

HEMs: Trends and Challenges

11.1 Introduction

From the first experiments with gunpowder and fireworks to the latest ultra-powerful high-explosive, octanitrocubane (ONC), or caged nitramine class of explosives such as CL-20, man has sought to unleash the force of chemical explosives in more powerful and controlled ways. However, the rapidly changing technology presents some tremendous opportunities and pitfalls. Now more than ever, success on the battlefield is dependent on the rapid access to information and the ability to act on that in a timely manner. The current trends in the field of high energy materials and the future challenges are discussed briefly in this chapter.

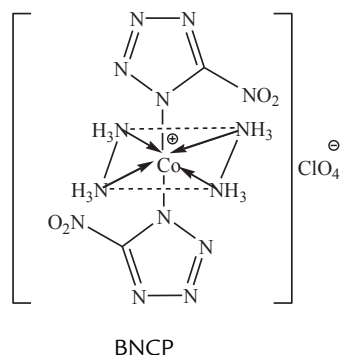
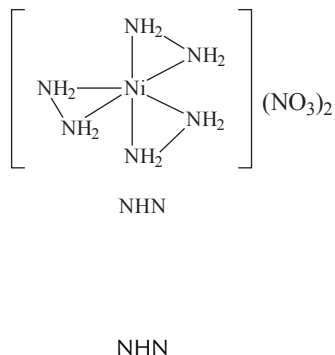
11.2 Primary Explosives

11.2.1 Problems

Mercury fulminate and lead azide are the foremost primary explosives, and they gained prominence in military ammunitions and civil applications. They ruled the world of initiatory compounds for more than 70 years. Despite being good in performance, they suffer from certain inherent drawbacks, such as hydrolytic instability, incompatibility with copper or its alloys (commonly used for encapsulation of primary explosive formulations), and high friction sensitivity. Globally, research and development is triggered for the development of potential primary explosives with figures of insensitivity greater than 20, which are then less prone to accidental initiation during storage, transport, or handling of the finished ammunitions and are stable and compatible with copper and its alloys.

11.2.2 Solutions

Lead-free coordination compounds are the choice of tomorrow in view of their additional advantage of being ecofriendly. Another desirable attribute of this class of compounds is the presence of almost stoichiometric fuel and oxidizer moieties. These compounds have been known for some time, but their applications in primary explosives were recently realized. Two important energetic coordination compounds are nickel hydrazine nitrate (NHN) and bis-(5-nitro-2H-tetrazolato-N²) tetramine cobalt(III) perchlorate (BNCP).



Apart from these, research is focused on the development of energetic coordination compounds without deleterious metal ions such as Co, Ni, and anions such as ClO₄⁻ and NO₃⁻.

11.3 High Explosives

High explosives are the major components of any weapon system. Today, the candidate molecules available for warhead applications are very limited. Any researcher always looks for better materials than the existing benchmark candidates. In this regard, any high-explosive scientists and technologists always look for better materials than HMX.

Three categories of importance under high explosives need to be mentioned here:

1. High-density, high-VOD (velocity of detonation) explosives, which, because of their superior power (due to high VOD and hence high detonation pressure) and volumetric efficiency (due to high density), hold great promise to impart enormous lethality to ammunitions of the future.
2. Insensitive explosives (or low-vulnerability explosives) assume their importance in view of the safety involved during transportation and storage and to prevent accidental initiation (e.g., due to enemy fire) during a battle. There are often battlefield situations in which the power of the explosives can be slightly compromised to ensure low vulnerability of the ammunition and avoid any disaster.
3. Thermally stable explosives (sometimes referred as heat-resistant explosives) play a vital role when a high-temperature environment may adversely affect the performance (or worse, prematurely initiate) of the explosive. Examples of such an environment are the explosives filled with warheads of supersonic missiles in which aerodynamic heating is involved and explosives are used in oil well exploration. Similar to the case of insensitive explosives, thermal stability is imparted slightly at the cost of the power of the explosives. As one can expect, imparting all three qualities of high power, high insensitivity, and high thermal stability in an explosive is impossible. To give an

example, a certain amount of thermal stability is imparted in an aromatic polynitro compound by converting one or more $-\text{NO}_2$ groups into $-\text{NH}_2$ groups (so that inter/intramolecular hydrogen bonding between $-\text{NO}_2$ and $-\text{NH}_2$ groups form a sort of a matrix in the explosive, introducing higher thermal stability). However, sacrificing one or more energetic $-\text{NO}_2$ groups to introduce nonenergetic $-\text{NH}_2$ groups results in the decreased power of the explosive. The choice of 1, 2, or 3 depends on the type of ammunition in which they are to be used.

11.3.1 High-Density, High-VOD Explosives

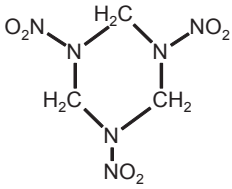
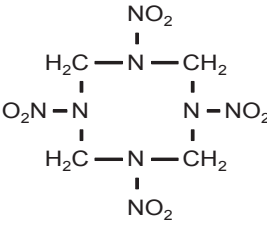
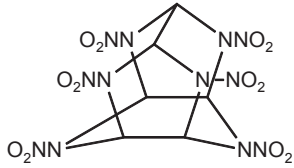
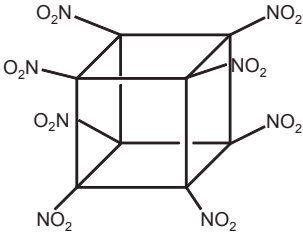
The challenges faced by an explosive chemist to achieve their goal of synthesizing an explosive more powerful (higher VOD) and with higher density are amazingly high. They must visualize a nonaromatic, polycyclic “caged” compound containing energetic groups such as $-\text{NO}_2$ or $\text{N}-\text{NO}_2$. Visualization is just the first step; they must assess its energetics by various empirical and quantum mechanical methods to calculate its expected VOD and density, if at all it is synthesized. Even if there are a 100 candidate molecules to start with, the chemist may ultimately end up with a few or even none. This is because their choices are ruthlessly narrowed down when most (if not all) of the candidates are rejected in terms of huge costs and hazards because of extreme sensitivity or instability of the final explosive or even intermediates.

If a new explosive with marginally better properties than HMX is going to be 100 times costlier than HMX, then no one is going to use it as ammunition. Or, if the same explosive is very sensitive to mechanical shock or has a poor thermal stability, then it holds no promise. This is the main reason why new powerful and promising explosives are made after long intervals of several decades. RDX was first made in the year 1899. Its higher homolog, HMX, was later made only in the year 1943 after a gap of 44 years.

Under this category, the only two high explosives exceeding the performance of HMX are hexanitrohexaazaisowurtzitane also called China Lake-20 (CL-20) and ONC. The synthesis and subsequent manufacture of CL-20 were established only in a few selected countries. The cost of CL-20 is much higher than that of HMX because it involves quite a few steps using very costly catalysts. Moreover, its sensitivity to impact and friction is more than that of RDX and HMX (see [Table 11.1](#)). Despite the cost and sensitivity factors, CL-20 holds great promise in futuristic warheads and its role as an ingredient in low-signature propellants because of its better oxygen balance than RDX and HMX.

Another interesting candidate in the series is ONC (see [Table 11.1](#)). ONC was synthesized in 1999 using a multistep synthesis approach. No reports appeared in the literature after its invention because of the difficulties in the preparation methods. Research and development efforts have to be focused for a viable and simple method for the preparation of ONC.

Table 11.1: Comparison of RDX, HMX, CL-20, and ONC.

Parameters	RDX	HMX	CL-20	ONC
Structure				
Year first made	1899	1943	1987	1999
Density (g/cm ³)	1.81	1.91	2.04	2.1
Oxygen balance (%)	-21.6	-21.6	-11	0
VOD (m/s)	8800	9100	9400	9800
Sensitivity to impact (h50%, cm)	46	38	24	Not reported
Friction (kg)	16	14	8	Not reported

In modern ordnance there is a strong requirement for explosives having thermal stability and mechanical insensitivity coupled with better explosive performance. Under normal conditions of use, munitions filled with conventional explosives are safe and effective to provide desired military capability. However, they violently respond to unintentional initiation such as getting exposed to enemy fire. In general, high explosives, gun propellants, and rocket propellants are sensitive to heat, mechanical shock, fire, and mechanical impact by bullets or fragments. Such secondary effects may lead to the violent initiation of the ammunitions and result in huge loss of men and materials on a battlefield.

11.3.2 Insensitive High Explosives

To avoid this kind of collateral damage to weapons, a new concept called “insensitive munitions” (IMs) has emerged. IMs are munitions designed to minimize the consequences of an accidental initiation without compromising the expected performance. IMs are designed such that they are difficult to be ignited accidentally or, in the case of an accidental initiation, it does not result in any detonation or mass fire.

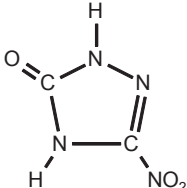
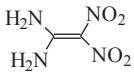
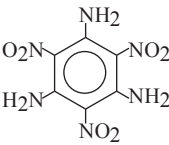
The synthesis of nitrotriazoles as insensitive energetic materials has received a great deal of attention in the past 20 years. The most studied nitrotriazole explosive is 3-nitro-1,2,4-triazole-5-one (NTO). NTO is currently being widely investigated in main charge warhead filling for IMs. It is used in cast-cured, pressed, and sheet explosive formulations.

Another new insensitive energetic material with promising properties is 1,1-diamino-2,2-dinitroethylene (FOX-7). In recent years, much interest has been devoted to RDX in another form (i.e., reduced sensitivity RDX (RSRDX) or insensitive RDX), which, when incorporated in cast-cured plastic-bonded explosive formulation, can confer reduced shock sensitivity as measured through the gap test. RSRDX is reported to possess improved crystal density and fewer crystal defects with smooth surface morphology, and these factors seem to reduce the mechanical sensitivity of RDX. These features also impart reduced vulnerability toward shock initiation. The preparation method of RSRDX is not disclosed in open literature because of its strategic importance. The properties of some of the insensitive explosives are given in [Table 11.2](#) in comparison with some thermally stable explosives.

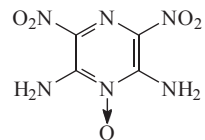
11.3.2.1 Is TNT Suitable for IM?

In the area of melt-cast explosives, trinitrotoluene (TNT) is the well-known explosive used in all possible ammunitions since World War I. The advantage of TNT is that it melts at 81 °C and can be cast alone or in combination with other ingredients such as RDX, aluminum, and ammonium perchlorate (AP) into various desired shapes. Although the performance is lower, TNT was well accepted by ordnance communities because of the above advantages. However, TNT and TNT-based ammunitions pose long-term health

Table 11.2: Performance comparison of insensitive and thermally stable explosives.

Name of HEM	Structure	Oxygen Balance (%)	Density (g/cm ³)	VOD (m/s)	Impact Insensitivity (h _{50%} , cm)	Friction Insensitivity (kg)
Insensitive High Explosives						
NTO		-24.6	1.93	8564	93	>36
FOX-7		-21.61	1.88	9090	126	>36
Thermally Stable Explosives						
TATB	 <p style="text-align: center;">TATB</p> <p style="text-align: center;">Decomposition temperature: 376 °C (T_{max})</p>	-55.78	1.94	8108	>177	>36

LLM-105



LLM-105

-37

1.91

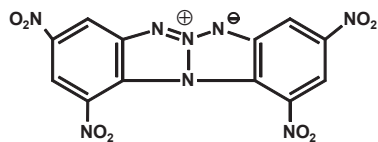
8560

117

>36

Decomposition temperature:
342 °C

TACOT



-74

1.82

7060

68

>36

Decomposition temperature:
403 °C (T_{max})

hazards to workers. Moreover, formulations containing TNT exude during storage. In addition, numerous problems involving TNT are noted during the melt-pour process, including high volume change from liquid to solid, supercooling, irreversible growth of crystals, and unpredictable sensitivity.

The main problem with TNT as a filling ingredient for modern projectiles is that it behaves violently if subjected to an accidental stimulus, such as being involved in a fire attack by enemy gun fire. The efforts pursued to make TNT safer ended in failure. Likewise, TNT-based ammunitions have failed all IM tests.

A promising compound to replace TNT as a melt-cast explosive is 2,4-dinitroanisole (DNAN) with a melting point of 94 °C. DNAN-based compositions with other ingredients such as RDX, aluminum, and AP successfully passed IM tests, which are internationally accepted. However, DNAN is inferior in performance to TNT. Hence, research and development efforts realized another potential compound, namely *N*-methyl-2,4,5-trinitro imidazole (MTNI), which melts at 82 °C. This compound possesses good thermal stability, impact insensitivity (50–70 cm), and better explosive performance than DNAN and TNT. However, the main problem with MTNI is its low yield in preparation.

Likewise, another high-performance melt-cast explosive realized in the last decade was 1,3,3-trinitroazetidine (TNAZ), which is a strained nitramine compound with a higher melting point (102 °C). This compound suffers in many aspects, such as a multistep cumbersome synthesis approach, high volatilization, exorbitant cost, and health hazards to the workers in the vicinity. Hence, not much seriousness was shown in the development of TNAZ-based ammunitions. Important melt-cast candidates are presented in [Table 11.3](#).

11.3.2.2 *Thermally Stable Explosives*

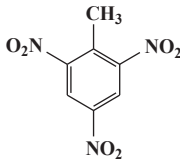
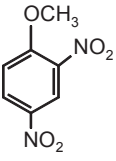
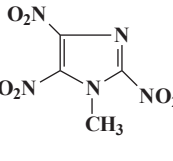
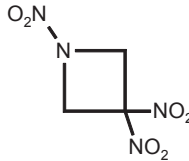
Warhead fillings of modern weapons are expected to function under various environmental conditions. Improved thermal stability of explosives in such warheads increases the shelf life of munitions. Their heat resistance decreases their vulnerability to accidental initiation. The development of explosives for space programs, applications in oil well exploration, transportation of munitions by supersonic aircrafts, etc., have resulted in the need for thermally stable explosives. The properties of some of the thermally stable explosives and which hold promise are given in [Table 11.2](#), along with a few insensitive explosives.

11.4 Propellants

11.4.1 *Ecofriendly Oxidizers*

In today's war scenario, a rocket propellant has the dual requirement of high performance and low signature (smoke). The major disadvantages of rocket propellant formulations

Table 11.3: Potential melt-cast explosives with performance.

Parameters	TNT	DNAN	MTNI	TNAZ
Structure				
Melting point (°C)	80.8	94	82	102
Density (g/cm ³)	1.65	1.55	1.76	1.84
Oxygen balance (%)	-74	-97	-25	-16.6
VOD (m/s)	6900	6800	8000	9000
Sensitivity				
Impact insensitivity (h50%, cm)	>170	>170	62	45–47
Friction insensitivity (kg)	>36	>36	>36	>36

with AP are that they produce huge signature because of the emission of hydrogen chloride (HCl) gas and they pollute the environment. Another drawback of AP is that it inhibits the functions of the thyroids of personnel involved in large-scale AP processing over a period of time. Therefore, a large amount of money is still being spent on the development of ecofriendly and low-signature oxidizers that will replace AP.

One such oxidizer is ammonium dinitramide (ADN). It is an inorganic oxidizer and was first made by a Russian scientist in the late 1970s, and the preparation details were kept under a high order of secrecy because of its strategic importance. ADN-based propellants offer high specific impulse with no secondary smoke because of the absence of HCl. The major application of ADN is that it can replace today's workhorse oxidizer AP in rocket propellants. The synthesis of ADN has been reported widely in the literature using various synthesis approaches. The main problem of ADN is that it is very sensitive to moisture. ADN readily absorbs moisture and rapidly decomposes. Stabilization of ADN is a critical issue and has been done through prilling or by coating techniques.

Hydrazinium nitroformate (HNF) is another ecofriendly energetic oxidizer for solid rocket propellants. The drawback of HNF is that it is very sensitive to mechanical stimuli, particularly to friction because of the sharp needle-shaped crystals. Hence, it is not possible to directly use it in propellant formulations. To overcome this problem, desensitization of HNF is necessary to process HNF-based propellants. Desensitization of HNF calls for elaborate trials involving the addition of proper ingredients at the time

Table 11.4: Performance comparison of various oxidizers.

Parameters	AP	ADN	HNF
Structure	NH_4ClO_4	$\left[\text{NH}_4 \right]^+ \left[\text{N} \begin{array}{l} \diagup \text{NO}_2 \\ \diagdown \text{NO}_2 \end{array} \right]^-$	$\begin{array}{c} \text{NO}_2 \\ \\ \text{O}_2\text{N}-\text{C}-\text{H} \\ \\ \text{NO}_2 \end{array} * \text{N}_2\text{H}_4$
Melting point ($^{\circ}\text{C}$)	452	92–93	115
Density (g/cm^3)	1.9	1.8	1.9
Oxygen balance (%)	34	26	13

of crystallization to modify its morphological characteristics. HNF can find applications in futuristic low-signature, high-performance green propellants in place of AP once the sensitivity issue is resolved. All said and done, despite the drawbacks of AP, there is a long way to go to replace AP because of its excellent oxygen balance, ease of preparation in large scale, and low cost. Table 11.4 gives a comparison of AP, ADN, and HNF.

11.4.2 Metallic Fuels

Composite rocket propellants use metallic powders as fuels. Most of the modern composite solid propellants contain finely powdered metallic fuels such as aluminum. They increase the chemical energy of the propellants by increasing the combustion temperature due to large thermochemical energy output.

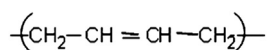
For several decades, aluminum has been the choice in propellant formulation because of its reasonably good thermochemical energy output, easy availability, nontoxicity of combustion products (mostly aluminum oxide), and low cost. The search is on to replace aluminum by metals that are more energetic and dense to boost the performance of the propellants. However, the alternative metallic fuels pose problems such as toxicity of products, combustion instability, high cost, etc. For example, boron is an alternative metallic fuel, but it is difficult to ignite/burn. Beryllium is energetically more favorable than aluminum, but it produces highly toxic products on combustion; therefore, it is not acceptable.

Zirconium has attractive properties in terms of density and energetics, but it is very hazardous in view of its pyrophoric nature (easy ignitability in the presence of air). In addition, there are certain metal hydrides that are also being tried as fuels in advanced propellant formulations in view of their attractive energetics. Lithium aluminum hydride is toxic and dangerous to handle because it may ignite and violently burn. It is incompatible

with water, alcohols, ammonium hydroxide, etc.; however, it acts as a high-energy fuel. Likewise, toxicity and sensitivity to initiation by mechanical shock ruled out the use of magnesium hydride and lithium borohydride. Similar to AP in the case of oxidizers, it will take quite some time to completely replace aluminum as a fuel in large-scale propellant processing.

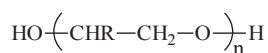
11.4.3 Energetic Binders

Binders are typically cross-linkable polymers (or sometimes called prepolymers) added in propellant formulations to bind the solids (oxidizer, fuel, additives) together with a plasticizer and to enhance the mechanical properties of the composition. For several decades, the choice of binders (which also act as nonmetallic fuels) for rocket propellants has been based on hydrocarbons such as polybutadiene. Carboxyl-terminated polybutadiene (CTPB) and hydroxyl-terminated polybutadiene (HTPB) are popular among them. Although the repeating unit of the polybutadiene chain

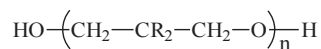


releases a good amount of heat on combustion, scientists have been working on the introduction of energetic functional groups, such as $-\text{NO}_2$, $-\text{NO}_3$, and $-\text{N}_3$, in the backbone of the polymeric binder (or sometimes as pendent groups attached to the backbone) to enhance the energy output during the propellant combustion. However, this does affect the easy processability of the propellant because the viscosity of the binder substantially increases due to the introduction of such energetic groups in the polymer backbone.

Some of the candidate polymers containing energetic groups such as $-\text{N}_3$, $-\text{NO}_3$, etc., are based on a polyethylene oxide



backbone (e.g., glycidyl azide polymer (GAP) and polyglycidyl nitrate (PGN) or a polypropylene oxide



backbone (e.g., poly-3,3-bis(azidomethyl) oxetane (polyBAMO) and poly-3-nitratomethyl-3-methyloxetane (polyNIMMO). Their molecular structures are shown in [Table 11.5](#).

At times, some of these polymers (the viscosities of which are quite high) are copolymerized with nonenergetic (low-viscosity) polymers such as polytetrahydrofuran

Table 11.5: Physicochemical properties of some energetic binders.

Polymer	Structure	Density (g/cm ³)	Oxygen Balance (%)	Glass Transition Temperature (°C)
HTPB	$\text{HO}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n\text{OH}$	0.92	-324	-65
GAP	$\text{HO}-\left(\text{CH}(\text{CH}_2\text{N}_3)-\text{CH}_2-\text{O}\right)_n\text{H}$	1.3	-121	-50
PGN	$\text{HO}-\left(\text{CH}(\text{CH}_2\text{ONO}_2)-\text{CH}_2-\text{O}\right)_n\text{H}$	1.39	-61	-35
PolyBAMO	$\text{HO}-\left(\text{CH}_2-\text{C}(\text{CH}_2\text{N}_3)_2-\text{CH}_2-\text{O}\right)_n\text{H}$	1.3	-124	-39
PolyNIMMO	$\text{HO}-\left(\text{CH}_2-\text{C}(\text{CH}_3)(\text{CH}_2\text{ONO}_2)-\text{CH}_2-\text{O}\right)_n\text{H}$	1.26	-114	-25

viz., $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$ for improving the processability. Table 11.5 compares the properties of some energetic binders.

11.4.4 Thermoplastic Elastomers

All of the polymers discussed so far are chemically cross-linked by a curing agent; hence, they have a certain amount of rigidity. They come under the category of thermosetting polymers and cannot be reprocessed. Thermoplastic elastomers (TPEs) are popular choices when one wants to process propellant compositions that can be reprocessed and that are easily disposed. TPEs contain macromolecules, each having a backbone containing “hard” (glassy) segments (e.g., aromatic rings) and soft (rubbery) segments (e.g., a polybutadiene moiety). Only physical cross-links give the polymer a physical or structural integrity, and they start disappearing near the melting point (like untying a complex knot). During cooling, these cross-links reappear. The thermoplastic and elastomeric nature of TPEs has been exploited in using them for processing the propellant

by extrusion methods. Some of the TPEs are also being tried for extrudable gun propellants for the same reason. One of the great advantages of TPE-based ammunitions is the ease of demilitarization (i.e., the ammunitions can be easily disposed by the process of melting).

11.4.5 Energetic Plasticizers

Plasticizers are low molecular weight liquids added to a polymer at the time of processing. The plasticizer molecules penetrate through the interstices between the long chains of the polymer and get linked to the polymer chain through weak physical bonds, thereby decreasing the interchain attractive forces in the polymer. This gives a “greasing” effect so that the polymer chains can slide among themselves. Thus, the plasticizer gives flexibility to the finished polymer. In addition, during the polymer processing, the plasticizer reduces the viscosity of the mix, thereby improving the processability. Many popular plasticizers used in the propellant industry have been nonenergetic, such as phthalate esters and a few aliphatic ones. The conventional energetic plasticizer well known in double-base propellants is nitroglycerine (NG). NG is an excellent plasticizer of nitrocellulose and it contains energetic $-\text{ONO}_2$ groups. However, NG is highly sensitive to impact; hence, its use as a plasticizer is limited.

Modern research replaces the nonenergetic plasticizers with an array of energetic nitrate esters such as butanetrioltrinitrate (BTTN), triethylene glycoldinitrate (TEGDN), butanenitrateoethylnitramine (BuNENA), bis-(2,2-dinitropropyl) acetal/formal (BDNPF/A), low molecular weight GAP (GAP plasticizer), and trimethylolethane trinitrate (TMETN). These plasticizers may be used independently or in combination with other plasticizers.

Table 11.6 compares the properties of some energetic plasticizers.

Apart from oxidizers, fuels, and binders, intense research and development has been going on for choosing better materials for other propellant ingredients such as burn rate modifiers and other process aids. As an example, to improve the solid loading characteristics, efforts are on to replace the conventional burn rate catalysts that are solids (e.g., iron(III) oxide or copper chromite) with liquid ones (e.g., ferrocene-based oligomers).

11.5 Polynitrogen Cages: Promising a Revolution in Future HEMs?

HEM scientists have ambitious plans for the future. On the basis of simple logic and extensive quantum mechanical calculations, the ultimate target molecules that will be the HEMs of the future must be those that have very high positive heats of formation, high densities, and very large heat release, resulting in very high VODs and detonation pressures if used as high explosives and very high I_{sp} values if used as propellants. If we

Table 11.6: Physicochemical properties of some energetic plasticizers.

Plasticizers	Structure	Density (g/cm ³)	Oxygen Balance (%)
NG	$\begin{array}{c} \text{H}_2\text{C}-\text{O}-\text{NO}_2 \\ \\ \text{HC}-\text{O}-\text{NO}_2 \\ \\ \text{H}_2\text{C}-\text{O}-\text{NO}_2 \end{array}$	1.59	+3.5
BTTN	$\begin{array}{c} \text{CH}_2-\text{O}-\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}-\text{O}-\text{NO}_2 \\ \\ \text{CH}_2-\text{O}-\text{NO}_2 \end{array}$	1.52	-16.6
<i>n</i> -BuNENA	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{O}-\text{NO}_2 \\ / \quad \backslash \\ \text{O}_2\text{N}-\text{N} \\ \backslash \quad / \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	1.20	-104
TMETN	$\begin{array}{c} \text{CH}_2-\text{O}-\text{NO}_2 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{O}-\text{NO}_2 \\ \\ \text{CH}_2-\text{O}-\text{NO}_2 \end{array}$	1.48	-34
BDNPF/A	$\begin{array}{c} \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \\ \qquad \qquad \qquad \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \\ \text{(50 \%)} \end{array}$ $\begin{array}{c} \text{NO}_2 \qquad \qquad \text{CH}_3 \qquad \qquad \text{NO}_2 \\ \qquad \qquad \qquad \qquad \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{O}-\text{CH}-\text{O}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \qquad \qquad \qquad \qquad \qquad \\ \text{NO}_2 \qquad \qquad \qquad \qquad \qquad \text{NO}_2 \\ \text{(50 \%)} \end{array}$	1.39	-51

compare RDX, HMX, CL-20, and ONC (in the same order), then we find that their densities, heats of formation, and VOD values significantly increase. One can visualize that as we go from RDX to ONC, the ring strain in the molecule increases. This strain and the nature of nitrogen bonding remarkably contribute to the positive values of heats of

formation and the energetics of the molecules. Extending this picture further, the hopes are pinned on those molecules that contain only nitrogen atoms in a strained ring structure. For example, imagine an N_8 molecule in which eight nitrogen atoms occupy the eight corners of a cube. The bond angle in this molecule becomes 90° , which is far less than 109° , a comfortable bond angle for the nitrogen compounds in which the nitrogen atom is bonded to three other atoms. Therefore, one can expect a very great degree of strain experienced by the cubic structure of N_8 , resulting in very high values of the heat of formation for the molecule. Such a molecule will be a dream molecule for any HEM scientist because when an N_8 molecule decomposes to give four molecules of nitrogen, the energy released will be stunningly high.

However, the problem is the huge challenges involved in their synthesis. Some years back, when polynitrogen compounds such as $Mg(N_5)_2$, $N_5^+SbF_6^-$, and $N_5^+SnF_6^-$ were made, it spurred the ambition of HEM scientists for planning the synthesis of polynitrogen molecules such as N_8 and N_{60} . N_8 and N_{60} will theoretically have the VOD values of 14.9 and 17.31 km/s, respectively (for HMX, it is 9.1 km/s), and heat of formation values of 407 and 546 kcal mol⁻¹, respectively (for HMX: 28 kcal/mol). However, the challenges involved in the chemistry of their synthesis are intimidating. Although some limited reports are available on the synthesis of some polynitrogen compounds such as those based on N_5^+ in the literature, it is going to be a very long and arduous journey for the HEM scientist to reach these goals.

Suggested Reading

- [1] J.P. Agrawal, R.D. Hodgson, *Organic Chemistry of Explosives*, first ed., Wiley, 2007.
- [2] J. Ledgard, *The Preparatory Manual of Explosives*, third ed., 2007.
- [3] T.M. Klapötke, *High Energy Density Materials Series: Structure and Bonding*, first ed., Springer, 2007.
- [4] R. Meyer, J. Kohler, *Explosives*, VCH Publishers, Germany, 1993 (Encyclopaedia — handy for referencing).
- [5] D.H. Liebenberg, et al. (Eds.), *Structure and Properties of Energetic Materials*, Materials Research Society, Pennsylvania, USA, 1993.
- [6] J. Akhavan, *The Chemistry of Explosives*, third ed., Royal Society of Chemistry, 2011.
- [7] N. Kubota, *Propellants and Explosives Thermochemical Aspects of Combustion*, 2007.

Questions

1. What is the necessity of lead-free initiators?
2. Initiator compounds should be sensitive. Justify the statement.
3. What is meant by coordination compounds? Name any two coordination compounds used for primary explosive purposes.
4. What is hydrogen bonding? How is it useful in achieving insensitivity/thermal stability of explosives?

5. What are the advantages of melt-cast explosives?
6. Explain the meaning of demilitarization?
7. Why is the viscosity of a polymer increased while introducing pendent groups?
8. What are the potential polymers that might replace HTPB in the future?