Strategic Environmentally Friendly High Energy Materials

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The development of environmentally friendly high-energy materials is essential for future generations, aiming to provide the necessary performance for propulsion and munitions while minimising environmental harm. Researchers are exploring various strategies to achieve this objective.

Green synthesis methods are being investigated to minimise the use of hazardous chemicals and reduce waste generation. Principles of green chemistry, such as solvent-free synthesis and catalytic reactions, are being employed to develop sustainable manufacturing processes.

One of the unconventional, innovative ways of using biomass is to use it as a component of high-energy material. According to conceptual assumptions, biomass can act as an energy carrier in modified high-energy materials explosives. Modification of the composition of the explosive requires development of a method for introducing an additional component, which changes its explosive and operational parameters (including safety). Utilising renewable feedstocks and bio-derived precursors presents a promising avenue for developing environmentally friendly energetic materials. Biomass-derived compounds can be converted into high-energy molecules through enzymatic or chemical processes, offering the advantages of renewability and biodegradability.

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Insensitive Munitions (IM) represent a crucial advancement in munitions technology, designed to mitigate the risk of accidental detonation and reduce collateral damage. The research in this field concentrates on formulating IM compositions with significantly lower sensitivity to external stimuli such as impact, friction and heat. By enhancing the stability of munitions, particularly during storage, handling and transportation, IM formulations ensure that heightened safety measures are upheld throughout the lifecycle of the ordnance. This focus on reducing the susceptibility to accidental detonation not only safeguards personnel and assets, but also aligns with broader efforts to promote safety and security within the military operations and civilian environments alike.

Top of Form

Efforts are underway to minimise the environmental and health hazards associated with energetic materials by reducing toxicity and emissions during production, usage and disposal. Formulation optimisation and advanced combustion technologies help mitigate environmental risks and improve sustainability.

Innovations in propellant and explosive formulations aim to enhance energy density, efficiency and environmental compatibility. Composite propellants and high-energy explosives with tailored properties, such as controlled combustion kinetics and reduced exhaust emissions, are being developed. Nano-energetic materials offer opportunities for optimising performance while minimising environmental impact.

Addressing the environmental footprint of energetic materials includes developing strategies for recycling, reuse and environmentally responsible disposal of waste products. Technologies for recovering and repurposing energetic materials from spent propellants and explosives promote circular economy principles.

Assessing the environmental impact and sustainability of energetic materials throughout their lifecycle is essential for guiding research and development efforts. Lifecycle assessment (LCA) methodologies evaluate factors such as resource consumption, energy use and greenhouse gas emissions. Sustainability analysis helps identify opportunities for improving environmental performance and guiding the development of next-generation materials and technologies.

Overall, the pursuit of environmentally friendly high-energy materials requires interdisciplinary collaboration, innovative technologies and a holistic approach to balancing performance, safety and sustainability considerations. Continued research, investment and collaboration are essential for advancing the development and adoption of these materials, ensuring a more sustainable future for defence, aerospace and other high-energy applications.

Ammonium Dinitramide (ADN) and 1-diamino-2,2-dinitroethylene (DADNE) offer fascinating competitive advantages over other high-energy materials. ADN boasts of a high specific impulse and relatively low toxicity compared to traditional propellants, making it an attractive option for propulsion systems in aerospace applications. Its compatibility with various fuels and binders enhances versatility in formulation. On the other hand, DADNE exhibits superior performance characteristics such as high energy density and stability, coupled with lower sensitivity to external stimuli, making it an ideal candidate for advanced explosive formulations. Both ADN and DADNE present significant advancements in energetic materials, promising enhanced safety, efficiency and environmental sustainability compared to conventional alternatives.

Ammonium dinitramide (ADN)

Ammonium dinitramide (ADN) has gained attention in the field of propellants due to its potential as a high-performance, environment-friendly alternative to traditional rocket propellants. It offers several advantages such as high energy density, low toxicity and relatively low sensitivity to shock and friction compared to conventional propellants.

ADN was first synthesized in the late 1960s by German researchers, but it gained renewed interest in the late 20th and early 21st centuries due to its promising properties. Research into ADN-based propellants has been conducted by various organisations and institutions, including government agencies, universities and private companies.

One of the significant advantages of ADN is its high nitrogen content, with each molecule containing four nitrogen atoms. During combustion, nitrogen is released as gas, contributing to the thrust generated by the rocket engine. This high nitrogen content results in a higher specific impulse, which is a measure of propellant efficiency.

Moreover, ADN exhibits good compatibility with various fuels and additives, allowing for the formulation of composite propellants tailored to specific requirements. ADN-based propellants can be used in both solid and liquid rocket engines, offering versatility in propulsion applications.

Despite its promising properties, there are challenges associated with the synthesis, handling, and storage of ADN. Its production on an industrial scale requires careful control of reaction conditions and purification processes. Additionally, ADN is hygroscopic, meaning it readily absorbs moisture from the atmosphere, which can affect its stability and performance.

Research efforts have focused on improving the synthesis methods, enhancing the stability of ADN-based propellants, and developing propulsion systems that can fully exploit the potential of this compound. Several studies have investigated the combustion characteristics, thermal decomposition behaviour and performance of ADN-based propellants through experimental testing and computational modelling.

Product Features of Ammonium Dinitramide (ADN)

New Energetic Oxidizer in Solid & Liquid Propellants
Energetic material highly soluble, strong oxidizer and high impulse

Applications

A. Ingredient in composite rocket motor propellants and depth charges for underwater ammunition.
B. Liquid monopropellant for rocket motors used in spacecraft propulsion.

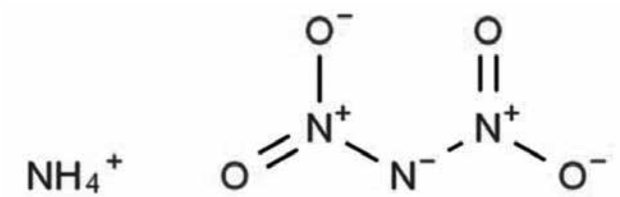

Figure 1 Chemical Structure of Ammonium Dinitramide (ADN)

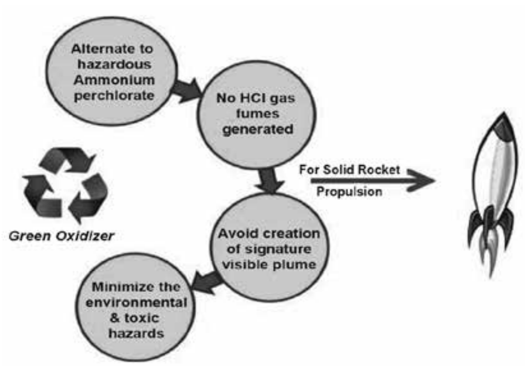

Figure 2 Features of AND

Table 1 Provisional Typical Properties

Characteristic	ADN
Density	1.81
Detonation Velocity	7000 m/s
Heat of formation	-35.8 kJ/Mole
3 Grades	Crystalline, prilled and coated, ultra pure
Green product	No HCl release

Synthesis of Ammonium Dinitramide (ADN)

Ammonium Dinitramide (ADN), an oxidizer used in advanced solid rocket propellants, is synthesized via nitration of sulfamate salts, typically ammonium sulfamate. The reaction involves converting ammonium sulfamate ($NH_4OSO_2NH_2$) into dinitramidic acid (HDN) through nitration using a mixed acid system (concentrated sulfuric acid and nitric acid). The process begins with protonation of ammonium sulfamate in sulfuric acid, forming a reactive intermediate, which undergoes electrophilic attack by the nitronium ion NO_2^+. Successive nitration steps lead to the formation of the dinitramide group ($N(NO_2)_2$), generating dinitramidic acid. Neutralisation with ammonia converts dinitramidic acid to ammonium dinitramide ($NH_4N(NO_2)_2$). Key precautions include maintaining controlled temperatures (typically below 20°C) to prevent side reactions or thermal decomposition, ensuring anhydrous conditions to avoid hydrolysis of intermediates, and conducting the reaction under inert atmospheres (e.g., nitrogen) to mitigate explosive hazards. Proper handling of nitric acid and waste by-products is crucial, as they can pose environmental and safety risks.

Step by Step process

The synthesis of Ammonium Dinitramide (ADN) involves the nitration of ammonium sulfamate ($NH_4OSO_2NH_2$) using a mixture of concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Below is a simplified chemical reaction mechanism for the process:

1. *Activation of Nitric Acid*: The concentrated sulfuric acid protonates nitric acid to generate the nitronium ion (NO_2^+), a strong electrophile.

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

2. *Nitration of Ammonium Sulfamate*: Ammonium sulfamate ($NH_4OSO_2NH_2$) reacts with the nitronium ion (NO_2^+) . This step involves electrophilic substitution, where the nitronium ion attacks

the nitrogen atom of the sulfamate group. This forms the nitro group ($-NO_2$) on the nitrogen, resulting in the formation of a nitrated intermediate.

$$NH_4OSO_2NH_2+NO_2^+ \rightarrow NH_4OSO_2N(NO_2)NH_2+H^+$$

3. *Formation of Dinitramidic Acid (HDN)*: The nitration proceeds further to introduce a second nitro group to the nitrogen atom, yielding dinitramidic acid (HDN), with two nitro groups attached to the nitrogen.

$$NH_4OSO_2N(NO_2)NH_2+NO_2^+ \rightarrow NH_4OSO_2N(NO_2)_2NH_2+H^+$$

4. *Neutralisation and Formation of ADN*: Dinitramidic acid (HDN) formed is neutralised by ammonia (NH_3), leading to the formation of ammonium dinitramide ($NH_4N(NO_2)_2$) through proton exchange.

$$HDN+NH_3 \rightarrow NH_4N(NO_2)_2$$

In summary, the overall reaction is:

$$NH_4OSO_2NH_2+2\,NO_2^+ \rightarrow NH_4N(NO_2)_2+HSO_4^-+H_2O$$

This process requires precise temperature control and careful handling of reagents due to the highly reactive nature of the intermediates and the potential for explosive decompositions if not managed correctly.

ENVIROX-7 (1,1-DIAMINO-2,2-DINITROETHYLENE) (DADNE)

ENVIROX-7, also known as 1,1-diamino-2,2-dinitroethylene (DADNE), is a powerful energetic material primarily used as an ingredient in advanced explosives and propellants. Its chemical formula is $C_2H_4N_4O_4$. ENVIROX-7 exhibits high energy density, good thermal stability, and low sensitivity to shock and friction, making it attractive for military and aerospace applications.

ENVIROX-7 was first synthesized in the 1990s as part of efforts to develop new energetic materials with improved performance characteristics. It has since garnered interest from the defence industry due to its favourable properties. ENVIROX-7 is notable for its relatively low sensitivity to mechanical stimuli, which enhances safety during handling and storage compared to some traditional explosives.

One of the key advantages of ENVIROX-7 is its compatibility with various binders and additives, allowing for the formulation of composite explosives and propellants tailored to specific requirements. It has been used in formulations for both solid rocket propellants and plastic-bonded explosives. Additionally, ENVIROX-7 exhibits good thermal stability, which contributes to its reliability and performance under a range of operating conditions.

Research into ENVIROX-7 continues, with ongoing efforts to optimise its synthesis, characterise its properties, and explore its potential applications in various energetic systems. However, challenges remain in terms of scalability and cost-effectiveness of production processes.

Overall, ENVIROX-7 represents a promising advancement in the field of energetic materials, offering improved performance and safety characteristics compared to some traditional explosives and propellants.

Product Features of ENVIROX-7 (1,1-diamino-2,2-dinitroethylene) (DADNE)

Nitrogen Rich Insensitive Energetic Materials

Greater resistance to impact and friction than standard explosive

Properties

1. Insensitive energetic material with UN-HD 1.1 class.
2. Excellent propulsive performance.
3. Good detonation properties.
4. Green synthesis.

Applications

A. Insensitive compositions for main charges and booster.
B. High performance propellants for tank ammunition.

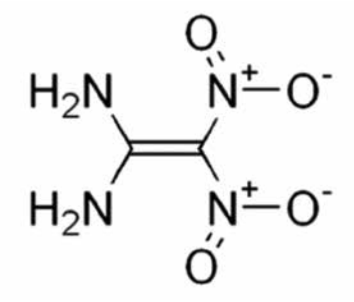

Figure 3 Chemical Structure (ENVIROX 7)

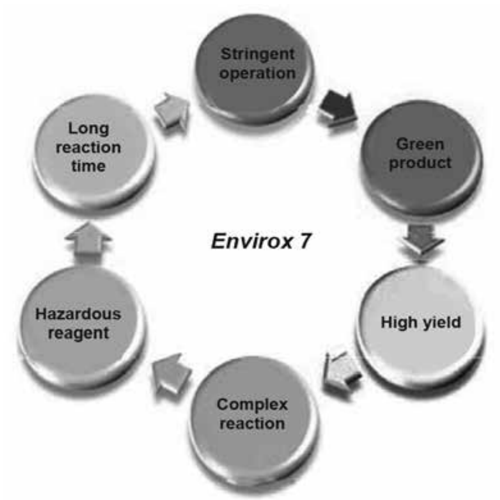

Figure 4 Product Features

Figure 5 Insensitivity visualisation as compared in Table 2

Table 2 Provisional Typical Properties

Characteristic	ENVIROX-7	RDX
Detonation Velocity (m/s)	9090	8800
Detonation Pressure (GPa)	36.6	34.7
Drop Weight Test (cm)	120	38
Friction Test (kg)	>36	12
Thermal Stability (^{0}C)	240	215

Synthesis of 1,1-diamino-2,2-dinitroethylene (DADNE)

The synthesis of 1,1-diamino-2,2-dinitroethylene (DADNE) using the paraformaldehyde route is a two-step process involving condensation and nitration reactions. The first step involves the reaction of paraformaldehyde with hydrazine hydrate under reflux conditions to produce glyoxal bis-hydrazone. This reaction occurs via the nucleophilic attack of hydrazine's nitrogen atom on the electrophilic carbon atom in paraformaldehyde, forming an intermediate hydrazone. Successive reactions result in the formation of glyoxal bis-hydrazone ($C_2H_6N_4$), a stable intermediate compound. This reaction is conducted under controlled reflux conditions to ensure complete conversion of formaldehyde units while minimising by-product formation. The resulting intermediate is then isolated and prepared for nitration.

In the second step, glyoxal bis-hydrazone undergoes nitration using cold fuming nitric acid. This reaction involves the generation of nitronium ions (NO_2^+) from nitric acid in the presence of a proton donor. These nitronium ions serve as powerful electrophiles, attacking the amino groups of the bis-hydrazone and replacing hydrogen atoms with nitro groups. The nitration process leads to the formation of DADNE ($H_2N–C(NO_2)=C(NO_2)–NH_2$). Temperature control is critical during this step to prevent side reactions, such as over-nitration or thermal decomposition, which can compromise product yield and safety. After the reaction, the product is precipitated by cooling, filtered, washed thoroughly (typically with cold water or dilute acid to remove residual reactants) and dried to obtain pure DADNE.

Chemical Equations:

1. Formation of Glyoxal Bis-Hydrazone:

$$(HCHO)_n + 2N_2H_4 \cdot H_2O \rightarrow C_2H_6N_4 + H_2O$$

2. Nitration of DADNE (FOX-7):

$$C_2H_6N_4 + 4\ HNO_3 \rightarrow C_2H_4N_4O_4 + 2H_2O + 2NO_2$$

Precautions

- Chemical Handling
  - ¤ Hydrazine hydrate is highly toxic and corrosive; use gloves, goggles and a fume hood.
  - ¤ Fuming nitric acid is a strong oxidizer and highly corrosive; handle it with extreme care.

- Temperature Control
  - ¤ During nitration, maintain the temperature between 0–5°C to prevent violent reactions or decomposition.
- Ventilation
  - ¤ Nitrogen dioxide (NO2) is released during nitration; ensure adequate ventilation or use a gas scrubber.
- Protective Gear
  - ¤ Use a chemical-resistant apron, gloves and a full-face shield to minimise exposure.

Equipment

1. Reflux Set-up
   - ¤ Round-bottom flask, reflux condenser and heating mantle for glyoxal bis-hydrazone synthesis.
2. Nitration Apparatus
   - ¤ Jacketed reactor or ice bath-equipped flask for temperature control during nitration.
3. Filtration Unit
   - ¤ Büchner funnel, filter paper and vacuum pump for product isolation.
4. Fume Hood
   - ¤ Required for all stages to safely handle volatile and toxic chemicals.

By carefully controlling reaction parameters and following safety protocols, the paraformaldehyde route provides an efficient synthesis method for high-purity DADNE.

Why Make These in India

Developing both molecules independently—whether it is DADNE (1,1-diamino-2,2-dinitroethylene) and ADN (Ammonium Dinitramide) or any other pair of energetic materials—could indeed be strategically advantageous for India.

Independently developing multiple energetic materials diversifies India's capability in the field of energetic materials. Different materials possess unique properties and characteristics, making them suitable for specific applications. By investing in the development of diverse energetic materials, India can cater to a wider range of defence and aerospace needs, from propellants to explosives, ensuring readiness for various scenarios and mission requirements.

Relying solely on a single energetic material poses risks, such as supply chain disruptions, technological obsolescence or geopolitical dependencies. Developing multiple materials ensures redundancy and risk mitigation. If one material faces issues, alternatives can be readily available, maintaining operational continuity in critical sectors like defence and aerospace.

Different energetic materials offer distinct performance characteristics, such as energy density, stability, sensitivity and environmental impact. By independently developing multiple materials, India can tailor solutions to specific needs and requirements. For instance, some materials might be better suited for high-performance rocket propellants, while others may excel in insensitive munitions, allowing for optimisation based on intended applications.

Developing indigenous capabilities in energetic materials enhances India's technological sovereignty. It reduces dependency on foreign suppliers and safeguards against potential export restrictions or geopolitical uncertainties. Moreover, mastering the synthesis, formulation, and application of multiple energetic materials strengthens India's strategic autonomy and defence preparedness.

Independent development projects stimulate innovation, research and expertise within India's scientific and industrial community. They encourage scientists, engineers and researchers to explore novel synthesis methods, improve material properties and innovate in formulation technologies. This fosters a culture of continuous improvement and technological advancement, positioning India as a hub for cutting-edge research and development in energetic materials.

Developing multiple energetic materials promotes competition within the domestic market, driving efficiency, quality and cost-effectiveness. It encourages collaboration among industry players, research institutions and government agencies, fostering a vibrant ecosystem of innovation and entrepreneurship. This competitiveness enhances India's global standing in the defence and aerospace sectors, attracting investment and partnerships.

In an evolving threat landscape, having a diverse portfolio of energetic materials provides strategic flexibility and adaptability. India can respond effectively to emerging threats, technological advancements and changing operational requirements by leveraging a range of materials optimised for different scenarios and mission objectives.

In conclusion, developing multiple energetic materials independently aligns with India's strategic interests by enhancing capability, resilience, sovereignty and innovation in defence and aerospace technologies. It strengthens national security, fosters technological leadership and ensures readiness to meet present and future challenges effectively.

Why It is Not Attractive to Industry

While there are strategic and technical reasons for independently developing multiple energetic materials, from a purely commercial perspective, there are several factors that may make such endeavours less appealing to industry and investors.

Developing new energetic materials involves significant research and development (R&D) costs. This includes investment in laboratory facilities, specialised equipment, skilled personnel and materials synthesis. The long and uncertain R&D timelines, along with the high risk of failure inherent in developing novel materials, can deter investors looking for shorter-term returns.

Energetic materials, especially those intended for military or aerospace use, are subject to stringent regulatory requirements and safety standards. Navigating the regulatory landscape, obtaining necessary permits, and ensuring compliance with safety and environmental regulations can add complexity and costs to the development process, potentially deterring commercial investment.

The commercial market for energetic materials is relatively niche and primarily dominated by defence and aerospace applications. Unlike consumer products or industrial chemicals with broader market appeal, the customer base for energetic materials is restricted to government agencies, defence contractors and aerospace companies. This limited market size may not be attractive to investors seeking scalable and diversified opportunities.

Established players in the defence and aerospace industries often have a significant advantage due to their expertise, infrastructure and existing relationships with government agencies and prime contractors. New entrants face formidable barriers to entry, including intellectual property challenges, competition from incumbents and the need to meet stringent quality and performance standards, making it difficult to gain market share and achieve profitability.

Sales cycles in the defence and aerospace sectors are notoriously long and unpredictable. Procurement decisions are influenced by factors such as budgetary constraints, geopolitical considerations and evolving strategic priorities, leading to lengthy evaluation processes and contract negotiations. This prolonged sales cycle can result in delayed revenue realisation and increased financial risk for companies investing in the development of new energetic materials.

The commercial viability of new energetic materials is inherently uncertain, as success depends on factors such as technological breakthroughs, market demand, regulatory approval and competitive dynamics. Investors may be hesitant to commit capital to projects with uncertain returns, especially given the high upfront costs and long timeframes associated with materials development.

Overall, while there may be strategic and technical motivations for independently developing multiple energetic materials, commercial viability depends on overcoming numerous challenges and uncertainties inherent in the defence and aerospace industries. Successful commercialisation requires careful consideration of market dynamics, regulatory requirements, competitive landscape and risk-return profiles to attract investment and achieve sustainable growth.

Our Approach

Despite the challenges and uncertainties associated with developing multiple energetic materials independently, there are compelling reasons for the industry to come forward from a nationalistic approach. Investing in the development of indigenous energetic materials enhances a country's strategic independence and security. Relying on foreign sources for critical defence and aerospace materials can pose risks to national sovereignty, especially in times of geopolitical tensions or disruptions in the global supply chain.

Developing advanced energetic materials domestically fosters technological leadership and innovation capabilities. It enables the country to stay at the forefront of scientific research and technological advancement, driving economic growth and competitiveness in high-tech industries. The development of a robust domestic industry for energetic materials creates jobs, stimulates economic growth and strengthens the industrial base. It provides opportunities for skilled employment, fosters innovation ecosystems and contributes to overall economic prosperity.

A strong domestic industry for energetic materials is vital for ensuring national security and defence readiness. It reduces dependence on external sources, mitigates supply chain vulnerabilities and enhances the resilience of the defence industrial base to external shocks and disruptions. By developing indigenous capabilities in energetic materials, a country maintains sovereign control over its defence and aerospace capabilities. It enables strategic decision-making, flexibility in procurement and ensures the availability of critical materials during times of crisis or conflict.

Nationalistic approaches to industry development encourage collaboration between government, academia and the private sector to drive innovation and technology transfer. It fosters a culture of entrepreneurship, research excellence and knowledge sharing, leading to breakthroughs in science and technology. Investing in indigenous energetic materials enhances a country's global competitiveness in the defence and aerospace sectors. It allows the nation to offer state-of-the-art solutions, attract international partnerships and compete effectively in the global market, strengthening its geopolitical position and influence.

Overall, embracing a nationalistic approach to industry development in energetic materials underscores the importance of strategic autonomy, innovation and self-reliance in securing a country's future in an increasingly competitive and uncertain world.