

1

New Energetic Materials

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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-trinitroazetidine);
- **HNIW** (hexanitrohexazaisowurtzetane or **CL-20**);
- **ONC** (octanitrocubane);
- **FOX-7** (1,1-diamino-2,2-dinitroethene);
- **ADN** (ammonium dinitramide). 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)
<i>Existing energetic materials</i>					
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
<i>New energetic materials</i>					
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:

$$D = A \cdot [N \cdot M^{0.5} \cdot (-\Delta H_d^\circ)^{0.5}]^{0.5} \cdot (1 + B \cdot \rho_0) \quad (1.1)$$

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

where

- D = detonation velocity (mm/ μ s);
- 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° = heat of detonation (cal/g);
- ρ_0 = density of the explosive (g/cm³);
- 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

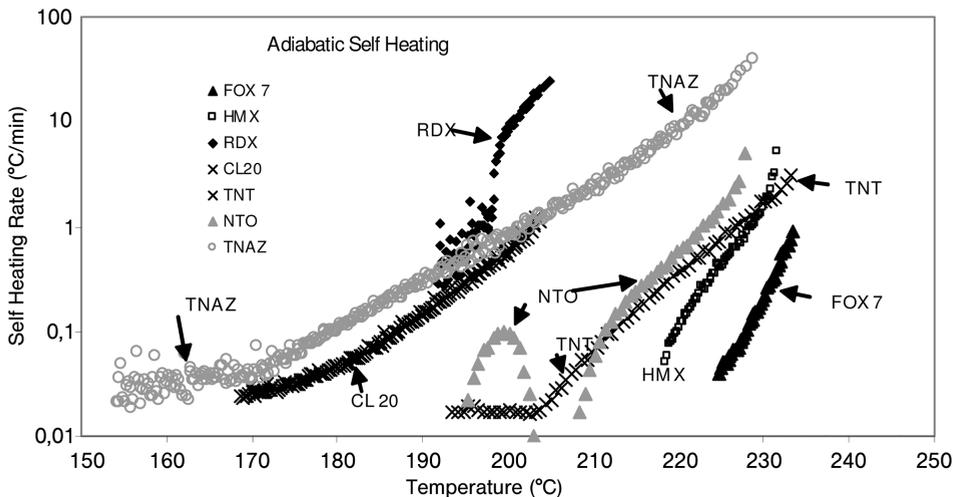


Figure 1.1. Adiabatic self-heating rate of various energetic materials.

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 adiabatic rate calorimeter (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, plastic bonded explosives (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 insensitive high explosive (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;

- A5 (99% RDX/1% stearic acid);
- LX-14 (95% HMX/5% estane).

Nitramine/wax and nitramine/estane formulations with high filler content are often employed as hollow charges.

For explosives, materials with high densities are attractive, because the detonation velocity and maximum detonation pressure are highly dependent on density. CL-20 has the highest density and, as a result, has the highest detonation velocity [1.2]. Due to the high energy content of this cage-like molecule, the detonation pressure and Gurney energy are also very high, with values more than double those of TNT.

Most properties of TNAZ fall between those of RDX and HMX. Of interest, however, is its low melting temperature of 101 °C, which is near that of TNT (80.8 °C). This indicates that TNAZ could be used instead of TNT in melt or casting processes, while potentially providing improved performance.

ADN is an oxidizer. A wide variety of explosive charges [1.3] exist, particularly for underwater use, including aluminum as fuel and AP as oxidizer. In general, AP reduces the detonation velocity of an energetic system because it is not an ideal explosive material. Using ADN in place of AP could result in improved properties in such formulations.

FOX-7 is extremely interesting as an insensitive explosive in the performance class of RDX. The complex synthesis required for this material, however, means that it is expensive and only small quantities are commercially available. Nevertheless, FOX-7 certainly has huge potential as a component of future formulations with improved IM properties. The emphasis in recent years on IM properties, even at the expense of performance increases, has resulted in increased attention on good IM candidate materials such as FOX-7.

1.2.2

Solid Rocket Propellants

The most important application properties for solid rocket propellant formulations are the specific impulse (I_{sp}) and burn rate characteristics:

$$I_{sp} = k_1 \cdot (T_c N)^{0.5} = k_2 \cdot (T_c / M)^{0.5} \quad (1.3)$$

where T_c = flame temperature in the combustion chamber; N = number of moles per unit weight; M = mean molecular weight of the combustion gases; and k_1, k_2 = constants. The specific impulse is high

- when the heat of reaction is high;
- when the products have a high flame temperature;
- when the mean molecular weight of the reaction products is small.

Other important parameters besides specific impulse include the burn rate and pressure exponent. In the ideal case, the burn rate is independent of pressure ($n = 0$;

i. e. plateau burning). Generally, however, the propellant's burn rate increases with increasing energy input into the system. If the pressure exponent is too high ($n > 0.7$), practical applications may not be feasible, even for an otherwise promising energetic system. The incorporation of specialized burn rate modifiers, which typically have a catalytic influence on the burn rate process, can alter the burn rate and pressure exponent sufficiently to enable practical applications to be realized:

$$r = a \cdot p^n \quad (1.4)$$

where r = burn rate; a = constant; p = pressure; and n = pressure exponent. This equation is not generally applicable and is relevant only over a small pressure range. Performance data for solid rocket propellants are given in Table 1.4.

Specific impulse is commonly compared at a chamber pressure of 7 MPa, which results from the American standard of 1000 psi, which equates to 6894 MPa.

Differences in the various types of solid propellants can be summarized as follows. Double-base (DB) solid propellants consist primarily of nitroglycerine and nitrocellulose mixed with processing and burn rate additives. The use of such propellants is widespread. Their specific impulse ranges from 2100 to 2300 N s/kg. DB propellants have a relatively low or moderate burn rate of $r = 10\text{--}25$ mm/s at 7 MPa with a pressure exponent $n = 0\text{--}0.3$. DB propellants are low signature, but they are relatively sensitive to detonation and pose difficulties under low-temperature conditions.

Composite propellants based on ammonium perchlorate, aluminum and HTPB comprise the second group of commonly employed propellants. They have significantly higher performance than DB propellants, with specific impulses in the range 2500–2600 N s/kg for aluminum-based formulations. So-called reduced smoke formulations without aluminum have a specific impulse of 2400–2500 N s/kg, with a burn rate r of 6–40 mm/s at 7 MPa and a pressure exponent of $n = 0.3\text{--}0.5$.

Table 1.4. Performance data for solid rocket propellants (values at 7 MPa).

Type	I_{SP} (N s/kg)	r (mm/s)	n	Signature	Status
Composite, AP/Al/HTPB/nitramine	2500–2600	6–40	0.3–0.5	High	Existing
Composite (reduced smoke), AP/HTPB/nitramine	2400–2500	6–40	0.3–0.5	Reduced	Existing
DB RP, NC/NG	2100–2300	10–25	0–0.3	Low	Existing
AN RP, GAP/AN/nitramine/plasticizer	2200–2350	5–10	0.4–0.6	Low	R&D tested
Nitramine RP, GAP/nitramine/AP/plasticizer	2300–2450	10–30	0.4–0.6	Low	R&D tested
ADN RP, GAP/ADN/nitramine/plasticizer	2400–2600			Low	R&D new
ADN/Al RP, GAP/Al/ADN/nitramine/plasticizer	2500–2700			Low	R&D new

Disadvantages of composite formulations include the primary and secondary signatures emitted and their relatively high friction and impact sensitivity. However, on the positive side, their detonation sensitivity is relatively low and HTPB-based formulations generally exhibit good mechanical properties. Another disadvantage of formulations containing ammonium perchlorate is the undesirable emission of hydrochloric acid as an exhaust product. High-performance propellants usually contain aluminum fuel (owing to its high heat of combustion) and AP as the oxidizer. Hot microparticles of aluminum oxide (Al_2O_3) are released as an exhaust product, as is HCl. This combination disperses and absorbs radiation over all relevant wavelengths, making detection by an adversary relatively simple. In addition, the rocket's own external radar- or laser-based guidance system is adversely affected by the strong exhaust signature. Moreover, the emission of large amounts of environmentally damaging hydrochloric acid is very undesirable from an environmental perspective [1.4].

Development of a smokeless, low-signature solid propellant with performance equivalent to currently employed AP/Al composite formulations ($\sim 2600 \text{ N s/kg}$) is a major goal of the energetic materials industry.

One development approach is to use nitramines such as RDX or HMX with a corresponding reduction in the AP content. CL-20 offers an attractive option as an alternative high-energy nitramine oxidizer. In fact, the possibility exists that CL-20-based formulations may allow the development of materials that contain little or no AP. A second possibility is to replace AP with the alternative oxidizer ADN. ADN is also chlorine free and propellants based on this oxidizer emit environmentally acceptable exhaust gases [1.5].

To achieve performance increases beyond existing AP/Al composite formulations requires the combustion of substances such as Al or AlH_3 with ADN as an oxidizer. Such formulations would still emit a significant signature as a result of Al_2O_3 in their exhaust gases. They would, however, exhibit performance advantages beyond anything previously developed in the area of composite solid rocket propellants.

In summary, ADN is the material of choice to be developed as an alternative oxidizer to AP. However, CL-20 combined with an energetic binder could allow the development of smokeless solid propellants with relatively high performance. Experimental studies still need to be conducted to determine whether the burn rates and pressure exponents of formulations based on such new components will be in the acceptable range for practical applications.

1.2.3

Propellant Powder

For propellant powders, the specific energy (force, E_s) is often used to compare different formulations:

$$E_s = N_G \cdot R_0 \cdot T_{\text{Ex}} \quad (1.5)$$

where N_G = number of moles of the gas; T_{Ex} = flame temperature; and R_0 = gas constant. Additional parameters shown in Table 1.5 include the combustion tem-

Table 1.5. Performance data of propellant powders (at charge density 0.1, calculated ICT code).

Powder type and formulation	E_s (J/g)	Q_{ex} (J/g)	T_{Ex} (K)	MM (g/mol)
<i>Conventional powders</i>				
Single-base A5020, 92% NC (13.2% N)	1011	3759	2916	23.98
Double-base JA-2, 59.5% NC/15% NG/25% DGDN	1141	4622	3397	24.76
Triple-base M30, 28% NC/22.5% NG/47.5% NIGU	1073	3980	2996	23.20
<i>HTPB formulations</i>				
30% HTPB/70% RDX	874	3702	2046	17.16
30% HTPB/70% HMX	867	3668	2034	17.19
30% HTPB/70% CL-20	930	4008	2286	17.99
30% HTPB/70% TNAZ	926	4020	2184	17.57
30% HTPB/70% ADN	915	3329	1935	17.58
<i>Semi-nitramine formulations</i>				
30% NC/30% NG/40% RDX	1248	5700	3921	26.11
30% NC/30% NG/40% HMX	1246	5681	3914	26.12
30% NC/30% NG/40% CL-20	1224	5972	4042	27.46
30% NC/30% NG/40% TNAZ	1239	5984	4016	26.95
<i>GAP formulations</i>				
30% GAP/70% RDX	1190	4116	2838	19.83
30% GAP/70% HMX	1181	4082	2816	19.83
30% GAP/70% CL-20	1280	4409	3332	21.64
30% GAP/70% TNAZ	1272	4420	3204	20.94
25% GAP/75% ADN	1294	5454	3604	23.15

perature and the mean molecular mass (MM) of the reaction gases. Studies conducted in the USA often consider the heat of explosion when comparing different powder formulations.

The lower the combustion temperature, the lower is the erosion within the combustion barrel or nozzle caused by the burning powder. For combustion temperatures above 3500 K, erosion within the combustion chamber can become critical. At combustion temperatures below 3000 K, erosion is typically negligible. Powders in which the mean molecular mass of the exhaust gases is low exhibit the best combustion efficiency.

The specific energy value of 1141 J/g exhibited by JA-2 is a yardstick for conventional high-performance propellant powders. JA-2, which consists of 59.5% NC, 15% NG and 25% DGDN, has close to the optimum energy achievable among compositions consisting purely of NC and nitrate acid ester plasticizers. However, various strategies can be employed to attain propellant powders with still higher performance characteristics. For instance, the so-called semi-nitramine powders use NC as the binder matrix and incorporate nitramine solid fillers. Such formulations exhibit higher performance than JA-2. This high energy content leads to a relatively high combustion temperature (~4000 K). The combustion temperature can, how-

ever, be suppressed to an acceptable level by the addition of appropriate plasticizers. In addition to the conventional nitramines RDX and HMX, CL-20 and FOX-7 can also be employed as the nitramine filler in semi-nitramine formulations.

Formulations with the inert binder HTPB and energetic filler up to solids concentrations of 70% exhibit relatively low performance, with a maximum specific energy <1000 J/g. Further increases in the solids content results in systems that are extremely detonation sensitive. An alternative approach is to use an energetic binder as the binder matrix. The use of GAP with nitramine fillers up to 70% solids results in formulations with specific energies well above conventional state of the art high-energy JA-2. Despite their high energy content, GAP-based propellants burn at reasonable combustion temperatures ranging from 2800 to 3300 K. In particular, GAP/TNAZ and GAP/CL-20 formulations exhibit significantly higher energy content at practical combustion temperatures. This indicates the enormous energy increases potentially available through the use of such formulations.

In addition to GAP, there are a number of other energetic binder candidates which, combined with other new energetic materials, have excellent potential for development as future high-energy propellant powders. However, as is the case for solid rocket propellants, the burn rate behavior of such formulations is very difficult to predict and must be determined experimentally through further research and development.

1.3

New Energetic Materials

New materials offer the potential for significant performance gains and other improvements for energetic systems used in all of the main practical energetic applications, i. e. explosives, solid rocket propellants and propellant powders. Realization of attractive, practical formulations will depend on the availability, processability, compatibility and the material property spectrum of such new materials. In this section, the known material properties of each of these new energetic materials are discussed.

1.3.1

CL-20

CL-20 or HNIW was first discovered by Arnold Nielsen [1.6, 1.7] in 1986 at the laboratory formerly known as the Naval Surface Weapons Center in China Lake, California. The molecular structure of this cage-shaped molecule is shown in Fig. 1.2.

1.3.1.1 Synthesis and Availability of CL-20

CL-20 is the highest energy single component compound known to date and, in addition, has the highest density of any known organic substance. Thiokol Corpora-

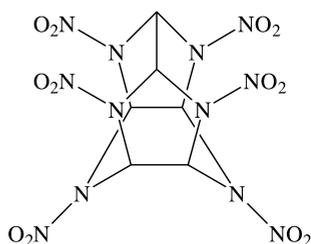


Figure 1.2. CL-20 or hexanitrohexaazaisowurtzitane (HNIW).

tion modified the original synthesis method pioneered by Nielsen [1.8–1.10] and constructed a pilot facility for small scale production of CL-20. Today, CL-20 is commercially available in kilogram quantities. It is also commercially available in various particle sizes from SNPE in France, which uses yet another modified synthesis method [1.11].

CL-20 is manufactured batchwise in lots of 50–100 kg. CL-20 has not yet been synthesized as a pure single phase, but instead exists in multiple solid phases, of which the ϵ -phase has the highest density. After the initial synthesis process, the raw product is recrystallized into ϵ -CL-20 in the presence of a suitable solvent. The resulting particle size distribution can be tailored based on the process parameters. Commercially available material is available with the following range of particle sizes:

$$120 < x_{50,3} < 160 \text{ } \mu\text{m};$$

$$20 < x_{50,3} < 40 \text{ } \mu\text{m};$$

and

$$x_{50,3} < 5 \text{ } \mu\text{m}.$$

Coarse particles are produced directly via the crystallization process, whereas fine particle fractions must be obtained by grinding the coarse material.

The chemical purity [1.12] of the SNPE and Thiokol products are 98 and 96%, respectively. Impurities include residual solvent and incompletely nitrated intermediate products with benzyl, acetyl or formyl groups. It is not yet known whether and how such impurities affect the sensitivity, phase transition or other material properties of CL-20.

The quoted price of CL-20 is considerably higher than € 1000/kg. It is therefore not yet attractive for most applications, solely on account of its high cost.

1.3.1.2 Chemical and Thermal Properties of CL-20

CL-20 is a white powder. The onset of thermal decomposition occurs at ~ 215 °C. An example differential scanning calorimetric (DSC) curve of CL-20 is shown in Fig. 1.3 [1.13].

CL-20 is soluble in acetone, esters and ethers, but is insoluble in water and aromatic or halogenated solvents. It is compatible with most solids and binders, such as RDX, HMX, AP, PETN, nitric acid esters, isocyanates, GAP and HTPB. It is incompatible with bases, amines and alkali metal cyanides (e.g. NaCN).

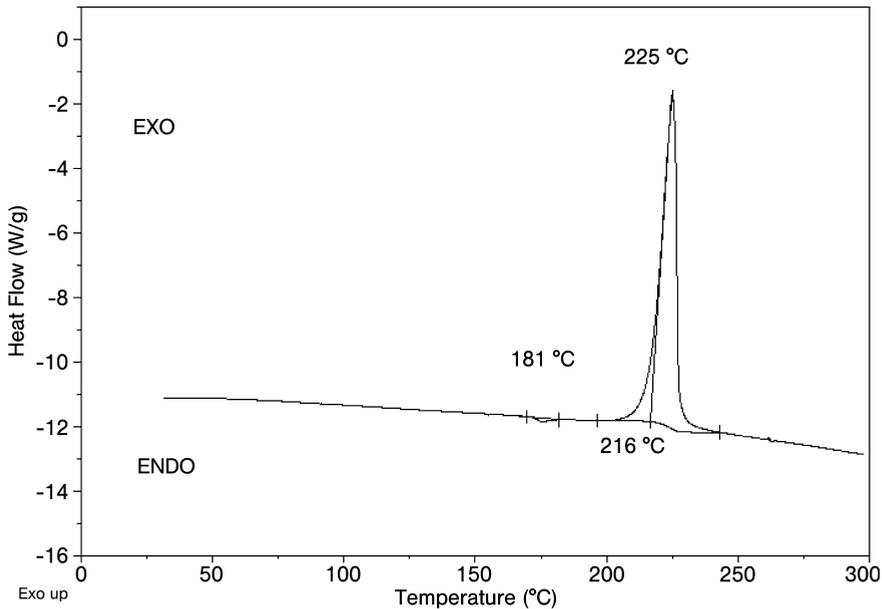


Figure 1.3. DSC curve of CL-20.

The material data sheet from SNPE lists the following properties for CL-20:

- deflagration temperature: 220–225 °C;
- decomposition temperature: 213 °C;
- maximum decomposition temperature: 249 °C;
- heat of decomposition: 2300 J/g;
- detonation velocity: 9650 m/s (experimental value);
- vacuum test, 193 h at 100 °C: 0.4 cm³/g.

1.3.1.3 Sensitivity and Phase Behavior of CL-20

The impact sensitivity of CL-20 is similar to that of PETN. As a result, extensive safety precautions must be employed during processing and handling of CL-20. As a result, many international research efforts are directed at reducing the sensitivity of CL-20 through methods such as improved crystallization conditions (to produce defect-free crystals) and the development of a suitable inert coating.

Table 1.6. Properties of CL-20 phases.

Property	γ -CL-20	α -CL-20	β -CL-20	ϵ -CL-20	HMX
Density (g/cm ³)	1.92	1.97	1.99	2.04	1.91
Detonation velocity (m/s)	9380	9380	9380	9660	9100
Phase transition temperature (°C)	260	170	163	167	280

Data available thus far indicate that CL-20 becomes more sensitive as the particle size is reduced. Crystallized CL-20 is therefore not as sensitive as the milled material. CL-20 exists in four polymorphic structures: α , β , γ and ϵ (Table 1.6). The ϵ -phase crystallizes with a very high density and is therefore the phase of interest. All the other phases have considerably lower densities. The α -phase is a semi-hydrate and crystallizes in the presence of water. The phases can be distinguished through IR spectroscopy and X-ray diffraction.

1.3.2

Octanitrocubane

In early 2000, Mao-Xi Zhang and Philip E. Eaton of the University of Chicago, in collaboration with Richard Gilardi of the Naval Research Laboratory in Washington, DC, successfully synthesized octanitrocubane [1.14]. Octanitrocubane is a cube-shaped carbon-based molecule with nitro groups at each corner of the cube (Fig. 1.4). Its chemical formula is $C_8(NO_2)_8$. The molecule's high energetic content derives from the large number of nitro groups per carbon atom and its highly stretched ring structure. The cubic form of the molecule forces the carbon atoms to assume bonding angles of 90° .

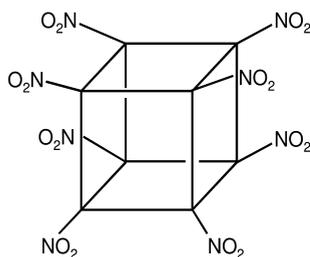


Figure 1.4. Octanitrocubane (ONC).

It could be said that octanitrocubane is a compound conceived on a drawing board. Its explosive properties were predicted years before even its precursors had ever been synthesized. Various theoretical calculations of octanitrocubane's density yielded values from 1.9 to 2.2 g/cm^3 . The densities of other explosive materials are given in Table 1.1.

Compared with conventional explosive materials such as TNT, RDX and HMX, even at the lower density value of 1.9 g/cm^3 , the energy content of octanitrocubane is comparable to that of HMX. If its density approaches the maximum theoretical value of 2.2 g/cm^3 , it would exceed that of CL-20, which is the highest known of any organic compound.

For over 10 years, synthetic chemists have labored to add nitrate groups to carbon-based cube-shaped molecules (cubanes). A milestone in this effort was achieved in 1997 with the synthesis of tetranitrocubane (containing four nitro groups), which has explosive properties comparable to those of RDX. From a chemical development standpoint, the synthetic efforts of the research group led by Philip E. Eaton, culminating in the synthesis of octanitrocubane, represent a monumental accom-

Table 1.7. Density of nitrocubanes [1.15].

Molecule	Density (calc.) (g/cm ³)	Density (g/cm ³)	DSC onset tempera- ture(°C)
Cubane	1.29	1.29	
1,4-Dinitrocubane	1.66	1.66	257
1,3,5-Trinitrocubane	1.77	1.76	267
1,3,5,7-Tetranitrocubane	1.86	1.81	277
1,2,3,5,7-Pentanitrocubane	1.93	1.96	–
Octanitrocubane	2.13	1.98	–

plishment. One could follow the developments in the literature, as nearly every year an additional nitro group was incorporated into the base molecule. The recent synthesis of octanitrocubane is incredibly complex and difficult, requiring numerous intermediate steps, including the preparation of tetranitrocubane as an intermediate compound (see Table 1.7). ONC is at present still available only in minute laboratory quantities, with each milligram more valuable than gold.

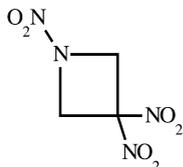
Now, to answer the long awaited question: does the synthesized octanitrocubane exhibit the high density predicted theoretically, thereby fulfilling the enormous expectations of the energetic materials community? The answer is: yes and no. The measured density of octanitrocubane is 1.979 g/cm³, which is of course high, but is near the low end of the theoretical range predicted. Hence ONC did not set a new record; instead, its density is comparable to the values exhibited by RDX and HMX. The density of ϵ -CL20 remains by far the highest of the newly synthesized organics.

It is still possible of course that, like CL-20, various polymorphic forms of octanitrocubane may exist. Thus far, crystal modification of ONC has only produced an isolated hydrate compound. Future work will certainly be focused on other crystal modifications of octanitrocubane. Theoretical calculations of the density of such a still fictional compound range from 2.123 to 2.135 g/cm³.

1.3.3

TNAZ

TNAZ (1,3,3-trinitroazetidine) [1.16], which has a performance roughly between those of RDX and HMX, was first synthesized by K. Baum and T. Archibald of Fluorochem in Asuza, California. The structural form of this compound is shown in Fig. 1.5.

**Figure 1.5.** TNAZ (1,3,3-trinitroazetidine).

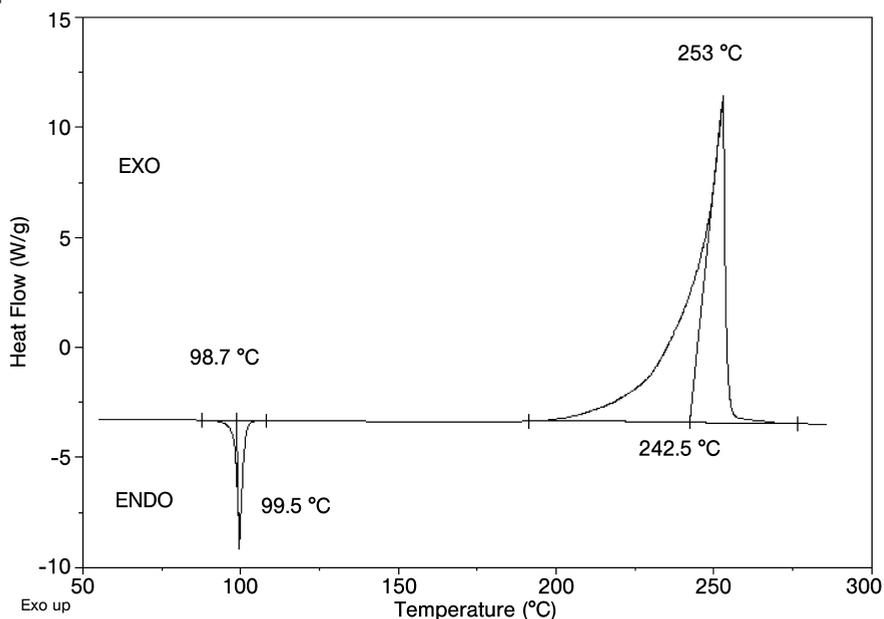


Figure 1.6. DSC diagram of TNAZ.

1.3.1.1 Chemical and Thermal Properties of TNAZ

The energy content of TNAZ is elevated owing to the tension in the four rings (the molecule has a positive heat of formation of 26.1 kJ/mol and a density of 1.84 g/cm³). The substance exhibits outstanding thermal stability, with the onset of decomposition occurring above 240 °C (Fig. 1.6) [1.17]. A particularly attractive property of TNAZ is its low melting temperature of about 100 °C. TNAZ is thus potentially suitable for casting processes such as those in which TNT is currently used. TNAZ is compatible with aluminum, steel, brass and glass and is not hygroscopic.

A number of studies have been conducted on eutectic mixtures of TNAZ [1.18]. The results indicate that mixtures of TNAZ with RDX or HMX exhibit only a slight melting point depression of 1–5 °C. There are few data to assess the suitability of TNAZ in casting processes. Obviously, its high vapor pressure and crystallization behavior in the melt state could cause processing difficulties.

1.3.3.2 Synthesis and Availability of TNAZ

TNAZ is not commercially available. The original synthesis accomplished in 1983 had far too many steps and insufficient yield (<5%) to make the material commercially viable. Subsequently, American researchers developed a simplified synthesis route and improved the yield to >70%. Today, batchwise lots of ~50 kg can be manufactured. Production costs exceed € 1000/kg, primarily owing to the high cost of the catalyst required [1.19].

1.3.4

ADN

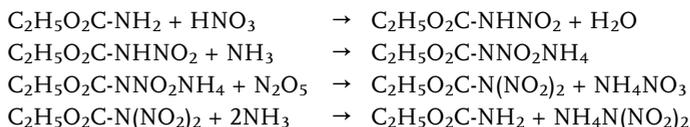
The third new component primed for application is ADN [ammonium dinitramide, $\text{NH}_4\text{N}(\text{NO}_2)_2$]. ADN is primarily of interest as an oxidizer for solid rocket propellants, particularly owing to its potential to replace ammonium perchlorate.

1.3.4.1 **Synthesis and Availability of ADN**

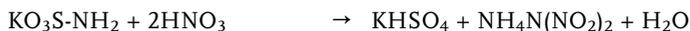
ADN was first publicly announced by Professor Tartakowsky at the ICT annual conference in 1993 [1.20]. Simultaneously, it was proposed as a new oxidizer for solid rocket propellants by Pak [1.21] in the USA.

ADN was synthesized in Moscow at the Zilinsky Institute and developed within the former Soviet Union for use in solid rocket propellants for tactical rockets. ADN was produced in ton-size quantities for this purpose. It is assumed that the manufacturing facilities for ADN were destroyed or dismantled; at any rate, it is certain that they no longer exist. The substance was unknown outside of the Soviet sphere and the Western world was neither aware of the large production facilities dedicated to ADN nor to its use in tactical rockets. Following the first publication about ADN in the West, researchers have attempted to duplicate the Russian development efforts and produce a material suitable for practical applications.

There are at least 20 different synthesis routes that successfully produce ADN, two of which have proved to be technically relevant. The first is the so-called urethane synthesis:



This synthetic method requires four synthesis steps and results in a yield of up to 60%. The processing method is not difficult and the amount of waste produced is relatively low. The urethane can be cleaned and recycled within the process. The second synthesis method uses salts of the amidosulfuric acid:



The nitration with amidosulfonates can be accomplished in the absence of organic solvents, but must occur in strongly acidic media, which can lead to decomposition of the dinitramide. This synthesis also concludes with a purification step to reclaim ADN. This process was extensively developed by FOI and Nexplor [1.22] and today it is used for the commercial manufacture of ADN.

A number of steps are required to manufacture ADN that is useful for practical formulations. ADN crystallizes into rod or lamellar structures, which are unsuitable for further processing as energetic formulations. The raw product therefore must be

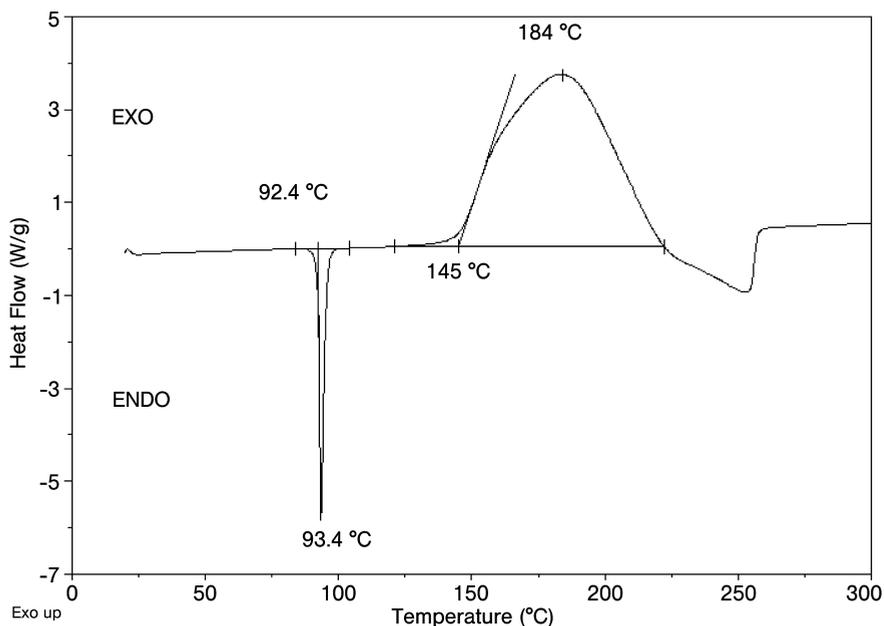


Figure 1.7. DSC diagram of ADN.

ground into spherically shaped particles of desired particle size (see Sect. 3.2.7). ADN also must be stabilized in order to attain the service life required for practical applications.

1.3.4.2 Thermal Behavior of ADN

ADN exhibits a melt temperature ranging from 91.5 to 93.5 °C (Fig. 1.7). Melt temperature values reported in the literature actually range from 83 to 95 °C. This large variation in the reported values is most likely attributable to impurities, which can have a significant influence on the ADN melt temperature even at very low concentrations. For instance, residues of water and especially of ammonium nitrate (AN) result in a clear decrease in the ADN melting temperature. Ammonium nitrate is not only a by-product of the ADN synthesis, it is also one of the primary alternative oxidizers to ADN. The AN concentration in ADN plays a key role in the long-term stability characteristics of ADN itself.

Further heating of the ADN melt (Fig. 1.7) results in exothermic decomposition. The decomposition is initiated by dissociation of ammonia and free dinitramide acid $[\text{HN}(\text{NO}_2)_2]$ [1.23]. The free dinitramide acid immediately breaks down into N_2O and HNO_3 . The latter condenses with NH_3 to form ammonium nitrate, which undergoes a second decomposition step, releasing N_2O and water. Other side reactions and the formation of NO , NO_2 , N_2 and O_2 occur along with the reaction sequence described. ADN decomposition is an acid-catalyzed process, due to the initial step. In addition to being thermally labile, ADN is also light sensitive.

1.3.4.3 Long-term Stability of ADN

Water content

As indicated above, small concentrations of impurities have a significant effect on the long-term stability of ADN. In general, the stability of ADN increases as the amount of water impurity decreases; however, completely water-free ADN is also unstable. It has been found that ADN stability is not degraded when the water content ranges from 0.1 to 0.5%. ADN is hygroscopic and must therefore be stored and processed in a dry environment.

Ammonium nitrate

Ammonium nitrate impurities in ADN cause problems because at certain AN concentrations a lower melting eutectic compound is formed. Ammonium nitrate is a salt of a weak base and strong acid and can thus lead to acid-catalyzed decomposition of ADN. However, residual concentrations of AN below 0.5% appear to be unproblematic.

Organic impurities

Because ADN is an oxidizer, organic impurities, such as organic solvent residues, are deleterious. Such compounds apparently take part in redox reactions that accelerate ADN decomposition. In contrast, long-chain organic compounds can lower the sensitivity of ADN. Therefore, short-chain solvents should never be used to purify ADN.

Stabilization of ADN

ADN stabilizers must fulfil two basic functions: suppress the acid-catalyzed decomposition (i. e. exhibit basic properties) and remove other possible free radicals from the system (i. e. function as a radical interceptor). Substances with such properties function well as ADN stabilizers. For practical applications, the choice of stabilizer and means of incorporating it into the ADN particles must be optimized. One elegant technical solution is to incorporate the stabilizer into the raw material during the recrystallization process.

1.3.4.4 Processability of ADN

As a result of its oxidizer nature, ADN tends to oxidize organic substances. However, in general ADN does not attack C-H and C-C single bonds. Compounds with double-bonded carbons also exhibit good compatibility with ADN. However, ADN is incompatible with isocyanates, spontaneously reacting and decomposing in their presence. This means that the large number of polymers that undergo polyurethane bonding cannot be used with ADN, at least in their common form. This eliminates the possibility of using HTPB or GAP binders with isocyanate as the curing agent. Because conventional polymeric binders used in solid rocket propellants are not compatible for use with ADN, the development of future ADN-based solid propellants is severely limited by the choice of suitable binders.

Good results have been obtained, however, using PCP (polycaprolactone polymer) as a binder with ADN [1.4, 1.24, 1.25]. The formulation with this binder also exhibited the best long-term stability observed by an ADN-based material. Despite these initial encouraging results, the long-term stability and aging mechanisms of such complex formulations must still be thoroughly examined before definitive statements about the applicability of such systems can be ventured.

1.3.4.5 Safety Properties of ADN

A range of different results has been obtained for the impact and friction sensitivity of ADN (Table 1.8). These results indicate that the impact and friction sensitivity of ADN are higher than the values for neat AP. Overall ADN is somewhat more sensitive than RDX. The comparison of neat materials may be misleading. For propellant applications, the sensitivity of formulations gives more relevant data in practice. So far there are no data available with such ADN formulations.

Table 1.8. Friction and impact sensitivity results for ADN compared with AP and RDX.

Substance	Friction sensitivity (N)	Impact sensitivity(N m)
RDX	120	7.4
AP	>320	15–25
ADN	64–72	3–5

1.3.5

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

This compound is a relatively new hope in the explosives world. It was introduced in the fall of 1998 by FOI collaborators in the USA [1.26, 1.27]. Three variations of the

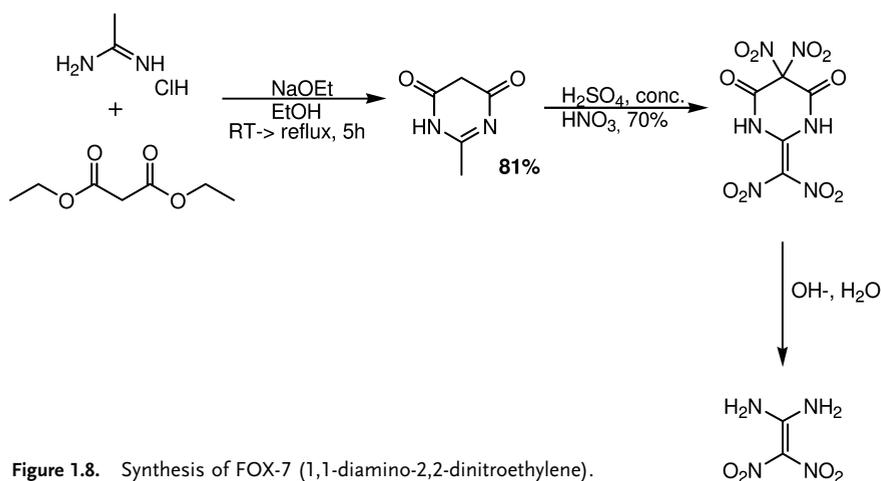


Figure 1.8. Synthesis of FOX-7 (1,1-diamino-2,2-dinitroethylene).

Table 1.9. Properties of FOX-7 (calculations with Cheetah 1.40 [1.23]) and comparison with RDX

Property	FOX-7	RDX
BAM impact sensitivity (N m)	>15	7.4
Petri friction sensitivity (N)	>200	120
Deflagration temperature (°C)	>240	230
Density (g/cm ³)	1.885	1.816
Formation energy (calculated) (kJ/mol)	-118.9	92.6
Detonation velocity (calculated) (m/s)	9040	8930
Detonation pressure (calculated) (GPa)	36.04	35.64

synthetic process have been developed [1.28–1.30], all of which involve the nitration of a heterocyclic compound followed by hydrolysis to form FOX-7. The most promising reaction path is shown in Fig. 1.8.

FOX-7 is commercially available; however, its cost of >€ 3000/kg makes it unrealistic for practical application at present.

FOX-7 has a performance in the range exhibited by RDX, but is considerably less sensitive. Little is known to date about its processability or compatibility with other materials. Such characteristics will surely be the subject of future investigations. Some properties of FOX-7 compared with those of RDX are given in Table 1.9. The very high performance of FOX-7 predicted theoretically remains to be confirmed experimentally. FOX-7 has the potential to contribute positively to the further development and improvement of insensitive munitions.

1.4

Conclusion

It is important to emphasize that the new energetic materials discussed, TNAZ, CL-20, ONC, FOX-7 and ADN, are still experimental. The material properties of these substances must be investigated further and improved before they find application in new or existing weapons systems.

Factors which must be considered when assessing whether such materials will find practical application include the following:

- availability and price;
- performance;
- sensitivity;
- processability;
- compatibility;
- chemical and thermal stability;
- temperature-dependent mechanical behavior;
- burn rate and pressure exponent.

CL-20 is currently commercially manufactured in 50–100-kg batches. As a raw product, CL-20 has a high sensitivity comparable to that of PETN, which is a significant limitation in terms of its processability. Lowering the sensitivity of the raw material by developing an improved crystallization process or coating method is a major challenge for CL-20 suppliers. When processed in a binder matrix, however, CL-20 formulations are not significantly more sensitive than RDX and HMX compositions.

CL-20 has the highest density, 2.04 g/cm^3 , of any organic explosive material. It is a nitramine with good chemical and thermal stability and is compatible with most binder and plasticizer systems. CL-20 has all the characteristics required for application in all three of the energetic material sectors.

Replacing HMX with CL-20 in explosive formulations results in a 10–15% performance increase.

CL-20 combined with an energetic binder in solid rocket propellant formulations results in a reduced smoke composition that approaches the performance of conventional HTPB/AP propellants. The favorable oxygen balance of CL-20 is particularly advantageous. As with other nitramine-based energetic materials, the high pressure exponent must be reduced through the addition of burn rate modifiers.

As a result of its high energetic content and favorable oxygen balance, CL-20 is also applicable as a component of propellant powders. Performance gains of 10–15% are possible if CL-20 is used instead of traditional oxidizers.

Unlike CL-20, TNAZ is not yet commercially available. The synthesis route currently used is so expensive that it is not yet possible to examine TNAZ even in test applications. A major goal is to develop improved methods to manufacture TNAZ at a reasonable cost.

TNAZ has a performance between those of HMX and RDX. The property of TNAZ that is particularly interesting is its low melting temperature of $101 \text{ }^\circ\text{C}$. TNAZ offers the possibility of functioning as a quasi-high-energy TNT. All charges that are manufactured via melt processing, such as Composition B or octol, could be formulated with TNAZ instead of TNT, resulting in compositions with considerably higher performance manufactured using the same basic technology.

ADN is commercially available. It has stability problems if the end product purity is inadequate. It crystallizes into rod-shaped structures and must therefore be ground in order to be used in practical applications. Technologies exist to grind ADN into spherical particles and stabilize it, and such methods must be incorporated into the production process. The aging behavior of ADN that has been properly stabilized is no worse than that of nitrocellulose.

Because of its strong oxidizing nature, ADN is compatible with other systems to only a limited extent. For instance, ADN is incompatible with isocyanates, which are commonly used as curing agents in the binder matrix of energetic materials. ADN is compatible with prepolymers, but requires a specialized curing agent. More research is required to solve the problems related to ADN compatibility.

The primary application for ADN would be for solid rocket propellants, in particular for replacing ammonium perchlorate while maintaining the high performance of AP-based systems. By using ADN in combination with an energetic binder, an impulse as high as the current space booster formulation ($I_{SP} = 2600$ N s/kg) is possible. Incorporating metal fuels in such a formulation, such as Al or AlH_3 , enable even higher specific impulses to be achieved, up to $I_{SP} = 2700$ – 2800 N s/kg. ADN formulations offer the possibility of higher specific impulse propellants and corresponding longer range rocket systems.

In the areas of propellant powders and explosives, ADN is likely to only find niche or specialized applications.

FOX-7 has a performance in the range of RDX but is less sensitive. It therefore has excellent potential as a substitute in formulations that currently use RDX. As such, it could be useful in explosives, propellant powders and solid rocket propellants.

At present, however, FOX-7 is commercially available only at an exorbitant price. Reducing the cost and improving the product quality are therefore the next essential steps in order to enable FOX-7 to be tested in new formulations. Only then it will be possible to determine whether the favorable sensitivity characteristics of this ingredient will lead to IM systems with correspondingly favorable properties.

Overall it appears that new substances exist that could significantly increase the performance of energetic materials in each of the major application areas. It is therefore crucial to explore thoroughly the development potential of these substances.

1.5

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1.6

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