Hydrazinium Nitroformate:
A High Performance Next Generation Oxidizer

Jeroen Louwers

TNO Prins Maurits Laboratory, Research Group Rocket Technology,
P.O. Box 45, 2280 AA Rijswijk, The Netherlands [e-mail: louwers@pml.tno.nl]

ABSTRACT

The use of chlorine-free high performance oxidizers in solid rocket propellants may reduce launch costs, while producing less polluting exhaust products. Hydrazinium nitroformate (HNF) is a candidate for such a next generation oxidizer. In this article the properties of HNF are addressed. Its combustion and decomposition characteristics, and its application in rocket propellants are discussed.

Keywords: oxidizer, hydrazinium nitroformate, HNF, monopropellant, composite propellant, decomposition

Introduction

Solid rocket propellants can be divided into two main categories. Double-base propellants, which are *homogeneous* mixtures, with main ingredients nitroglycerin and nitrocellulose. Another group consists of the so-called composite propellants, which are *heterogeneous* mixtures of oxidizer and fuel. The oxidizer is an inorganic salt, which is held together by a polymer matrix, which also acts as a fuel. Double-base propellants are mostly used in small military missiles. The mechanical properties and performance of composite propellants are better than those of double-base propellants. Therefore, most larger systems (e.g., the boosters of the Space Shuttle) are based on composite propellants.

The majority of the composite propellants use hydroxyl-terminated polybutadiene (HTPB, $\sim CH_{1.5}$) as binder and ammonium perchlorate (AP, NH_4ClO_4) as the oxidizer.[1] Often fine aluminum is added as a fuel to increase the combustion temperature and hence performance. These types of composites are cheap, reliable, and can be tailored to a large range of regression rates by using burn-rate modifiers and varying AP particle-size distribution. However, there is a lot of research on new oxidizers to replace AP. Reasons for this are:

- By replacing AP composites with more energetic composite propellants, launch costs can be decreased dramatically. Reduction of launch costs is important in the current period of increased competition between launcher organizations.

- AP-based composites are characterized by a large amount of hydrochloric acid (HCl) in their exhaust products. During each launch of the Space Shuttle, 162 metric tons of HCl are ejected into the earth's atmosphere! HCl is known for it ozone depletion properties.

- The presence of HCl causes a large smoke trail behind missiles. This so-called secondary smoke consists of condensed water. (Primary smoke is caused by solid particles in the exhaust products, for example, aluminum oxide and soot.) In the presence of HCl, water condenses more easily, as HCl decreases the effective saturation pressure of water (like the white trail behind airplanes). The secondary smoke increases the signature of a missile and is therefore unwanted.

New Oxidizers

The introduction explains the search for new oxidizers that may replace AP. Several alternatives have been identified, and some of them have already been applied in actual systems.

Ammonium nitrate (AN, NH_4NO_3) is an oxidizer that does not contain chlorine. AN-based composite propellants are characterized by their low flame temperature. This makes them ideal for gas generator applications. However, their performance is lower than that of AP-based composite propellants.

The cyclic nitramines, cyclotrimethylenetrinitramine (RDX, $C_3H_6N_6O_6$) and cyclotetramethylene tetranitramine (HMX, $C_4H_8N_8O_8$), are not real oxidizers, as they are stoichiometrically balanced. Both nitramines have a high flame temperature and generate combustion products with a low molecular weight. By replacing AP in AP-based composites with these nitramines, the performance may be increased. RDX- and HMX-based propellants do not show a strong particle-size dependent burning rate.[2] This has been attributed to the melt layer formed during decomposition of these materials. Regression rates of nitramine-based composites can therefore not be tailored by particle-size distribution control. Also combustion catalysts have only been proven partially successful. AP is therefore often only partially replaced by HMX or RDX. The performance gain of nitramine composites is still not the maximum that can be obtained as the binder decomposition products cannot be oxidized, because the nitramines are stoichiometrically balanced.

A new energetic filler is CL20 or hexanitrohexaazaisowurtzitane (HNIW, $C_6H_6N_{12}O_{12}$).

Unlike RDX and HMX, CL20 is not yet used in operational systems. Its main advantage over the cyclic nitramines is its high density, 2.04 g/cm^3. CL20 research is carried out in France and the United States.

Ammonium dinitramide [ADN, $NH_4N(NO_2)_2$] and hydrazinium nitroformate [HNF, $N_2H_4C(NO_2)_3$] are two "new" high-performance oxidizers that do not contain chlorine and have a positive oxygen balance. In the United States, research focuses on the development of ADN-based propellants. There are also ADN programs in France and Sweden. There are indications that Russian rocket engines based on ADN have already been operational for many years.[3] However, ADN is hampered by its low melting point (93 ºC) and hygroscopicity.[4]

HNF was part of a large research project for new high-performance propellants in the 1960s in the United States. HNF appeared to be incompatible with the double bonds in unsaturated binders like HTPB.[5] The recent commercial production of saturated energetic binders, like glycidyl azide polymer (GAP), led to a renewed interest in HNF. The theoretical performance of HNF-based composites is unmatched by any other energetic material. Because of HNF's high performance, the European Space Agency (ESA) decided to fund HNF research.

Several properties of the oxidizers discussed are summarized in Table 1.[6,7] The performance of some typical propellants with some of these oxidizers is given in Figure 1.

Table 1. Properties of Several Oxidizers and Energetic Fillers.[6,7]

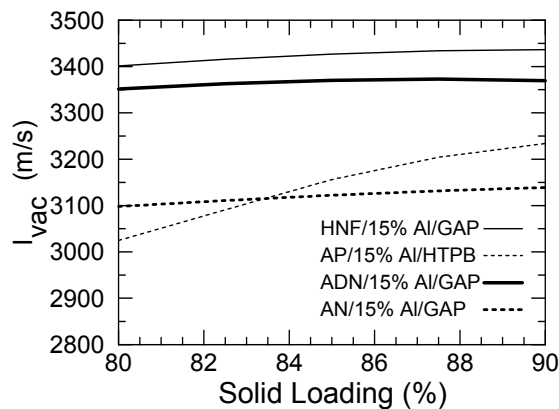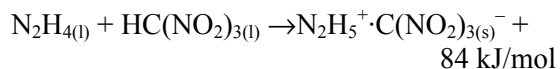|	AN	AP	RDX	HMX	HNF	ADN	CL20
Molecular weight [kg/mol]	80	117.5	222	296	183	124	438
Density [kg/m³]	1720	1950	1820	1960	1860	1800	2040
Heat of formation [kcal/kg]	−1028	−601	+72	+61	−94	−282	+208
Melting point [ºC]	169	230	>170	275	124	93	>195
Oxygen balance $CO+O_2$ [%]	20	34	0	0	21.8	25.8	10.9
BAM friction sensitivity [N]	353	>100	120	120	18–36	350	90–120
BAM impact sensitivity [Nm]	49	15	7.5	7.4	2–4	3–6	3.5–13

Figure 1. Performance of several propellants (Chamber pressure 10 MPa, expansion ratio 100, equilibrium flow).

Hydrazinium Nitroformate

HNF is an orange-yellow solid of formula $N_2H_5 \cdot C(NO_2)_3$. HNF is made by a precipitation reaction between hydrazine (N_2H_4) and nitroform [$HC(NO_2)_3$]:

$$N_2H_{4(l)} + HC(NO_2)_{3(l)} \rightarrow N_2H_5^+ \cdot C(NO_2)_{3(s)}^- + 84 \text{ kJ/mol}$$

As this reaction is exothermic, the process vessel must be thoroughly cooled. After reaction, the HNF crystals are recrystallized, to improve the purity of the raw HNF and to obtain different particle sizes. HNF is now commercially produced in batch quantities by Aerospace Propulsion Products (APP) in Hoogerheide, The Netherlands. At the moment, about 50 kg of HNF are produced each year.

Purity is an important factor for the stability of HNF. Friction and impact sensitivity increase in the presence of even trace impurities. Also, the melting point and thermal stability are very sensitive to the purity of the HNF. Because of this sensitivity, the melting point of HNF is used as a simple method to determine its purity.

HNF particles tend to crystallize into needle-shaped crystals, with large length to diameter ratio's (L/D). Needle-shaped HNF is more sensitive to impact and friction and is not desirable for propellant production. Furthermore, the rheology of needle-shape-based propellants prevents the manufacturing of propellants with high solid loadings. Cubic or spherical crystals would be ideal for both sensitivity and casting properties. By recrystallization, the L/D ratio can be reduced to values between 4 and 5 (see Figure 2), and the different processes also influence the mean particle size. At the moment it is possible to manufacture HNF crystals with particle size varying between 5 and 2000 µm.
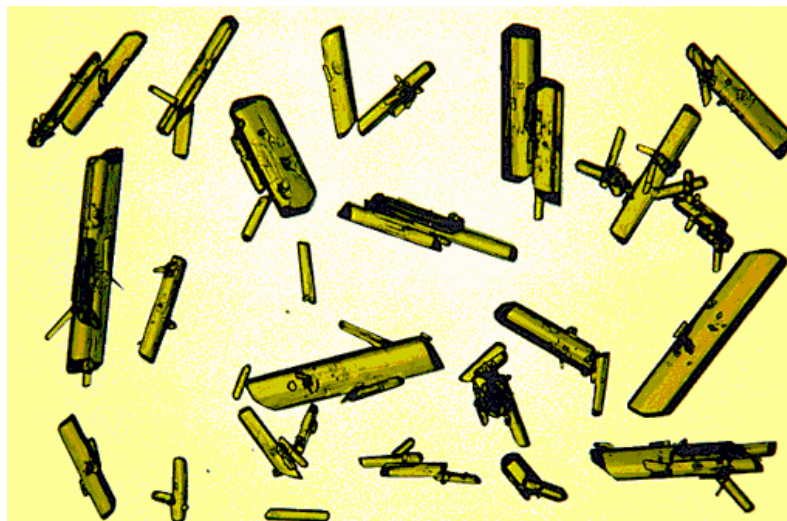

Figure 2. Recrystallized HNF with length to diameter ratio's between 4 and 5, mean diameter about 500 µm.

Monopropellant Combustion

Because of the highly exothermic HNF decomposition, self deflagration of pressed neat HNF is possible, at least in the experimental pressure range of 0.025 to 10 MPa.[8,9] The regression rate, r_b, of HNF monopropellants was determined by McHale and von Elbe.[10] They determined the burning rate of HNF-filled Pyrex tubes at approximately 75% of the theoretical maximum density (TMD). For safety reasons, the HNF was only loosely packed in the Pyrex tubes and not pressed. More recently, regression rates of pressed HNF at 96% TMD were measured.[9,11] The results of both measurements are shown in Figure 3. Neat HNF regression rates are high, reaching more than 40 mm/s at 10 MPa. HNF also burns nicely at subatmospheric pressures down to 0.025 MPa.
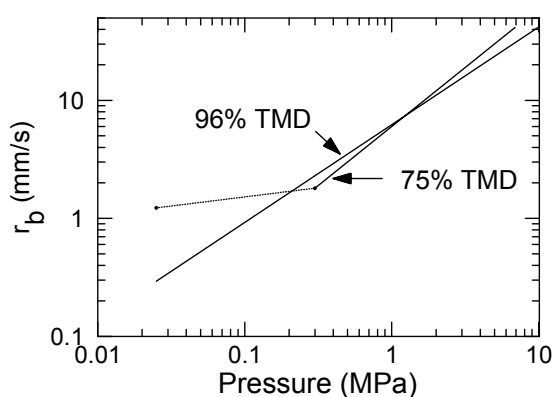

Figure 3. Experimentally determined regression rates of HNF monopropellants for two different TMD values. The beginning and ending points of the lines indicate the experimental pressure range.

Parr and Hanson-Parr measured the species profiles of HNF flames using several optical techniques.[11] The transient combustion of HNF was studied by Finlinson using a laser recoil method.[12] The HNF oscillations were found to be of the same order of magnitude as HMX.

Decomposition

To study the decomposition behavior of HNF under combustion-like conditions, temperature-jump (T-jump) experiments were conducted by Williams and Brill.[13] Species were detected with a Fourier Transform Infra-Red (FT-IR) apparatus.
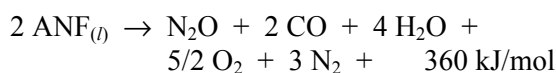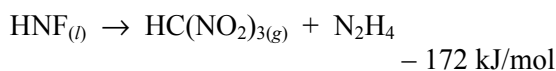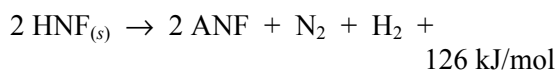
The T-jump studies show a strong dependence of the species formed during decomposition on temperature. It was found that the same three temperature regions as for HNF monopropellant combustion can be distinguished:

1) *Decomposition below 123 ℃:*
   Below the melting temperature of HNF, preheating only; no decomposition occurs.
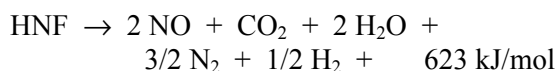
2) *Decomposition from 123 to 260 ℃:*
   This temperature range corresponds with the foam zone found during HNF monopropellant combustion. Ammonium nitroformate (ANF, $NH_4C(NO_2)_3$) aerosol, $HC(NO_2)_3$, N_2H_4, N_2O, H_2O, and CO were detected in the gaseous phase. HNF aerosol was not detected; so the evaporation of HNF followed by gas decomposition was concluded to be negligible. The following reaction scheme was proposed:

$$2\,HNF_{(s)} \rightarrow 2\,ANF + N_2 + H_2 + \qquad 126\,kJ/mol$$

$$HNF_{(l)} \rightarrow HC(NO_2)_{3(g)} + N_2H_4 \qquad -172\,kJ/mol$$

$$2\,ANF_{(l)} \rightarrow N_2O + 2\,CO + 4\,H_2O + \\ 5/2\,O_2 + 3\,N_2 + \quad 360\,kJ/mol$$

Taken together, the reactions above yield 314 kJ/mol of HNF. This exothermicity is confirmed by the thermocouple experiments; this might explain the self-sustained combustion of HNF at subatmospheric pressures.[8]
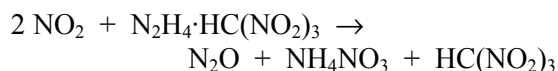
3. *Decomposition above 260 ℃:*
   This temperature region corresponds with the combustion zone found during HNF monopropellant combustion. Above 260 ℃, the formation of CO_2 is observed for the first time. The amount of CO_2 increases with increasing temperature; hence, the exothermicity increases with temperature. Above 350 ℃, the amount of ANF, N_2O, and CO decreases. At 400 ℃, the reaction can be described by

$$HNF \rightarrow 2\,NO + CO_2 + 2\,H_2O + \\ 3/2\,N_2 + 1/2\,H_2 + \quad 623\,kJ/mol$$
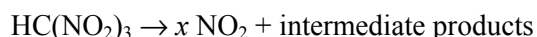
This reaction is the most strongly exothermic of the above reactions. The products of this reaction are not in the thermodynamic equilibrium concentrations that exist at the theoretical, adiabatic flame temperature. Further reaction at higher temperature is expected.

The above reaction pathways differ from those proposed by von Elbe et al.[8] By simple analytical techniques, they determined that NO_2 was released during HNF monopropellant combustion. This NO_2 reacts with the hydrazine component of HNF, liberating nitroform, according to

$$2\ NO_2\ +\ N_2H_4{\cdot}HC(NO_2)_3\ \rightarrow$$
$$N_2O\ +\ NH_4NO_3\ +\ HC(NO_2)_3$$

Because the free nitroform is unstable well below 120 °C, this reaction is immediately followed by

$$HC(NO_2)_3 \rightarrow x\ NO_2 + \text{intermediate products}$$

where x is presumably >1, but cannot exceed 3. It was concluded that at elevated temperatures, confinement of HNF in a closed container constitutes a severe explosion hazard, because a run-away increase of the NO_2 concentration, terminating in an explosion, may be expected. Effective venting of the container to remove trace amounts of NO_2 would mitigate this hazard.

The difference between the results from Williams and von Elbe is remarkable. During combustion von Elbe found that NO_2 plays an important role, whereas Williams found no evidence of NO_2 in T-jump experiments at combustion-like temperatures and temperature gradients. These differences may be explained by the fact that NO_2 is very unstable and might not be detected above the platinum filament, because it is already reduced to NO by, for example, the released hydrazine. The decomposition to NO in one step is very unlikely, for example, HMX and RDX also decompose into NO_2 first.

HNF Propellants

Compatibility of HNF with Propellant Ingredients

Application of HNF in a composite rocket propellant requires the use of energetic binders for two reasons. As stated earlier, HNF is incompatible with the double bonds in conventional solid propellant binders like HTPB. Modern energetic binders do not show this incompatibility as they do not contain double bonds. However, apart from the binder prepolymer, HNF has also shown incompatibility with many isocyanates, which are used for curing the binder.[14] A reaction between the hydrazine moiety of HNF and the isocyanate groups seems most logical, as similar effects were also found with hydrazine diperchlorate.

As HNF is not a very strong oxidizer like AP (oxygen balance +21.8 and +34%, respectively) performance with hydrocarbon binders like HTPB is not maximized due to lack of oxygen for binder combustion. Energetic binders have energetic groups attached to their backbones and often contain oxygen. This reduces the amount of oxygen needed to fully oxidize the binder decomposition products. Glycidyl azide polymer (GAP) is the only energetic binder that is produced in large quantities. Therefore GAP was chosen as the binder for propellant testing, although better performance may be obtained with some of the new binders like polyNIMMO and polyGLYN, produced by ICI Explosives.

The azido group in GAP contributes to its energy content (Figure 4). During combustion, the exothermic scission of the $-N_3$ bond structure forms $N_{2(g)}$, releasing 685 kJ/mol. Due to this highly exothermic decomposition, neat GAP gumstock is able to sustain combustion with appreciable regression rates (more than 10 mm/s at 10 MPa).[15]

Propellant Combustion

At the moment there is little experimental regression rate data on HNF propellants. TNO-PML has tested several propellant combinations. The most important are summarized in Table 2.[14] Due to the crystal-shaped oxidizer particles, the high mixture viscosity made casting impossible; therefore, the propellants were
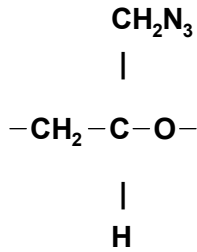
CH₂N₃

CH_2N_3

$|$

$-CH_2-C-O-$

$|$

H

Figure 4. Molecular structure of glycidial azide polymer (GAP).

Figure 5. Experimentally determined regression rates of HNF-based propellants.

pressed. Figure 5 shows the regression rates for two different propellants, as measured in a chimney burner. The uncatalyzed propellant has a very high combustion exponent of 0.81. This makes the propellant unsuitable for application in rocket engines. By introducing a combustion modifier (catalyst), the regression rates are increased in pressure from 0.1 to 10 MPa. No data above 10 MPa are available, but it is expected that the catalytic effect will disappear above this pressure, and regression rates will become similar. Due to the higher regression rates at lower pressure, the pressure exponent decreased from 0.81 to 0.59.

Experiments have been conducted to compare the specific impulse of the HNF/Al/GAP propellants to that of conventional AP/Al/HTPB propellants.[14] These experiments have confirmed the theoretical calculations.

Conclusions

HNF-based composite rocket propellants have a higher performance than any other solid rocket propellant at the moment. This, and the fact that its exhaust gases are chlorine-free, makes it a very likely candidate for replacement of AP in many commercial and military solid-propellant rocket engines. HNF has a high sensi-
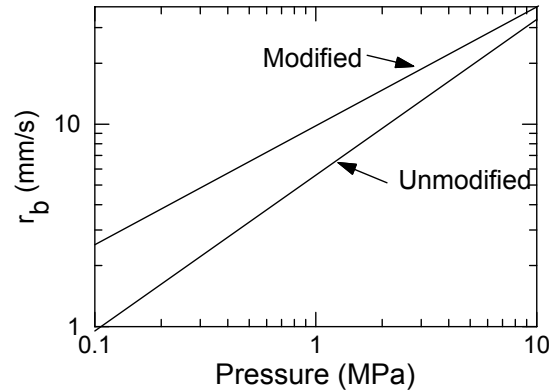
tivity and has shown incompatibility with many usual propellant ingredients. Therefore, much research still has to be conducted. This makes the application of HNF in operative systems very unlikely in the short term. However, HNF's advantages are many, and its use as a next-generation, solid-propellant oxidizer is promising.

References

1) R. R. Sobczak, "Ammonium Perchlorate Composite Basics", *J. Pyrotechnics*, No. 3, 1996, p 35.

2) K. Klager and G. A. Zimmerman, "Steady Burning Rate and Affecting Factors: Experimental Results", In: *Nonsteady Burning and Combustion of Solid Propellants*, AIAA Inc., New York, Vol. 143, 1992, p 59.

3) Z. Pak, "Some Ways to Higher Environmental Safety of Solid Rocket Propellant Application", AIAA, 1993, Paper 93-1755.

4) M. D. Pace, "Nitrogen Radicals from

Table 2. Two Typical HNF-Based Propellants Tested at TNO-PML.

Propellant Composition	Regression rate (in mm/s, pressure in MPa)
Baseline 59% HNF, 18% Al, 23% GAP binder	$5.75 \cdot p_c^{0.81}$
Modified 59% HNF, 14% Al, 4% catalyst, 23% GAP binder	$9.86 \cdot p_c^{0.59}$

Thermal and Photochemical Decomposition of Ammonium Perchlorate, Ammonium Dinitramine, and Cyclic Nitramines", *Mat. Res. Soc. Symp. Proc.*, Vol. 296, 1993, p 53.

5) G. M. Low, Hydrazinium Nitroformate Propellant with Saturated Polymeric Hydrocarbon Binder, U.S. Patent 3,708,359, Jan 2, 1973.

6) G. Doriath and B. d'Andrea, "New Solid Propellants Formulations and Production Processes", *5th Int. Symp. Propulsion in Space Technology*, Paris, 1996.

7) J. Köhler and R. Meyer, *Explosives*, 4th rev. & extended ed., VCH, Weinheim, Germany, 1993.

8) G. von Elbe, R. Friedman, J. B. Levy, and S. J. Adams, *Research on Combustion in Solid Rocket Propellants: Hydrazine Nitroform as a Propellant Ingredient*, Atlantic Research Corp., Technical Report DA-36-034-AMC-0091R, 1964.

9) J. Louwers, G. M. H. J. L. Gadiot, M. Q. Brewster, and S. F. Son, "A Model for Steady-State HNF Combustion", *International Workshop on Combustion Instability of Solid Propellants and Rocket Motors*, Milan, Italy, 16–18 June 1997.

10) E. T. McHale and G. von Elbe, "The Deflagration of Solid Propellant Oxidizers", *Combustion Science and Technology*, Vol. 2, 1970, p 227.

11) T. Parr and D. Hanson-Parr, "HNF: Neat and Diffusion Flame Structure", *32nd JANNAF Combustion Subcommittee Meeting*, 1995.

12) J. C. Finlinson, "Laser Recoil Combustion Response of HNF Oxidizer from 1 to 6 atm", AIAA Paper 97-3342, 1997.

13) G. K. Williams and T. B. Brill, "Thermal Decomposition of Energetic Materials 67. Hydrazinium Nitroformate (HNF) Rates and Pathways under Combustionlike Conditions", *Combustion and Flame*, Vol. 102, 1995, p 418.

14) H. F. R. Schöyer, A. J. Schnorhk, P. A. O. G. Korting, and P. J. van Lit, "First Experimental Results of an HNF/Al/GAP Propellant", AIAA Paper 97-3131, 1997.

15) N. Kubota and T. Sonobe, "Combustion Mechanism of Azide Polymer", *Propellants, Explosives, Pyrotechnics*, Vol. 13, 1988, p 172.