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Review of Promising Insensitive Energetic Materials

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Abstract: During the last twenty years military explosives, and energetic materials in general, have changed significantly. Worldwide, research and development programs are active in developing promising insensitive HEMs with higher performance. This has been due to several factors, which include new operational requirements such as Insensitive Munitions (IM), but it is also due to the availability of new materials and to new assessment and modelling techniques. The present review focuses on the basic idea and necessity for IM, and the conditions, technical requirements and tests for IM. The review also explains the various promising insensitive high explosives, their synthesis and formulation used in different propellants.

Keywords: ammunition, azoxyfurazan, insensitive munitions, safety, vulnerability

1 Introduction

In the past twenty years, military explosives and energetic materials in general have changed significantly. Worldwide, research and development programs have focused on developing insensitive HEMs with higher performance. This has been due to several factors, which include new operational requirements such as Insensitive Munitions (IM) [1], but it is also due to the availability of new materials and to new assessment and modelling techniques. This permits more effective use of materials and a more detailed understanding of the processes involved in applying the technology. In the past 50 years, many new energetic

compounds have been found as potential ingredients for explosive, propellant and pyrotechnic formulations [2]. Some of these compounds find utility in military munitions. One way of attempting to improve the performance of munitions without compromising safety is to make changes in particle size, particle shape and sensitivity mitigation by making insensitive formulations of the energetic materials. An ideal explosive [3] is one, which has high performance, but which is insensitive enough to permit safe handling. Common explosives like TNT [4], RDX [5] and HMX [6] used to be considered adequate for all weapons applications, but are no longer so due to the number of accidents involving initiation of ammunition by impact or shock. So there is a need to develop new ingredients and formulations that are insensitive to common stimuli while maintaining the desired performance characteristics [7].

The development of this class of explosives has led to the reduction of quantity distances between storage locations, decreased battle field vulnerability of armoured vehicles and personnel, and increased capacity to carry a large quantity of ordnance [8]. New explosives have been developed with promising blends of insensitivity and performance. The application of these materials is due to their exceptional properties, such as insensitivity to accidental impact and the ability to withstand high temperatures [9]. In the past two decades, the most incredible contribution of scientists/technologists working in the field of HEMs is the development of high explosive formulations that are extremely insensitive to high temperatures, shock and impact, for the initiation of nuclear explosives [10]. These insensitive high explosive (IHEs) formulations significantly advance the safety and survivability of munitions, weapons, and personnel. The central requirement is to diminish the hazards to personnel and material on accidental initiation of a weapon due to environmental stimuli, such as rough handling, fragment impact and thermal cook-off [11]. IM means ammunition or explosives that reliably fulfill their performance, readiness and operational requirements on demand, but which minimize the probability of inadvertent initiation and the severity of subsequent collateral damage to weapon platforms, logistic systems and personnel when subjected to unplanned stimuli. IMs are always filled with fire resistant and shock insensitive HEMs [12]. IM is one that will not react violently in an accident situation. IMs are munitions with enhanced safety. IMs can be achieved mainly through the incorporation of energetic materials exhibiting remarkable insensitivity.

2 Tests Required for IMs

The slow cook-off, fast cook-off, and bullet impact tests for munitions were well defined in the past as they had been performed as part of the WR-50 [13] tests. There were however no documented tests or procedures for fragment impact, sympathetic detonation, and sensitivity to electromagnetic radiation. These were new requirements [14]. DOD-STD-2105 required tests on only two munitions per stimulus, *i.e*. two for slow cook-off, two for fast cook-off, *etc*. To minimize the costs and provide additional information for use in IM assessments, NAVSEAINST 8010.5 stated the following: in addition to the requirements of [15], new energetic materials will undergo testing in munition-size hardware such as described in [16, 17]. The following data are required:

1. **Slow Cook-off** − The requirement to test for a slow increase in the thermal environment such as a fire in an adjacent magazine, store or vehicle. These types of incidents require exposure to a gradually increasing thermal environment at a rate of 6 °K/h.
2. **Fast Cook-off** − The requirement to test for a fast heating hazard comes from the ignition of liquid fuel fires such as burning aircraft fuel on a flight deck or burning diesel fuel from a truck as a result of a transportation accident. These types of incidents thus require exposure of the test item configuration to heat fluxes generated within the incandescent flame envelope of a large liquid hydrocarbon fuel fire.
3. **Sympathetic Detonation** − The requirement for this test is to determine if a sympathetic reaction response results when a detonation of an adjacent munition occurs as a result of an accident or hostile event.
4. **Multiple Bullet Impact** − The requirement to test for bullet impact threat from small arms during terrorist or combat events. These events require the test item to be impacted by a three-round burst of 0.50 caliber AP projectiles.
5. **Multiple Fragment Impact** − The requirement to test comes from combat or terrorist events where bombs, artillery shells or IEDs are detonated. These types of events thus require the test item to be subjected to the effects of a high-velocity impact of a calibrated fragment representative of a bomb or artillery fragment.
6. **Shaped Charge Jet Impact Testing** − The requirement to test for a shaped charge jet threat comes from combat or terrorist events where rocket propelled grenades, land mines, airborne bomblets or guided weapons are deployed. These types of events thus require the test item to be subjected to a direct hit from a representative shaped charge jet.

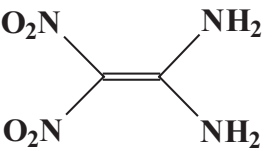
   These tests will provide the reliable data necessary to assess the relative

sensitivity of the materials in realistic situations and at a more reasonable cost than all-up munitions testing.

3 Promising Insensitive High Explosives and Their Applications

3.1 1,1'-Diamino-2,2'-dinitroethylene (FOX-7)

1,1'-Diamino-2,2'-dinitroethylene (FOX-7, or DADNE) is emerging as a potential candidate for use as an insensitive high explosive. The R & D work on FOX-7 is continuously pursued with great interest in many developed countries, where the process has been scaled up to pilot plant level.



FOX-7

Figure 1. Structure of FOX-7

The Swedish Defence Research Agency [18] has developed FOX-7, which attracted considerable attention because of its sensitivity being lower than TATB [19] and its performance being comparable with RDX and HMX [20]. Politzer *et al*. [21] have pointed out that this compound has the same molecular stoichiometry as RDX and HMX. It is interesting to note that the reported activation energy of decomposition (E_a = 58 kcal/mol for the temperature interval 210 °C to 250 °C) for FOX-7 is higher than that of RDX (E_a = ~40 kcal/mol) and HMX (E_a = ~35 kcal/mol), which favours FOX-7 as an insensitive explosive. The sensitivity of FOX-7 to physical stresses, such as impact, friction, heat *etc*., has been extensively studied [22]. These studies support FOX-7 as a prime candidate as an energetic filler in insensitive munitions. FOX-7 was first synthesized in 1998 by Latypov *et al.* [23], however since then different synthetic methods have been developed and FOX-7 is now synthesized in a pilot plant on a multi-kilogram scale by NEXPLO Bofors, Sweden. Baum *et al*. [24] synthesized several 1,1-bis-(alkylamino)-2,2-dinitroethylenes by reacting 1,1-diiodo-2,2-dinitroethylene (DIDNE) with alkylamines. FOX-7 is prepared by the hydrolysis of 2-(dinitromethylene)-4,5-imidazolidinedione with aqueous ammonia. It has interesting properties as a high explosive and also finds application in the

synthesis of nitrogen heterocycles. Thus, this compound is a potential candidate for LOVA (Low Vulnerability Ammunition) [25].

RDX is considerably cheaper than FOX-7, however increasing demand for low vulnerability explosives (LOVEX) for IMs [26] has led to the initiation of exhaustive applied research on high explosive formulations based on FOX-7, reported by many researchers to be a promising candidate. Lochert *et al*. [27] has reported that FOX-7 is significantly less sensitive than RDX, particularly to impact and friction stimuli and is compatible with TNT-based, melt-cast compositions. The velocity of detonation and detonation pressure of FOX-7 charges are marginally higher than those for RDX charges, the detonation pressure showing a 5% increase [28]. Wild and Teipel [29] have also reported that the performance of FOX-7 is better than that of TNT and close to those of nitramines, with relatively insensitive characteristics.

A plastic bonded explosive (PBX) formulation of FOX-7 with a polyGlyn binder has been reported by Karlsson *et al*. [30]. This formulation does not detonate up to a diameter of 25 mm in large-scale detonation and small-scale slow cook-off tests. The composition ignites at 220 °C on slow heating (3.3 °C/h) and burns without damage to the container [31]. A new formulation based on FOX-7 and HMX (called FOF-5), with the same theoretical performance as Composition B, has been developed by FOI Weapons and Protection Division, Swedish Defense Research Agency [32]. This composition has been tested with respect to its low sensitivity properties by applying fast heating, slow heating and bullet impact tests. The response of a FOF-5 loaded 40 mm gun munition (with an HNS II-based fuse) in the fast heating test was Type IV (deflagration), Type V/IV (fire/deflagration) in the slow heating test, and Type V (fire) in the bullet impact test. Composition B shows a detonation response in all of the above tests. The loading of FOX-7 in these formulations has been restricted to a maximum of 30% by weight in non-aluminized formulations and a maximum of 25% by weight in aluminized formulations. Melt cast formulations [33] based on FOX-7 and TNT showed that these formulations will find application as insensitive high explosive formulations for future applications in insensitive munitions.

3.2 Guanylurea dinitramide (GUDN or FOX-12)

Energetic dinitramides are interesting high energy materials for present and future demands [34]. N-Guanylurea dinitramide (GUDN or FOX-12) is a stable salt of dinitramidic acid, with good thermal stability and low water absorbency [35]. It does not respond to mechanical stimuli, which makes it an excellent component for many insensitive energetic material applications.

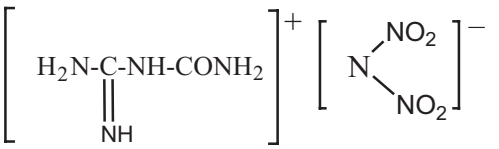
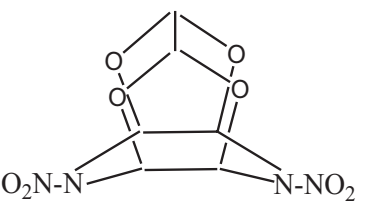


Figure 2. Structure of GUDN

GUDN is an insensitive energetic ingredient for insensitive munitions, such as LOVA propellants for artillery modular charges, the main component in warhead fillings like general purpose bombs, artillery, tank and mortar ammunition. The use of powerful, safer and eco-friendly explosives is the main criteria of ammunitions during propellant formulations [36]. GUDN is a low vulnerability energetic material, to impact and friction stimuli and is a good candidate for IM [37]. Its thermal stability is comparable to RDX and superior to that of ammonium dinitramide (ADN). GUDN can find application in LOVA propellants [38], melt cast and PBX high explosive formulations [39]. Besides the advantages of low sensitivity, GUDN burns with an extremely low temperature, which is important in automatic guns where barrel erosion is often a problem. The synthetic route to FOX-12 involves the nitration of ammonium sulphamate using mixed acid at low temperature [40].

3.3 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX)

TEX has a crystal density of 1.99 g/cm^3, the highest known density of all CHNO based explosives. The high density is due to its isowurtzitane structure, having a close-packed crystal lattice, with nitro groups occupying the free space between the cages. TEX [41a] is very energetic (due to the strained cage structure), combining a high velocity of detonation with low sensitivity to mechanical stimuli and good thermal stability. The insensitive nature of TEX [41b] suggests that it may be a suitable high performance alternative to TATB, NTO and RDX.



TEX

Figure 3. Structure of TEX

TEX was synthesized in two steps, namely synthesis of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP) followed by nitration of the latter using commercially available fuming nitric acid. TEX was formed by the cyclization and nitration of the DFTHP. Glyoxal dihydrate trimer and DFTHP underwent cyclization in the presence of sulphuric acid to yield diformyltetra oxo-isowurtzitane (DFIW). DFIW was further nitrated by nitric acid *in situ* to give TEX.

3.4 3-Nitro-1,2,4-triazol-5-one (NTO)

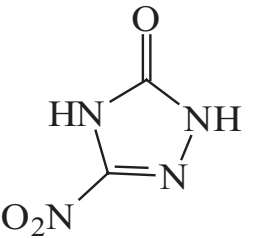


Figure 4. Structure of NTO

3-Nitro-1,2,4-triazol-5-one (NTO) is an insensitive high explosive ingredient, a potential replacement for RDX in explosive formulations [42]. Although its performance is slightly less than that of RDX, NTO is more thermally stable and less sensitive to hazard stimuli.

The problems associated with calamitous mishaps, sympathetic detonations and dimensional instability at elevated temperatures have made common explosives, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrohexahydro-s-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) less attractive in certain applications, where materials are subjected to extreme conditions while being transported or stored.

3-Nitro-1,2,4-triazol-5-one (NTO) has emerged, albeit recently, as a strong candidate as an IHE and development of IM-class formulations containing NTO is underway worldwide. NTO has performance levels close to those of RDX and its insensitivity is comparable to TATB. Its thermal stability is also high and decomposes exothermically around 272 °C. NTO-based pressable and castable explosive formulations exhibit superior mechanical and thermal properties and are insensitive [43]. NTO-based PBX development has been performed, predominantly at SNPE, where much work was undertaken on the "B series" compositions [44].

3.5 Reduced shock sensitivity RDX (RSS-RDX)

RDX [45, 46] is the foremost military explosive used in most warheads, alone or in combination with other materials such as TNT, binders or some additives. RDX is sensitive to mechanical stimuli such as impact and friction, as well as being also sensitive to shock [47]. In recent years much interest has been devoted to RDX in another form, namely reduced sensitivity RDX (RSRDX) [48] or insensitive RDX (IRDX), which when incorporated in cast-cured plastic bonded explosives (PBX-109), can confer reduced shock sensitivity, as measured by the gap test [49]. I-RDX [50] was first realized by SNPE, France, in the 1990s. Later many manufacturers claimed RSRDX having special features, such as high quality crystals and high density, and cast PBX formulations based on RSRDX having less shock sensitivity than that based on standard RDX [51].

Figure 5. Shock sensitivity test set up

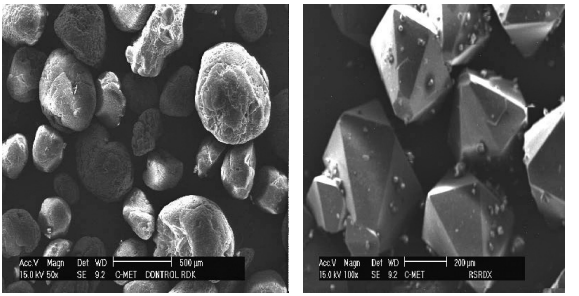


Figure 6. SEM image of RSSRDX

Reduced sensitivity RDX (RS-RDX) offers the potential to reduce the vulnerability of munitions [52]. RSS-RDX has been identified and distinguished from RDX by a flotation density method using anhydrous zinc bromide solution. RDX crystals floated completely and RSSRDX crystals sedimented completely.

An RSS-RDX-based PBX formulation is less shock sensitive than a conventional PBX formulation [53]. RSS-RDX based weapons exhibit low vulnerability to accidental initiation − IM [54].

3.6 Amino nitro heterocyclic N-oxides as HEMs

Difficulties in synthesizing several heterocyclic compounds bearing nitro, amino and N-oxide substituents have been studied, as potential replacements for existing insensitive explosives such as FOX-7 and NTO [55]. The use of nitro compounds of different heterocycles such as pyridines, pyrimidines, pyrazines and their bicyclic analogues had been reported as insensitive explosives by Millar and coworkers [56]. Molecular modelling studies indicated that ANPZ-i would have a similar performance to RDX, with an anticipated greater insensitivity. ANPZ-i as a novel high energy insensitive explosive has therefore been reported by Philbin *et al*. [57].

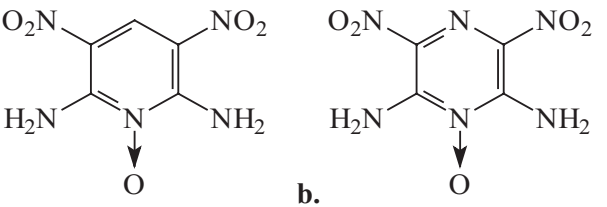


Figure 7. Structure of (a) 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) and (b) LLM-105

Ritter and Licht [58] reported the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO, Figure 7a) by the nitration of 2,6-diaminopyridine (DAPy) followed by oxidation with a mixture of acetic acid and 30% hydrogen peroxide. Hollins *et al*. [59] extended this work and synthesized 2,4,6-triamino-3,5-dinitropyridine N-oxide by the amination of ANPyO with hydroxylamine in aqueous potassium hydroxide in 39% yield. Tran *et al*. [60] synthesized 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105, Figure 7b) by reacting 2,6-dichloropyrazine with sodium methoxide to yield 2-methoxy-6-chloropyrazine. This compound was then nitrated with mixed acid at 70 °C and treated with NH_4OH in CH_3CN at 60 °C to yield 2,6-diamino-3,5-dinitropyrazine (ANPZ) [61]. The oxidation of ANPZ with a mixture of trifluroacetic acid and 30% H_2O_2 yielded LLM-105 in 48% yield from 2,6-dichloropyrazine. LLM-105 has a density [62] of 1.918 g/mL and a decomposition point of 354 °C.

Pagoria *et al*. [63] have synthesized LLM-105 from ANPZ. LLM-105, first synthesized at Lawrence Livermore National Laboratory, USA, is a dense

molecule ($\rho = 1.91$ g/cm^3) with excellent physical properties, good safety characteristics and 20% more energy than TATB [64]. It is insensitive to spark and friction and has impact insensitivity ($h_{50\%} = 117$ cm) approaching that of TATB (>177 cm) [65].

3.7 3-Amino-5-nitro-l,2,4-triazole (ANTA)

3-Amino-5-nitro-l,2,4-triazole (ANTA), an amino-nitro-heterocyclic compound has received some interest as an energetic material due to its greater heat of formation [66]. Explosives containing a triazole ring are of multipurpose interests because the heterocyclic ring system confers a high density, thermal stability, high nitrogen content, high volume of detonation products, and insensitivity to impact [67]. ANTA was found to be an insensitive energetic material with a density of 1.81 g/cm^3, heat of formation 61 kcal/mol, m.p. 238 °C and performance less than that of TATB.

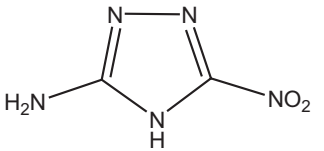


Figure 8. Structure of ANTA

ANTA was first prepared by Pevzner *et al*. [68] starting from commercially available 5-amino-1,2,4-triazole. A second route to ANTA, reported by Pevzner *et al*. in 1982, involves the oxidation of 1-acyl-3,5-diamino-l,2,4-triazole with hydrogen peroxide. A further alternative route to ANTA was developed by Lee, Storm [69] starting with commercially available 3,5-diaminotriazole. Lee *et al*. [70] subsequently reported an improved synthesis that involves treatment of 3,5-diamino-1,2,4-triazole with $NaNO_2$ in H_2SO_4 and heating to 60 °C to yield 3,5-dinitro-1,2,4-triazole.

3.8 Triaminotrinitrobenzene (TATB)

TATB is currently the most important IHE and is used in modern nuclear warheads worldwide. Its attributes are greater thermal, physical and shock stability, all of which are greater than those of any other known material of comparable energy [71]. TATB was first obtained in 1888 by Jackson and Wing [72]. TATB can be readily obtained from aniline and is qualified as a heat resistant explosive. The unique structure of TATB confirms its properties, which include high density and extreme insensitiveness to impact and shock.

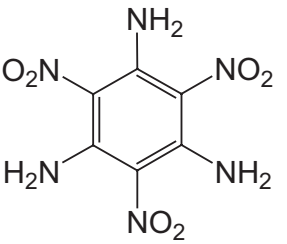


Figure 9. Structure of TATB

It is used extensively in military applications, mainly because of the cost of the materials. Recently a synthesis of TATB from picramide or 1,3,5-trinitrobenzene was reported in three patents by Mitchell *et al*. [73] at Lawrence Livermore National Laboratory, which may significantly reduced the cost of TATB. A series of new explosive compositions (PBXs) were developed with a promising blend of insensitivity, performance and thermal stability [74].

Several compositions based on TATB have been reported as main-charge explosives. PBX-9502 (TATB 95% and Kel-F 800 5%) is a main-charge explosive [75] formulation with comparatively low performance but very low shock sensitivity; RX-26-AF (HMX 49.3%, TATB 46.6% and Estane 4.1%) is another main-charge explosive formulation with comparable performance but increased shock sensitivity; PBX − 9503 (TATB 80%, HMX 15% and Kel-F 800 5%) was developed as a booster formulation for PBX-9502. TATB/Kel-F 800 and TATB/Viton compositions are the most stable and attractive for long-term use [76]. To improve the performance of TATB-based PBX compositions, HMX and TATB mixture-based PBX formulations were explored to find a favorable compromise between the prime properties of explosive safety and excellent performance. For this purpose, HMX, which has excellent power performance but is more sensitive to impact, was mixed with IHE TATB. Some explosive formulations based on HMX, TATB and KeL-F were characterized for density, VOD, initiation sensitivity, ignition temperature and other explosive properties [77].

3.9 Diaminoazoxyfurazan (DAAF)

Diaminoazoxyfurazan (DAAF) is an insensitive high explosive [78] first synthesized in Russia in the 1980s, and the synthesis was developed at Los Alamos National Laboratory in the early 2000s. DAAF has safety characteristics (impact, friction) similar to those of TATB [79], but a critical diameter of less than 3 mm and shock sensitivity similar to HMX. The combination of these characteristics is unusual and makes DAAF an interesting explosive that is suitable for booster applications.

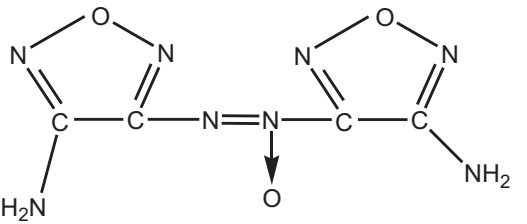


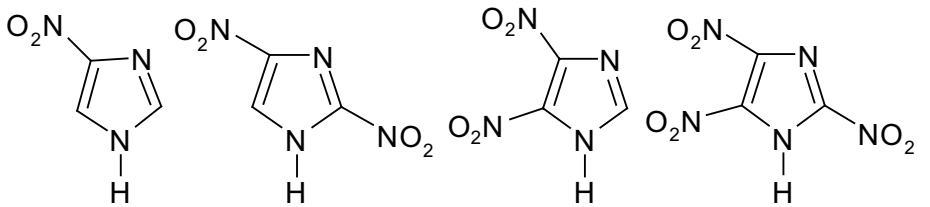
Figure 10. Structure of DAAF

3,4-Diaminofurazan (DAF), first synthesized by Coburn [80] in 1968, has been an important precursor for a series of furazan-based energetic materials that are interesting as both propellant and explosive ingredients. DAF may be synthesized by the condensation of hydroxylamine with a variety of reagents, including dithiooxamide, cyanogen, glyoxal, and glyoxime, to yield diaminoglyoxime followed by cyclization to DAF by treatment with aqueous base at 180 °C in a pressure vessel. Solodyuk *et al*. [81] reported that the oxidation of DAF with hydrogen peroxide under various conditions yields 3-amino-4-nitrofurazan (ANF), 4,4'-diamino-3,3'-azoxyfurazan (DAAF), or 4,4'-diamino-3,3'-azofurazan (DAAzF). Hiskey *et al*. [82] scaled-up the synthesis of DAAF and performed measurements of its explosive properties, including a poly-r test, a mini-wedge test and a standard 1 in cylinder test. DAAF has a crystal density of 1.747 g/mL, a ΔH_f of 106 kcal/mol and DH_{50} >320 cm (2.5 kg, Type 12). DAAF is pure orange-yellow, has a DSC onset of 248 °C and an X-ray crystal density [83] of 1.747 g/cm^3. The heat of formation (ΔH_f) was measured as +443 kJ/mol by combustion calorimetry. DAAF has a drop height (H_{50}) greater than 320 cm (2.5 kg, Type 12) and elicits no response to spark (>0.36 J) or friction (>36 kg, BAM) [84].

3.10 Imidazole based HEMs

Imidazole is a five membered heterocyclic compound containing two nitrogen atoms in its structure. Imidazole derivatives with more than two nitro groups are expected to be powerful insensitive explosives. 2, 4-Dinitroimidazole (DNI) is much less sensitive than RDX and HMX and is 15-20% more energetic than triaminotrinitrobenzene (TATB). It is expected to be relatively cheap since it is made from inexpensive starting materials. Various nitroimidazole derivatives (structures 2-5), including 2,4-dinitroimidazole [85], 4,5-dinitroimidazole [86], 2,4,5-trinitroimidazole and 4,4',5,5'-tetranitro-2,2'-benzimidazole [87], have been investigated so far. One of the problems concerning these molecules is their chemical stability associated with the hydrogen attached to

the 1-position, which is known to be quite acidic. The nitration of position 1 is possible and the synthesized 1,4-dinitroimidazole is easily isomerised to 2,4-dinitroimidazole by heating at a modest temperature, in solution or in the solid state. Polynitroimidazole derivatives (Figure 11: 1-4) have attracted renewed attention of high energy materials (HEMs) chemists due to their favorable explosive performance [88]. Bulusu *et al*. [89] synthesized 2,4-dinitroimidazole (2,4-DNI) and found it to be a highly promising, high energy material.



4-nitro-1H-imidazole **(1)** | 2,4-dinitro-imidazole **(2)** | 4,5-dinitro-imidazole **(3)** | 2,4,5-trinitro-imidazole **(4)**

Figure 11. Structures of various imidazoles (**1**-**4**)

3.11 Dihydroxylammonium 5,5′-bis-tetrazole-1,1′-diolate (TKX-50)

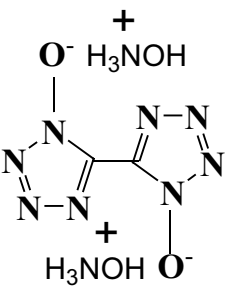


Figure 12. Structure of TKX-50

Dihydroxylammonium 5,5′-bis-tetrazole-1,1′-diolate (TKX-50) [90] is a recently synthesized energetic material (EM) with a most promising performance, having high energy content, high density, low sensitivity, and low toxicity. TKX-50 forms an ionic crystal in which the unit cell contains two bis-tetrazole dianions {c-((NO)N_3C)-[c-(CN_3(NO)], formal charge of -2} and four hydroxylammonium $(NH_3OH)^+$ cations (formal charge of +1). TKX-50 is one of the most promising ionic salts, as a possible replacement for RDX [91]. The

thermal behaviour of TKX-50 and the kinetics of its thermal decomposition were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It was found that the thermal decomposition [92] of TKX-50 starts in the range 210-250 °C, depending on the heating rate.

3.12 Application of nanotechnology for insensitive munitions

The recent introduction of nanomaterials into the science of energetic materials has resulted in many exciting new developments. It has opened new applications for existing materials by significant improvement in their properties. For example, the slow energy release of conventional thermite materials makes them suitable only for some traditional applications such as welding; on the other hand, nanothermites [93] with their fast reaction velocities have been proposed for use in a variety of contexts such as igniters, actuators, microthrusters [94], micro- and nanoelectromechanical systems, as well as lead-free primers for ammunition [95]. On the other hand, the detonation of an explosive can be used for synthesizing nano materials, for example nanodiamonds [96], which have many potential applications. Energetic materials are usually sensitive to mechanical stress, impact and friction, and to electrostatic discharge. Accidental initiation by one of these types of stress can lead to grave injury or to the destruction of the device in which the energetic material is embedded. This is why safety has become the prime criterion of choice in selecting energetic materials for industrial applications. In some cases, even a slight reduction in the performance of a material is acceptable if it is correlated with a reduction in sensitivity. From a military point of view, there is another consideration: high sensitivity means high vulnerability, for example to nearby impacts of projectiles. Thus, concepts like LOVA [97] have been created, leading to propellant and explosive formulations with reduced sensitivity.

3.13 Insensitive high energy materials for advanced gun propellants

All of the globally produced gun propellants have been focused on the utilization of nitrocellulose (NC), with NC-based and higher energy double base propellants (also with nitroglycerine or related energetic plasticizers). However, developments have been made with the use of new materials that raise the energy density without unacceptable increases in flame temperature. Much work has addressed the use of the crystalline, cyclic nitramines RDX and HMX, and by the 1980s, joint efforts by the U.S. Navy and Army had led to the first service-qualified nitramine-based gun propellant for low-vulnerability (LOVA) ammunition [98]. Since then, unusually high energy density ingredients such as CL-20 [99], TNAZ (1,3,3-trinitroazetidine), and ADN (ammonium dinitramide)

Table 1. Physico-chemical properties of promising Insensitive High Explosives

Properties	RDX [5, 6]	RSSRDX [48, 49]	FOX-7 [19, 21, 22, 27]	FOX-12 (GUDN) [34, 35, 36]	NTO [42, 43]	TEX [41a, 41b]	DAAF [78, 79, 84]	LLM-105 [55, 57, 58]	TATB [64, 65, 72]	TKX-50 [90-92]
DSC, Decomp. temp. [°C]	204	238.8	260	217	272±2	>250	249	354	> 350	221
Oxygen balance [%]	−21.6	−21.6	−21.6	-19.1	−24.6	−42.7	−22.64	−37	−55.8	−27
PcJ [GPa]	34.1	34.1	33.7	25.7	349	365	306	341	300	424
Velocity of Detonation, VOD [m/s]	8750	8750	8800	8210	8500	8749	7930	8560	8100	9687
Impact sensitivity [cm]	42	39	126	>49	87	170	>320	117	170	110
Friction sensitivity [kg]	16	16	36	>33.5	36	49	>36	>36	> 36	15
ΔHf [kcal/mol]	16	16	−32	−355	3.1	−106	+106	+124	−33.4	+106
Density [g/cm^3]	1.82	1.82	1.87	1.75	1.93	1.99	1.74	1.91	1.93	1.91

have been recognized and evaluated in promising new superior gun propellants. CL-20 is extremely attractive as an energetic filler because of its heat of formation (+100 kcal/mol), density (2.04 g/cm^3), and influence on burning rates. Concurrently, new binders were developed to replace the historical workhorse NC. Thermoplastic elastomers (TPEs) process like thermoplastics but behave like elastomers at gun operating temperatures, while offering the opportunity for easy inclusion of energetic fillers, good physical properties, and recycling. Early LOVA formulations were based on energetic fillers in nonenergetic binders, but the quest for higher performance led to the focus on the use of energetic TPEs (or ETPEs, such as the oxetanes BAMO (3,3-bis(azidomethyl)oxetane) and AMMO (3-azidomethyl-3-methyloxetane)) (Figure 13) [100].

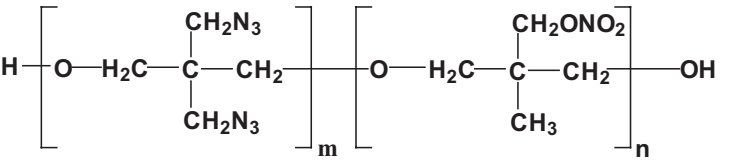


Figure 13. BAMO-AMMO co-polymer

4 Conclusions and Perspectives

This review covers the synthetic aspects along with the applications of various promising insensitive energetic materials. The development of these classes of explosives have led to a reduction in quantity distances between storage sites, a decrease in the battle field vulnerability of armoured vehicles and personnel, and an increased capacity to carry a large quantity of ordnance. A series of new explosives have been developed with promising blends of insensitivity and performance. The application of these materials is due to their special properties, such as insensitivity to accidental impact and ability to withstand high temperature. The review compiles informative data on various promising insensitive high explosives and their emerging applications in propellant applications. The review also emphasizes the application of nanotechnology for insensitive munitions and advanced materials for gun propellant formulations.

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