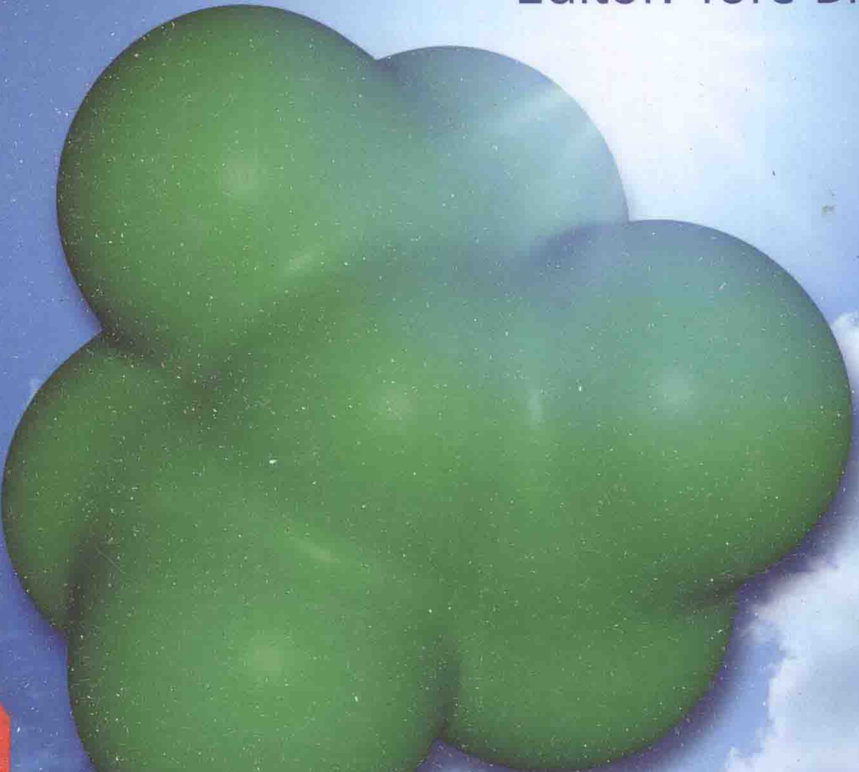
Green Energetic Materials

Editor: Tore Brinck



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Editor

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Preface

It has become increasingly apparent that the use, or production, of many common energetic materials leads to the release of substances that accumulate in nature and can be harmful to humans or to the environment. As a consequence, the use of several important compounds has already been restricted or banned, and many more are expected to face restrictions in the near future. This has resulted in considerable research efforts aimed at developing sustainable alternatives with preserved performance. This book is an attempt to review the current status of the field of green energetic materials. My objective has been to cover the entire process in the development of a new energetic material, from the initial theoretical design to the optimization of the manufacturing process. In addition, the aim has been to consider all different types of energetic materials, including propellants, explosives and pyrotechnics, and both military and civilian applications. To ensure the quality and relevance of the description, I have invited active scientists that are all highly regarded experts in their respective fields to write the individual chapters.

The book is intended as a reference and an inspiration for academic, industrial, and government researchers active in the field of energetic materials. It should also find use as a textbook for courses at the graduate level.

In the first chapter I introduce the concept of green energetic materials and define it in the context of the principles of green chemistry. The particular issues that separate the production and use of energetic materials from other chemical products are highlighted and discussed. Furthermore, the development of green propellants for civil space travel is used as a case study to analyze the problems of taking an energetic material from the initial design phase to its final application.

In the subsequent chapter, Martin Rahm and I discuss the use of quantum chemical methods to design green energetic materials with targeted properties. We show that, while such procedures are very effective for identifying compounds with extreme performance levels, the real challenge often lies in devising routes for their synthesis and large-scale production. The focus of Chapter 3 is on the sensitivity for detonation of energetic materials. Peter Politzer and Jane Murray describe the current understanding of sensitivity at the molecular level, and identify molecular and crystalline features that can be used to design compounds with decreased risks of unintended detonations.

The advances in the development of green pyrotechnics are impressive, considering the diversity of the applications and the large number of toxic chemicals that traditionally have been used to achieve the special effects. Jesse Sabatini reviews the efforts that have been made to remove perchlorates, toxic heavy metals, and harmful organic compounds from pyrotechnic applications. In the subsequent chapter, Karl Oyler writes about similar developments in the field of primary explosives. Here, the main challenge has been to find replacements for lead azide and lead styphnate. Thomas Klapötke and Jörg Stierstorfer describe current efforts to develop greener secondary explosives. Their chapter focuses on the synthesis and properties of tetrazole *N*-oxides; a class of compounds that shows great promise to hold a green alternative for the most common military explosive, RDX.

The following two chapters turn attention to the development of green propellants. In Chapter 7, Martin Rahm and I discuss recent advances in the understanding of ammonium dinitramide (ADN). This oxidizer, first synthesized in the 1970s in the former Soviet Union, has long been considered a potential green replacement for ammonium perchlorate in solid propellants. However, its implementation in solid formulations has been plagued with stability and compatibility issues. Due to new knowledge, gathered from theoretical and spectroscopic analyses, the chemical rationale behind these issues has been resolved and the potential for designing stable ADN-propellants has improved. In the following chapter, Carina Eldsäter and Eva Malmström discuss binder materials for green solid composite and homogeneous rocket propellants. They consider propellants based on ADN as well as other green oxidizers. This chapter highlights the many factors that need to be optimized in order to obtain a functional propellant formulation.

David Chavez reviews the development of sustainable manufacturing technologies for energetic materials in Chapter 9. According to the principles of green chemistry, it is not sufficient that the end product is benign, the entire manufacturing process should be environmentally friendly and make efficient use of natural resources. Challenges that are discussed include minimization of waste, reduced use of organic solvents, and the introduction of energy efficient synthesis procedures. Electrochemical synthesis is one such procedure that is discussed in more detail in Chapter 10. In this chapter, Lynne Wallace also describes the use of electrochemical methods for remediation of wastewater arising from the use and manufacture of energetic materials.

I am very grateful to all the authors that have contributed to this book. My hope is that you will appreciate their chapters as much as I have, and that you will find this book useful for your future endeavors in the exciting field of green energetic materials.

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Contents

1

Introduction to Green Energetic Materials

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1.1 Introduction

The first energetic materials were developed in ancient China. Around 200 BC, Chinese alchemists were already starting to experiment with heating mixtures of saltpeter and sulfur. In the seventh century, saltpeter and sulfur were combined with charcoal to create an explosive material resembling what we today refer to as gunpowder. It was originally used for fireworks but soon became increasingly important for a range of military applications. The use of gunpowder in mining and civil engineering did not begin until the seventeenth century. Gunpowder remained the base for all energetic materials in practical use until the isolation of mercury(II) fulminate in 1799 by Edward Charles Howard. However, the first revolution in the development of energetic materials since the discovery of gunpowder started with the inventions of nitrocellulose (NC) in 1846 and nitroglycerine (NG) in 1847. NC was used as a propellant, whereas NG was mainly an explosive. Both these compounds had greatly enhanced performance compared to gunpowder. In 1866, Alfred Nobel introduced the original dynamite, a mixture of 75% NG with 25% kiselguhr, with a minor addition of sodium carbonate. It had much reduced sensitivity compared to pure NG and was, in contrast to NG, relatively safe to handle and transport. Nobel later developed gelatinous dynamite by combining NG with NC in a jelly. This material performed considerably better than the original

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dynamite and additionally improved safety. These examples illustrate the two main objectives, to improve performance and safety, that have traditionally driven research on energetic materials. It is important to remember that, in the wider definition of energetic materials – which include propellants, explosives, and the large area of pyrotechnics – the definition of performance depends largely on the purpose of the intended device. For example, in the area of pyrotechnics, performance can relate to light intensity, gas generation or smoke production.

Since the end of the twentieth century it has been increasingly realized that the use, or production, of many energetic materials leads to the release of substances that are harmful to human health or to the environment. In some instances the use of certain compounds has been restricted, or even banned, as a consequence of legislative actions. The result is that new objectives have been enforced on the development of energetic materials. Today, almost all research in the area is focused on designing new materials that can be considered "green." This book intends to summarize the most recent developments in the area of green energetic materials, and to introduce the reader to some tools that are used in the research. However, before we embark on this journey, it may be valuable to try to define "green", and how this extra requirement relates to the objectives of maximizing performance and safety of handling.

1.2 Green Chemistry and Energetic Materials

The concept of "green chemistry" was first introduced in 1990s by the US Environmental Agency (EPA), and is briefly defined on their web site as [1]:

> To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products.

Since its first appearance, green chemistry has gradually evolved due to organized efforts in both Europe and the USA, and has been widely adopted within the chemical industry as a method to promote sustainability in the design and manufacturing of new chemicals. The basic ideas behind green chemistry were concretized in 1998 by Anastas and Warner by their definition of the Twelve Principles of Green Chemistry [2]:

The Twelve Principles of Green Chemistry

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1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals**
   Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The principles of green chemistry are largely geared towards guiding the design of the manufacturing process, since for many chemicals the manufacturing has the largest impact on human health and the environment. Energetic materials are to some extent different, in that their use prohibits recycling and proper waste disposal; they disintegrate, and the decomposition or combustion products are directly released into the environment. It is, therefore, particularly important to consider the health and environmental effects of the final product and its usage. With this aspect in mind, the principles of green chemistry can be applied to the design of energetic materials and their manufacturing. It may seem very difficult to adhere to some of the principles, such as 2, 5, 8, and 9. After all, most energetic materials are complex structures that are very high in energy. Energy and complexity are often afforded by employing reactive reagents, specialized solvents, extreme reaction conditions, and through the use of protecting groups or other derivatization. However, most drugs are of equal or larger complexity, and therefore it is encouraging that green chemistry has been very successfully implemented in the pharmaceutical industry [3,4]. It is also obvious from reading Chapter 9 that great progress is currently being made in adopting green chemistry principles to the design of manufacturing processes for energetic materials. In some cases the achievements are clearly at the forefront of sustainable manufacturing, such as the use of biocatalysts or the implementation of continuous processes. The implementation of electrochemical methods is also likely to become of increased importance. Electrochemical processes often constitute energy efficient approaches for synthesis and for remediation of chemical waste. The use of water as the prevalent solvent in many such processes is an added advantage.

The principles of green chemistry provide no direct indication of how to determine the sustainability of a chemical or manufacturing process. One attempt to remedy this deficiency is the E-factor, which has been introduced as a method for quantifying the greenness of processes and products [5–7]. It is defined as the quotient of mass of waste over the mass of product, that is, $m_{\text{waste}}/m_{\text{product}}$. The waste is often considered to include all compounds formed during the process, including gases and water. It is generally a better measure for comparing different processes for making the same product than for comparing products, since it does not explicitly consider the constitution of the waste or its toxicity. Even if the E-factor is a relatively blunt tool, it provides a rapid and often very revealing method for assessing different process alternatives from an environmental perspective. A lifecycle assessment (LSA) is a much preferred approach as it attempts to give an assessment of the overall environmental impact of a product. It considers the entire process from the extraction and acquisition of the raw material, via the manufacturing and use of the product, to the end-of-life management [5,8]. There are also methods that attempt to combine LSA with lifecycle cost analysis to get a total assessment of the costs for a product. Such a technique was recently used to analyse the life-cost of a toxic monopropellant (hydrazine) propellant versus a green one [9]. The analysis demonstrated that replacing the toxic propellant would give large cost reductions, even though the actual manufacturing cost for the green replacement is higher. It is a common observation that it pays off, from a direct cost perspective, to replace old products with greener alternatives. This also holds for the manufacturing of chemical products; converting to processes that adhere to the green principles of chemistry is often cost effective.

Reduction of costs can actually be considered one of main forces that drive the implementation of green products and manufacturing technologies; the others are societal pressure due to public awareness and government legislation. In Europe, chemicals and their use are regulated through the European Community regulation REACH (**R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emical substances) [10]. REACH was introduced in 2007 and will be gradually phased in over 11 years. "The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances" [10]. REACH significantly increases the responsibilities of manufacturers and importers of chemicals. They are required to gather information on the properties of their chemical substances and provide safety information that ensures their safe handling. The Regulation further calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified. This also has implications for the energetic materials industry. It is becoming increasingly important to identify early on energetic materials that are in danger of being phased out, and to begin the development of green replacements.

So far we have not touched on the subject of whether the considerations according to the principles of green chemistry should be prioritized over performance and safety of handling when designing green energetic materials. Safety of handling is partly considered in principle 12. However, the potential consequence of an accident in the case of an energetic material is often of such magnitude that safety of handling must take precedence over other priorities. The prioritization of performance is a slightly more complicated matter, and is somewhat dependent on the application. It is obvious that the performance of a product will affect its atom-economy, for example, if a new material has half the performance of an old material, we need to use twice the amount of the new material to accomplish the same task. However, for some applications the consequence of lowered performance can be detrimental. In the case of rockets for space exploration, the mass of the propellant can easily be up to 90% of the total weight, whereas the payload typically constitutes only a few percent; even a minor reduction in performance (specific impulse) will significantly reduce the size of the payload. Thus, high performance is essential for efficient energy utilization and is often needed for mission completion. There are many other applications of energetic materials where high performance is also of great importance.

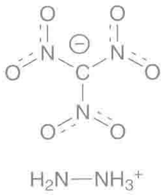
With this discussion in mind we can attempt to define the concept of a green energetic material:

> A green energetic material is a material designed and manufactured in accordance with the principles of green chemistry, with the minimum requirement to preserve the performance level, and safety of handling, of the energetic material it is intended to replace.

It is important to remember that it is not always possible to design a material that fully satisfies this definition and, if the need to replace an old composition is sufficiently urgent, it may be necessary to settle for something that is not entirely green, just greener. In many cases, such an approach can lead to a significant improvement over the existing situation.

1.3 Green Propellants in Civil Space Travel

We are facing environmental challenges related to the use of energetic materials in many areas of society. In the following section, we will use the civil space sector as an example, and discuss some past and present attempts to develop and implement green propulsion technology. This is not intended to be a comprehensive survey, but rather to indicate some of the challenges associated with taking a green material from the initial development state to its final application.



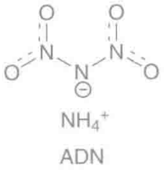
HNF

Scheme 1.1

1.3.1 Green Oxidizers to Replace Ammonium Perchlorate

Ammonium perchlorate (AP, NH_4ClO_4, Scheme 1.1) is the most common oxidizer in solid propellants. Its use extends from civil pyrotechnics, via a range of military applications, to the large booster engines in space shuttles and heavy-lift launchers. One of the environmental concerns relating to AP is its high chlorine content, which is converted to hydrochloric acid (HCl) upon combustion. As an example, it is easy to calculate that each launch of the European heavy-lift launcher, Ariane 5, produces HCl corresponding to 270 metric tons of concentrated hydrochloric acid at full conversion [11,12]. The large amount of HCl released into the atmosphere as consequence of the extensive use of AP may contribute to acidic rain and ozone depletion. The direct release of perchlorates into the environment, either due to incomplete combustion, or leakage from undisposed material, is considered to be an even bigger problem. It is estimated that drinking water in at least 35 of the states in the USA is contaminated by perchlorates [13]. This is a matter of concern since it has been suggested that high intakes of perchlorates may lead to an increase in thyroid disorders [14]. The EPA published in 2009 an interim health advisory with a maximum limit of 15 ppb for drinking water, and announced in 2011 that they are moving forward with regulations [15,16].

Hydrazinium nitroformate (HNF) has been considered as a potential green oxidizer in solid booster propellants. HNF was discovered already in 1951 [17]. However, the real interest in HNF as a replacement for AP started in the late 1980s, when the European Space Agency (ESA) began to realize the potential environmental problems associated with acid release from AP combustion. The ESA initiated a large research program with the aim of developing a green solid propellant for use in space applications. This included the establishment of a production plant for producing HNF at a scale of 300 kg per year [17]. HNF is not considered to be entirely green, since one of the reactants used to manufacture HNF is hydrazine, which is a highly toxic and carcinogenic compound. Still, HNF is chlorine free, and the burning is clean and without acid release. It was soon realized that HNF has severe compatibility issues with common binder systems. However, HNF was later shown to be compatible with the energetic binder glycidyl azide polymer (GAP), and a propellant based on HNF, aluminum (Al), and GAP has been developed [18]. The performance, in terms of specific impulse, is reported to be 2–7% higher than for a standard formulation of AP-Al with hydroxyl-terminated polybutadiene (HTPB) as the binder [19]. This increase would, according to some estimates, translate into a reduction in the cost/kg payload of a launch system of 5–50% [19]. In spite of these very encouraging results, and the large investments made, ESA seems to have largely lost interest in the



Scheme 1.2

development of an HNF-based propellant; the research has almost halted and there are no indications of industrialization in the near future. We can only speculate about the reasons. However, it may be connected to problems with the thermal stability and sensitivity of HNF [17]. In addition, the manufacturing costs of both HNF and GAP are high and it is expected that a HNF propellant would be too expensive to use on a larger scale. This should be added to the large costs associated with the development of a new engine system and the related infrastructure.

Ammonium dinitramide (ADN, Scheme 1.2) is another oxidizer that has received considerable interest as a potential green replacement for AP. ADN was first prepared in 1971 in Moscow, and is believed to have been used for propulsion of Soviet intercontinental missiles during the Cold War [11]. Reportedly, the main advantage of the propellant was the smokeless signature (a consequence of the clean burning of ADN), which prevented radar detection of the missiles. ADN was rediscovered in the late 1980s by US scientists. Since then, it has been the focus of intense research efforts worldwide. Like HNF it is chlorine free, and combustion of pure ADN without a fuel leads to formation of N_2, H_2O, and O_2 as the thermodynamic products. ADN is today produced on a large scale in a relatively green process at the SNPE Eurenco plant in Karlskoga, Sweden.

ADN is very hygroscopic in nature. Although it is relatively stable in pure form, it has, like HNF, been found to be incompatible with a number of binder and curing systems, most notably the common isocyanate curing system [17,20] (see Chapter 8 for details). The reactivity of ADN has been very difficult to understand and anomalous solid state decomposition behavior has been reported [17,20]. As described in Chapter 7, many of the issues with ADN are now finally beginning to be resolved. New compatible binder systems have also recently been presented [11,21] (see also Chapter 8). Although they need considerable optimization before a working solid ADN propellant can be realized, the preliminary results are promising. Theoretical calculations indicate that an optimized ADN-propellant would have a high performance and increase the specific impulse over a standard AP-Al propellant by up to 5–7% (see Chapter 2).

Even though ADN-based solid propulsion is on the verge of becoming a mature propulsion technology, we do not see any initiative that in the near future is likely to lead to the implementation of ADN in a larger propulsion system. In 2008, NASA signed an agreement with the Swedish Defence Research Agency (FOI) with the title *Initial evaluation of ADN as oxidizer in solid propellants for large spacelauncher boosters* [22], and it was rumored that ADN was considered for the next-generation ARES booster. However, NASA, in an unoffical statement, denounced this rumor and explained that ADN needed further evaluation and development before eventual implementation [23]. The reason for the current relatively low interest in an ADN-based launch system from private investors and space agencies is not obvious. However, the answer is probably connected to the size of the