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# THERMAL ANALYSIS OF THE HIGH-ENERGETIC MATERIAL HNF

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## Abstract

In a search for new storable high performance propellants for the European Space Agency (ESA), the solid oxidiser hydrazinium nitroformate (HNF) has been identified as a very promising ingredient for a new storable composite propellant.

The purity and stability of HNF after production are very important indicators for the quality of HNF. In order to characterise HNF, many thermal analysis techniques as DSC and TG/DTA were performed to obtain more information about its stability and its (in)compatibility with other materials. Also some less familiar techniques such as the vacuum stability test and microcalorimetry have been performed.

In relation to the safety, a relation between the friction and impact sensitivity and the physical-chemical properties is made.

**Keywords:** compatibility, DSC, HNF, microcalorimetry, propellant, TG, thermal stability

## Introduction

In order to increase the performance of the presently used AP/HTPB based propellants, new oxidisers which could replace the AP are searched for. One of these new oxidisers is hydrazinium nitroformate (HNF). The production and characterisation of this energetic material can be found in several literature references [1–4]. Apart from an improved theoretical and experimental performance of an HNF/Al/GAP based composite propellant [2], an additional advantage is that HNF is chlorine free. This implies that it is more environmentally friendly and it has an improved (lower) signature compared to the conventional AP/HTPB propellants. Another advantage of the replacement of AP by HNF in an HTPB based binder system is that the existing HTPB processing knowledge and infrastructure can be maintained.

In patent literature [5, 6] it has been mentioned that HNF is incompatible with unsaturated C=C bonds which are present in the backbone of CTPB. For this reason

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pre-polymers with saturated bonds were used [5] or nitroguanidine was added as a stabiliser in a CTPB based propellant [6]. It is also known that HNF reacts with isocyanates so this reaction competes with the desired polyurethane reaction, which leads to curing of the pre-polymer. However, the purity and product characteristics of HNF were considerably improved in the last decade, which led to a renewed interest in HNF/HTPB based composite propellants.

In the early 90s, researchers at TNO Prins Maurits Laboratory renewed their interest in HNF, which was abandoned in the 60 in the US due to its stability, compatibility and sensitivity problems. After extensive research, a new method was identified with the help of which HNF could be produced in a safe way [5]. Later, HNF/Al/GAP based propellants were prepared on 350 g scale, so the theoretical performance of these kind of propellants could be demonstrated and experimentally verified [1]. In the meantime, Aerospace Propulsion Products was founded where the scale-up of the production of HNF up to pilot scale was realised. During scale-up, the production process of HNF was further improved and optimised in order to increase its purity, to control the crystal size distribution and to improve the shape of the crystals from long needles to much more isomorphic shapes [12].

## Experimental

This study focuses on the analytical results with regard to the thermal properties of HNF and of HNF combined with two potential propellant ingredients.

### *Techniques*

#### Thermoanalytical methods

DSC and TG/DTA are techniques that are generally used and well known. The experimental equipment comprises a TG/DTA-320 and a DSC-220-C, both manufactured by Seiko Inc. Open aluminium cups were used and a heating rate of 5°C min$^{-1}$ was applied for the compatibility measurements on the TG/DTA. The temperature range, from room temperature to ~200°C was quite limited, because of the fact that HNF starts to decompose at around 125°C.

The DSC technique was used for kinetic calculations.

#### Manometric vacuum stability test

The manometric vacuum stability test (MVST) is performed according to MIL-STD-286B [8]. This guideline describes that a compound is considered to be thermally stable if the gas evolution during 40 h storage under vacuum at 100°C is less than 5 mL g$^{-1}$. In practice, however, the temperature for HNF at which the test is performed cannot be too high due its decomposition. Just above its melting temperature of about 124°C. In the past, experiments indicated that a test temperature of 60°C in combination with a gas evolution less than 3 mL g$^{-1}$ during 48 h is acceptable. For both the stability and compatibility test, a sample size of about 1 g is used. In a period of 48 h, the gas production is measured in an initial vacuum. For compatibility investigations, the volume of gas evolved (calculated at STP=standard temperature and pressure) by the mixture is compared to the volumes evolved when testing the single components.

### Heat flow calorimetry

The heat flow calorimeter (HFC) is a sensitive heat generation measuring instrument. The technique is in use, for energetic materials as propellants, at TNO-PML since the beginning of the seventies [10–12]. This technique is used for the determination of the thermal stability of a certain sample.

### Safety tests: UN Test 3(a) – BAM impact sensitivity [9]

The BAM test equipment is used to measure the sensitivity of solids and liquids to drop-mass impact and to determine if the substance is too dangerous to transport in the form tested.

### UN Test 3(b) – BAM friction sensitivity [9]

The friction apparatus is used to measure the sensitivity of the substance to frictional stimuli and to determine if the substance is too dangerous to transport in the form tested.

### Electrostatic discharge

Electrostatic discharge is commonly considered as an electrical charge, modelled by a capacitor loaded to a specified voltage, flowing to ground through a discharge circuit presenting a given electrical stimuli.

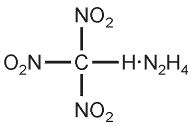
### UN Test 3(c) – Thermal stability at 75°C [9]

This test is used to measure the stability of the substance when subjected to elevated thermal conditions to determine if the substance is too dangerous to transport. When dealing with a new substance, several screening tests, involving heating small samples at 75°C for 48 h, are performed to explore its behaviour. A sample of 100 g is heated in an oven. The temperature inside the sample is measured by a thermocouple. The criterion is that the difference between the sample and the temperature of the reference material may not exceed +3°C.

### *Sample description*

Hydrazinium nitroformate (HNF) is a yellow, crystalline material, which is manufactured by Aerospace Propulsion Products (APP) in the Netherlands (Fig. 2). HNF is an energetic material to be used as an oxidiser. Since HNF does not contain any chlorine, its combustion products do not contain any chlorine gases, either. The material can be used as an oxidiser in a composite solid rocket propellant.

| | | |
|---|---|---|
| Molecular formula | $N_2H_5C(NO_2)_3$ | |
| Molecular mass | 183.08 | g $mol^{-1}$ |
| Appearance | yellow crystal | |
| Crystalline form | monoclinic | |
| Melting point | ~124°C | |
| Combustion energy | –5824 | kJ $kg^{-1}$ |
| Density | 1840–1910 | kg $m^{-3}$ |



$$O_2N-\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{C}}-H\cdot N_2H_4$$

For the compatibility research, the following additives are used:

- HTPB: hydroxy terminated polybutadiene, inert binder
- GAP: glycidyl azide polymer, energetic binder.

## Results and discussion

### *Stability increase during process optimisation*

During the production research and development, which started in 1992 on lab-scale and evolved via bench-scale to the present pilot-scale production of HNF, numerous production characteristics have been analysed and improved. Important production characteristics are purity, melting point, thermal stability and morphology. Especially, thermal stability and morphology improvement have been focussed on. Stability improvement at temperatures ≥60°C is important for military applications and morphology improvement is necessary to obtain a high solid load in the propellant [7].

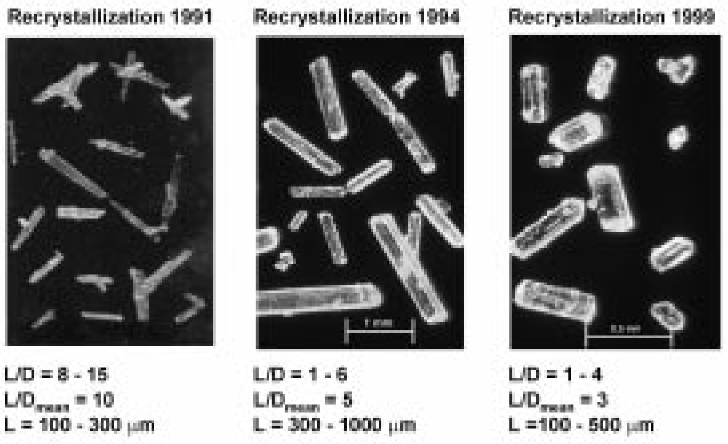


**Fig. 1** Change of morphology during process improvements

Table 1 gives an indication of the stability improvement of HNF and HNF compositions over the years. Figure 1 shows the evolution of the morphology of HNF.

**Table 1** Improvement of stability of HNF and HNF compositions over the years

| Composition | 1992 | 1994 | 1995 | 1997 | | 1999 |
|---|---|---|---|---|---|---|
| Measuring period: | 2 days | 2 days | 2 days | 3 days | 11 days | 42 days |
| HNF | 1.5–10 | 0.1–1.5 | | 0.1–0.4 | 0.4–1.0 | 1.0 |
| 50% HNF/50% GAP | 4 | 0.4 | | | | |
| 60% HNF/20% GAP/20% Al | 3.9 | | | | | |
| PoC propellant 1995 | | | 4.4 | | | |
| HNF propellant 1997 | | | | 0.5 | | |
| HNF propellant-stabilised | | | | | <1 | |

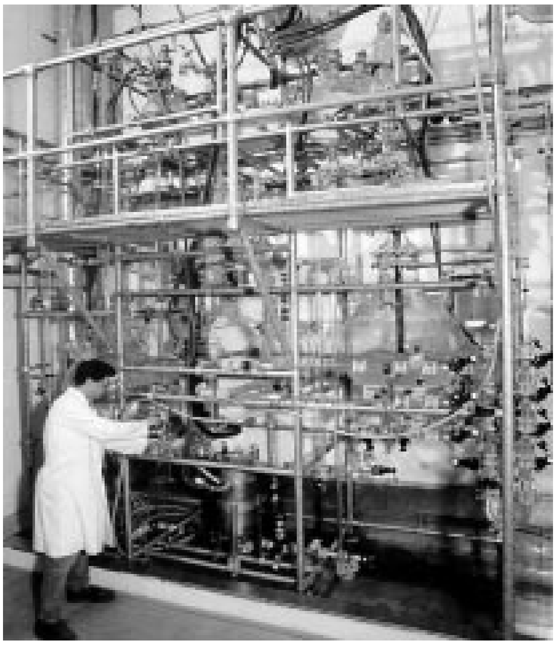


**Fig. 2** Photograph of the production facilities at APP; equipment in contact with HZ and NF is made of glass or is Teflon coated

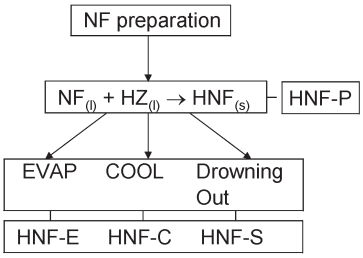


**Fig. 3** HNF production scheme

The values in Table 1 are expressed in the gas volumes in mL $g^{-1}$ after the period as mentioned in the second row, at 60°C. The used method is the vacuum stability test (VST).

The batches mentioned in Fig. 3 result in different stability parameters. One of the stability parameters which is checked for every batch is the VST-value.

**Table 2** VST results for different HNF batches

| HNF | Previous specifications/ mL gas/2.5 g | Most recent specifications/ mL gas/2.5 g |
|---|---|---|
| Raw material (P-batch) | <6.3 | <1.3 |
| S-batch | <4.5 | <4.5 |
| C-batch | <1.3 | <1.3 |
| E-batch | <0.5 | <0.5 |

Table 2 shows the difference in typical VST values for the different grades. Furthermore, comparison of the measured values with the up-to-date specification shows that the raw material has drastically improved and HNF-E grade still has the lowest VST value. The study was performed on two different batches of HNF namely the S-batch and E-batch. For the stability research, techniques as DSC, TG/DTA and MVST were used.

### *DSC and TG/DTA experiments*

In both techniques the measurements were performed with a heating rate of 5°C $min^{-1}$. In the case of DSC experiments closed SuS-vessels were used. They can withstand a pressure of about 80 bar. TG/DTA experiments were performed with open vessels in a nitrogen atmosphere.

**Table 3** Results of TG/DTA and DSC experiments on HNF

| | | S-batch | E-batch |
|---|---|---|---|
| TG/DTA | DTA-onset/°C | 129 | 129 |
| | Mass change/% | 97 | 97 |
| | Enthalpy/μVs $mg^{-1}$ | ~1040 | ~850 |
| DSC | Melting point/°C | 123.8–124.4 | 124.2–124.3 |
| | DSC-onset/°C | 125.4–126.1 | 126.0–126.2 |
| | Enthalpy/mJ $mg^{-1}$ | 3961–4035 | 4139–4143 |

According to the results in Table 3, it could be concluded that the purity of the E-batch is higher than the S-batch. This follows from the small range in melting point and enthalpy as measured by DSC.

The enthalpy as given by TG/DTA is only an indicative value, because all the measurements are performed in open cups.

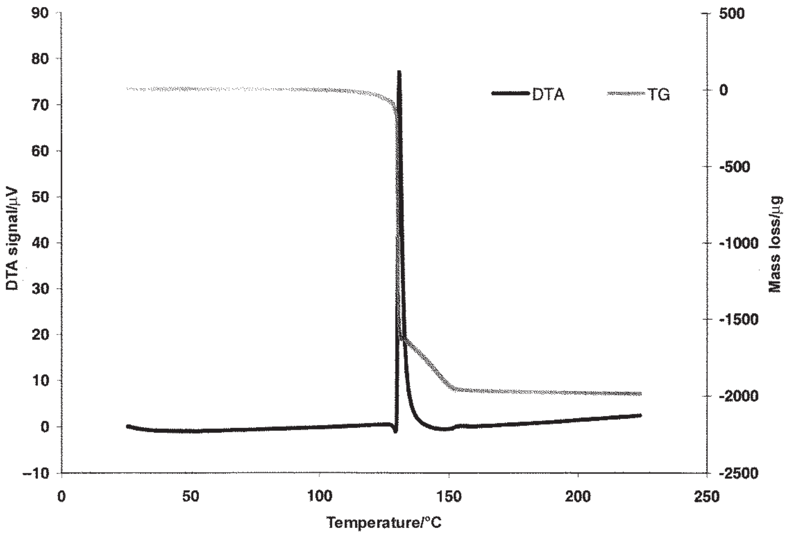


**Fig. 4** Typical TG/DTA curve of HNF S-batch

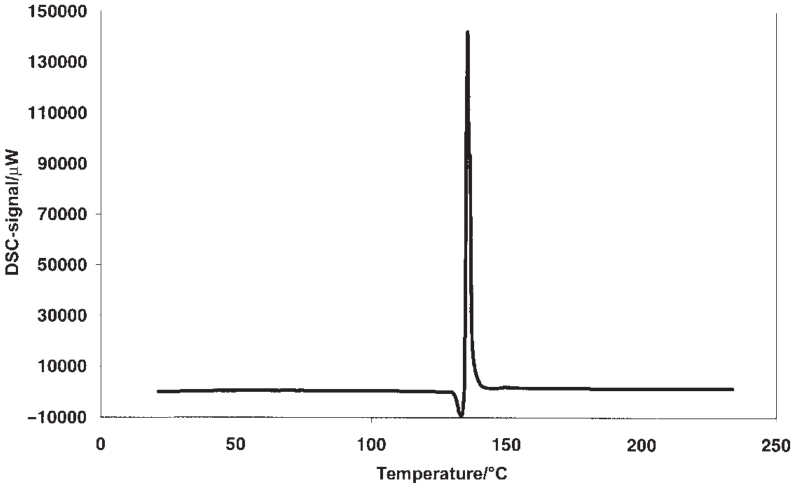


**Fig. 5** Typical DSC curve of HNF E-batch

### *Heat flow calorimetry measurements*

In the HFC, measurements at 60°C are performed with pure HNF and for the combination HNF/GAP, with a burning additive (aluminium). The sample amount was about 2 g, in both cases. In Fig. 6, the curve of pure HNF, results in a large increase of the heat generation, as a consequence of decomposition of the material. After the measurement period of 1 week, 4% of the material has decomposed, based on the decrease of enthalpy.

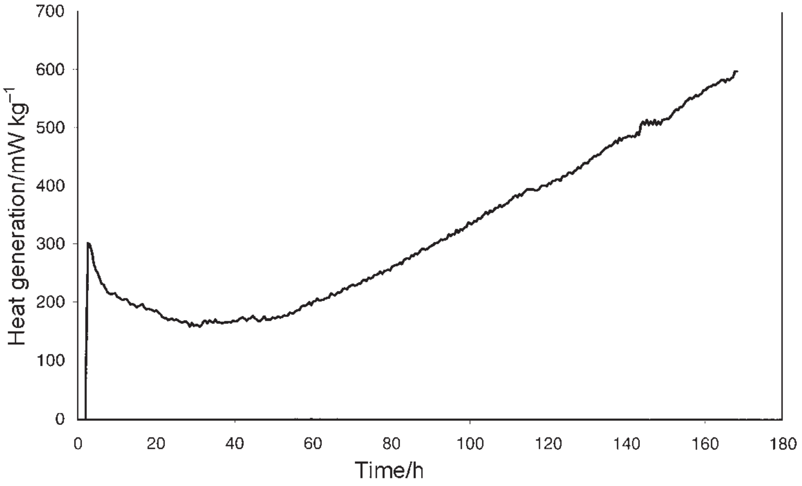


**Fig. 6** HFC-curve of pure HNF

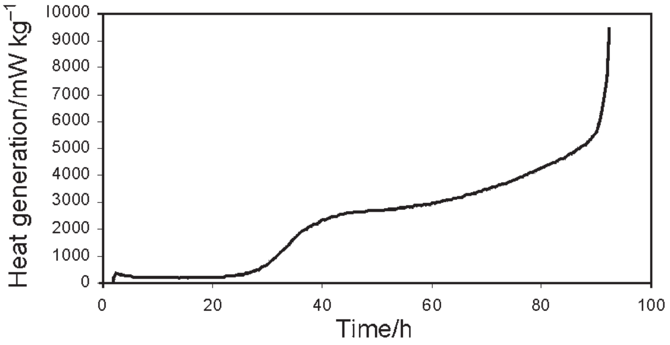


**Fig. 7** HFC-curve of HNF with GAP and an additive

Figure 7 shows a twostep decomposition reaction, the first step is related to the decomposition of GAP, followed by a fast second step, the decomposition of HNF. In comparison to Fig. 7, the level of the heat generation is much higher, and after 94 h, a run-away reaction occurs. This method illustrates that the addition of aluminium and/or GAP decreases the stability of the composition and/or HNF.

### *Compatibility with inert and energetic binders*

It has been demonstrated theoretically and experimentally that solid propellants based on HNF and GAP or HTPB will lead to a higher performance and a more environmentally friendly propellant. In relation to this, the compatibility of HNF in combination with HTPB and GAP has been investigated.

According STANAG 4147 [13], the vacuum stability test is used for the compatibility research. In this situation the MVST is chosen, since a large database has been generated with this technique over the years.

**Table 4** Results of MVST compatibility research, 48 h at 60°C

| Sample | mL gas/2.5 g |
|---|---|
| HNF S-batch | 1.88 |
| HTPB | 0.41 |
| GAP | 1.68 |
| HNF S-batch / HTPB mixture | 38.11 |
| HNF S-batch/HTPB cured propellant | 3.19 |
| HNF S-batch / GAP mixture | 1.68 |

The criterion for compatibility is that the amount of extra gas may not be more than 3 mL 2.5 $g^{-1}$, for the mixture. From the results as presented in Table 4 it is obviously clear that the cured propellant composition with HTPB and the HNF/GAP mixture are compatible.

The second technique used for assessing the compatibility of HNF with other propellant ingredients, is isothermal and scanning TG/DTA. The isothermal measurements were performed at the same temperature as in the MVST. During the scanning TG/DTA measurements a heating rate of 5°C $min^{-1}$ is used. Criteria for this technique are given in STANAG 4147 and in MIL-STD-286B.

**Table 5** Results of TG/DTA compatibility research

| Sample | DTA-onset/°C |
|---|---|
| HNF S-batch | 129 |
| HTPB | 273 |
| GAP | 160 |
| HNF S-batch / HTPB mixture | 122 |
| HNF S-batch/HTPB cured propellant | 122 |
| HNF S-batch / GAP mixture | 124 |

According to these results there is a small indication of incompatibility between HNF and HTPB (Figs 8 and 9), because the temperature shift in DTA-onset is more than 5°C. This mixture was also measured isothermally in TG/DTA during a period of 48 h. After that period the mass loss was 2.51 mass%. The amount of gas for the HNF/HTPB mixture (in the MVST) can be calculated back to a mass%. Taking into account that 2.5 g of pure HNF gives 1836 millilitres gas when it totally decomposes, the measured gas volume can be compared with a decomposition degree of 2.1%. This value is in line with the result of the isothermal TG/DTA. The small difference could be explained by the evaporation of the sample that takes place when using open aluminium sample vessels.

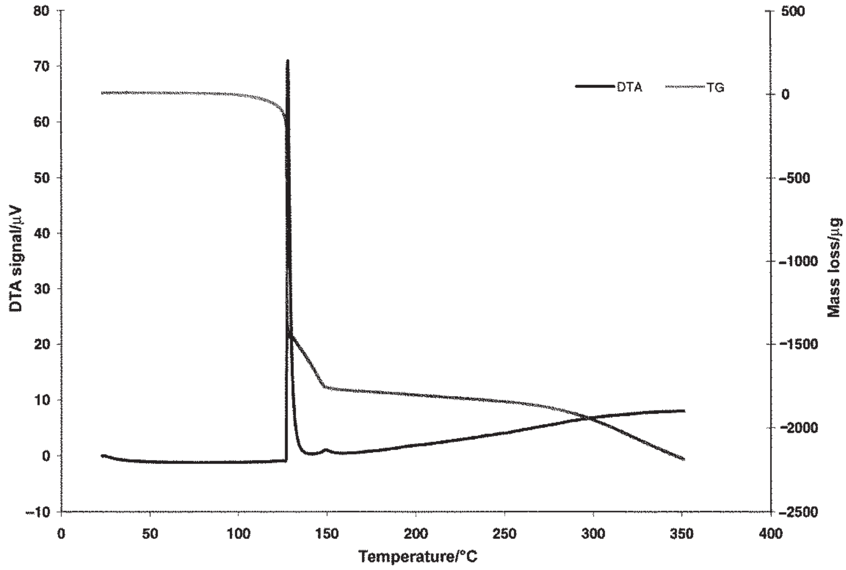


**Fig. 8** Typical TG/DTA curve of HNF S-batch with HTPB

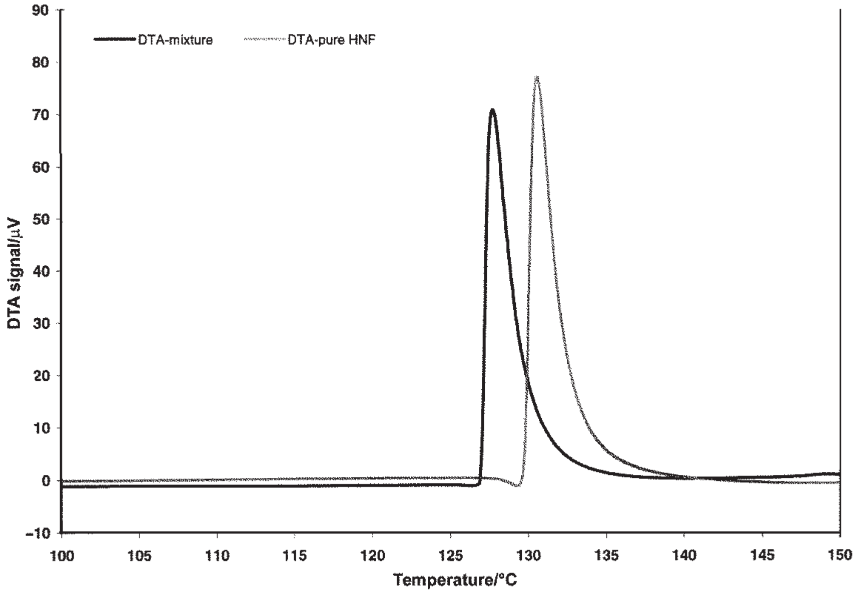


**Fig. 9** Typical DTA curve of HNF S-batch with HTPB and HNF separately

Figure 9 shows the result from the compatibility study, based on the DTA signal. The difference in $T_{onset}$ is quite small, only 5°C. According to STANAG 4147 there is no incompatibility.

Comparing all the results for the compatibility study, it may be concluded that both, the HNF/GAP mixture and the HNF/HTPB mixture are compatible, when the compounds are mixed and cured. In the situation of only mixing the two components, the combination indicates to be incompatible.

### *Safety and handling*

The hazard properties – comprising BAM impact, BAM friction and ESD – of HNF have been determined for a large number of batches produced under different process conditions. Table 6 summarises the ranges of values found for these sensitivity data.

**Table 6** Hazard properties of HNF

| BAM impact/Nm | BAM friction/N | ESD/J |
|---|---|---|
| 2–5 | 14–36 | 4.5[a] |

[a] Limited number of batches

These values show that HNF is particularly sensitive towards friction. The values for the impact sensitivity and sensitivity to spark are moderate to low, respectively. Despite the relatively low impact sensitivity values, handling of HNF and its processing in propellant mixtures is very well possible. This is probably due to the fact that during mixing the mechanical forces and the rate, at which these forces are applied, are relatively low. Furthermore, the HNF particles will be phlegmatized by the presence of the binder, which prevents direct contact between the particles and the moving parts in the mixing equipment.

In an attempt to relate the physico-chemical properties of HNF with regard to purity (melting point, hydrazine content and nitroform content), VST, aspect ratio and mean size to its sensitivity (friction and impact), an elaborate study was carried out covering the analytical data of over 120 different batches of HNF produced on lab, bench or pilot scale [14]. Although a vast amount of data on HNF, generated over the past 8 years, has been reviewed, no firm conclusions could be drawn with regard to the dependence of impact and friction sensitivity on one or more of these characteristic HNF properties. This implies that no clues could be identified regarding one or more properties of HNF which should be improved in order to reach an intrinsically less sensitive material. Based on the finding that in particular the impact sensitivity is always in a relatively small range of roughly 2 to 5 Nm, one might conclude that this is an intrinsic property of HNF, practically independent of its purity or other properties [14].

HNF was also subjected to the UN 3(c) test where 100 g of HNF is stored at 75°C during 48 h. At the end of this test the temperature difference between the sample of HNF and an inert reference sample, e.g. due to self-heating, should not be larger than 3°C. Taking the criterion into account, HNF successfully passed this test. For the transport classification the sensitivity for impact, friction, UN 75 test and 12-meters drop test has to be performed. On the basis of the results of the UN3 (a), (b) and (c) tests, the only test that pure HNF fails to satisfy, is the friction sensitivity test.

However, recently HNF has been classified for transport as a 1.1D material under UN number 0475, after passing the 12 meters drop-test for the material in a restricted packaging. This implies that HNF does not have to be transported anymore in a so-called explosafe container, which is limited to a maximum of 333 g of HNF per container but can be transported as a 1.1D material.

## Conclusions

From this study the following conclusions could be drawn:

- HNF decomposes during the melting process, an endothermic effect followed by a fast exothermic.
- HNF and GAP are compatible. Incompatibility of HNF with HTPB and GAP; nevertheless, experimental results have clearly shown that cured propellants can be prepared based on both HNF/HTPB and HNF/GAP.
- Recently produced HNF results in a higher purity, which is expressed by a clear melting peak in DSC and DTA experiments.
- Hazard properties (impact and friction) seem to be ‘intrinsic’ properties of HNF, which cannot be desired from the physical-chemical properties of HNF. However, sensitivity characteristics have not resulted in any problems relating to processing HNF in binder systems on bench scale (350 g propellant).
- Transport of HNF in larger quantities is possible, under UN number 0475 and properly packed, class 1.1D.

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## List of abbreviations

| | |
|---|---|
| AP | ammonium perchlorate |
| APP | aerospace propulsion products |
| CTPB | carboxy-terminated polybutadiene |
| GAP | glycidyl azide polymer |
| HNF | hydrazinium nitroformate |
| HTPB | hydroxy-terminated polybutadiene |
| PoC | proof of concept |
| STANAG | Standard NATO Agreement |
| TNO | Netherlands organisation for applied scientific research |
| VST | vacuum stability test |

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