2650
Heat of explosion (kJ/kg)	4262	4001
Heat of explosion (gaseous water) (kJ/kg)		
Average heat of explosion (kJ/kg)	4057	3796
Gas vol (cm^3/g)	904	904
OB (%)	-52.7	-52.7

HMX/FOX-7 : 22, AP: 50, Binder (PBAN/Epoxide/DOA): 23

Table 11. Theoretically computed ballistics of Hy-At/ADN propellants[51]

ADN	Hy-At	Density (g/cm^3)	Ω (%)	T_c (K)	I_{sp} (s)
60-10	40-90	1.704 – 1.573	-14.6 to-65	2903-1857	251-220
90-70	10-30	1.782 – 1.730	+15.7to-4.5	2563-3063	221-251
CP(AP:70, Al:30)		2.178	-2.9	4199	232
DBP(NC:50,NG:50)		1.63	-13.3	3287	248
TBP(NC:25,NG:25,NQ:50)		1.70	-22	2663	235

Table 12. Performance [I_{sp} (s)] of solid propellant formulations based on advanced binders and oxidisers

Oxidiser	Binders			
	GAP	P-BAMO	P-NIMMO	PGN
ADN	310	312	309	306
HNF	314	317	313	310

ADN by Hy-At. However, there was an increase in flame temp. from 2563 to 2903 K accompanied by increase in I_{sp} from 221 to 251 s. Subsequently replacement of ADN by Hy-At led to decrease in all the ballistic parameters. It can be inferred that a judicious combination of Hy-At and ADN can offer superior I_{sp} compared to both composite and DB propellants.

It is predicted that a combination of HNF / ADN with energetic binders like GAP, BAMO, NIMMO can offer I_{sp} of the order of 300 s. However, such claim need to validated[58,65] in a practically useful propellant.

3.2 Gun Propellants

Attempts to realise low vulnerable gun propellants have led to exhaustive research in the area of RDX and HMX-based propellants with polymeric binders as alternate to currently used TBPs**.** This class of propellants can be tailored to realise force constant and flame temperature comparable to TBP with the advantage of low vulnerability to unplanned stimuli like impact, friction, shock and high velocity metal fragments as well as improved mechanical properties.

Energetic polymers are also reported as component of LOVA. A typical RDX (58 %), NQ (17 %) and BAMO-AMMO 35:65 (25 %) is reported with ballistic parameters equivalent to M30 propellant (F 1078 J/g and 1081 J/g respectively) with the advantage of low flame temperature (2548 K) compared to M30 propellants (3000 K). It is designated as TGD-008. Energetic polymers can offer superior *F*. However, increase in flame temperature leading to increase in barrel erosion is cause of concern. An RDX and BAMO-AMMO TPE propellant designated as BAT-5RDX composition is prepared by Thiokol, USA. CL-20 has also been reported as a component of gun propellant. Selected compositions

Table 14. Combustion characteristics of CL-20 incorporated gun propellants[75-77, 22]

Composition	Impetus (J/g)	Flame temperature (K)
76 % RDX; BAMO/AMMO	1182	2827
76 % CL-20; BAMO / AMMO	1297	3412
CL-20; 5-30 % BAMO-AMMO/BAMO- NMMO/ BEMO-NMMO	1278- 1349	-
CL-20; NC; BDNPF/A	1253	3698
RDX; NC; BDNPF/A	1220	3390
TBP	950-1140	2400-3300

Table 15. Ballistic parameters of propellants containing nitrogen rich compounds[78]

Composition	Force constant (J/g)	Flame temperature (K)	B1 (cm/s/Pa)	A
RDX: 65	1200	3210	0.14	0.84
RDX: 50, TAGN: 15	1163	2900	0.30	1.40
RDX: 50, TAGAZ: 15	1158	2850	0.30	1.40
RDX: 50, GN 15	1118	2915	0.13	0.80
RDX: 50, GA15	1160	2870	0.15	0.95

reported in literature are given in Table 14.

US Army's M-900 programme has embarked on LOVA gun propellants and has reported an alternative propellant system for MK 66 (NOSIH-AA-11) based on TMETN/ TEGDN. The use of Hy-At is also suggested in gun propellants to realise less erosivity, and high N_2/CO ratio.

Nitrogen rich compounds have been evaluated[78] as ingredient of gun propellants in closed vessel (Cv) like triamino guanidine nitrate (TAGN), guanidium nitrate (GN), triaminoguanidium azotetrzolate (TAGAT), and guanidium-5-aminotetrazolate (GA). Table 15 shows the ballistic parameters of propellants containing nitrogen-rich compounds. Researchers concluded that rapid exothermic decomposition of nitrogen-rich compounds like TAGN and TAGAZ is responsible for higher burn rates of propellants compared to RDX-based reference. Slow decomposition of GA and GN results in lower burn rates.

3.3 High Explosives

In the area of explosives, attempts are on to develop more powerful and/or less vulnerable explosive composition to currently used RDX/HMX based melt cast TNT formulations[4,79-81]. HTPB appeared as preferred polymer for this class of compositions[82]. It has been reported that the RDX/ HTPB composition ROWANEX-1100 is selected for 105 mm and 155 mm projectiles[83-86]. A large number of explosive formulations based on cast cured polymers are developed for naval applications. Most of these compositions are based on NTO and are designated as French 'B' and US PXW systems. This class of compositions is designated as GD in Sweden. Energetic polymers are also being investigated as component of explosive formulations. RDX and AP combination based composition with GAP as binder is designated as GHX[87-88]. In UK and Germany the compositions incorporating energetic binder poly-NIMMO and plasticizer K-10 (2,4-dinitroethyl benzene and 2,4,6-trinitroethyl benzene 65:35) with HMX and NTO combination are designated as CPX.

TATB has been explored in pressed explosive formulations to realise IM applications referred as SHEE explosives[89]. Both NTO and TATB have also been evaluated in melt cast TNT-based compositions to realise optimum performance and low vulnerability owing to its strategic importance. During recent times, TEX and FOX-7 have also been investigated as low vulnerable explosives both as component of melt cast and cast cure compositions. Both non-energetic and energetic systems with thermoplastic elastomers are explored as binders for pressed explosives[90]. RS-RDX has been investigated in pressed and cast-cured compositions[53]. However, it is found to be more effective in cast-cure explosives. Parallelly, melt-cast explosive DNAN is also studied in detail despite its relatively lower explosive power compared to TNT. RS-RDX/DNAN-based compositions are reported by ARDEC under the nomenclature of PAX. MTNI can offer a superior alternative to DNAN.

CL-20 has been extensively evaluated in all the classes of explosives, i.e., melt cast, cast cure, and pressed explosives. However, major work is reported on CL-20-based pressed explosives[91-94].

Table 16. Density and VOD of selected high performance PBXs[22]

Composition	Density (g /cm^3)	VOD (m / s)
66.8-72.1 % CL-20; HTPB	1.618-1.710	8325-8470
66.8-72.1 % HMX ; HTPB	1.575-1.648	8030-8107
LX-19 : 95 % CL-20; Estane	1.959	9440
LX-14: 95 % HMX; Estane	1.835	8790
PATHX-1: 88-95 % CL-20; Estane	1.868-1.944	8890– 9370
PATHX-2: 92-95 % CL-20; Estane	1.869-1.923	8850- 9220
95.5 - 95.8 % CL-20; Estane	1.942±0.001	9208±10
PBXC-19:95 % CL-20; EVA	1.896±0.002	9083±9
96 % HMX; 1 % Hy Temp; 3 % DOA 96 %	1.817	8748
CL-20; 1 % Hy Temp; 3 % DOA	1.901	9018

Table 17. Aluminised CL-20-based PBX compositions[94]

Composition	Density 99% TMD (g/cm^3)	CJ pressure (GPa)	VOD (m/s)
PAX-11 (Aluminised) CL-20: 79, Al: 15, CAB: 2.4,BDNPF/A: 3.6	2.023	39.5	8870
PAX-29 CL-20: 77, Al: 15, CAB: 3.2,BDNPF/A: 4.8	2.002	38.3	8770
A-3 (Aluminised) RDX: 64, Al: 30, wax: 6	1.824	21.0	7420
PAX-3 HMX: 64, Al: 20, CAB: 6.5, BDNPF/A: 9.5	1.859	28.1	8060

Table 18. Selected GHX compositions[87]

Composition	RDX	GAP	*Al* (5 μm)	AP (200 μm)	AP (5 μm)	Density (g/cm^3)	VoD (m/s)	Sensitivity	
								Impact (Nm)	Friction (N)
GHX 82	27	18	30	25	--	1.91	6810	2.0-3.0	20-24
HXA-174	27	18 (HTPB)	30	25	--	1.70	5870	--	--
GHX 116	27	18	25	30	--	1.88	6750	3.0	24
GHX 117	27	18	25	15	15	1.87	7080	4.0	30

Considering the superior energy release probability, nano *Al* has also been evaluated both in cast-cure and melt-cast compositions. However, it is found to be more effective in TNT-based formulations. Considering the agglomeration and surface oxidation problems, exhaustive data need to be generated to assess the potential of nano *Al* in compositions. Heavy metals like tungsten are also being used to achieve reduction in blast area to reduce collateral damage to the surroundings. Tables 16-19 show the computed properties of reported high performance PBXs, CL-20-based PBXs, GHX and TEX-based compostions respectively.

3.4 Thermobaric Compositions

Thermobaric explosives[95] providing combined blast and incendiary effects are emerging as systems of interest in view of increase in terrorist activities. Russia has developed technology of thermobaric system, popularly known as 'Father of all Bombs' and claimed it more effective than 'Mother of all Bombs' of US. Naval Surface Warfare Centre Indian Head Division (NSWC IHD) and the Talley Defence Systems (TDS)[87] developed solid thermobaric compositions for light weight shoulder launched penetrating/anti-cave warhead for M-72 LAW system. The jointly developed aluminised HMX-based compositions with HTPB/PCP/Hytemp binder are designated as PBXIH or HAS (Table 20).

4. INDIAN SCENARIO

Production base for conventional explosives like TNT and RDX exists in Ordnance Factories of India. HMX is being produced at limited scale in DRDO Laboratories. The melt cast and cast cure compositions based on of these explosives have been developed for wide range of applications in missile warheads and gun projectiles. CL-20 has been productionised at kg level in Defence and Private Sectors. CL-20 has been evaluated in explosive compositions based on and increase in penetration of shaped-charge has been established. FOX-7 and TATB are being produced at pilot scale in DRDO. TEX and NTO have been synthesised. The investigation on RSRDX has been undertaken and encouraging results have been obtained in cast cure explosives.

The production base for AP/Al/HTPB exists in the private sector. Ordnance factories are well equipped to produce double-base propellants. The composite propellants are being produced in both ordnance factories and pilot plant facilities in DRDO. Investigative studies have been undertaken in DRDO for elastomer-modified double-base (EMDB) propellants. HNF has been synthesised in DRDO Labs. and attempts are on to tackle its sensitivity problems. Double-base and triple-base propellants are being produced in ordnance factories to meet all the gun propellant requirements. RDX and HMX are also being evaluated in LOVA propellant with thermoplastic elastomers and conventional polymers as binders. A large number of nitrogen rich compounds have been synthesised and evaluated as components of gun propellants. Nitrogen-rich compounds have also been evaluated in other systems.

The production of energetic polymers and plasticizers like GAP, BAMO and TMETN/TEGDN has been established in private sector. These energetic binders are extensively evaluated in gun propellants. Feasibility studies are also under taken on rocket propellants and explosive compositions.

Table 19. TEX-based compositions

Formulation	Density (g/cm^3)	VOD (m/s)	P_{CJ} (GPa)
RDX / TNT (75/25)	1.773	8435	32.47
TEX / TNT (75/25)	1.893	8306	32.85
H-6 (RDX)	1.773	300	23.24
H-6 (TEX)	1.852	7236	23.28
AFX-644 (NTO)	1.903	7312	24..25
AFX-644 (TEX)	1.934	7487	26.02

Table 20. Explosive compositions developed at NSWC IHD[87]

Explosive	Composition	P (g/cm^3)
PBXIH-135	HMX/Al/HTPB	1.68
PBXIH-135EB	HMX/Al/PCP-TMETN	1.79
PBXIH-136	RDX/AP/Al/PCP-TMETN	2.03
HAS-4	HMX/Al/HTPB	1.65
HAS-4 EB	HMX/Al/PCP-TMETN	1.73
PBXIH-18	HMX/Al/Hytemp/DOA	1.92

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