Overview of the Development of Hydrazinium Nitroformate-Based Propellants

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Recent improvements in the quality of hydrazinium nitroformate (HNF) and binder polymer developments have shown that it is possible to produce HNF-based propellants with hydroxyl-terminated polybutadiene (HTPB), glycidyl azide polymer (GAP), and poly 3–nitromethoxy–3–methyl oxetane [poly nimmo (PNM)] as binders. Especially when considering space applications, HNF-based propellants show results that encourage further research and development. An alternative method to cure GAP has been evaluated. This curing method eliminates the use of isocyanates, which always require special attention when used together with HNF. Combustion studies, experimental and theoretical, led to a good understanding of the steady-state combustion of HNF/GAP sandwiches and HNF/GAP propellants. Burning-rate modifiers have been identified, which lower the burning-rate exponent in GAP/HNF propellants by at least 25%. HNF/GAP and HNF/PNM propellants have a low temperature sensitivity. Liquid HNF monopropellants look attractive as a hydrazine replacement. They offer the same or a substantially higher I_{sp}, combined with a 30–40% higher density. The progress made in the manufacture of HNF and the HNF-based propellants (solid and liquid) was possible through extensive international cooperation.

Nomenclature

a	=	burning-rate coefficient in $r = a \cdot p^n$
c^*	=	characteristic velocity
D	=	diameter
E	=	modulus of elasticity (Young's modulus)
G^*	=	complex shear modulus
I	=	impulse
L	=	length
n	=	burning-rate exponent in $r = a \cdot p^n$
p	=	pressure
pH	=	$-^{10}\log(H_3O^+)$
r	=	burning rate
T	=	temperature
ε	=	strain
π_r	=	burning-rate sensitivity to temperature variation
σ	=	stress

Subscripts, Superscripts, and Indices

b	=	binder
i	=	initial
max	=	maximum
rupt	=	at rupture
sp	=	specific
T	=	temperature
vac	=	vacuum
δ	=	density
50	=	for which 50% of the total distribution is smaller

I. Introduction

DURING the last half decade, the development of hydrazinium nitroformate (HNF) and HNF-based propellants has been accelerated substantially. Recent publications, among others, give an overview of the advances in HNF.[1,2] A number of different laboratories and industries have been involved in the research and development efforts. As a result, not all approaches are exactly the same; some data are overlapping, most is complementary. Curing of glycidyl azide polymer (GAP) together with HNF was investigated, during which another method to polymerize GAP was identified. As in combination with energetic binders, HNF has the promise of making solid propellants with a very high I_{sp}, and GAP and poly 3–nitromethoxy–3–methyl oxetane- [poly nimmo (PNM-)] based HNF propellants have successfully been manufactured. One of the remarkable findings is the very low temperature sensitivity of PNM–HNF propellants. It was also demonstrated that hydroxyl-terminated polybutadiene-(HTPB-) based HNF propellants can be made without showing degradation effects. The combustion of HNF/GAP sandwiches and HNF/GAP propellants was investigated experimentally and compared with theoretical models. This showed good agreement between theory and experiment. Work was started on the development of HNF-based liquid monopropellants as a hydrazine monopropellant replacement. Because HNF-based liquid monopropellants offer at least the same performance as hydrazine, possibly using the same catalytic ignition system, while the propellant density is 30–40% higher than for hydrazine, this may become very attractive for small or low-budget satellites. Moreover,

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the propellant purchase and handling costs are expected to be substantially lower than for hydrazine, while the propellant has a much lower toxicity and does not pose the hazards associated with hydrazine.

The results of this work are summarized in this paper. It is concluded that much progress has been made over the past five years. It is possible to manufacture HNF-based PNM, GAP, and HTPB propellants where the first impression is that mechanical properties and aging behavior seem acceptable. The steady-state combustion of HNF/GAP is well understood by now.

II. HNF Solid Propellants with Energetic Binders

HNF, together with energetic binders and aluminum, theoretically yields propellants with very high specific impulses (≥ 3100 m/s or ≥ 316 s). Some background has been given by Schöyer et al.[3] Experimental propellants have been made successfully with GAP and PNM. There were compatibility problems between HNF and poly glycidyl nitrate. Both GAP and PNM are being manufactured in Europe and are, therefore, easily available. According to Schöyer et al.,[3] the combination GAP/HNF/Al gives a slightly higher I_{sp} than PNM/HNF/Al, and higher solids loads can be obtained more easily with PNM than with GAP, due to the lower density and lower viscosity of PNM.

D'Andrea and Lillo,[4] manufactured and tested PNM/HNF/Al propellants with a 70% solids load. Although these propellants had not yet been optimized, for an Ariane 5 booster application they would give 2.7% more I_{sp} than the presently used Ariane 5 propellant while being chlorine free. The importance of clean exhausts from solid rocket motor boosters is also stressed by D'Andrea et al.[5] Of all known solid propellants, HNF-based propellants yield the highest specific impulse. Experiments showed that HNF-based composite solid propellants offer an I_{sp} of 7–9% higher than the best available AP propellant. Part of this higher I_{sp} is due to improved aluminum combustion.[6]

A. Status of HNF/GAP Propellants

Curing of GAP or PNM usually takes place with an isocyanate. For the GAP/HNF propellant to be cured with isocyanates, the best results are obtained at low curing temperatures[7] (20°C). Depending on the isocyanate used, curing at 40 and 60°C gave a greater chance of swelling of the samples after some days. Because various types of HNF have been used, it became obvious that the HNF quality strongly affects the results. This is shown in Table 1. There are two aspects: the effect of the different grades of HNF on the propellant quality, and the effect of improvement in HNF quality on the propellant over the years.

The different HNF grades [cooling crystallization (C), evaporation (E), and solvent-nonsolvent (S)] show an effect: When the 20% HNF-C in the experimental propellant F19 was replaced by HNF-E (F20 and K1) it led to a large increase in gas production. Some gas escaped in the vacuum thermal stability test (VTS), and so it is only known that the gas production exceeded 12.5 and 25.5 ml/g. Table 2 suggests that E and S grade slightly improve the mechanical properties.

The experimental propellants P1–P3 are identical except for the HNF grades. The effect of HNF grade on the VTS is clearly visible.

Over the years no exactly identical propellant has been produced. However, the 1995 propellant[6] contained 60% HNF with 18% Al and 22% GAP. In 2000 a propellant with 60% HNF and 40% PNM was produced. In earlier work,[3] it had already been established that Al is compatible with HNF and does not affect the VTS values of HNF propellants. Therefore, the strong reduction in VTS values for the 2000 propellant compared to that made in 1995 is considered indicative of the improvement in HNF quality.

1. Mechanical Properties

The mechanical properties of these propellants are reasonable, as is obvious from Table 2. At low temperatures (-10°C) the mechanical properties are better than at room temperature. For comparison, typical data for a representative HTPB/AP/Al propellant are also given.

2. Ballistic Properties

Strand burner tests have been performed with a number of propellant formulations; the results have been summarized in Table 3. These propellants did not contain burning-rate modifiers and have burning rate exponents ranging from 0.65 to 0.88. The variation in the burning-rate exponent may be related to the propellant quality. The latter is expressed in Table 3 as a relative propellant quality, based on visual observations and thermal stability data. The burning rate at 7 MPa ranges from 17.6 mm/s for the K1 propellant (30% HNF) to 27.8 mm/s for the 1995 propellant (60% HNF). With a burning-rate modifier the exponent of the 1995 formulation can be reduced[6] to at least 0.6.

In Sec. V, tests with other HNF/GAP propellants are reported; even without burning-rate modifiers, lower burning-rate exponents have been observed there.

3. Curing

Because HNF shows a certain degree of incompatibility with most isocyanates, it has been investigated[8] whether GAP could be modified in such a way that HNF-compatible curing agents could be used. It has been tried experimentally to modify GAP by giving it an epoxy end group, so that it might be cured with acid anhydrides. The other solution that has been investigated was to replace the

Table 2 Some mechanical properties of HNF/GAP test propellants

Sample	Test, temperature, °C	σ_{max}, MPa	$\varepsilon_{\sigma_{max}}$, %	σ_{rupt}, MPa	ε_{rupt}, %	E, MPa
F-19	20	0.56	22	0.49	26	5.2
F-20	20	0.66	38	0.57	42	3.1
F-21	20	0.53	18	0.43	25	4.5
K-1	20	0.69	27	0.58	32	4.4
K-1	-10	1.16	76	1.08	80	5.5
HTPB/AP/Al (reference)	20	0.49	43.5	0.45	52	2

Table 1 Effect of HNF quality on HNF propellants

Year	Propellant	HNF, % C	HNF, % E	HNF, % S	Binder, %	Al, %	Cooxidizer, %	VTS, ml/g
					Effect of HNF grade			
1996	F19	20	——	10	55	10	5	11.1
1996	F20	——	20	10	55	10	5	>12.5
1996	K1	——	20	10	55	10	5	>22.5
1998	P1	50	——	——	50	——	——	1.9
1998	P2	——	50	——	50	——	——	4.6
1998	P3	——	——	50	50	——	——	5.5
					Effect of improvement of HNF itself over time			
1995			60		22% GAP (+ isocyanate)	18		4.4
2000			60	——	40% PNM			0.2

Table 3 Some ballistic properties of experimental HNF/GAP propellants

Sample	HNF, %	GAP + isocyanate, %	Al, %	Cooxidizer, %	Burning-rate law, r, mm/s, $\times P$, MPa	Relative propellant quality[a]
K1	30	55	10	5	$3.17 \times p^{0.88}$	——
	20 coarse					
	10 fine					
1995	60	22	18	——	$5.75 \times p^{0.81}$	0
	41 coarse					
	18 fine					
HGU-19-1	55	45	——	——	$5.3 \times p^{0.71}$	+
	55 coarse					
	0 fine					
HGU-20-1	55	45	——	——	$6.0 \times p^{0.67}$	+
	0 coarse					
	55 fine					
HGU-23-1	50	32	18	——	$6.6 \times p^{0.65}$	+
	35 coarse					
	15 fine					

[a]Based on a combination of visual properties and thermal stability.

Table 4 Compatibility tests HNF—AC

Weight ratio AC/HNF	Temperature, °C VTS (193 h)	Gas evolution, ml/g	DTA, °C		
			Begin	Onset	Maximum
5/95	40	2.7			
5/95	30	1.6			
50/50	40	10.4			
80/20			47	101.5	111.4

Table 5 Thermal stability of GAP/HNF propellant

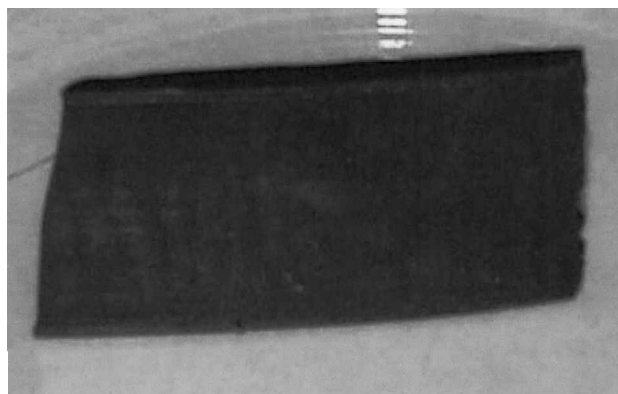| Composition GAP/AC/HNF	Test temperature, °C	Time, h	Gas evolution, ml/g
85.4/9.82/4.78	40	193	1.3
81.53/9.38/9.09	40	193	3.1
85.4/9.82/4.78	60	48	2.8
	70		3.4
81.53/9.38/9.09	60	48	4.8

GAP end groups by an acid group, so that epoxy compounds could be used as curing agents. However, these approaches did not meet with success. It was tried to give GAP epoxy end groups by a reaction between GAP and acryloyl chloride (AC). Instead of providing GAP with epoxy end groups, curing of GAP was observed. This probably involves a reaction between the azido groups in GAP and the double bond in AC.

This new curing system is extremely interesting for GAP because it 1) allows curing at room temperature, which leads to a low stress-free temperature, eliminates the need for heating during curing, and because incompatibility reactions are faster at higher temperatures, reduces incompatibility problems; 2) is less sensitive to moisture than isocyanate curing; 3) allows tailoring the mechanical properties of the propellant by adjusting the amount and functionality of the curing agent; and 4) does not require a modification of GAP for use with HNF. It is important that the new curing agent is compatible with HNF. To this end AC with HNF was subjected to VTS and differential thermal analysis (DTA) tests. The results are shown in Table 4 and demonstrate acceptable compatibility of HNF with the curing agent at temperatures up to 20°C above the curing temperature.

Thereafter GAP has been cured without HNF. Although no detailed mechanical properties have been determined as yet, a flexible, nonbrittle polymer was obtained within a wide range of ratios of GAP prepolymer/AC (8.6–21.7). If this ratio decreased below 4, a tough and brittle material resulted. For the flexible, nonbrittle GAP, the Bundes Anstalt für Materialforschung und Prüfung (BAM) friction and impact data are 11 J and >55 N, respectively, which are very acceptable values. AC cured GAP is compatible with HNF as follows from VTS tests at 40°C (193 h). After having assured that curing GAP/HNF/AC will not pose a safety hazard, the first test samples were prepared. Two different compositions (with 5 and 10% HNF) were made. In both cases a well-cured, flexible, and homogeneous material resulted. VTS tests did not give any indication of incompatibility, as may be seen from Table 5. For comparison, VTS data for HNF/isocyanate cured GAP yielded, after 48 h at 65°C, 3–12 ml/g, and after 193 h, >20 ml/g. However, these propellants had a higher percentage of HNF (30–60%), whereas VTS testing was done shortly after manufacturing, and the present samples had


Fig. 1 AC cured GAP with 10% HNF.

been in storage for more than 4 months before the VTS measurements were made. Also, the propellants used different grades of HNF. Note that these GAP/AC/HNF trial samples after 6 months storage had not undergone any observable change. Figure 1 shows a sample of the GAP/AC/10% HNF. The new curing method looks very promising; however, more development work is needed to arrive at a high solid load propellant based on AC cured GAP.

B. Status of HNF/PNM Propellants

A number of experimental PNM/HNF propellants have been made at several laboratories. The objective was not to maximize ballistic performance but to investigate how to make such propellants and to establish ballistic, safety, and hazard aspects. In some cases,[10] only HNF with a rather large L/D ratio (7) and large particle size ($D_{50} \approx 1200\,\mu$m) was available, which hampered mixing the ingredients and obtaining a castable propellant. Adding 10% ammonium perchlorate (AP) with $D_{50} \approx 200\,\mu$m led to a castable propellant. Table 6 gives an overview of the composition and the results to obtain a castable propellant. For large motors, such as the Ariane 5 boosters, a long pot life is required. Although an HNF/PNM propellant could be cured with long-chain multifunctional isocyanates,

Table 6   Investigation of castability of HNF–PNM propellants

Ingredients, %				
PNM	Al	HNF	AP	Castability
25	15	60		NC[a]
25	20	55		NC
30	20	50		NC
35	15	50		CGD[b]
35	15	40	10	CD[c]
40	15	35	10	C[d]

[a]Not castable.
[b]Castable with great difficulty.
[c]Castable with difficulty.
[d]Castable.
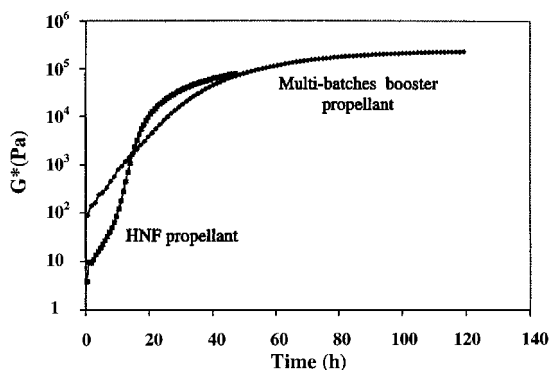
Fig. 2   Comparison of PNM/HNF/AP/Al propellant with multibatches booster propellant.

the pot life (measured by the complex shear modulus G^*) is shorter than for the standard HTPB/AP/Al propellant used in the Ariane 5 boosters (see Fig. 2). Varying the curing temperature and curing catalyst allows increasing the pot life somewhat. When, recently, more spherical HNF became available, very good PNM/HNF/Al propellant samples could be prepared (personal communication, B. D'Andrea, December 1999) with a higher solids loading fraction than for the castable ones in Table 6.

The 60°C DTA and VTS stability properties of the first set of PNM/HNF/Al propellants were acceptable; the later produced series gave even better results (personal communication, B. D'Andrea, December 1999).

1.   Mechanical Properties

For isocyanate curing, the NCO/OH ratio is important. This holds for GAP-based as well as for PNM-based propellants. The effects of the NCO/OH ratio and the test temperature on the mechanical properties are shown in Table 7. The results indicate that increasing the binder functionality increases the rigidity (Young's modulus), but decreases strength and strain. These effects are more pronounced at lower temperatures than at room or elevated temperature.

2.   Ballistic Properties

A number of burning-rate modifiers (BM) has been tested with HNF/PNM propellants. Two groups of BM have been used: metal powders and organic compounds. The metal powders gave a positive contribution to the theoretical I_{sp}. In some cases, it was possible to reduce the burning-rate exponent by ~25%; in other cases, the opposite of what was intended was achieved. Table 8 summarizes the results. It also gives the correlation coefficient for the De Vieille law with experimental results. BM allow for a reasonable range of variation, although a substantially lower n would be desirable. Burning-rate measurements of HF21 at temperatures ranging between −50 and 40°C showed very little effect of temperature. It was found that the temperature sensitivity, $(1/r)(\partial r/\partial T)_p = 0.55 \times 10^{-3}/K$, which is lower than for conventional composite propellants or for double-base propellants. Note, in this respect, that the tempera-
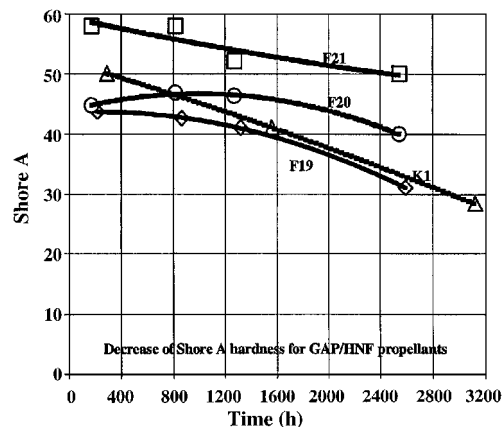
Fig. 3   Evolution of Shore A hardness for some GAP/HNF propellants.

ture sensitivity of neat HNF was about 2 to 4 times as large (see Sec. V).

3.   Storability/Aging

If HNF is stored at elevated temperatures (40°C) for a long period (1872 h), small amounts of N_2 and CO_2 may be detected, where the latter gas is dominant. PNM stored under the same conditions generates larger amounts of N_2 and CO_2. Storing HNF and PNM together reduces the amount of N_2 emitted, but now significant quantities of N_2O are detected. The strong reduction in N_2 is too large to come from the HNF. It is, therefore, believed that HNF may affect the degradation pathway of PNM.[7]

GAP/HNF propellant samples have been stored for 2600–3100 h at room temperature.[7] To assess the aging behavior the Shore A hardness was measured over time. For the propellants F20 and F21, the Shore hardness has only decreased by ~14% after 2500 h. In fact, initially the hardness slightly increases for these two propellants. For the propellants F19 and K1, the hardness decreases by 29% after 2600 h and by 43% after 3100 h, respectively. The hardness history is given in Fig. 3.

4.   Sensitivity

HNF/PNM propellants tested for Rotter impact indicate that these propellants have a sensitivity comparable to nonaluminized AP/HTPB propellants, but are more sensitive than aluminized AP/HTPB propellants. The rotary friction tests indicated that HNF/Al/PNM propellants have a substantially lower friction sensitivity than HNF and that friction sensitivity is approximately the same or a bit less than for a nonaluminized AP/HTPB propellant. One of the hazard classifications concerns the detonability of a propellant. No full-scale tests have been performed to determine the HNF propellant hazard class. Some initial small-scale tests[4] indicate that high-performance HNF-based propellants might be class 1.1. However, these tests were performed with a propellant based on an earlier production type of HNF without any effort to make the propellant less sensitive. Possible desensitization measures are phlegmatization, coating the oxidizer crystals, and adjusting the oxidizer particle size.

III.   HNF Solid Propellants with Conventional Binders

For a long time it was assumed that HNF and carboxy-terminated poly butadiene (CTPB) (and similarly HTPB) were incompatible[11,12] because of the unsaturated C=C bonds in the prepolymers. In the work on HNF development, it rapidly became clear that the relationship between epoxides and isocyanates (the standard curing agents for CTPB and HTPB) and HNF may be troublesome and this might be another reason for the earlier observed incompatibility. Recent developments show that HTPB-based HNF propellants are well feasible.[13] The advantages of using HTPB instead of GAP or PNM are that only one of the major ingredients in a new propellant formulation has to be changed and, also, HTPB has excellent mechanical properties.

Table 7   Mechanical properties of HNF/PNM propellants

Sample	PNM			Temperature, °C	σ_{max}, MPa	$\varepsilon_{\sigma\,max}$, %	E, MPa
	Diol/C8	Triol/C8	NCO/OH				
HF21	0	0.25	1/1	−10	0.83	42.9	3.14
HF21	0	0.25	1/1	20	0.48	23.3	3.33
HF21	0	0.25	1/1	50	0.29	18.8	2.38
HF31	0.121	0.129	1/1.2	−10	0.93	33	4.79
HF31	0.121	0.129	1/1.2	20	0.44	21	3.13
HF31	0.121	0.129	1/1.2	50	0.32	16	3
HF30	0.059	0.191	1/1.2	20	0.56	18	4.95
HF32	0.184	0.066	1/1.2	20	0.46	24.6	2.9

Table 8   Ballistic properties of HNF/PNM propellants

Sample	BM (%)	a	n	Correlation coefficient
HF21	ref (0)	3.38	0.898	0.978
HF13	BM1 (15)	6.46	0.676	0.967
HF33	BM2 (2)	16.52	0.758	0.924
HF35	BM3 (2)	4.14	0.812	0.994
HF36	BM4 (2)	3.46	0.937	0.979
HF37	BM5 (2)	4.90	0.817	0.981

Table 9   Stability tests of HNF/HTPB propellant compositions

HNF/HTPB/Desmodur VL +	TGA		VTS 48 h at 60°C, ml/g
	Days at 40°C/ mass loss, %	Days at 60°C/ mass loss, %	
HNF only	7/0.09	2/0.40	1.73
Baseline	7/0.13	2/1.96	——
Stability 1	7/0.17	2/0.23	——
Stability 2 + stability 3	6/0.09	2/0.26	0.73
Stability 2 + stability 3 + DOA	6/0.13	2/0.47	0.76

A.   Performance Aspects

Compared to the best AP/HTPB/Al propellants, an HNF based propellant in conjunction with HTPB may give performance gains up to 4%. Maximum performance is achieved for a propellant with ~70% HNF, ~18% Al, and ~12% HTPB (by weight). Because no HCl is present in the exhaust products, a significantly more environmentally friendly and reduced smoke propellant is obtained.

B.   Thermal Stability

Nonaluminized propellants with a solids loading up to 80% using HNF with different crystal sizes, resulting in castable mixtures, have been prepared. Further enhancements in the solids loading are feasible with the introduction of aluminum and improved HNF crystal shapes ($L/D \leq 2$). Casting and curing took place at 40°C. Different isocyanates were tried; the best results were obtained with Desmodur-VL. In conjunction with stabilizers, very acceptable stability data were obtained for the propellant samples. To improve the processability, an inert plasticizer di–n–octyl adipate was added to the mixture. This combination led to a propellant with good stability characteristics. The results of (thermal) stability tests are summarized in Table 9. The main stability tests were thermogravimetric analysis (TGA) and VTS, with the remark that the TGA tests comprised mass loss tests at 40 and 60°C on samples of ~10-g HNF/HTPB compositions. Table 9 also shows the beneficial effect of the stabilizers by the strong reduction in the mass loss at 60°C.

Furthermore, the stability of the HNF/HTPB propellants is illustrated by the current compositions, which even after a year's storage at room temperature, show no severe degradation effects such as discoloration, swelling, softening, or outgassing. Whereas, in 1973, Low and Haury[11] reported that, without 10% stabilizer, some of these effects were already observed after 6 days room temperature storage.

C.   Ballistic Properties

At this moment, the propellants have a burning-rate exponent $n \sim 1$, which slightly exceeds the burning-rate exponent of pure HNF. The burning-rate coefficient a is from ~2.5 to ~3.6 (pressure in MPa, burning rate in mm/s). However, because successful BM have already been identified in the GAP and PNM-based HNF propellants, it is expected that suitable BM will also become available for the HTPB-based HNF propellants.

D.   Mechanical Properties

From compression tests, values for Young's modulus ranging from 7.9 to 8.4 MPa and maximum stresses ranging from between 0.7 and 0.8 MPa were found. The Shore A hardness is in the range of 55–65. These values agree with typical values for conventional composite propellants.

E.   Hazard Properties

The BAM impact data range from 2 to 3 Nm, and the BAM friction data from 36 to 42 N. Although these are relatively low values, this does not prohibit safe handling, cutting, and testing of these propellants.

IV.   HNF Liquid Propellants

For solid propellants, one needs to mix HNF in dry form with prepolymers and metallic fuels. To obtain a high solids loading in the propellant, spherical or cubic HNF crystals are preferred. Much of the research and development efforts for HNF itself are, therefore, oriented toward lowering the crystalline aspect ratio. Other development work is directed toward lowering (friction) sensitivity and making actual solid propellants. However, HNF may also be used as a liquid monopropellant. It is especially interesting as a hydrazine replacement because it may overcome the expensive handling and preparation of spacecraft associated with hydrazine.

A.   Propellant Combinations

Hydrazine monopropellant thrusters are commonly used on smaller spacecraft. The $I_{sp_{vac}} \sim 2265$ m/s (231 s) for steady-state firings. This low I_{sp} is acceptable because of the simplicity of the propulsion system. However, because small and simple spacecraft usually are also budget limited, the expense of handling the highly carcinogenic hydrazine is counterproductive. On the other hand, although HNF crystals require an elaborate manufacturing process, and even for a large-scale production the unit price will only be comparative to AP, liquid HNF only requires the mixing (under well-controlled conditions) of water, hydrazine–hydrate and nitroform. In comparison to the standard purified anhydrous hydrazine (PAH), the cost of this HNF-based propellant will be orders of magnitude smaller than PAH, while simultaneously the costs of handling will also be reduced substantially.

B.   Performance

For HNF-based liquid monopropellants,[14] a large number of propellant combinations with HNF as an oxidizer is possible. In all cases, the propellant consists of HNF dissolved in water together with a fuel which is soluble in water. Some interesting combinations

are listed in Table 10, where hydrazine is listed for comparison and HNF/water is listed as a reference.

Table 10 also lists the combustion temperature because this to a large extent determines the simplicity of the thruster. Ammonia (NH_3) and methanol (CH_3OH) are interesting fuels in this respect: they are easily available, and contrary to most other fuels, while the I_{sp} increases with increasing fuel contents, the chamber temperature decreases. With 20% NH_3, about the same performance as with hydrazine can be obtained, although the combustion temperature is of the same order as for hydrazine. On the other hand, with nitromethane (CH_3NO_2) substantially higher performances are possible, but the combustion temperature is also substantially higher. From a performance point of view, hydrazine azide ($N_2H_5N_3$) is a potentially interesting candidate; contrary to NH_3, CH_3OH, and CH_3NO_2, the compatibility of $N_2H_5N_3$ with HNF dissolved in water has not yet been demonstrated.

The water/HNF/fuel mixtures have a density ranging between 1300 and 1400 kg/m^3, which is a 30–40% improvement over hydrazine ($\rho = 1010$ kg/m^3), which allows smaller propellant tanks for the same performance.

C. Thermal Stability of HNF–Water Solutions

The thermal stability of HNF–water solutions was investigated for a 65/35 HNF/H_2O solution. Contrary to the boiling-point increase that was expected, boiling started at 100°C. At this point, the vapors did not show any acidity (pH measurement). At 110°C, the pH indicator turned red, indicating vapors with a pH around 1–2. This is caused by the release of N_xO_y gases due to the decomposition of HNF. The experiment indicates that water evaporates before HNF starts to decompose significantly. This observation leads to three important conclusions:

1) HNF does not decompose (significantly) below the boiling point of water.

2) Ignition by a heated bed will require significant energy because water has to be evaporated first.

3) A water-HNF mixture is stable; no HNF (decomposition) vapors are formed. This is a significant advantage over N_2H_4, which is susceptible to decomposition and explosion due to adiabatic compression. Spacecraft propellant feed systems for N_2H_4 propellant systems have to take this aspect into account in their design.

D. Ignition

In principle, there are five types of ignition that might be used for an H_2O/HNF/fuel mixture:

1) The first type is catalytic ignition: experiments show that catalysts similar to the ones used for catalytic ignition of N_2H_4 also work well with H_2O/HNF/fuel mixtures. In addition, a number of other catalysts could be identified.

2) Pyrotechnic (or pyrogen) ignition is a second type. While in principle possible, this method is not very attractive because many of the thrusters that might use this monopropellant will have to operate in pulse mode [attitude and orbit control system (AOCS) thrusters].

3) Heated bed ignition is another type. This has not (yet) been investigated. Bed heating will have to be on the order of 120°C, which is lower than the catalyst temperature for N_2H_4. On the other hand, there may be the danger of separating water vapor, fuel vapors, and HNF decomposition products, which might hamper proper pulse mode operation. For purely steady-state operation, it may be an attractive option.

4) The forth type is electrolytic ignition. This is a very interesting and promising concept. It has been studied by Russel and Fondrk.[15] Because the HNF solutions in water are highly conductive (electrically), a current may be passed through the propellant to heat and ignite it. Electrolytic ignition usually requires much less energy than bed heating, is effective, and has a quick response at sufficiently high currents.

5) The last is hypergolic ignition. At this moment, no hypergolic reactants suitable to ignite a H_2O/HNF/fuel mixture are known. However, the system would become more complex as an additional propellant tank and line would have to be added to the propulsion system. It would become a bipropellant system. Experience with N_2H_4/N_2O_4 and mono methyl hydrazine/N_2O_4 systems shows that pulse mode operation is well possible.

Whereas experiments already have demonstrated the feasibility of catalytic ignition, electrolytic ignition and heated bed ignition are also good candidates for rapid and controlled ignition and operation of H_2O/HNF/fuel monopropellant thrusters. Because the same catalysts that work for hydrazine also work well with the HNF-based monopropellants, such a system would require the least number of modifications to existing monopropellant hydrazine thrusters and the satellite AOCS.

V. Combustion of HNF Propellants

The combustion of HNF, HNF/GAP sandwiches, and HNF-based propellants has been investigated experimentally and theoretically.

A. Sandwiches and Propellant Samples

HNF/GAP propellants have been vacuum mixed and cast into propellant blocks $30 \times 40 \times 150$ mm^3. This propellant was then used to prepare strand burner samples $7 \times 7 \times 125$ mm^3 or 4-mm-thick slices for window-bomb samples.

For experimental purposes, HNF/GAP/HNF sandwiches and HNF/GAP propellants have been made. The binder thickness in the sandwich is ~250 μm; the HNF has a thickness of ~2 mm. HNF propellants have been manufactured based on GAP, HTPB, and PNM; the composition of some GAP and HTPB-based propellants is given in Table 11 with their measured burning-rate characteristics.

Table 10 Performance of HNF + fuel dissolved in water

Constituents				
HNF, %	Fuel/(%)	I_{sp},^{a} m/s	I_{sp},^{a} s	T_c, K
N_2H_4 (100%)		2265	231	1311
50	——	1783	182	1100
50	CH_3OH/(5)	2185	223	1567
50	CH_3OH/(10)	2207	225	1516
50	CH_3OH/(20)	2248	229	1412
50	NH_3/(5)	2194	224	1556
50	NH_3/(10)	2227	227	1503
50	NH_3/(20)	2294	224	1411
50	CH_3NO_2/(16.67)	2563	262	2157
50	CH_3NO_2/(20)	2631	268	2285
50	CH_3NO_2/(25)	2728	278	2446

^{a}Vacuum specific impulse, $p_c = 1$ MPa, expansion ratio $A_e/A_t = 50$.

Table 11 Composition and burning characteristics of some experimental HNF-based propellants

Ingredients	HGU-19-1	HGU-20-1	HGU-23-1	HTPB/HNF
HNF C15 (474 μm)	0.55		0.35	0.73
HNF S16 (100 μm)		0.55	0.15	
Aluminium			0.18	
GAP + isocyanate	0.45	0.45	0.32	
HTPB + isocyanate + plasticizer				0.25
Additives				0.02
Burning-rate exponent, n	0.71 ± 0.03	0.67 ± 0.01	0.65 ± 0.05	1.01 ± 0.05
Burning rate, at 1 MPa, mm/s	5.36	5.95	6.78	5.33

The only difference between the propellants HGU-19-1 and 20-1 is the size of the oxidizer crystals. Classical HTPB/AP propellants show a large effect of the AP-crystal size on the burning-rate, which is explained by the Beckstead–Derr–Price (BDP) model. These two HNF propellants hardly show a difference in burning rate (see Table 11), which is also explained by the BDP model (see following section). Their burning-rate exponents are very close and are acceptable for rocket motor applications.

Also the Al containing propellant shows a burning rate of the same order of magnitude and a slightly lower burning-rate exponent. PNM- and HTPB-based propellants until now have shown high burning-rate exponents. The results for the propellants HGU-19-1 and 20-1 agree very well with the theoretical analysis (see following section).

B. Modeling

Louwers[16] has extensively modeled the combustion of HNF and HNF propellants. Steady-state combustion, temperature sensitivity, surface temperature, and flame standoff distances turn out to be best modeled by a low gas-phase activation energy model as proposed by Ward et al. (WSB).[17] The experimental results for HNF combustion match this model better than older models by Denison and Baum[18] and Williams,[19] which assume a high gas-phase activation energy.

The flame temperature of HNF strongly varies with pressure ($T_f = 2766$ K at 0.1 MPa and 3112 K at 10 MPa); therefore, the gas phase heat release Q_g has been varied in such a way that the flame temperature calculated by this model (modified-WSB) matches the adiabatic flame temperature. Figure 4 shows a comparison of the calculated and measured burning rates for HNF. The temperature sensitivity $(\pi_r)_p = [\partial \ell n(r)/\partial T_i]_p$ is predicted to decrease with increasing pressure. The predicted $(\pi_r)_p = \sim 0.23\%$ at 0.1 MPa and $\sim 0.12\%$ at 10 MPa agree reasonably well with the measured $(\pi_r)_p$ data, for example, $\sim 0.21\%$ at 0.5 MPa and $\sim 0.14\%$ at 5.5 MPa, but the uncertainty in the measured data is too large to be able to validate the modeling unambiguously. According to the model, the surface temperature increases from ~ 535 K at 0.1 MPa to 815 K at 4 MPa. The agreement with thermocouple measurement data by Shöyer et al.[2] and Louwers[16] is excellent.

A more detailed insight in the flame and decomposition chemistry is obtained by applying a combustion model, closely resembling the Kee et al.[20] premix model. This model confirms the WSB results and also shows a good agreement between the measured and calculated concentrations of combustion products, with the exception for OH and NO concentrations. NO measurements show lower concentrations (by a factor of 2) than the calculated concentrations. Within 0.5 mm above the burning HNF surface, a temperature of ~ 2550 K is predicted, which is in agreement with experimental data.

Application of the BDP model,[21] properly modified for HNF propellant combustion, confirmed that oxidizer particle size has a negligible effect on the propellant burning rate. Changing the oxidizer particle size from 10 μm to 1 mm decreases the 80%HNF/20%GAP propellant burning rate by 6%; for an 88%AP/12%HTPB propel-

lant the change would have been 90% (Ref. 22). This is because the HNF monopropellant flame standoff distance rapidly decreases with pressure, and all HNF decomposition products react in the monopropellant flame and not in a primary diffusion flame anymore. Because of the relatively large distance of the final diffusion flame to the burning surface, and because the HNF decomposition flame close to the surface already is very hot (2766 K as compared to 1377 K for the AP monopropellant flame), the final diffusion flame hardly affects the burning rate. This high monopropellant flame temperature is believed to be one of the reasons that HNF-based propellants demonstrate a very good aluminum combustion and high c^* efficiency, especially above ~ 3 MPa (Refs. 6 and 23).

To model the gas-phase structure above an HNF/GAP sandwich, the BIGMIX[24] code was modified and applied. The results confirm the other analyses: a steep temperature rise above the HNF and above the binder the temperature rise is slower. Close to the surface, on the border of HNF and GAP, ~ 0.5 mm from the sandwich center, the highest temperature is reached, indicating the occurrence of a small diffusion flame that disappears above 1 MPa.

There is a very promising agreement between experimental data and theoretical analyses: the absence of an effect of crystal size on the burning rate of HNF propellants, and the temperature sensitivity, and the overall decomposition of HNF and HNF propellants. For steady-state processes, it is fair to state that most fundamental aspects of the combustion of HNF and HNF propellants are well understood.

VI. Further Developments

In the near future, the focus of HNF solid propellant development will be mainly on space applications because these are believed to be the first practicable applications due to the less severe high-temperature constraints in comparison to, for example, military applications. A number of experimental propellants have shown that good quality propellants with GAP and PNM can be made that do not show deterioration over time. Propellants for actual motor firings have not yet been prepared, and manufacturing such propellants followed by motor firings on a 1–5 kg scale is a next logical step. Steady-state combustion experiments and modeling of HNF composite propellants demonstrate that the steady-state combustion process is well understood. The much-improved combustion of aluminum (as compared to an AP propellant) is explained by the very high flame temperature of HNF; the same high flame temperature contributes to the very low temperature sensitivity of HNF propellants as well. Nonsteady combustion (combustion instability) has not received any attention as yet. This will have to be investigated. In addition to making propellants that will perform well in solid motors, further lowering of the burning-rate exponent and obtaining the proper mechanical and aging characteristics of the propellant are other subjects of interest that will receive attention.

The new curing method of GAP, in conjunction with HNF, will have to be developed further. For liquid monopropellants, the demonstration of proper ignition (pulse trains) by catalytic, electrolytic, and/or heated bed ignition systems will be demonstrated before implementing this on a small monopropellant thruster.

VII. Conclusions

A coordinated international effort, involving universities, laboratories, industries, and agencies, has brought significant improvements and advances in the development of HNF composite solid propellants and liquid monopropellants. Curing GAP and PNM with isocyanates has led to propellants with an acceptable storage life, and an alternative curing method for GAP was found that looks extremely promising.

Various detailed experiments have clarified the steady-state combustion processes of HNF solid propellants. It was possible to model the combustion processes (steady state) with excellent agreement between model and experiment. This has given confidence that the steady-state combustion process is well understood and makes the propellant development less a process of trial and error than it was in the past.
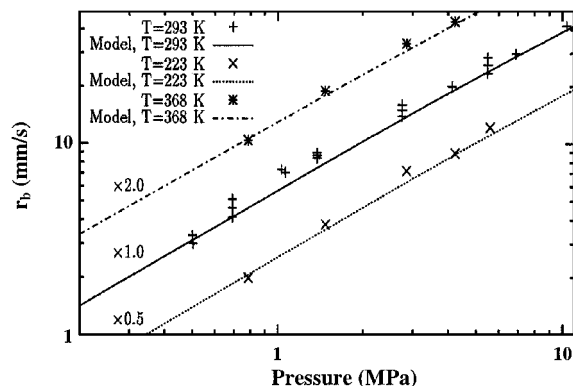

Fig. 4   Comparison of calculated and measured burning rates of neat HNF (multiplication factor used to prevent overlap of data).

HNF-based composite solid propellants offer a substantially higher I_{sp} (7–9%) than the best available AP propellants; part of this higher I_{sp} is achieved by an improved aluminum combustion.[6] Surprisingly, it was possible to make an HNF/HTPB/Al propellant with good mechanical and aging properties. The ballistic properties need improvement before the propellant can find applications in real rocket motors.

Liquid HNF-based monopropellants offer an attractive alternative to hydrazine monopropellants. At similar combustion temperatures, similar I_{sp} can be achieved, while the density impulse is 30–40% higher. At higher combustion temperatures, substantially higher I_{sp} can be achieved. Compatibility and storability for a number of HNF/water/fuel mixtures has been demonstrated, as well as rapid catalytic ignition.

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