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Review

Emerging Trends in Green Primary Explosives: A Review

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Abstract: This review emphasizes the noteworthy and diverse kinds of primary explosives (PEs), and the prerequisites for substance to act as a PE. In addition, it describes the limits of the presently used PEs. It also emphasizes the significance of green PEs and probable candidates as green PEs by revised information.

Keywords: green primary explosives, high energy materials, lead azide, lead styphnate, nitrotetrazole

Synonims and abbreviations:

BLA	Basic lead azide
BNCP	Tetraammine-bis-(5-nitrotetrazolato-N^2) cobalt(III) perchlorate
DBX-1	Copper(I) salt of 5-nitrotetrazole
DDT	Deflagration to detonation transition
DNDTF	*Di*(triaminoguanidinium)-3-nitramino-4-(3-(dinitromethanidyl)-1,2,4-triazol-5-yl) furazanate
EM	Energetic material
HEM	High energy material
HNT	5-Nitrotetrazole
ICM-103	6-Nitro-7-azido-pyrazol[3,4-d][1,2,3]triazine-2-oxide
KDNBF	Potassium 4,6-dinitro-7-hydro-7-hydroxybenzfuroxanide
KDNP	Potassium salt of 4,6-dinitro-7-hydroxybenzofuroxan
K2ABNAT	Potassium 5,5’-azobis(1-nitraminotetrazolate)
K2BDFOF	Dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan
K2DNABT	Potassium 1,1’-dinitramino-5,5’-bis(tetrazolate)
K2DNAT	Dipotassium salt of 1,5-dinitramino tetrazole
LA	Lead azide
LS	Lead styphnate
MF	Mercury fulminate
MTX-1	1-[(2E)-3-(1*H*-Tetrazol-5-yl) triaz-2-en-1-ylidene]methanediamine
ONPP	Octanitropyrazolopyrazole
PE	Primary explosive
PE-13	*Bis*-(5-nitrotetrazolato) copper(II)
TAT	1,3,5-Triazido-2,4,6-triazine

1 Introduction

1.1 Energetic materials (EMs)

EMs play a crucial role in a range of aspects of modern life, with significant implications for defence, industry, and scientific research. Materials that discharge a huge amount of energy in a short time span are defined as high-energy materials [1-11]. EMs should contain enormous amount of power in a dense and readily deliverable form. EMs includes various classes of chemical compositions of fuel and oxidant that respond rapidly upon initiation. In this process, they generate power during the production of product species and progress at high-speed, releasing important quantities of power in the form of heat and light [12-20]. The power of an EM is a function of the rate at which energy is liberated. These

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features have been utilized in many industrial, space and military applications. However, these have not been entirely optimized. This is primarily due to the inability to identify and know the basic chemical and physical steps that control the material changing to its final products. The requirements in developing capabilities for war-fighting within the military, space applications including satellites for daily life, mining, construction, road building, automobile safety airbags, and other related industries, necessitates the search for new high energy materials (HEMs) [21-27]. EMs are primarily of three types, explosives, propellants, and pyrotechnics.

1.2 Types of explosives

Explosives have been classified according to their chemical nature (sensitiveness), performance and applications. As a primary understanding, chemical explosives have been classified as primary explosives (PEs) and secondary explosives, depending on the sensitivity of an explosive to stimuli. PEs refer to those that readily detonate upon exposure to minimal energy sources, such as light or mechanical forces. By contrast, secondary explosives, often referred to as high explosives, require a substantial shock or high-energy impulse to initiate detonation. PEs typically detonate when subjected to heat, while some secondary explosives can burn when present in small quantities. Sensitivity tests have been designed to evaluate the response of a particular explosive to thermal and mechanical stimuli. Certain energetic compounds exist at the boundary between primary and secondary explosives [28-31].

Low explosives, which contain the essential oxygen content for their ignition, are primarily composed of flammable materials that pass through deflagration when ignited on their surface. Although low explosives can also explode when confined, this occurs due to the increased pressure resulting from the discharge of gaseous products. Certain explosives can detonate under confinement when triggered by the shock from an additional explosive. Light explosives comprise materials such as gunpowder, smokeless powder and propellants for weapons. By contrast, high explosives do not depend on confinement for detonation, as their chemical reactions are significantly faster and lead to physical detonation. In these substances, a high-pressure shock wave initiates the chemical reaction, propagating it through the explosive material. High explosives are expected to detonate with a detonation velocity (VoD) ranging from 5500 to 9500 m/s. The VoD serves as a proportional metric for evaluating the action of diverse explosives. High explosives comprise compounds similar to trinitrotoluene (TNT), nitroguanidine (NG), hexogen (RDX) and octogen (HMX) [33-37].

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PEs are highly responsive substances that can be effortlessly detonated when exposed to a choice of stimuli, such as fire, spark, impact, friction, and more. Handling them requires extreme caution due to their high reactivity, and they are typically utilized in small quantities. PEs find common use in applications like primers, detonators, and percussion caps. Some examples of PEs include lead azide (LA), mercury fulminate (MF), silver azide, basic lead azide (BLA), and others [38-40].

Secondary explosives, by contrast, exhibit much lower sensitivity to both mechanical shock and open flame. They necessitate a more considerable shock to be initiated to detonation, typically achieved by detonating a small adjacent quantity of a PE. Major examples of secondary explosives include RDX, HMX, CL-20, and others. PETN is often regarded as a reference explosive in this category [41].

The basic distinction between primary and secondary explosives lies in their initiation mechanisms: PEs are triggered by a flame, while secondary explosives are triggered by shock waves. One vital characteristic of PEs is their capacity to show a rapid transition from deflagration to detonation (DDT). As a result, the strength and susceptibility of PEs are measured by the speed of this DDT. A good PE should exhibit a rapid DDT. However, the rapidity of DDT becomes a weakness when an accidental deflagration initiation leads to a detonation event [42, 43]. The basic requirements of substances to act as PEs are:

(i) The substance has to be safe to handle and have a rapid deflagration to detonation transition (DDT).
(ii) It should be thermally stable up to > 150 °C and should have a melting point >90 °C.
(iii) The substance should also possess high detonation performance and sensitivity.
(iv) The substance should be chemically stable for long periods.
(v) The substance should not contain toxic heavy metals or other known toxins that endanger health, and should be environmentally safe.
(vi) Synthesis of the substance should be cost effective.

1.3 General data on substances that are already used as PEs

Lead azide (LA, PE-1, see Section 2.2), lead styphnate (LS, PE-2, see Section 2.3), and mercury fulminate (MF, PE-3, see Section 2.4), have served as PEs for general and armed applications, such as detonators, blasting caps and detonators, and were produced in the 19th century. Despite around one hundred years of research, no suitable alternatives for MF, with the required stability, sensitivity and performance, have been found [42].

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Mercury and its compounds were known to be extremely toxic to living organisms, particularly warm-blooded species. Consequently, the use of MF in civil primers and blasting caps is now banned worldwide, due to its harmful effects on human health and ecosystems.

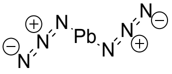
The environmental criteria for any initiating explosive should cover the following attributes [32-40]:

- **Resistant to moisture and light:** It should exhibit insensitivity to both moisture and light to ensure stability and reliability.
- **Initiation sensitivity, yet safe to handle and transport**: It must be sensitive enough for consistent initiation but not extremely sensitive, ensuring safe handling and transportation.
- **Thermal stability up to 200 °C:** The explosive should maintain its stability and integrity when exposed to temperatures as high as 200 °C.
- **Long-term chemical stability:** It should remain chemically stable for extended periods to guarantee consistent performance over time.
- **Free of toxic metals:** The explosive should be free from lethal metals such as lead, mercury and others, to avoid harm to the environment and living organisms.
- **Absence of perchlorate:** It should not contain perchlorate, which is teratogenic and can affect thyroid function, to ensure safety and environmental friendliness.

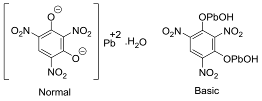
2 Characteristics of Substances Regarded as PEs

2.1 Comparison of substances taken into consideration

The chemical structures of chemical compounds taken into consideration in this paper, (PE-1 to PE-29), are presented in Figure 1. Their most important data, taken from the literature, are listed in Table 1.



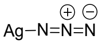
PE-1



PE-2 (two structures)

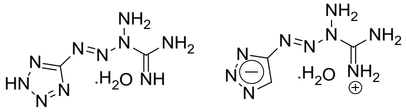
$Hg(CNO)_2$

PE-3

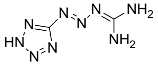


$Ag-N=\overset{\oplus}{N}=\overset{\ominus}{N}$

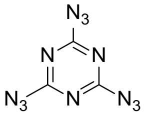
PE-4



PE-5 (the chemical and zwitter ionic structures)



PE-6



PE-7

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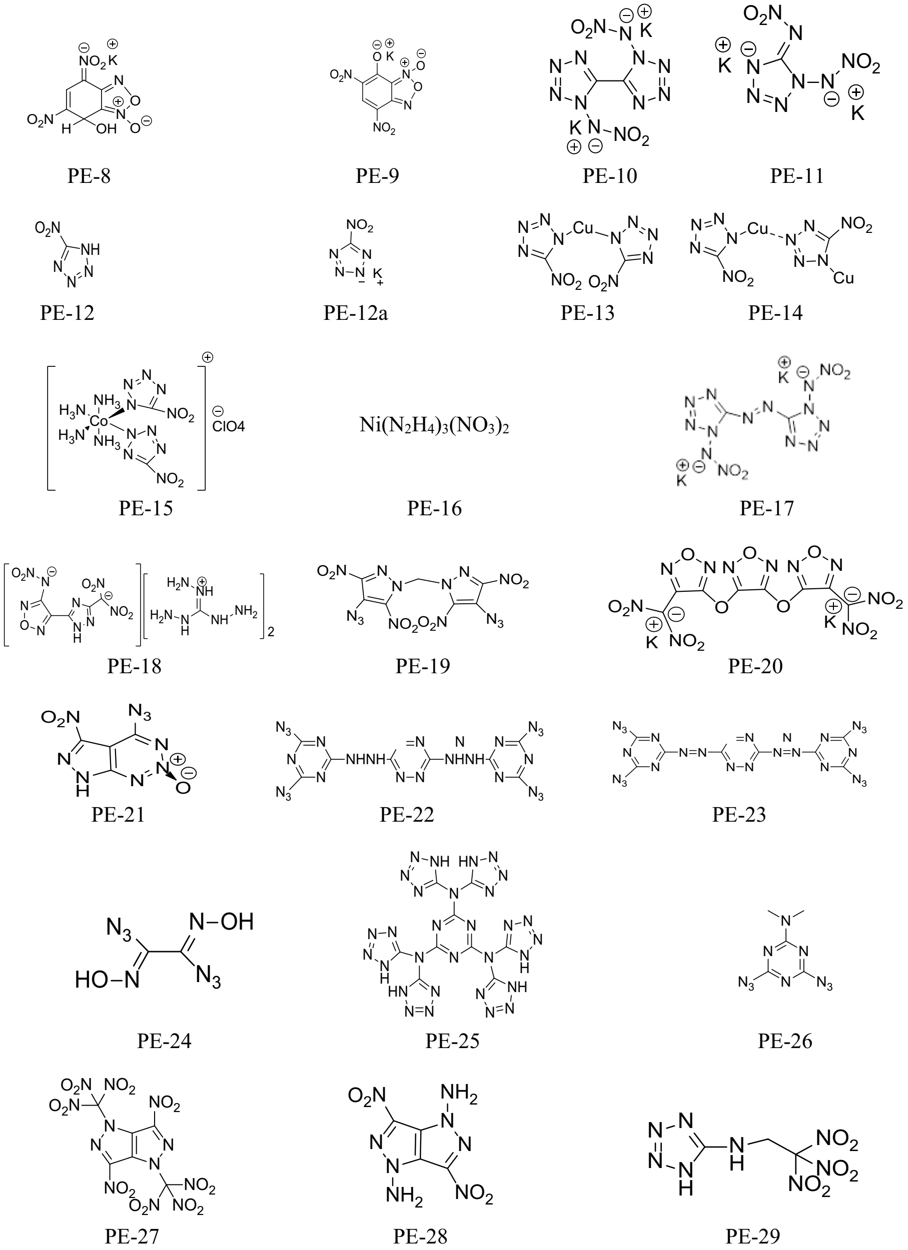

Figure 1. Chemical structures of known and possible PEs

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Table 1. Fundamental explosive properties of the substances discussed as PEs: – density (*D*), T_i – ignition temperature, T_d – thermal decomposition temperature, IS – impact sensitivity, FS – friction sensitivity and VoD – detonation velocity

Abbreviation		*D* [g/cm^3]	T_i [°C]	T_d [°C]	IS [J]	FS [N]	ESD [mJ]	VoD [m/s] at density ([g/cm^3])	Ref.
PE	Commonly known as								
PE-1	LA	4.80	350	315	0.089	<1	4.7	4500 (3.8) 5300	[43-44]
PE-2	LS	3.02$^{a)}$; 1.4-1.6$^{b)}$	267-268	282	2.5-5	0.1	0.2	5200	[45-47]
PE-3	MF	4.42$^{a)}$	170	<170	2.5	5	0.5-0.6	4250 4740 (3.96)	[47-52]
PE-4	SA	4.42$^{a)}$	272	340	<1	<0.1	18	3000	[53-61]
PE-5	Tetrazene	1.64-1.65$^{a)}$	160	135-140	1-2	27	2.7	5300	[62, 63]
PE-6	MTX-1	1.64	214	214	0.016	7.85	3.30	–	[64-67]
PE-7	TAT	1.91	205	175-180	0.4-0.5	5	<360	7350 (1.86)	[68, 69]
PE-8	KDNBF	_	210	190	7	5	6	–	[70, 71]
PE-9	KDNP	1.9-2.01	–	270	2	20	–	–	[72, 73]
PE-10	K2DNABT	2.11	–	200	1	<1	–	8330	[74]
PE-11	K2DNAT	2.17	–	240	1	5	–	10000	[75]
PE-12	HNT	1.73	–	–	–	–	–	8900 (1.73)	[76-78]
PE-12a	–	2.027	195	–	3.0-6.5	0.1-1.0	–	–	[81]
PE-13	–	1.7-2.0	–	278	3-4	30-47	–	–	[83-86]
PE-14	DBX-1	2.58	356	333	0.04	0.4	7.3	>7000	[87]
PE-17	K2ABNAT	2.11$^{a)}$	–	189$^{c)}$	1-2	<1		8367	[92]
PE-18	DNDTF	1.75	260-280	183$^{c)}$	17.4	240	0.225	8806$^{d)}$	[93-95]
PE-19	–	1.76	–	159	2	353	–	8459	[96-98]
PE-20	K2BDFOF	2.09	–	221	1-2	≤1	–	8431	[99-102]
PE-21	ICM-103	1.86	–	160	4	60	130	9111	[103]
PE-22	–	1.755$^{a)}$	–	194	7.4	120	0.205	8365	[104-106]
PE-23	–	1.763	–	189	5.3	29.1	0.174	8602	[104-106]
PE-24	–	–	–	170	1.5	<5	7	–	[107, 108]
PE-25	–	1.88$^{d)}$	–	300	>50	>360	–	7430	[109]
PE-26	–	1.45	–	152	>40	>360	–	5990	[110]
PE-27	ONPP	1.997	–	160	7	40	–	9182	[111, 112]
PE-28	–	1.95	–	145	3	20	–	9460	[113]
PE-29	–	1.85	–	150	15	–	–	8771	[114]

$^{a)}$ crystal density; $^{b)}$ bulk density; $^{c)}$ heating rate of 5°C/min; $^{d)}$ – calculated value

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2.2 Lead azide (LA, PE-1)

LA, see PE-1 in Figure 1, exhibits high sensitivity and is frequently stored underwater in insulated rubber containers to mitigate risk. The synthesis route for LA is shown in Scheme 1. Some key properties of LA are listed in Table 1. It has an immediate deflagration to detonation transition, although even minute quantities can pass into complete detonation when exposed to flame or static electricity. It is usually transported in a desensitized solution to reduce its sensitivity. Despite its disadvantages, such as complexity in ignition, LA is favoured over mercury fulminate (MF) due to its stability, cost-effectiveness, and ease of use. It finds extensive use in armed ammunition and industrial blasting caps. A key advantage is its ability to transition quickly from fire to explosion. When used in small quantities, it can trigger detonation in other explosives, making it suitable for detonators but not for primers.

$$1/2\ Pb(NO_2)_2 + 2\ HN_3 \xrightarrow{\qquad\qquad} {}^1/_2\ Pb(N_3)_2 + N_2 + N_2O + H_2O$$

Scheme 1. Synthesis of LA

The main drawback of LA is its environmental impact. Tons of lead-containing super-toxicants are released into the environment teach year due to the use of LA and lead styphnate (LS) in primers and detonators for industrial and armed purposes. These super-eco-toxicants exhibit a broad spectrum of toxic effects, and lead, in particular, is considered a super-eco-toxicant with harmful effects on various life-supporting systems [43]. LA is typically obtained through the reaction of lead nitrate and excess hydrazoic acid in aqueous solution (Scheme 1) [44]. Lead acetate may also be used.

Lead contamination poses significant risks to various systems in the human body and the environment:

- **Blood-Producing Systems:** Excess lead contact can lead to anaemia, a condition characterized by a reduced number of red blood cells. Extreme exposure to lead compounds in experimental animals has been shown to decrease red blood cell counts by more than half.
- **Central Nervous System:** Lead and its compounds can have detrimental effects on the neural network and impairs human memory in particular. Youngsters are particularly susceptible to lead poisoning. Children who live in lead-contaminated areas often have less success at school. Bones and Osteoporosis: lead tends to accumulate in bones, displacing calcium salts. This can lead directly to osteoporosis, a condition characterized by weakened and brittle bones. Lead can remain within bones for more than 25 years.

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- **Impact on Metabolic Processes:** Lead is classified as a thiolic poison and powerfully interacts with the SH-groups in a mixture of proteins. This interaction disrupts various metabolic processes in diverse organs, leading to inefficiencies and health problems.
- **Environmental Impact:** Lead pollution is highly hazardous to terrestrial ecosystems, as it efficiently accumulates in the soil and becomes part of food chains. This can lead to prevalent contamination of the environment and pose risks to both wildlife and humans who rely on these ecosystems for nourishment and habitat.

2.3 Lead styphnate (LS, PE-2)

LS see PE-2 in Figure 1, also identified as lead trinitrorescorcinate, gained significant recognition in the early twentieth century [45-47], just like LA. It exists mutually in its normal (lead(II) 2,4,6-trinitro-m-phenylene dioxide) and primary forms. Some key properties of LS are listed in Table 1.

It is less responsive to IS and FS compared to MF or LA. However, it is more brisant, meaning it produces a shattering effect when it detonates. LS is used as a coating charge for LA and is a component of PE compositions. Basic LS is chosen because of its better thermo-stability and compatibility with LA.

A method for the preparation of α-normal LS involves the reaction of an aqueous solution containing lead cations with a solution of styphnate ions at high temperature in the presence of a mineral acid. The mineral acid is usually present in a concentration of about 1 to about 15 g per litre of the styphnate ion solution. This route is used to produce the desired form of LS for various applications [47].

2.4 Mercury fulminate (MF, PE-3)

MF, see PE-3 in Figure 1, is an extremely sensitive explosive recognized for its susceptibility to friction, heat, and shock. Some key properties of MF are listed in Table 1. It has been used historically primarily as an initiator for other explosives in percussion caps and blasting caps. However, in modern times, more efficient and safer chemical substances have replaced MF primers. These alternatives are non-corrosive, less toxic, and show superior stability over time. Examples of such replacements include LA, LS, and tetrazene derivatives. These compounds do not contain mercury, which can be difficult to source during wartime. MF has several noteworthy properties:

- Its thermal decomposition can be initiated at below 100 °C, with the rate of decomposition rising at higher temperatures.
- MF is highly sensitive to both impact and friction. It will burn strongly if not confined but will detonate if constrained.

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- One of its most important attributes is that it can easily transition from burning at a moderate rate to detonation when ignited, impacted, or subjected to friction. Although it is not hygroscopic in the presence of humidity, it can react with metals, especially aluminium.

Due to its hazardous nature and the availability of safer alternatives, the use of MF has been largely discontinued in most countries. It was historically synthesized by dissolving 1 g of mercury in 12 g of nitric acid and adding 11 g of ethanol to the solution in two portions [47-52].

2.5 Silver azide (SA, PE-4)

SA (AgN_3), see PE-4 in Figure 1, like other heavy metal azides, is an essentially unstable PE. Its decomposition can be triggered by contact with ultraviolet light or by impact. The decomposition of SA produces free electrons and azide radicals, so the reaction rate increases on addition of semiconducting oxides. Some key properties of SA are listedin Table 1. The most important properties of SA include:

- Pure SA explodes at 340 °C, although the presence of impurities can lower this temperature to around 270 °C.
- The decomposition of SA has a lower activation energy and early delay than the equivalent decomposition of LA.

SA is synthesized by a metathesis reaction, involving the reaction of an aqueous solution of silver nitrate with sodium azide (Scheme 2). However, due to its inherent instability and the potential for hazardous decomposition, the use of SA is limited and requires careful handling and storage [53-61].

$$AgNO_3 + NH_4OH + NaN_3 \xrightarrow[H_2O]{CH_3COOH} AgN_3 + NH_3 + NaNO_3$$

Scheme 2. Synthesis of SA

2.6 1-Amino-1-(1*H*-tetrazol-5-yl)-azoguanidine hydrate (tetrazene, PE-5)

Tetrazene is an environmentally friendly PE as it contains no heavy metals or perchlorate ions. Its molecular structure is characterized as a zwitter ion with a hydrogen-bonded water molecule (see PE-5 in Figure 1). Tetrazene forms a monohydrate and appears as a soft solid with colourless to pale yellow crystals. It is almost insoluble in water and many organic solvents, such as alcohol, acetone, ether, benzene and ethylene dichloride. It does not react at room temperature with concentrated ammonia, metals (such as steel, copper or aluminium) or highly explosive substances (*e.g.* TNT, tetryl, pentrite(PETN), RDX) [52-56]. However, tetrazene does have some drawbacks, *viz* poor thermal stability and sensitivity

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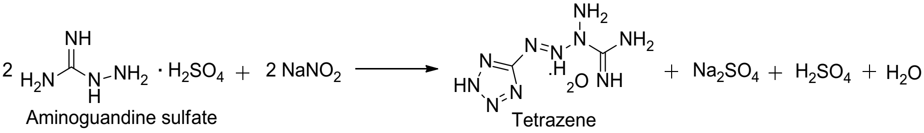
to moisture. In the presence of moisture, tetrazene can become degraded, even at fairly low temperatures, around 60 °C. Boiling water can lead to significant decomposition, producing a range of products, 5-azidotetrazole, which is an extremely sensitive PE.

Tetrazene is susceptible to pressure desensitization, which can reduce its sensitivity. It is more sensitive to impact than MF, and its sensitivity to friction is as good as that of MF. When pressed at 20.7 MPa, tetrazene reaches a density of 1.05 g/cm³. It can be easily ignited by a flame, and when used in small quantities, it deflagrates without producing a visible flame. However, its initiation ability is relatively low, even under conditions optimized for maximum brisance. Tetrazene can initiate tetryl but not TNT. It is classified as an initial igniter, but its effectiveness is low. Tetrazene is heavy-metal-free, making it suitable for various applications. Current percussion primer mixes may contain varying amounts of tetrazene, typically in the range of 2-5%. A typical composition might include LS (37%), barium nitrate (V) (32%), antimony sulfide (15%), aluminium powder (7%), PETN (5%), and tetrazene (4%). However, the main disadvantages of tetrazene are its reduced thermal stability, its short initiation competence and its susceptibility to pressure desensitization.

Tetrazene is usually formed by reaction of sodium nitrite with an aminoguanidine salt dissolved in acetic acid at temperatures between 30-40 °C (Scheme 3) [62, 63].



Scheme 3. Synthesis of tetrazene

2.7 1-[(2E)-3-(1*H*-Tetrazol-5-yl) triaz-2-en-1-ylidene] methanediamine (MTX-1, PE-6)

MTX-1, see PE-6 in Figure 1, exhibits sharp sensitivity to mechanical stimuli. Its thermal decomposition is initiated around 214 °C. Remarkably, even after exposure to water for 120 days, MTX-1 exhibits remarkable stability, with the ability to be re-isolated in nearly quantitative yield. MTX-1 has been reported to have similar impact and friction sensitivities to tetrazene, making it an attractive latent substitute for this commonly used organic sensitizer in primer compositions [64-67].

MTX-1 is synthesized by the reaction of tetrazene with sodium nitrite and nitric acid in aqueous acidic conditions at 70 °C (Scheme 4) [64-67].

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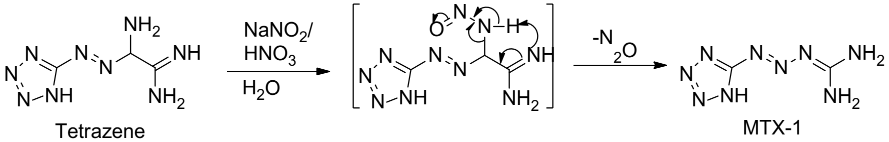
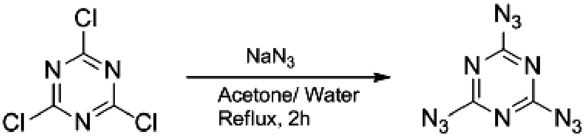


Scheme 4. Synthesis of MTX-1

2.8 1,3,5-Triazido-2,4,6-triazine (TAT, PE-7)

TAT, see PE-7 in Figure 1, also known as cyanuric triazide, is acknowledged for its moderate toxicity, environmentally friendly nature, and its role as an organic PE. With a melting point of 94 °C, TAT exhibits favourable characteristics. The gaseous detonation products are considered safe. TAT surpasses LA in efficiency as a PE, making it a suitable alternative for LA in larger detonators. Compatibility tests using techniques like DSC have confirmed that TAT works well with materials such as aluminium and stainless steel. Additionally, it exhibits compatibility with various energetic nitramines, including RDX, HMX, and hexanitrohexaazaisowurtzitane (CL-20). TAT has been successfully utilized as an alternative for both LA and LS in specific explosive mixtures, exemplified by its use in the NOL-130 stab detonator mix. Moreover, it has been explored as a probable replacement for LS in percussion briefing formulations. TAT crystals, as free-flowing crystalline materials appropriate for detonator applications, are obtained by emulsion crystallization using a non-solvent at a higher temperature. These crystals are uniformly shaped, free-flowing, and have a higher bulk density compared to typical TAT crystals prepared by crash precipitation. [68, 69]. Nevertheless, it is crucial to highlight that TAT is a volatile organic substance, sublimation commencing above 30 °C. Moreover, it undergoes decomposition when exposed to hot water and when heated over 100 °C in its solid state. These characteristics do not allow TAT to meet the criteria for a “green”EM.

The synthesis of TAT involves reacting cyanuric chloride with sodium azide in aqueous acetone under reflux for 2 h (Scheme 5), following a specific chemical reaction scheme.



Scheme 5. Synthesis of 1,3,5-triazido-2,4,6-triazine (TAT) from cyanuric chloride

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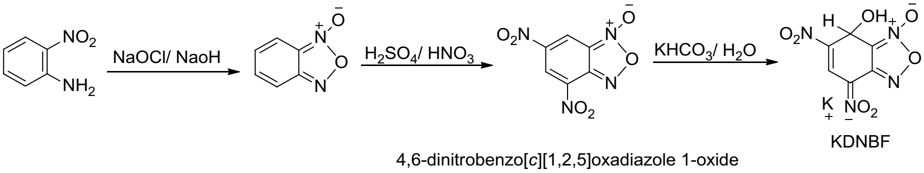
2.9 Potassium 4,6-dinitro-7-hydro-7-hydroxybenzfuroxanide (KDNBF, PE-8)

KDNBF, see PE-8 in Figure 1, is considered a low-toxicity, environmentally friendly energetic compound. The use of potassium in this compound is seen as a safer and less toxic alternative to lead, contributing to its "green" attributes. The sensitivity of KDNBF to impact and friction is comparable to that of lead styphnate (LS). The key properties of KDNBF are listed in Table 1. KDNBF has an initiation capability that is less than that of MF [70,71].

Like 2-diazo-4,6-dinitrophenol (DDNP), KDNBF serves as a "green" PE, replacing LS in resident detonators. It is employed in formulations with low toxicity, incorporating the environmentally friendly oxidizing agent potassium nitrate (KNO_3) and diverse additives during the production of civil detonators in the USA and other nations. Nevertheless, KDNBF has not been widely used for military applications, and its lower thermal stability results in it not being used as a general substitute for LS in PE compositions. While KDNBF is considered a "green" explosive, it may not meet all the criteria necessary for its categorization as a "green" EM.

The starting material for the synthesis of KDNBF is *o*-nitroaniline. This is treated with NaOCl and NaOH to give Benzofurazanoxide, which is subjected to mixed acid nitration to form dinitrobenzofurozanoxide. The K salt is then formed by further treatment with potassium bicarbonate, as shown in Scheme 6 [70,71].



Scheme 6. Synthesis of KDNBF

2.10 Potassium salt of 4,6-dinitro-7-hydroxybenzofuroxan (KDNP, PE-9)

KDNP, see PE-9 in Figure 1, has attracted interest as a likely replacement for LS, exhibiting similar energetic characteristics in militarily applicable detonators and superior thermo-stability. The key characteristics of KDNP include:

Structural differences: Unlike KDNBF (PE-8), KDNP has one less hydrogen atom, leading to the re-establishment of aromaticity in the benzofurazan ring system. This structural variation possibly contributes to the better thermo stability of KDNP relative to KDNBF.

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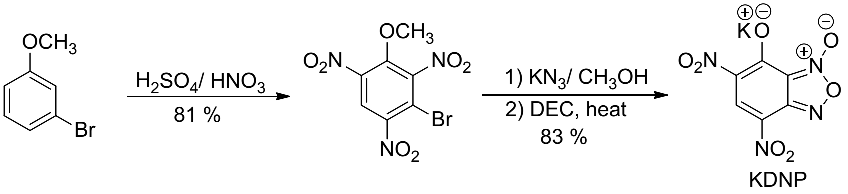
Decomposition temperature: PE-9 has a decomposition temperature of 270 °C, by DSC. KDNP has been tested and evaluated against lead styphnate in various applications, including the CCU-63, the TOW rocket fuse and the PVU-12/A percussion fuse. It has an equal or better suitability than lead styphnate for various artillery materials and shows considerably better productivity on a weight basis in pressure-time tests (closed bomb). One of the important advantages of KDNP is its ease of recrystalization to achieve a particle size appropriate for various applications. It can be customized for use as a small particle constituent in bridge wire slurries or as a large particle component in stab primers.

KDNP exhibits lower sensitivity to IS, FS and ESD compared to regular lead styphnate. It is a rapidly deflagrating material with superior thermo-stability and safe treatment characteristics [72, 73].The synthetic process (Scheme 7) starts with commercially available 3-bromoanisole, which is nitrated with a mixed acid system to form 3-bromo-2,4,6-trinitroanisole. This is further reacted with potassium azide in methanol under reflux to yielded KDNP [72, 73].



Scheme 7. Synthesis of KDNP

2.11 Potassium 1,1'-dinitramino-5,5'-*bis*(tetrazolate) (K2DNABT, PE-10)

In 2014, Klapötke *et al.* [74] described the synthesis and performance of K2DNABT, see PE-10 in Figure 1. This compound was designed as a prospective substitute for LA in detonator applications, with the two 1-nitraminotetrazole moieties contributing to its high explosive power. The key characteristics of K2DNABT include:

- similar sensitivities to impact and friction as LA,
- significantly higher calculated VoD of 8330 m/s, compared to LA's VoD of 5400 m/s,
- no mass loss or decomposition after exposure to 100 °C for 48 h. However, aggressive decomposition was observed at 200 °C by DSC,
- tests indicated that K2DNABT is considered fundamentally harmless, as determined by its toxicity in water using the luminescent bacteria method.

The synthesis of K2DNABT is a multi-step process (see Scheme 8):

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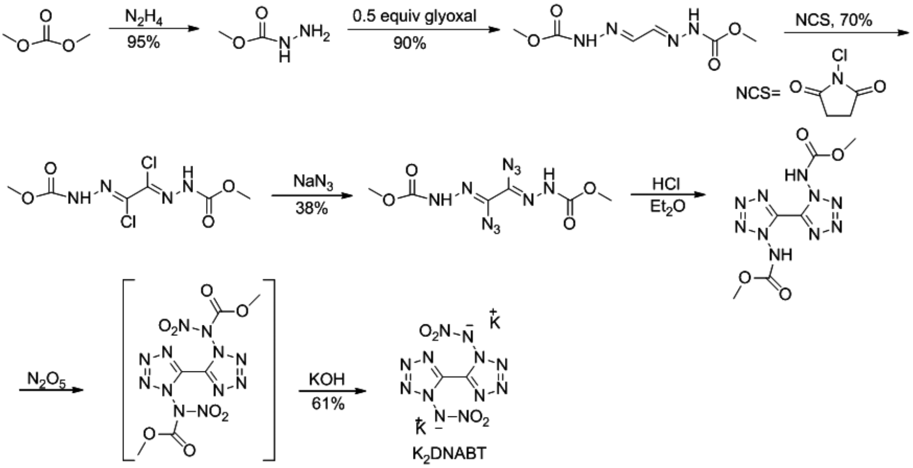
1) Starting from readily accessible available dimethyl carbonate, this is reacted with hydrazine hydrate to form methyl carbazate.
2) A condensation reaction with half an equivalent of glyoxal follows.
3) The resulting intermediate is oxidized with NCS (N-chlorosuccinimide) to obtain the subsequent dichloride.
4) This is then treated with sodium azide to form the diazide.
5) The diazide is then cyclized with a suspension of hydrochloric acid in diethyl ether.
6) The resulting N-methoxycarbonyl-protected 1,1’-diamino-5,5’-bistetrazole is nitrated with N_2O_5.
7) Treatment of the resulting dinitro intermediate with KOH removes the protecting groups to yield K2DNABT.

K2DNABT is a capable candidate for replacing LA in various explosive applications [74].



Scheme 8. Synthesis of K2DNABT

2.12 Dipotassium salt of 1,5-dinitraminotetrazole (K2DNAT, PE-11)

In 2015, Klapötke *et al.* [75] introduced a similarly structured compound known as K2DNAT, see PE-11 in Figure 1. This compound exhibits an outstanding calculated VoD of approximately 10,000 m/s. This VoD is particularly superior to the experimental value of the modern secondary explosive CL-20, which is approximately 9570 m/s. This indicates that K2DNAT is the most effective high-energy material synthesised to date. K2DNAT was specifically designed as a thermally stable candidate with the intention of replacing tetrazene as

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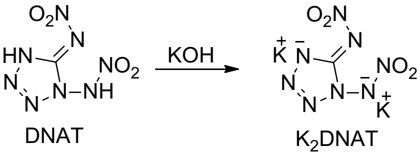
a sensitizer in PE formulations. The features listed below make K2DNAT a remarkable and promising explosive material, showcasing its potential for various applications in the field of EMs.

Key properties of K2DNAT include:

- high level of thermal stability, with completed decomposition being initiated at approximately 240 °C, as shown by DSC,
- high sensitivity to both impact and friction,
- the shockwave generated by a mere 50 mg of K2DNAT is sufficient to detonate the secondary explosive RDX.

K2DNAT is obtained through a reaction involving KOH and DNAT, following a specific chemical reaction scheme. K2DNAT demonstrates remarkable explosive properties, and its high calculated VoD places it as one of the most potent explosives known to date (Scheme 9) [75].



Scheme 9. Synthesis of K_2DNAT

2.13 5-Nitrotetrazole (HNT, PE-12)

The salts of the energetic compound 5-nitrotetrazole (HNT) represent a useful class of low-toxicity, environmentally benign PEs suitable for use in commercial detonators and blasting caps [76-80]. HNT is characterized as a strong NH acid (pKa = –0.82) and a weak base (pKbH+ = –9.3). Key properties and characteristics of HNT and its metal salts include:

- high enthalpy of formation of 2273 kJ/kg, contributing to its explosive properties,
- significant detonation velocity, making it suitable for explosive applications.

The EM properties of various stable metal salts of HNT were studied earlier. In recent times, there has been a renewed interest in exploring these metal salts of HNT as potential low-toxicity and ecologically benign PEs.

The production of metal salts of HNT and of HNT itself (see Scheme 10) involves several chemical reactions. Copper 5-nitrotetrazolate salt can be obtained, for example, by diazotization of 5-amino-1*H*-tetrazole with nitrous acid in the presence of copper(II) sulphate. Sodium 5-nitrotetrazolate can be obtained from the very insoluble copper salt by digestion with sodium hydroxide. After removal of black copper(II) oxide by filtration, the basic solution can be treated *in situ* with acid and then reacted with ammonia to precipitate ammonium

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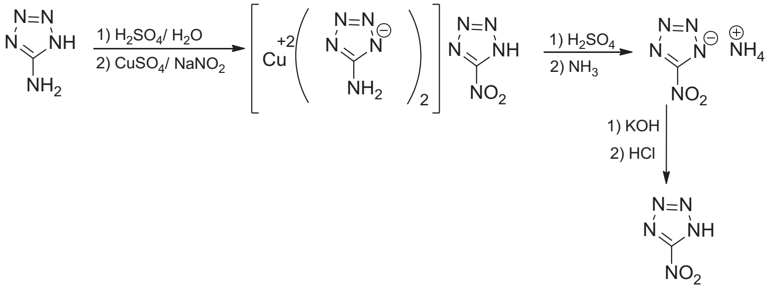
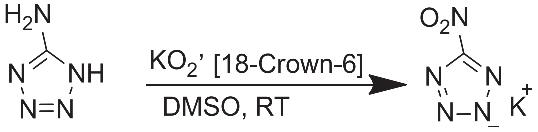
5-nitrotetrazolate. This, in turn, can be reacted with potassium hydroxide and HCl to obtain HNT .These methods of synthesis allow for the production of various stable metal salts of HNT, which can serve as low-toxicity and eco-friendly alternatives in various explosive applications.



Scheme 10. Synthesis of HNT

The potassium salt of HNT, denoted as PE-12a (see Figure 1), was prepared and thoroughly studied with the aim of it potentially serving as a 'green' PE. These explosive salts, *e.g.* PE-12a, exhibit the characteristics of PEs and demonstrate IS and FS that are similar to industrial grade LA (see Table 1). It has been proven that these salts, *e.g.* PE-12a, have the ability to initiate in a detonator No. 8 blasting cap and can be regarded as 'green' PEs. Although, it is worth noting that the decomposition temperatures of these salts do not exceed approximately 195 °C. As a result, they do not meet the necessary criteria for 'green' EMs, as their thermal stability falls short of the desired standard.

The synthesis of the PE-12a involves treating 5-aminotetrazole with potassium superoxide in the presence of 18-crown-6, following a specific chemical reaction protocol (Scheme 11).While PE-12a displays promise as a 'green' PE, its thermal stability remains a limiting factor, and further development may be needed to meet the criteria for environmentally friendly EMs [81].



Scheme 11. Synthesis of PE-12a

2.14 *Bis*-(5-nitrotetrazolato) copper(II) (PE-13)

PE-13 (see Figure 1) is a PE with high initiation capability comparable to LA. PE-13 exhibits a significant temperature for the onset of complete decomposition,

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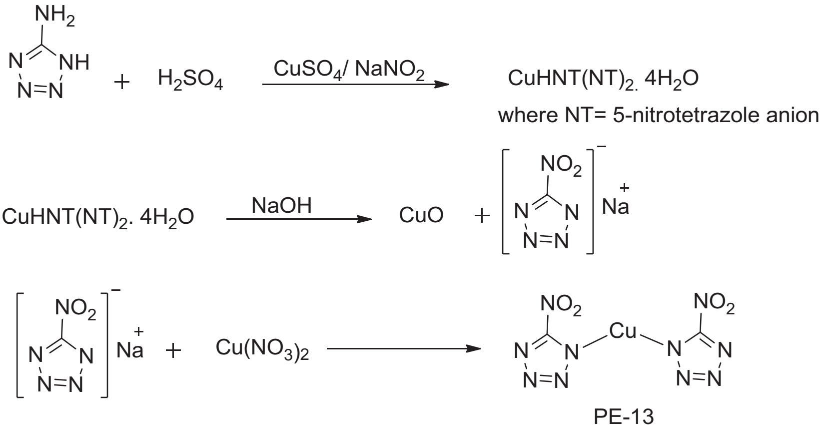
estimated to be around 278 °C. It has been planned as a probable eco-friendly PE for use in primers and detonators, representing a step towards the development of "green" initiation devices. However, it is important to note that while copper is being explored as an alternative for lead and mercury in PEs in order to create safer alternatives, it is also important to be aware of the potential environmental impact of copper. Copper is considered a bio-metal and, in high concentrations, can be toxic to nature. Increased concentrations of copper can result in the generation of reactive oxygen species, leading to oxidative damage to proteins and nucleic acids. On the other hand, a lack of copper can lead to the inactivation of important antioxidant enzymes and disrupt energetic processes in living organisms. Therefore, maintaining the optimal concentration of copper in ecological systems is crucial. The development of copper-based PEs is a modern industrial development aimed at producing safer explosives, and represents a step towards creating "green" PEs.

The synthesis of PE-13 involves a series of chemical reactions, starting with the reaction of 5-aminotetrazole with copper sulphate and sodium nitrite in an acidic solution, to produce the acid copper salt of HNT. Subsequent successive reactions with sodium hydroxide and copper nitrite yield the corresponding desired product (Scheme 12) [83-86].



Scheme 12. Synthesis of PE-13

2.15 Copper(I) salt of 5-nitrotetrazole (DBX-1, $Cu_2(NT)_2$, PE-14)

DBX-1, see PE-14 in Figure 1, also referred to as $Cu_2(NT)_2$, is a low-toxicity substitute for LA. Compound PE-14 exhibits sensitivity to IS and FS that is just about equivalent to that of LA. The temperature at which the complete decomposition of PE-14 begins is 333 °C (by DSC). It also has a high ignition

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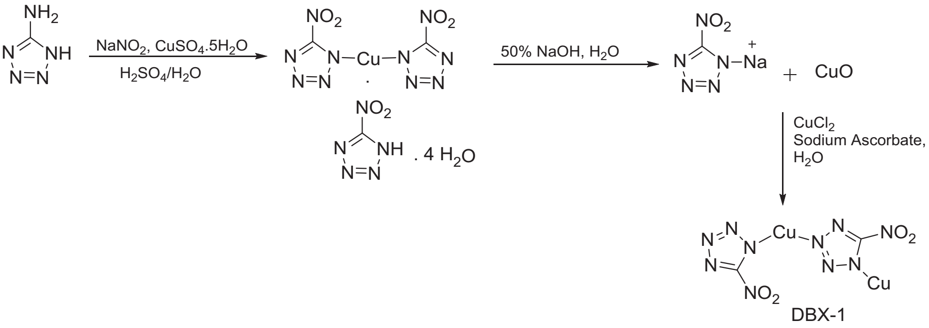
temperature, with DBX-1 igniting at 356 °C and LA igniting at 351 °C. Furthermore, DBX-1 exhibits exceptional thermal stability, as indicated by the absence of weight loss after 24 h at 181 °C, in contrast to LA, which loses 14.57% of its weight under the same conditions. DBX-1 has confirmed good compatibility with a series of high explosives, including RDX, HMX, CL-20, and others, in addition to a wide range of structural materials [87]. Experimental tests have demonstrated that PE-14 can efficiently replace LA in transmitting charges and in the NOL-130 stab mixture for the M55 stab detonator (USA). This substitution can be achieved directly, volume-for-volume, without the need for hardware changes. Compound PE-14 can be considered as a substitute for LS in definite applications considering its notable properties; DBX-1 is thus on track to emerge as a lead-free PE suitable for applications in detonators and primers. The knowledge required for preparing the copper salt PE-14 has been developed and implemented in pilot plants in the USA, as outlined in Scheme 13.



Scheme 13. Synthesis of DBX-1

2.16 Tetraammine-*bis*-(5-nitrotetrazolato-*N*²) cobalt(III) perchlorate (BNCP, PE-15)

Complex perchlorates of cobalt(III) amines with ligands derived from tetrazole derivatives are considered low-toxicity compounds. Complex cobalt(III) salts with amines, such as BNCP, demonstrate enhanced safety compared to traditional PEs like LA or LS. These complexes possess non-hygroscopic properties and exhibit satisfactory thermal stability. Additionally, their initiation capability is adequate, qualifying them for use as PEs in secure blasting caps [88, 89].

BNCP (see PE-15 in Figure 1) is used in safe explosive devices. The temperature at which BNCP begins to decompose completely is approximately 270 °C, by DSC. Its sensitivity to impact is similar to that of the industrial high explosive PETN. BNCP finds widespread use as both a primary and a secondary explosive charge within blasting caps. Notably, this composite exhibits sensitivity

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to light and can be initiated through exposure to a pulsed laser beam. This light-sensitive character of BNCP has been harnessed in the development of secure ocular detonators employed in pyrotechnic usual control systems for rocket complexes in the United States. It is important to note that the complex BNCP contains the very poisonous perchlorate anion, which means it does not comply with the criteria for “green” EMs. BNCP is typically prepared by condensing the sodium salt of nitrotetrazole with carbonatotetrammino cobalt(III)acetate (CTCA) [88, 89].

2.17 Complex *tris*-hydrazinenickel(II) nitrate (PE-16)

Complex hydrazinates of nickel(II) with outer-sphere anions have been studied as potential PEs. These complexes exhibit some properties of PEs, but have several negligible charge aspects compared to LA, and their thermostability is lower than that of LA. Initially, nickel(II) hydrazinate complexes with anion-oxidizers were not deemed suitable for primer ingredients. However, the growing requirement for lead-free and environmentally benign PEs spurred further investigation into this category of metal complexes.

Successive studies have identified the complex *tris*-hydrazinenickel(II) nitrate ($Ni(N_2H_4)_3(NO_3)_2$), see PE-16 in Figure 1, as a viable substitute for LA in commercial blasting caps. PE-16 demonstrates sensitivity to impact similar to LA, and is light-sensitive, ignitable by a pulsed CO_2 laser beam. Over 10 million detonators and electric blasting caps loaded with PE-16 charges have been successfully prepared and tested in China. Consequently, PE-16 has become a commercial PE, finding use in lead-free civilian detonators in China. The temperature at which PE-16 begins to undergo excessive decomposition is around 220 °C, by DSC. PE-16 exhibits and IS similar to that of LA. However, it is important to note that nickel, along with copper, is considered a bio-metal and is necessary for the operation of some enzymes. Nickel has been found to show carcinogenic activity according to the International Agency for Research on Cancer. While nickel concentrations in the environment are relatively low, they persist in ecological systems for extended periods. Unfortunately, complex PE-16 is not thermally stable enough to meet the criteria for a “green” PE. PE-16 is typically prepared by slow addition of a nickel nitrate solution to hot, well-stirred 98% hydrazine hydrate, resulting in the precipitation of PE-16 (Scheme 14) [90, 91].

$$Ni(H_2O)_6^{2+} + 2\,NO_3^{-} + 3\,N_2H_4 \longrightarrow Ni(N_2H_4)_3(NO_3)_2 + 6\,H_2O$$

Scheme 14. Synthesis of PE-16

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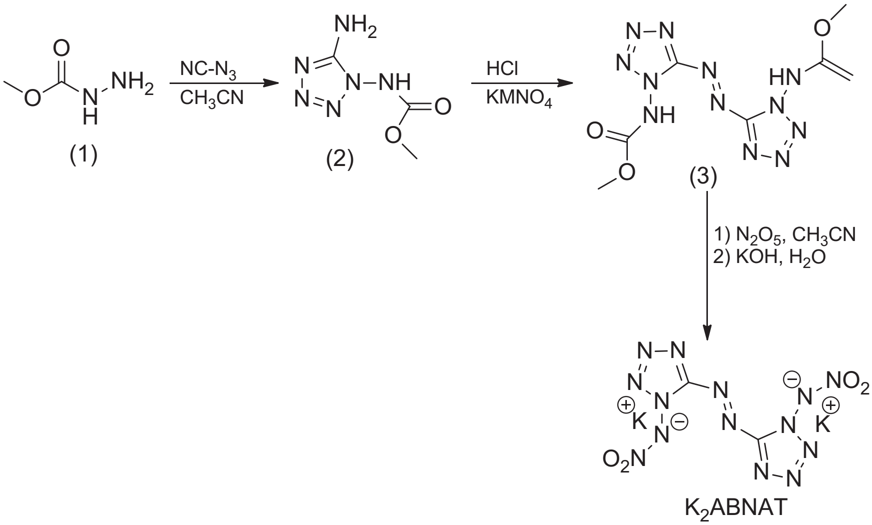
2.18 Potassium 5,5’-azo*bis*(1-nitraminotetrazolate) (K2ABNAT, PE-17)

Li *et al.* [92] reported K2ABNAT (see PE-17 in Figure 1) as a new “green” PE with promising characteristics. Some key properties of K2ABNAT are listed in Table 1. This explosive exhibits excellent overall performance, in terms of IS and FS.K2ABNAT is considered an appropriate and safe substitute for LA, and can be synthesized in three steps from readily available chemicals.

The synthetic steps (Scheme 15) involve treating methyl carbazate **(1)** with cyanogen azide to produce the *N*-methoxycarbonyl-protected 1,5-diaminotetrazole **(2)**, which is then oxidized in concentrated hydrochloric acid with $KMnO_4$ to form 5,5’-azobis(1-ethoxyformamidotetrazole) **(3)**. Finally, compound **(3)** is mildly nitrated with N_2O_5 in acetonitrile and then decomposed in solution with aqueous KOH to yield K2ABNAT. This synthetic process makes K2ABNAT a useful and eco-friendly alternative for diverse EM applications [92].



Scheme 15. Synthesis of K_2ABNAT

2.19 *Di*(triaminoguanidinium) 3-nitramino-4-(3-(dinitromethanidyl)-1,2,4-triazol-5-yl)furazanate (DNDTF, PE-18)

Ma *et al.* [93-95] reported the compound DNDTF (see PE-18 in Figure 1), as a new and capable PE. It contains only carbon, hydrogen, nitrogen and oxygen in its composition. DNDTF exhibits outstanding gas-generating ability and fast combustion reactions, making it a suitable PE. Importantly, DNDTF meets the criteria for an insensitive PE with sensitivity similar to that of the insensitive secondary explosive, TNT. This original approach of using

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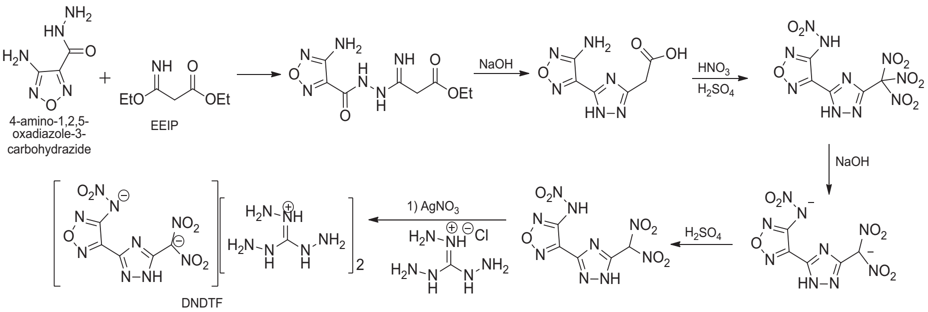
a polynitro-functionalized triazolylfurazanatetriaminoguanidine as PE could open the door for new "green" and insensitive PEs. The maximum detonation pressure is 9.03 MPa, which results in a pressure rise rate of almost 201.5 GPa/s. DNDTF demonstrates excellent gas-generating capabilities and combustion performance, with higher gas productivity and pressure increase rates compared to other traditional gas-generating compositions like nitroguanidine (NG). The combustion of DNDTF on a nickel-chromium wire under rapid heating leads to a further aggressive reaction with faster energy discharge and rate of pressure rise. DNDTF is considered a green and insensitive PE, and its properties make it a promising candidate for various applications in the high energy materials sector. This compound could contribute to the reduction of the dependence on lead-based PEs and to promoting more eco-friendly alternatives. The synthesis of DNDTF involves several steps, starting from 4-amino-1,2,5-oxadiazole-3-carbohydrazide (Scheme 16) [93-95].



Scheme 16. The synthesis of DNDTF

2.20 *Bis*(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane (PE-19)

Kim *et al.* [96-98] first reported the compound *bis*(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane, (see PE-19 in Figure 1), as an innovative PE with properties that make it a probable candidate for "green" PE applications. PE-19 is obtained by a double azidation reaction of *bis*(4-chloro-3,5-dinitro-1*H*-pyrazol-1-yl)methane in a single step [96-98].

The physical and explosive properties of PE-19 demonstrate its PE potential. Its characteristics are similar to previous newly reported bis(nitropyrazolyl) alkane-type PEs, indicating its potential as an environmentally benign alternative for various applications in EMs. The use of compounds like PE-19 can contribute to reducing the environmental impact of PEs and the reliance on traditional, more hazardous materials [96]. Compound **(1)** is treated with Li_2CO_3 and diiodomethane in the presence of DMSO at 70 °C, to give compound **(2)** [89]. This

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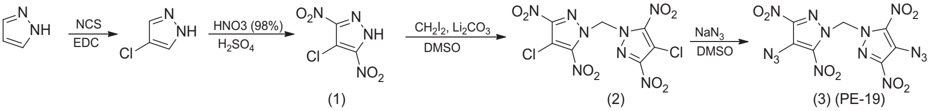
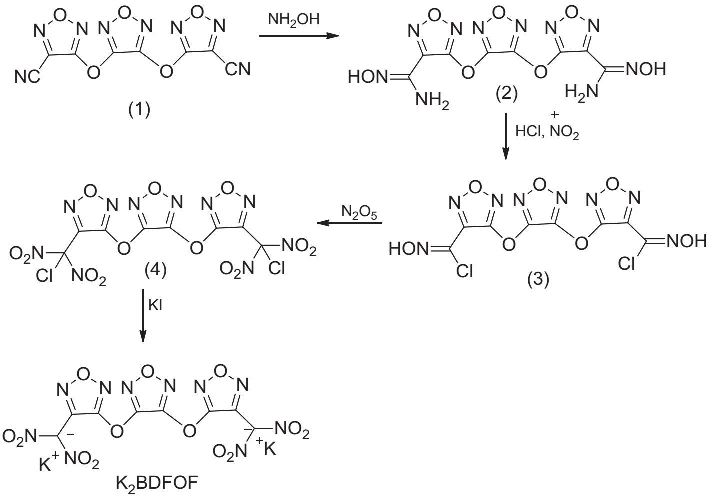
intermediate, compound **(2)**, is then reacted with sodium azide in the presence of DMSO to yield compound **(3)**, PE-19 (Scheme 17) [96-98].



Scheme 17. Synthesis of PE-19

2.21 Dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan (K2BDFOF, PE-20)

Zhai *et al.* [99-102] first reported the compound dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan, often referred to as K2BDFOF (see PE-20 in Figure 1), as a novel green PE that has been prepared through a 4-step synthetic procedure (Scheme 18). The properties of PE-20 (see Table 1) indicate that it is a promising contender as a green PE. It exhibits a relatively high thermostability, low sensitivities to impact and friction, and a substantial VoD, making it suitable for various applications in the domain of high energy materials. The uses of compounds like PE-20 contribute to the progress of environmentally benign alternatives to traditional PEs [99-102].



Scheme 18. Synthesis of K_2BDFOF

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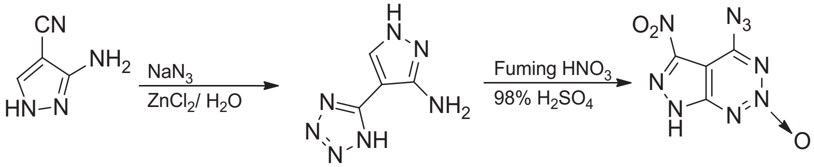
2.22 6-Nitro-7-azido-pyrazol[3,4-d][1,2,3]triazine-2-oxide (ICM-103, PE-21)

Deng *et al.* [103] reported the compound 6-nitro-7-azido-pyrazol[3,4-d][1,2,3] triazine-2-oxide, also known as ICM-103 (see PE-21 in Figure 1) as a PE with several notable characteristics (see Table 1).

PE-21 offers a range of advantages that make it a capable PE: absence of lethal metals and perchlorates, higher density, strong priming capability, abnormal resistance to non-explosive stimuli, exceptional ecological stability, good thermal stability, high explosive performance, acceptable flow ability, and resistance to pressure, cost-effectiveness and synthetic scalability. These properties and performance characteristics surpass those of 2-diazo-4,6-dinitrophenol (DDNP), the commonly used organic PE.

The synthesis of PE-21 (Scheme 19) involves several steps, starting from 3-amino-1*H*-pyrazole-4-carbonitrile. This is reacted with sodium azide and zinc chloride and the resulting intermediate is then nitrated. PE-21 is environmentally friendly and its high-performance characteristics make it a valuable addition to the science and technology of HEMs [103].



Scheme 19. Synthesis of ICM-103

2.23 3,6-*Bis*-(2-(4,6-diazido-1,3,5-triazin-2-yl)-hydrazinyl)-1,2,4,5-tetrazine (PE-22)

Tang *et al.* [104-106] reported the explosive material PE-22, as a metal-free compound (see PE-22 in Figure 1). PE-22 exhibits characteristics that make it a potential candidate for a green PE (see Table 1). The overall features and properties of PE-22 are favourable for its prospective use as a PE, with improved environmental friendliness and performance.

It is synthesized through a series of reactions *via* 3,6-*bis*(2-(4,6-dichloro-1,3,5-triazin-2-yl) hydrazinyl)-1,2,4,5-tetrazine [104-106] (Scheme 20). 3,6-Bis(2-(4,6-dichloro-1,3,5-tria-zin-2-yl)hydrazinyl)-1,2,4,5-tetrazine is obtained from the reaction of DHT with cyanuric chloride by nucleophilic substitution. DHT synthesis was reported in [104-106]. Further reaction with sodium azide in the presence of water at 5 °C yields PE-22 [104-106].

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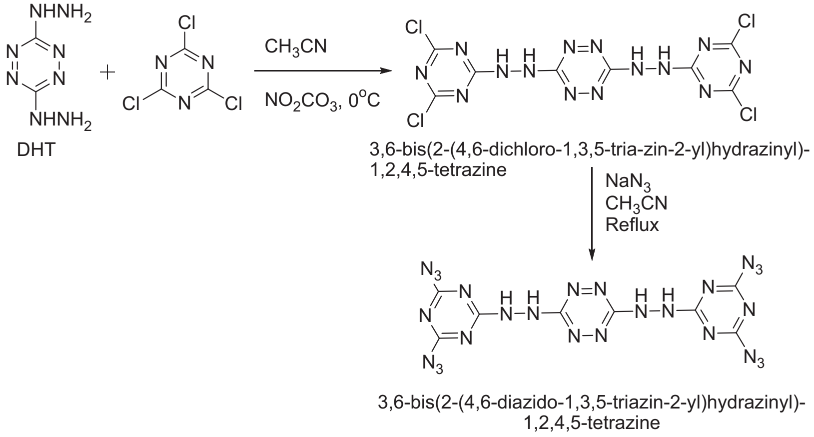

Scheme 20. Synthesis of PE-22

2.24 3,6-*Bis*-(2-(4,6-diazido-1,3,5-triazin-2-yl)-diazenyl)-1,2,4,5-tetrazine (PE-23)

The most important properties of PE-23 (see Figure 1) are listed in Table 1. PE-23 has been used for its priming capability to detonate RDX. These results demonstrated that PE-23 is a plausible environmentally-friendly replacement for lead-based PEs. PE-23 is synthesised by the reaction of PE-22 (synthesis described in Scheme 20) with N-bromosuccinamide in the presence of CH_3CN at 40 °C [104-106].

3 Miscellaneous Potential Candidates for Green PEs

3.1 (1Z,2Z)-*N*'1,*N*'2-dihydroxyoxalimidoyl diazide (PE-24)

Fischer *et al.* [107, 108] reported that PE-24 (see Figure 1) is a metal-free explosive material. Its most important properties are listed in Table 1. Based on its better physical properties, PE-24 showed its attractiveness as one of the potential target molecules for green PEs [107, 108]. The synthesis of PE-24 was achieved by the reaction of dichloroglyoxime with sodium azide in the presence of DMF at 0 °C (Scheme 21) [107-108].

Scheme 21. Synthesis of PE-24

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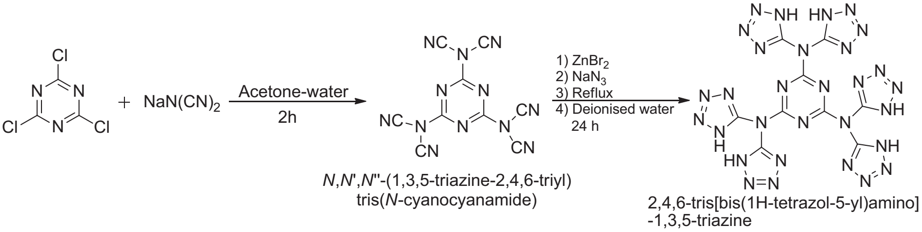
3.2 2,4,6-*Tris*[*bis*(1*H*-tetrazol-5-yl)amino]-1,3,5-triazine (PE-25)

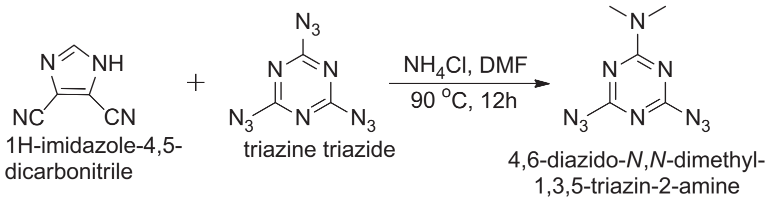
Rao *et al.* [109] reported that PE-25 (see Figure 1) is a metal-free explosive material. Its most important properties are listed in Table 1. PE-25 is the very first example of an energetic substance with six tetrazole units in a single molecule built on a triazine ring, and has 79% nitrogen content, making it one of the potential target molecules for a green PE. PE-25 has been successfully obtained by the reaction of sodium dicyanamide with cyanuric chloride to give *N*,*N*',*N*''-(1,3,5-triazine-2,4,6-triyl) *tris*(*N*-cyanocyanamide), which is then further reacted with zinc bromide and sodium azide in the presence of deionised water under reflux for 24 h (Scheme 22) [109].



Scheme 22. Synthesis of PE-25

3.3 4,6-Diazido-*N*,*N*-dimethyl-1,3,5-triazin-2-amine (PE-26)

Rao *et al.* [110] reported that PE-26 (see Figure 1) is a metal-free explosive material. Its most important properties are listed in Table 1. The physical and explosive properties of PE-26, with 68% nitrogen content, showed that PE-26 makes it one of the potential target molecules for a green PE. The explosive material has been synthesized reacting 1*H*-imidazole-4,5-dicarbonitrile and triazine triazide with ammonium chloride in DMF at 90 °C for 12 h (Scheme 23) [110].



Scheme 23. Synthesis of PE-26

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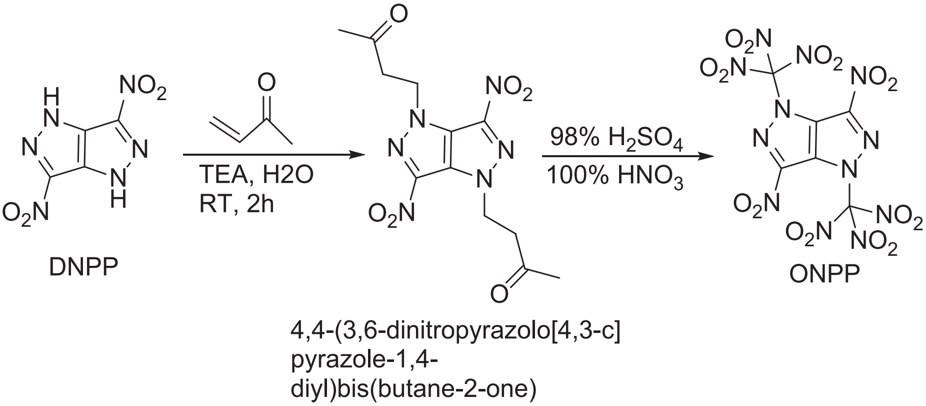
3.4 Octanitropyrazolopyrazole (ONPP, PE-27)

ONPP, see PE-27 in Figure 1, is reported as a metal-free explosive material [111, 112]. Its most important properties are listed in Table 1. ONPP contains of 51% oxygen and 33.88% nitrogen. PE-27 is one of the possible target molecules for a green PE.

The synthesis of PE-27 has been fruitfully achieved by the reaction of DNPP with methylvinylketone in the presence of triethylamine in aqueous media. This reaction yields 4,4-(3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diyl) bis(butane-2-one),which is further nitrated with 98% H_2SO_4 and 100% HNO_3 at room temperature for 18 h to give PE-27 (Scheme 24).



Scheme 24. Synthesis of ONPP

3.5 1,3,4,6-Tetranitro-1,4-dihydropyrazolo[4,3-c]pyrazole (PE-28)

Shreeve *et al.* [113] reported that PE-28 as a metal-free explosive material. Its most important properties are listed in Table 1. With 44.43% oxygen and 38.90% nitrogen, PE-28 is one of the potential target molecules for green PEs.

According to [113] PE-28 was synthesized the reaction of DNPP with NH_4NO_3 in the presence of trifluoroacetic acid, *via* N-nitration. Another synthetic route to PE-28 involved reacting DNPP with 1,8-diazabicycloundec-7-ene (DBU) and O-tosylhydroxylamine ($TsONH_2$) to give 3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diamine, and then this intermediate was reacted with nitric acid in presence of trifluoroacetic acid (Scheme 25).

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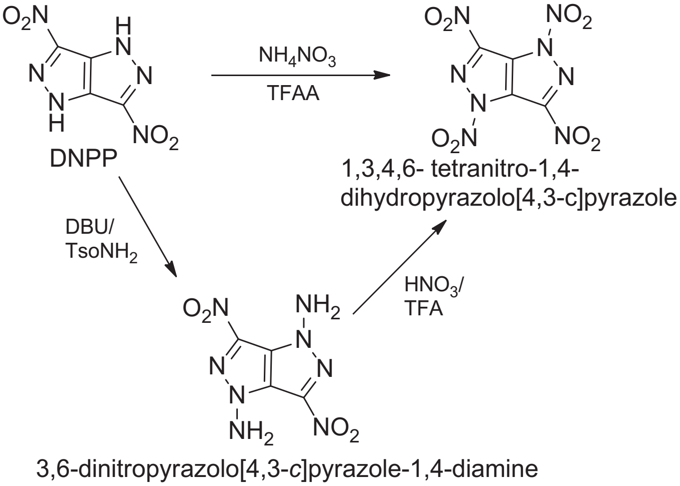
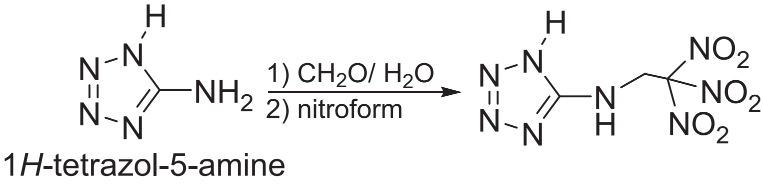


Scheme 25. Synthesis of PE-28

3.6 *N*-(Trinitroethyl)-1*H*-tetrazol-5-amine (PE-29)

Zhang *et al.* [114] reported that PE-29 (see Figure 1) is a metal-free explosive material. Its most important properties are listed in Table 1. With 41.01% oxygen and 47.87% nitrogen, PE-29 is one of the potential target molecules for green PEs.

PE-29 was obtained by the condensation of 1*H*-tetrazol-5-amine with hydroxymethyl derivatives (obtained by the reaction of 1*H*-tetrazol-5-amine with formaldehyde) with nitroform, without the need to isolate the hydroxymethyl derivative. Their aqueous solutions are used for the reaction with nitroform [115]. Nitroform was synthesized according to the method reported previously (Scheme 26) [116].



Scheme 26. Synthesis of PE-29

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4 Conclusions and Future Perspectives

- This review has emphasized the importance of developing and implementing lead-free PEs, often referred to as “green” PEs, in order to improve safety and reduce the environmental hazards associated with common PEs like LA and LS. These green PEs are not only aimed at improving the safety of military and industrial applications, but also at protecting the environment.
- The authors have discussed the developments made in synthesizing and applying these lead-free PEs in various applications, such as primers, blasting caps, and detonators. However, they have also emphasised that the complete industrialization and widespread adoption of these “green” PEs is still ongoing.
- The review underscores the need for continued research and development in the field of high-energy materials, focusing on environmentally friendly and safer alternatives to traditional PEs.
- The authors have covered recent research in PEs and anticipate that more powerful and eco-friendly EMs will materialize. They emphasize the importance of safety, both for humans and the environment, in the design and development of PEs. In summary, this review highlights the ongoing efforts being made to develop and implement green PEs for a safer and more environmentally friendly future.

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Authors declare there is no conflict of interest.

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