Energetic Materials

Particle Processing and Characterization

Edited by Ulrich Teipel

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Edited by Ulrich Teipel

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Preface

Nowadays, propellants, explosives and pyrotechnics are composed mainly of particulate energetic materials. These are gaining in importance as a way to optimize the performance, burning behavior, stability, detonation properties, processing characteristics and, above all, the low sensitivity of these systems. By varying the characteristic profile of these materials, product design provides for particulate components specially optimized for the application in question. Well-known solid formation processes are often used to create particles of energetic materials, such as crystallization or precipitation, comminution or atomization. Although there is a certain amount of information available about these processes for particle syntheses or processing, there is currently a lack of detailed comprehension in some points, which is needed to be able to completely control the particle formation process or to make reliable predictions about the profile required by the user for the particles so created. Vital questions and tasks remaining for particle technology of energetic materials are the comprehensive characterization of particulate components, the experimental determination of the kinetics of particle formation processes, the influence of the manufacturing process on important particle characteristics, such as particle size distribution, morphology or polymorphy, the simulation and modeling of particle formation processes and particulate materials, as well as the creation of low-defect particles with regard to the sensitivity of propellants and explosives. This book is targeted at those working in industry, government or R&D, and involved in the fascinating field of energetic or other special materials. It will hopefully contribute to summarizing our current level of knowledge.

This volume begins with an introduction to the topic, with a focus on novel energetic materials. One of the main subjects, namely production, is described in chapters two to four, beginning with a look at processes used to reduce the size of the materials, followed by a detailed treatment of crystallization. After covering certain basics, the possibilities of designing hexogen, octogen, CL 20, NTO, ammonium nitrate and ammonium dinitramide in particular using crystallization are examined. In addition, the possibilities currently offered by simulation and the potential of crystallization with compressed gas are looked at. Alongside the mixing process of disperse systems important for particle processing, a whole chapter deals with the product design of particulate materials using microencapsulation and particle coating. This is followed by the increasingly important topic of nano-

particles. The remaining chapters deal primarily with the second main topic of this book, the characterization of particle characteristics. They present the possibilities and limitation of particle size analysis, microstructures, polymorphy and morphology as well as the analysis of chemical and thermal properties and wettability. The rheological behavior of dispersions composed of particulate energetic materials and the relevant binder materials as well as that of solids are treated separately in Chapter 12. The whole is rounded off with a look at the performance of energetic materials, including the influence of particle size on reactions, that of crystal defects on the sensitivity of formulations and the diagnostics of shock wave and combustion processes.

The authors have incorporated in this work their excellent scientific expertise, knowledge and experience in particle technology as related to energetic materials. It was vital for this publication to win renowned colleagues as expert co-authors, and as its editor, I would like to thank all the authors for their willingness to work on this book. My gratitude is also extended to those who worked in different ways "in the background" for the individual authors and the editor. In particular I wish to sincerely thank Ulrich Förter-Barth and Hartmut Kröber as well as Irma Mikonsaari for their continuous and varied support in the preparation and carrying out of the project, as well as the reviewing, processing and correcting of the manuscripts. I also wish to thank the staff at Wiley-VCH for their cooperation from the start of the project until completion of the book.

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1
New Energetic Materials

Horst H. Krause

1.1
Introduction

For many years there was little discussion of or activity to develop new energetic materials for military applications. However, since the end of the Cold War there have been significant new activities in such materials. Particularly in the last 10 years, a number of new synthesized energetic materials have been reported and generated much discussion. Some of the most interesting newly developed materials include the following:

- **TNAZ** (1,3,3-**tri**nitro**az**etidine);
- **HNIW** (**h**exa**n**itrohexaza**i**so**w**urtzetane or **CL-20**);
- **ONC** (**o**cta**n**itro**c**ubane);
- **FOX-7** (1,1-diamino-2,2-dinitroethene);
- **ADN** (**a**mmonium **di**nitramide). A number of questions can be raised with respect to this new generation of explosive materials:
- Do the new substances offer significant advantages compared with currently existing materials?
- What range of applications might be expected for the new materials?
- Have the new substances been sufficiently characterized and developed?
- Does processing or manufacture of these new substances pose particular compatibility or safety problems?
- Will the chemical stability and aging behavior of these new substances result in formulations with adequate service life?

1.1.1
Applications of Energetic Materials

To assess the potential of the newly developed materials, their energetic characteristics must be compared with those of contemporary materials. The values of some key characteristic properties of energetic materials, such as density, formation

Table 1.1. Properties of existing and new energetic materials.

Abbreviation	Name	Applications[a]	Density (g/cm^3)	Oxygen balance (%)	Formation energy (kJ/mol)
Existing energetic materials					
TNT	2,4,6-Trinitrotoluene	HX	1.65	−74.0	−45.4
RDX	Cyclo-1,3,5-trimethylene-2,4,6-trinitramine	HX; RP; GP	1.81	−21.6	92.6
HMX (β)	Cyclotetramethyl-enetetranitramine	HX; RP; GP	1.96	−21.6	104.8
PETN	Pentaerythrol tetranitrate	HX	1.76	−10.1	−502.8
NTO	3-Nitro-1,2,4-triazol-5-one	HX	1.92	−24.6	−96.7
NG	Nitroglycerine	RP; GP	1.59	3.5	−351.5
NC	Nitrocellulose (13% N)	RP; GP	1.66	−31.8	−669.8
AN	Ammonium nitrate	HX; RP	1.72	20.0	−354.6
AP	Ammonium perchlorate	RP; HX	1.95	34.0	−283.1
New energetic materials					
TNAZ	1,3,3-Trinitroazetidine	HX; RP; GP	1.84	−16.7	26.1
CL-20 (HNIW)	2,4,6,8,10,12-(Hexanitro-hexaaza)tetracyclododecane	HX; RP; GP	2.04	−11.0	460.0
FOX-7	1,1-Diamino-2,2-dinitroethene	HX; GP; RP	1.89	−21.6	−118.9
ONC	Octanitrocubane	HX	1.98	0.0	465.3
ADN	Ammonium dinitramide	RP; HX; GP	1.81	25.8	−125.3

a HX, explosive; RP, solid rocket propellant; GP, gunpowder.

energy and oxygen balance, are listed in Table 1.1, providing a comparison of these new substances with currently existing energetic materials. A wide variety of materials are currently used in the energetic materials sector, some of which required decades of research and development. Table 1.1 lists the most important contemporary energetic materials and their primary application(s) in one or more of three key areas: explosives (HX), gunpowder (GP) and solid rocket propellants (RP).

Nitrocellulose remains the leading major ingredient of gunpowder formulations. One distinguishes between single- and double-base formulations, i.e. between pure nitrocellulose and a combination of nitrocellulose and a high-energy plasticizer. Triple-base formulations are also possible, where the third component is a solid energetic component such as nitroguanidine (NIGU).

Most solid rocket propellants fall into one of two classes: double-base (NC/NG) and so-called composite propellants. Composites consist of a fuel and oxidizer (e.g. aluminum and ammonium perchlorate) bound together in a polymeric matrix. Only a limited range of oxidizer candidates can be employed in solid propellants. It is therefore crucial to consider the oxidizer properties (including a positive oxygen balance) in the propellant development process. The property data shown in Table 1.1 indicate that ADN is probably the only viable oxidizer alternative to AP for solid rocket propellants; it therefore holds considerable promise for future development efforts.

The most important property for a good explosive is the material's density. CL-20 (or HNIW) has the highest density (2.04 g/cm^3) of the organic substances listed. It also exhibits the highest formation energy. This results from the stored energy, which is due to the highly stretched bonds in the ring system of this so-called 'cage' molecule.

Octanitrocubane belongs to the same group of cage compounds as CL-20. Octanitrocubane was synthesized only recently. The measured density of the ONC molecule, 1.979 g/cm^3 is unfortunately much lower than that expected based on computer-based simulation predictions.

1.2 Application Requirements

Of the materials listed in Table 1.1, the primary candidates that offer potential to increase the performance of future energetic materials are ADN, TNAZ and CL-20. The energy content of FOX-7 is comparable to that of RDX; however, it is significantly less sensitive and therefore a promising material for further development. Except for NC-based formulations, polymeric binders are used as the matrix of energetic materials. Newly developed energetic binders offer the possibility of improving the performance of composite systems. The optimal combination of solid material and binder is critical to the development of improved performance systems across the range of applications.

Based purely on chemical structure, CL-20, TNAZ and ADN are promising candidates as formulation ingredients for any of the three application areas (HX, GP or RP), because of their performance advantages. However, performance is not the only criterion that determines a material's suitability for practical application; other important considerations include the following:

- availability (and price);
- thermal and mechanical sensitivity [insensitive munitions (IM) characteristics];
- processability;
- compatibility;
- chemical and thermal stability;
- temperature-dependent mechanical behavior;
- burn rate behavior (for solid rocket propellants and propellant powders).

Each of the application areas has its own specific requirements with respect to the properties listed above.

1.2.1 Explosives

Material density clearly plays the most important role in developing a high-performance explosive. For example, the density is directly related to detonation

velocity and Gurney energy of the formulation. This relationship is described by the Kamlet-Jacobs [1.1] equations:

$$D = A \cdot \left[N \cdot M^{0.5} \cdot (-\Delta H_{\mathrm{d}}^{\circ})^{0.5} \right]^{0.5} \cdot (1 + B \cdot \rho_0) \tag{1.1}$$

$$P_{\mathrm{CJ}} = K \cdot \rho_0^{\,2} \cdot \left[N \cdot M^{0.5} \cdot \left(-\Delta H_d^{\circ} \right)^{0.5} \right] \tag{1.2}$$

where

D = detonation velocity (mm/μs);
A = 1.01;
B = 1.3;
K = 15.85;
N = mol gas per g explosive;
M = mean molecular weight of the gas (g);
ΔH_d^o = heat of detonation (cal/g);
ρ_0 = density of the explosive (g/cm^3);
P_{CJ} = detonation pressure (kbar).

In addition to the goal of high density, other primary considerations in developing explosives include processability and the ability to attain insensitive munitions (IM) characteristics. IM properties actually depend on the complete system rather than single ingredients. However, one can often make good predictions of the IM properties of the system based on single-ingredient properties such as thermal or friction/impact sensitivity. Finally, in developing a formulation one must search for the optimal balance of chemical architectures, because generally as the performance increases, so does the material's sensitivity. However, there are certain chemical combinations that yield relatively insensitive compounds despite their relatively high energetic content.

Again, it is important to distinguish between the sensitivity of individual ingredients and that of the final, tailored formulation. For instance, pure CL-20 is relatively sensitive to both impact and friction. However, as a component in a PBX formulation, the sensitivity of the resulting formulation is only slightly greater than that of a comparable formulation based on HMX. The fact that the CL-20-based formulation exhibits higher performance makes it an interesting candidate for certain applications.

In fact, the potential to develop energetic materials with IM properties is not limited to new materials. The sensitivity of well-established energetic materials can be reduced through various material improvements, such as better crystal quality, reducing crystal or molecular defects, eliminating voids, chemical impurities or the existence of multiple phases. Properties that are advantageous for IM systems include the following:

- high decomposition temperature;
- low impact and friction sensitivity;
- no phase transitions when the substance is subjected to rapid volume expansion or contraction;

- no autocatalytic decomposition;
- spherical crystal morphology;
- good adhesion of the binder matrix;
- no voids brought about by solvent or gas bubbles;
- high chemical purity;
- phase purity. Performance characteristics and IM properties of various materials are given in Tables 1.2 and 1.3.

Table 1.2. Performance characteristics of explosive components and example formulations[a].

Substance	ΔH_f (kcal/kg)	ϱ (g/cm^3)	D_{calc} (m/s)	P_{CJ} (GPa)	ΔE at $V/V_0 = 6.5$ (kJ/cm^3)	V_{gas} at 1 bar (cm^3/g)
TNT	−70.5	1.654	6881	19.53	−5.53	738
RDX	72.0	1.816	8977	35.17	−8.91	903
HMX	60.5	1.910	9320	39.63	−9.57	886
PETN	−407.4	1.778	8564	31.39	−8.43	852
TATB	−129.38	1.937	8114	31.15	−6.94	737
HNS	41.53	1.745	7241	23.40	−6.30	709
NTO	−237.8	1.930	8558	31.12	−6.63	768
TNAZ	45.29	1.840	9006	36.37	−9.39	877
CL-20	220.0	2.044	10065	48.23	−11.22	827
FOX-7	−85.77	1.885	9044	36.05	−8.60	873
ADN	−288.5	1.812	8074	23.72	−4.91	987
LX-14:						
95% HMX/5% estane	10.07	1.853	8838	35.11	−8.67	880
LX-19:						
95% CL-20/5% estane	161.6	1.972	9453	42.46	−10.07	827
Composition B:						
60% RDX/40% TNT	9.55	1.726	7936	27.07	−7.23	840
60% RDX/40% TNAZ	55.4	1.801	8827	34.16	−8.81	894
Octol:						
75 HMX/25 TNT	27.76	1.839	8604	33.54	−8.41	850
75 HMX/25 TNAZ	56.73	1.892	9237	38.69	−9.52	883

a ΔH_f = heat of formation; ρ_0 = density (TMD = total maximum density); D_{calc} = calculated detonation velocity; P_{CJ} = calculated detonation pressure; ΔE at $V/V_0 = 6.5$ = calculated Gurney energy at an expansion ratio of 6.5; V_{gas} = gas volume at 1 bar of 1 g of explosive

Table 1.3. Insensitive munitions properties of existing and new energetic materials.

Substance	Friction sensitivity (N)	Impact sensitivity (N m)	Deflagration point (°C)
TNT	353	15	300
RDX	120	7.4	230
HMX	120	7.4	287
CL-20	54	4	228
TNAZ	324	6	>240
TATB	353	50	>325
FOX-7	216	15–40	>240

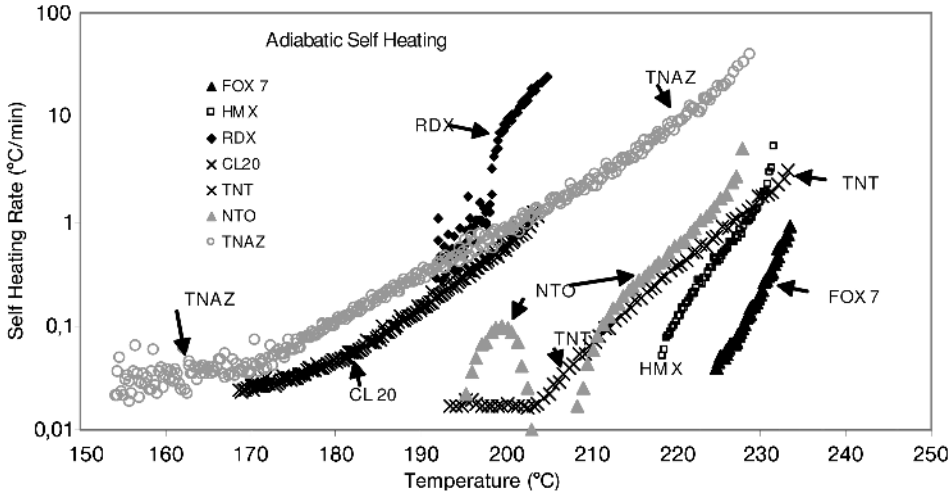

Figure 1.1. Adiabatic self-heating rate of various energetic materials.

The onset of decomposition temperature is only one criterion that impacts IM properties. Just as important is the material's heat quantity release characteristics, which cause material self-heating and accelerated decomposition. The **a**diabatic **r**ate **c**alorimeter (ARC) can be used to measure self-heating temperatures and rates, allowing these properties to be compared for different materials. Fig. 1.1 shows values of the self-heating rate for various pure compounds. The most sensitive substances tend to exhibit a low decomposition temperature and a rapid increase in self-heating rate over the temperature range examined.

It is important to distinguish between the sensitivity of raw materials and that of the finished product. A goal of modern explosive processing methods is to reduce considerably the sensitivity characteristics of the formulation compared with those that of the individual components.

In addition to active charges such as Composition B or octol, which use castable TNT more or less as a binder, **p**lastic **b**onded e**x**plosives (PBX) also consist of a polymeric binder that serves as a matrix for energetic fillers. Cleverly tailored formulations can be developed for specific applications by incorporating specially selected additives. NTO (3-nitro-1,2,4-triazol-5-one) has proven to be an important component of **i**nsensitive **h**igh **e**xplosive (IHE) formulations. Incorporating NTO significantly reduces a formulation's sensitivity, with only a relatively small decrease in performance characteristics. Nevertheless, the majority of active charge formulations currently used are still based on well-known energetic components such as TNT, PETN, RDX and HMX. Common examples include the following:

- Composition B (60% RDX/40% TNT) and
- octol (75% HMX/25% TNT);
- C4 (91% RDX/9% polyisobutylene) as explosive plasticizer;