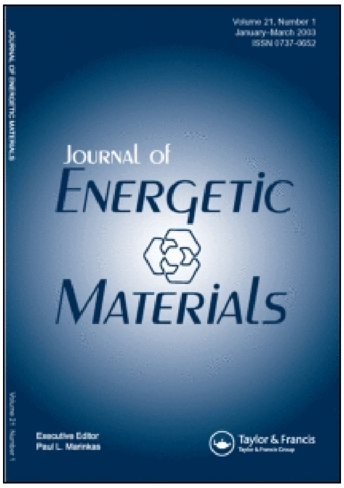

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Dendage, P. S. , Sarwade, D. B. , Asthana, S. N. and Singh, H.(2001) 'Hydrazinium nitroformate (HNF) and HNF based propellants: A review', Journal of Energetic Materials, 19: 1, 41 — 78

To link to this Article: DOI: 10.1080/07370650108219392

URL: http://dx.doi.org/10.1080/07370650108219392

HYDRAZINIUM NITROFORMATE (HNF) AND HNF BASED PROPELLANTS: A REVIEW

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ABSTRACT

This paper reviews the studies carried out so far on HNF, which is emerging as potential oxidizer for futuristic propellant systems. Methods of synthesis of HNF including efforts to obtain HNF of desired particle size/shape have been discussed in detail. As purity of HNF has bearing on its thermal, physical and chemical characteristics, process parameters are being optimized to obtain high quality HNF with reproducible characteristics. Potential of HNF based propellants as propulsive force to missiles and space vehicles is also discussed in this paper. Problem areas in processing HNF based propellants have also been identified.

INTRODUCTION

The primary function of an oxidizer in a propellant composition is to provide oxygen for the combustion of fuel species. Positive oxygen balance, high heat of formation, high density and high thermal stability are the other important criteria for an energetic oxidizer. Ammonium perchlorate (AP) is the most widely used oxidizer in composite (CP)

Journal of Energetic Materials Vol. 19, 041-078 (2001)
Published in 2001 by Dowden, Brodman & Devine, Inc.

and composite modified double base (CMDB) rocket propellants. However, AP has its own inherent disadvantages, as it produces chlorine rich combustion products (30%), posing environmental hazards such as ozone depletion and acid rain. Further, it produces white smoke trail during inclemental weather, which is detrimental for specific applications demanding smokeless plume. Among other conventional oxidizers, ammonium nitrate (AN) offers chlorine free propellant formulations. However, it has drawbacks of hygroscopic nature and multiple transition phases in the temperature range of practical importance and comparatively lower energy. Therefore, attempts are on all over the globe to develop propellant formulations based on eco-friendly energetic oxidizers. Ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are emerging as potent candidates in global scenario[1]. Hexa nitro hexa aza iso-wurtzitane (CL–20) is also being evaluated as rocket propellant component[2]. HNF has certain advantages over ADN such as its simple method of synthesis, non-hygroscopic nature, higher density and melting point[1]. This paper reviews the work done so far on HNF and propellant systems based on HNF.

HYDRAZINIUM NITROFORMATE [HNF]

HNF is a salt of hydrazine, a weak base and nitroform [NF], a weak acid. Its synthesis is two step process involving preparation of NF followed by its conversion to HNF. NF, the key intermediate in the preparation of HNF is a brown, toxic and volatile

Molecular weight: 151

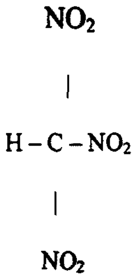
Oxygen balance: + 37.1%

Nitrogen content: 27.83%

Density*: 1.59 g/ml.*

Melting point: 22^{0}C

Boiling point: 48^{0}C



$$\begin{array}{c} \mathrm{NO_2} \\ | \\ \mathrm{H-C-NO_2} \\ | \\ \mathrm{NO_2} \end{array}$$

Nitroform (NF)

liquid at room temperature. W. Hunter[3] first reported its synthesis by nitration of acetylene gas to tetranitromethane (TNM), followed by its conversion to NF by reacting with KOH & H_2SO_4. This method has potential hazard due to high exothermicity and the hazardous nature of the intermediate, potassium nitroformate (KNF). The method is uneconomical due to low yield of NF. The method developed by Hatano et.al.[4, 5] involving nitration of acetic anhydride with fuming nitric acid also has similar drawbacks particularly due to formation of KNF as an intermediate. In 1970 Welch et.al.[6] prepared NF by nitration of acetone preferably with 90% HNO_3 (molar ratio of 1:3). This method is beset with hazards due to volatility and flammability of acetone. On the other hand, method reported by Frankel et.al.[7] is considered safe particularly, due to use of isopropanol instead of acetone as a starting material. Moreover, it afforded 25 % yield.

Until 1978, the separation of NF from the reaction mixture was carried out by vacuum distillation. This technique is hazardous as NF forms azeotropic mixture with nitric acid and, thereby requiring high temperature for separation leading to possibility of explosion. Consequently, progress on introduction of HNF, as key oxidizer was slow. Frankel et.al.[8] developed an easy and safe method of NF isolation from nitric acid by its extraction in methylene dichloride in the presence of concentrated H_2SO_4. Frankel et.al.[9] modified their earlier method of NF synthesis and its isolation in 1987 to prepare NF on industrial scale. The modified method utilizes an inert organic solvent like ethylene dichloride as reaction medium to reduce the exothermicity of the reaction. Zee et.al.[10] of Prins Maurtis Laboratory, TNO Netherlands, developed a reliable and safe production process for preparation of HNF (from NF). It is reported that Rockwell International division of USA has developed a safe method of NF synthesis and its conversion to HNF on commercial scale.[9] Aerospace Propulsion products is also reported to be producing HNF on commercial scale since 1993.

Authors have carried out synthesis of NF on the lines of methods reported by Frankel et.al.[7-9] and its conversion to HNF by following the method described by Lovett and Edision[11]. The reaction conditions were optimized to obtain high yield. Pure HNF was obtained by recrystallization process reported by Meulenbrugge[12]. The purity was found to be > 98% as determined by HPLC method (fig.1).

PHYSICO – CHEMICAL PROPERTIES

Various physico-chemical properties of HNF reported in the literature are given in table1. Unlike ADN, it is a yellow needle shaped crystalline solid which is non-hygroscopic in nature[1]. The particle size of HNF plays an important role in its sensitivity and loadability in propellants. In the earlier crystallization process, HNF was dissolved in a suitable solvent followed by its addition to a non-solvent. The major drawback of this process is sudden oversaturation leading to rapid crystallization resulting in formation of agglomerates. Meulenbrugge et.al.[12] reported that physico-chemical properties of solvent have influence on shape of the crystal. They have recommended water and lower alcohols as the most suitable solvents for crystallization of HNF. Controlled particle size can be obtained by addition of a non-solvent to HNF solution. Particles can be obtained in the form of granules by adjusting the process parameters.[12] The granular particles (spherical /cubical) are preferred for processing propellant formulations to realize high solid loading. This is important because HNF achieves stoichiometry at higher solid loading than AP due to its lower oxygen balance. Schoyer el.al.[1] of Prins Maurtis Laboratory, TNO Netherlands, developed two methods of recrytstallization of HNF on bench scale. Fine particles of HNF (~ 20 μm) are produced by addition of non-solvent into the solution of HNF, while the coarse HNF (~ 200 μm) is generated by evaporation of solvent from HNF solution.

The melting point of HNF is reported in the temperature range of 110-124^{0}C. The data reported by various researchers varies due to difference in purity level of HNF.[13-16] The probable impurities in HNF are hydrazine, nitroform and the double salt of hydrazine with nitroform[17]. The density of HNF ranges between 1.86 to 1.93 g/cc. The high density of HNF is due to extensive hydrogen bonding, which influences the packing of HNF crystal lattice[18]. It has theoretical oxygen balance of 13.1 % and heat of formation from -71 to -72 kJ/mol [1,14,16,19-23] .Its heat of combustion [20] (ΔH_c), is reported to be -1066 kJ/mol (-5824 kJ/kg). The reported elemental analysis values are close to the theoretical values. HNF is sparingly soluble in most of the organic solvents except alcohols in which it is moderately soluble. On the other hand, it is highly soluble in water (112.21 %). The reported frequency assignments [24-26] of the infrared absorption spectrum (fig. 2,3&4) and Raman spectrum (fig. 5) of HNF conform to theoretically proposed structure (Table 2).

UV spectrum of pure HNF in water (fig. 6) exhibits λ_{max} at 352 nm[11]. UV and IR spectra of the HNF synthesized by the authors were in agreement with the reported spectral pattern (fig.7&8). Mass spectrometric[17] studies (fig. 9 & 10) of HNF are required to be carried out on TP-MS spectrophotometer due to low decomposition temperature of HNF. The negative ion spectrum of HNF shows only one nitroform ion $[C(NO_2)_3]^-$. The positive ion spectrum shows two peaks with mass 33 and 51 corresponding to $N_2H_5^+$ & $N_2H_5^+ . H_2O$

CRYSTALLOGRAPHY

HNF is a yellow needle shaped crystalline solid with monoclinic packing. The crystal structure reveals that $N_2H_5^+$ ions are hydrogen-bonded to neighboring $C(NO_2)_3^-$ ions[18]. The unit cell of HNF contains two crystallographically independent and structurally different formula units. One of the $N_2H_5^+$ ion is staggered while the other is eclipsed. The CN_3 frame work of both $C(NO_2)_3^-$ ions is planar, but these propeller-shaped ions have $N_2C\text{-}NO_2$ dihedral angles between 4^0 and 74^0.

TOXICITY

Toxic properties of HNF were investigated by number of researchers. For dermal toxicity, [17,27,28] LD_{50} value is ≥ 2000mg/body weight, suggesting that HNF is non toxic when exposed to skin and eyes. However, LD_{50} value of 128mg/body weight for oral toxicity suggest that it is toxic in this respect as per European Community (EC) Standard.[17, 21-23] Preliminary mutagenic tests [17,27-29] showed activity in two out of five strains of different sat-monella bacteria.

SENSITIVITY ASPECTS

Impact and friction sensitivity of HNF is determined[17, 30,31] by using BAM apparatus (table 3). It is found that the results strongly depend not only on purity, but also on particle size, shape of HNF crystals and the kind of contaminants. Impure HNF shows values of impact sensitivity of < 1Nm, while the purified product of the same batch exhibits an improvement to the level of ≥ 15Nm. Some of the researchers have reported friction sensitivity of 25N. Authors subjected HNF synthesized in the laboratory to impact and friction stimuli in Julius Peter apparatus. h_{50} obtained in the impact test for 2 kg. drop wt. is 25 cms. In the friction test sample does not under go explosion up to 2 kg. Limited data on other sensitivity tests like drop ball test, drop hammer test, electrostatic spark test, shock sensitivity, detonation velocity and critical diameter is also available[20, 30] (Table 3,4). In general HNF is more sensitive than AP, RDX and HMX.[30, 32]

STABILITY

Considering the lower decomposition temperature of HNF (~ 120°C), a test temperature of 60°C and criterion of gas evolution less than 3 cc/g during 48 hours heating is fixed for vacuum stability (VS) test. Gas evolution in the range of 2 – 10 cc/g. is reported by various researchers.[12, 17] Excessive gas evolution for raw HNF is attributable to presence of solvent and other impurities. Pure HNF with controlled particle size is reported to evolve 0.1 – 0.5 cc gas /g. Recrystallized HNF prepared by the authors exhibits more or less similar trend. This brings out that the purification of HNF is

THERMAL DECOMPOSITION

Thermogravimetric analysis (TG) of HNF carried out by Hordijk et.al.[17] (in air at 4^0C/min heating rate) revealed no mass change up to 90^0 C. A very small mass decrease (~ 1.4%) was observed in the temperature range of 90 - 105^0C. The rapid decomposition of HNF was observed above 105^0C. The DTA studies at 2^0C/min heating rate carried out by McHale and Von Elbe[15] indicate a strong exotherm at ~ 120^0C. DTA measurement at 10^0C/min heating rate reported by Shoyer et.al.[1]exhibit a weak exothermic effect at ~ 109^0C with T_{max} at 110^0C followed by two exotherms with T_{max} at 134 and 139^0C respectively. It is believed that the discrepancy between these results is due to impurities in the earlier samples. Decomposition of HNF in 3 steps at temperature > 131^0C is also reported by Toshiyuki et.al.[32].

DSC studies carried out by various researchers [11,14,19,21-23] exhibit onset temperature of decomposition, (DSC-To) in the temperature range of 110 - 125^0C. Hordijk et.al.[17] reported energy release of 4700 kJ/kg during its decomposition. The DSC curve (fig. 11) reported by Hatano et.al.[30] shows two exotherms at 130 & 140^0C respectively corresponding to release of 4800 J/g energy.

Koroban et.al. [16] reported formation of ammonium nitroformate (ANF) as intermediate during slow decomposition of HNF in the temperature range of 70-100^0C.Williams and Brill[33] carried out heating of partially confined HNF between two

NaCl plates and monitored its IR pattern. They observed decrease in all absorbances corresponding to HNF and formation of AN rather than ANF. They proposed that water (gaseous product formed during decomposition of HNF) gets absorbed on NaCl plates and ionic pathway favored by H_2O-NaCl results in the preferred formation of AN. Decomposition of ANF to AN was confirmed by Williams and Brill[33] in TGA experiments conducted at heating rate of 1^0C/min. They found that ANF decomposes to AN at 112^0C and subsequent weight loss pattern corresponds to AN decomposition/sublimation at 170^0C. Thus, formation of ANF can not be totally ruled out in Williams and Brill's [33]experiments.

Micro thermocouple data revealed that HNF combustion progresses with melting at 123^0C followed by foaming due to gas generation. At about 260^0C, rate of gasification accelerates rapidly followed by deflagration. These results bring out that there are two regions of special interest in the combustion of HNF i.e. between $123\text{-}260^0$C and $260\text{-}400^0$C.

Williams and Brill[33] subjected HNF to the heating rate of 600^0C/s on Pt ribbon filament and monitored the gases evolved by applying FTIR and FT-Raman spectroscopy method. Absence of HNF aerosol in gaseous products brings out that the decomposition is not accompanied with its evaporation. Gaseous products comprising of ANF aerosol, NF, N_2H_4, N_2O, H_2O and CO obtained in the temperature range of $123\text{-}260^0$C can be explained on the basis of following reaction scheme,

$$HNF \rightarrow 2ANF + N_2 + H_2 \quad (-30 \text{ kcal / mole.}) \ldots(1)$$

$$HNF \rightarrow HC(NO_2)_3\ (g) + N_2H_4\ (g) \quad (+41 \text{ kcal / mole.}) \ldots(2)$$

Although N_2 and H_2 formed during reaction (1) are IR inactive, formation of N_2 is confirmed by Koroban et. al.[16] in separate set of experiments. Presence of N_2O, CO and H_2O suggest that other reactions occur simultaneously as shown bellow,

$$2ANF \rightarrow N_2O + 2CO + 4H_2O + 5/2O_2 + 3N_2 \qquad (-86\ \text{kcal/mole.})$$

The over all exothermicity of surface reaction corresponds to 73 kcal /mol., which may be responsible for its self sustained deflagration. Above 260^{0}C, formation of CO_2 takes place and its amount increases with increase in temperature. NO is also detected in this temperature zone. In these experiments ratio of NO and CO_2 is found to be 2. ANF, N_2O and CO are not detected above 350^{0}C. These results suggest that following strong exothermic reaction takes place above 260^{0}C,

$$HNF \rightarrow 2NO + CO_2 + 2H_2O + 3/2N_2 + ½H_2 \qquad (-149\ \text{kcal/mole.})$$

All these reactions are expected to describe semi-global surface deflagration process. The thermal experiments of Williams and Brill[33] correspond to the activation energy of 25 kcal /mole. for decomposition of melt /foam layer. These values are at variance with activation energy reported for solid HNF which may be because of the complexity of semi-global reaction.

COMPATIBILITY

HNF is found to be incompatible with HTPB and isocynates.[34, 35] The presence of carbon double bond in the HTPB backbone is reported to be the cause of the HNF/HTPB incompatibility. It is proposed that the carbon-carbon double bond get oxidized by HNF leading to deterioration of mechanical properties of HTPB binder. The incompatibility of isocyanates is possibly due to transfer of hydrogen from HNF to nitrogen in – N=C=O group of isocyanate.[36] This was confirmed by Schoyer et.al. [1] on the basis of 88% decrease in the isocyanate absorption peak (2270 cm^{-1}) in IR spectra of HNF/isocyanate mixture after an interval of 48 hours. It is opined that isocyanate should be allowed to react completely with the binder to avoid such interaction. Schoyer et.al.[1] also observed poor compatibility of various aliphatic, cyclic polymeric di / poly isocyanates with HNF in VS test. These researchers established that HNF is compatible with GAP and Al.

HNF PROPELLANTS

The development work on HNF based propellant was started in PML-TNO Netherlands in 1988[1] in view of the dual advantage of higher specific impulse and chlorine free exhaust. Schoyer et.al.[1] selected HNF/GAP propellant systems for detailed study. They found that optimum performance could be achieved at 85% solid loading. However, in view of the anticipated processibility problems due to physical characteristic of GAP, they selected composition with 80% solid loading. For compositions comprising of 55-60% HNF, 20-25% Al and 20-25% GAP, theoretically predicted I_{sp} (vacuum) ranges from 2973 to 3080 m/s (considering 8% loss). The density of these compositions ranges from 1.91 to1.98 g/cc. They have predicted the potential of HNF/Al/GAP propellant vis-a-vis currently used AP/Al/HTPB propellant (I_{sp}=2660 s.) in Ariane 5 booster by applying ESTEC ASTROP code. This analysis suggests that payload mass can be increased by ~ 10% by using HNF based propellants in place of current Ariane 5 booster propellant used for HERMES launch. They have also predicted 7% increase in I_{sp} on replacing AP/Al/CTPB propellant (I_{sp}=2825-2884 s.) by HNF/Al/GAP system for MAGE booster.

In view of the problems encountered in preparing slurry cast composition because of non-availability of a suitable curing system and HNF of desired morphology, Schoyer et.al.[1] prepared a pressed propellant formulation containing 60% HNF (150-200 μm: 33% & 10-20 μm: 67%), 20% Al and 20% GAP. They subjected circular discs of pressed formulation (OD: 50 mm & web thickness: 10 mm) with end burning (achieved by inhibition) to L* burner test (fig.12). Their studies brought out that HNF propellants are easily ignitable. They obtained C* value of ~1590 m/s. (Theoretical C*: 1667 m/s at 5.1 MPa) The burn rate realized was > 30 mm/s. (at 5.5 MPa) with pressure index value of 0.81-0.83. More or less similar results are reported by researchers from ESSO and Thiokol.[37] Although the impact and friction sensitivity of HNF /Al/GAP propellant is higher than that of AP/Al/HTPB propellant, the values are within the acceptable limit for practical use. (Table 5)

Schoyer et.al.[20] made further study on these compositions containing 70-59% HNF, 0-18% Al and 19-20% GAP with other additives (curing agents & burn rate catalysts). They obtained burn rate of 1-40 mm/s, in the pressure range of 0.1-10 MPa. Incorporation of burn rate catalyst brought down the pressure exponent from 0.81 to 0.58. The burn rate-pressure relationship obtained for these systems are given below,

* Non-catalyzed propellant: $r = 5.75\ Pc^{0.81}$

* Catalyzed propellant (with 4% catalyst): $r = 9.86\ Pc^{0.58}$

Shoyer et.al.[20] subjected catalyzed GAP/HNF/Al propellant grains (100 mm dia. and 10 mm length) to static test in test motor of 100 mm ID and 40 mm length. Data obtained gave burn rate of 11-28 mm/s in the pressure range of 2-7 MPa corresponding to the relationship r = 7.062Pc.$^{0.6436}$ The C* value is in the range of 1532-1656 m/s. The reference AP/Al/HTPB formulation (70% AP, 18% Al, 6.8% HTPB, 4.1% IDP, 0.4% additives, 0.7% IDPI) tested under same conditions exhibited much lower burn rate (6-9 mm/s. at 2.5-7.5 MPa) corresponding to the relationship of r = 4.5523 Pc.$^{0.3315}$ The C* value for the above composition was also on lower side. (1455-1559 m/s.) Schoyer et. al.[29]could prepare a slurry cast formulation with low HNF loading (35-47% HNF, 43-47% GAP & 5-8% curatives). This composition also gave burn rate close to those for aluminized composition (fig.13).

These researchers have patented HNF/NP/AP based high performance propellants with GAP and BAMO as energetic binders and B, Al or AlH_3 as fuels.[38] Mul et.al.[39] patented a method of manufacture of propellants based on HNF, ANF, NP or AP as oxidizers, B, boranes, Al or AlH_3 as fuels and PLN, GAP, PGN or BAMO as energetic binders. Gadiot et.al.[40] have developed "clean" propellants based on AN and HNF for commercial applications.

Authors theoretically predicted performance of HNF based aluminized composite propellant and CMDB propellant formulations vis-à-vis corresponding AP based propellant formulations (Table 6&7). An increase in C* value by 74 m/s and I_{sp} by 11 s. is observed on replacement of 66% AP by HNF in composite propellant. On replacement of 18% AP by HNF in CMDB propellant, an increase in C* value by 28 m/s and I_{sp} by 4 s. is observed.

OTHER POTENTIAL DERIVATIVES OF NITROFORM

Various NF derivatives (other than HNF) are also reported in the literature with potential applications as oxidizers, explosives and plasticizers. Tetrakis (2,2,2-trinitroethyl) orthocarbonate (TNEOC) and Bis (2,2,2- trinitroethyl) nitramine (BTNEN) are the potential oxidizers for smokeless propellants.[41] 1,4 Dinitro-3, 6-bis (trinitroethyl) glycouryl [42] is an explosive material having high density (1.95 g/cc), high VOD (9037 m/s), with acceptable thermal and hydrolytic stability. 5 - (Trinitro - N - ethylamino) - tetrazole [43] (~161% TNT) and N-nitro-N (2,2,2-trinitroethyl) guanidine [44] are also powerful explosives. 2,2,2-Trinitroethyl -1,2-nitroxyethyl ether is a high-energy plasticizer for explosives and propellants.[45] It has high energy content between NG and butanetriol with advantage of low volatility and less toxicity as well as high thermal stability than NG. It is especially useful in LOVA gun propellants. Bis (b, b, b-trinitroethyl-N-nitro) ethylenediamine [46,47] finds use in plastic bonded explosives.

This review reemphasizes tremendous potential of HNF as an eco-friendly energetic oxidizer. Although, its pilot plant scale production has commenced in Netherlands, various process parameters need to be finalized to obtain HNF of high purity and controlled particle size / shape. Pure HNF has desired stability and sensitivity characteristics to obtain propellant composition of practical value. Controlled particle size / shape is essential to achieve high solid loading. Another major problem to be tackled is the incompatibility of HNF with HTPB, the current work horse polymer binder and its curatives (isocynates). HNF formulations based on azido polymers need to be developed on top priority to meet futuristic needs. It is necessary to develop technology for processing slurry cast propellant formulations to obtain defect free monolithic propellant grain. Combustion studies also need to be undertaken in much more detail in order to understand the mechanism of energy release leading to high performance and super burn rate. In view of the limited and scattered data available in the literature, there is a wide scope of detailed study on these aspects in near future to arrive at system of practical value.

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TABLE 1

Physico-Chemical Properties of HNF

Sr. No.	Property	Value	Reference
1.	Molecular formula	$N_2H_5C[NO_2]_3$	
2.	Molar Mass[kg/kmol]	183.03	
3.	Appearance	Yellow crystals	
4.	Crystalline form	Monoclinic	20
5.	Melting Point (^{0}C)	110 – 124	1,11,12,14-17,19-23,30,35
6.	Density (g/cc)	1.86 – 1.93	1,7,11,17-20,22,23,30,39
7.	Oxygen Balance (%)	13	
8.	Heat of Combustion ΔH_c (kJ/mol)	-1086	20
9.	Heat of Combustion ΔH_c (kJ/kg)	-5824	20
10.	Heat of Formation ΔH_f (kJ/mol)	-71,-72	1,11,16,19,20,23
11.	TNT Equivalent (theoretical %)	130 – 150	20
12	Elemental Analysis	Exp. (Theo.)	30
	C	6.68% (6.56%)	
	H	2.65% (2.75%)	
	N	28.24% (38.25%)	
13	Solubility in g/100g of Solvent		30
	Methanol	22.28	
	Ethanol	5.98	
	2-Propanol	1.14	
	Ethyl acetate	1.12	
	Water	112.21	

TABLE 2 (Ref. 33)

IR and Raman Frequencies of Neat Solid HNF[a]

IR	Raman	
2578-3350 m[b]	2950-3350 w[c] 1618 w	N-H str.
1615 w, sh	1595w	NH_3^+ def.
1595 w	1522 w	
1512 s		NO_2 antisym str.
1496 s	1463 m	
1474 m, sh		
1421 m	1385 s	NH_3^+ bend
1396 w	1345 m	
1380 w	1276 s	
1271 s	1237 s	NO_2 sym str. and
1241 m	1166 w, sh	NH_2 rock
1177 s	1151 s	NH_3^+ wag
1153 w, sh	1099 m	
1098 m	1075 m	N-C-N asym str.
1084 m,sh	1075 m	
1069 m	968 m	
971 m	954 m	N-N str.
955 m	879 s	
879 w		C-NO_2 in phase str.
872 w	793 m	
794 s	785 m	NO_2 bend
788 w, sh	731 m	
734 s		

[a] S = strong, m = medium, w = weak, sh = shoulder,

[b] A broad envelope containing 13 resolvable absorbances

[c] A broad envelope containing 6 resolvable bands

TABLE 3

Sensitivity Data of HNF

Sr.No.	Test	Results	Reference
1.	Impact [BAM] Nm	2 – 20	11,12,17,19-23,31,35
2.	Friction [BAM] N	12 – 36	12,17,20,21,23,31
3. *	Critical diameters (mm)	< 10	20
4. *	Shock sensitivity [ϕ 30 mm] (Gpa)	3	20
5. *	Detonation velocity (km/s)	8.2 – 8.5	20
6.	ESD (J)	Ignition at 4.5 No. ignition at 0.726	20

*** Test material: 91 % HNF; 9 %Wax; ρ=1680 kg/m^3**

TABLE 4
Sensitivity Data of HNF vis-a-vis RDX & HMX

Sr.No.	Test	HNF		RDX	HMX	Ref
		NEEDLE	GRANULE			
1.	Friction test	Class 3	Class 3	Class 5	Class 6	30
2.	Drop hammer test (cm)	24.7	11.6	27.6	34.7	30
3.	Drop ball test(cm) Direct	2.75	4.43	>4.70	>4.70	30
	Indirect	0.25	0.47	0.48	0.49	30
4.	Electrostatic spark test	1.71	1.81	0.65	2.55	30

<u>Note:</u> Test No 2,3&4 were carried out according to the Dixon's up-and-down method. The values are for 50% probability.

TABLE 5 (Ref. 1)
Sensitivity Data of HNF and HNF (pressed) Propellant Mixtures in Comparison to Typical AP and AN Based Propellant Systems

Composition	Impact Sensitivity, Nm	Friction Sensitivity, N
HNF	7.5	24
60% HNF / 20% Al / 20% GAP	3	30
59% HNF /21% Al /20% GAP	15	24
Literature [48]		
AP/Al based propellants	15-25	30
AN/GAP/BDNPA-F	15-25	>360

TABLE 6
Theoretical Performance Prediction of Various Oxidizers
Composite Propellant

X	T_f ^{0}C	M_w	C* (m/s)	I_{vac} (s)	I_{sp} (s)
AP	3499	30.11	1572	286.6	261.7
ADN	3435	26.62	1637	295.7	271.1
HNF	3399	26.49	1646	297.9	272.7

Propellant composition: energetic oxidizer (X): *66%, Al: 19%, HTPB: 7.5%, DOA: 5%, TDI: 1.5%,* Fe_2O_3*:*

TABLE 7
Theoretical Performance Prediction of Various Oxidizers
CMDB Propellant

X	T_f (^{0}C)	Mw	C*(s)	I_{vac}(s)	I_{sp} (s)
AP	3646	31.29	1573	285.3	260.8
ADN	3634	30.17	1592	288.2	263.6
HNF	3661	30.08	1601	289.5	264.8

CMDB composition: *NC (12.2% N): 27%, NG: 30.19%, Carbamite: 0.81%, DEP: 6.3, 2NDPA: 0.7%, X: 18%, Al: 17%*

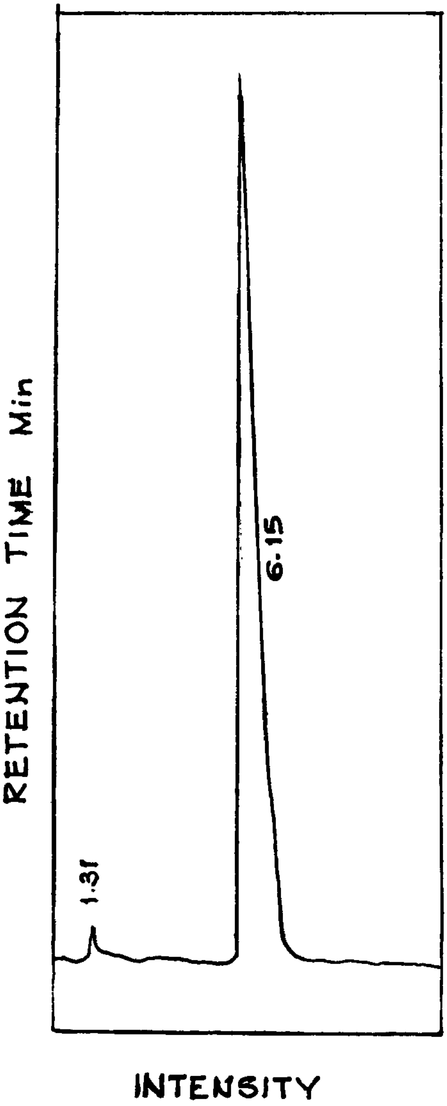

FIG.1 HPCL OF HNF

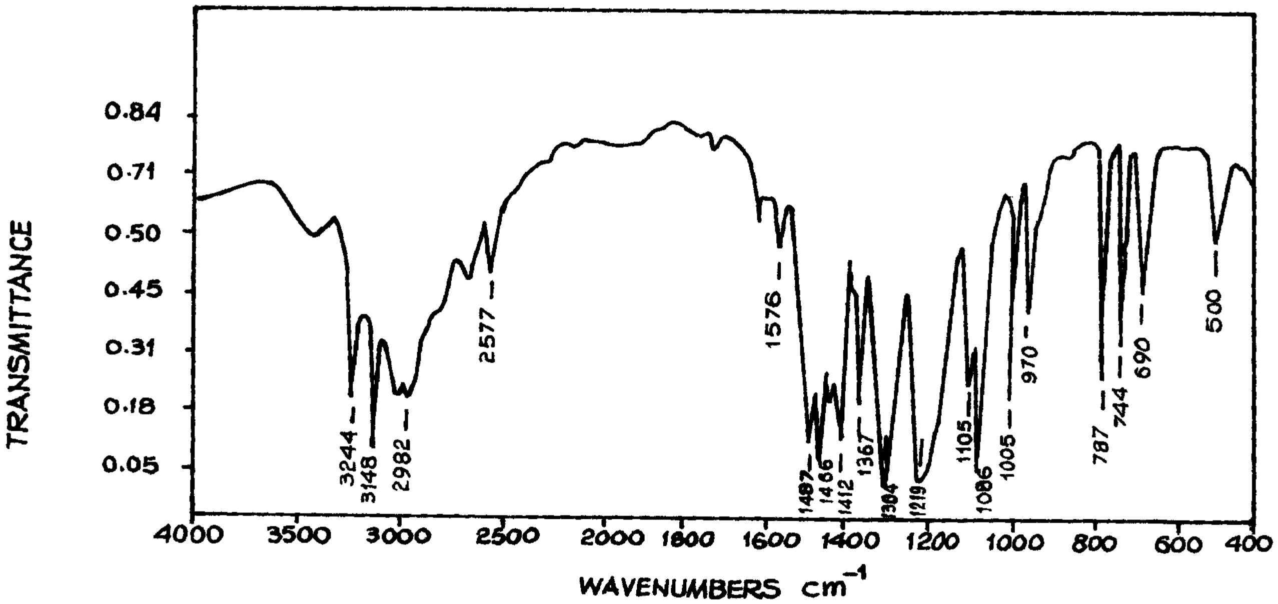

FIG.2 – INFRARED SPECTRUM OF HNF (REF.17)

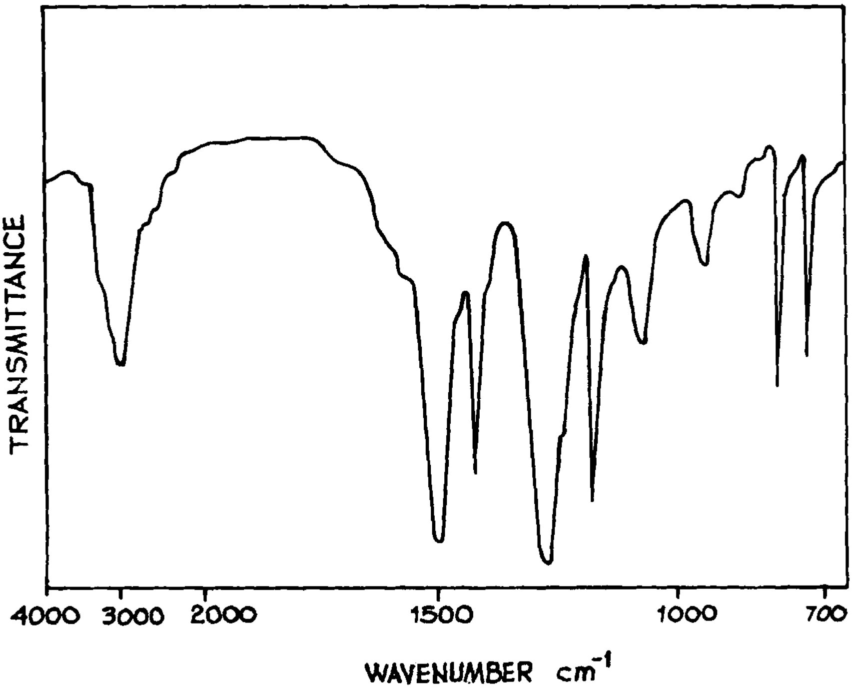

FIG. 3 - INFRARED SPECTRUM OF HNF
(REF.30)

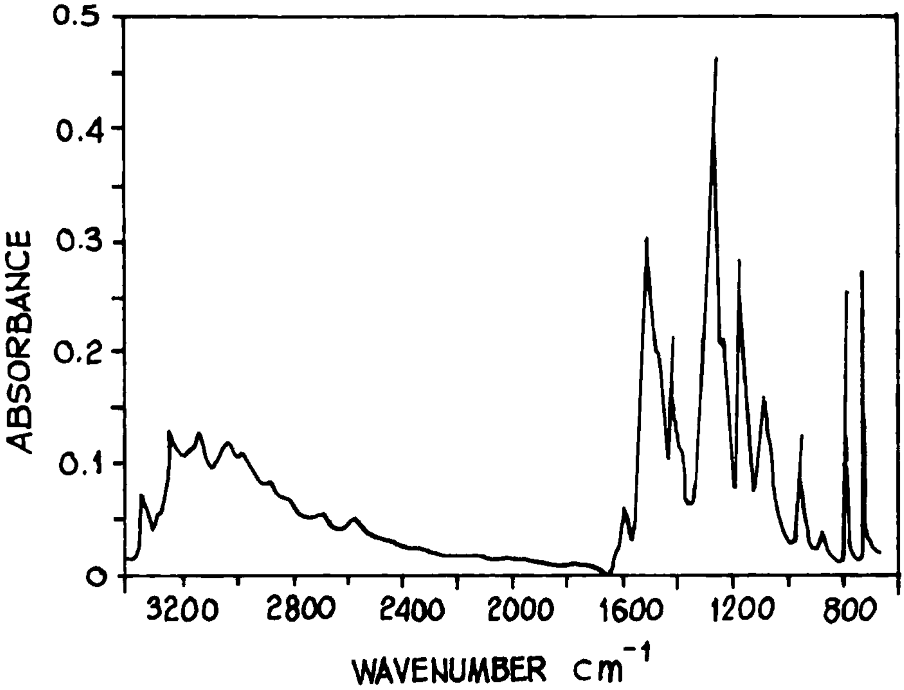

FIG. 4 - IR SPECTRUM OF DRY SOLID HNF
(REF. 33)

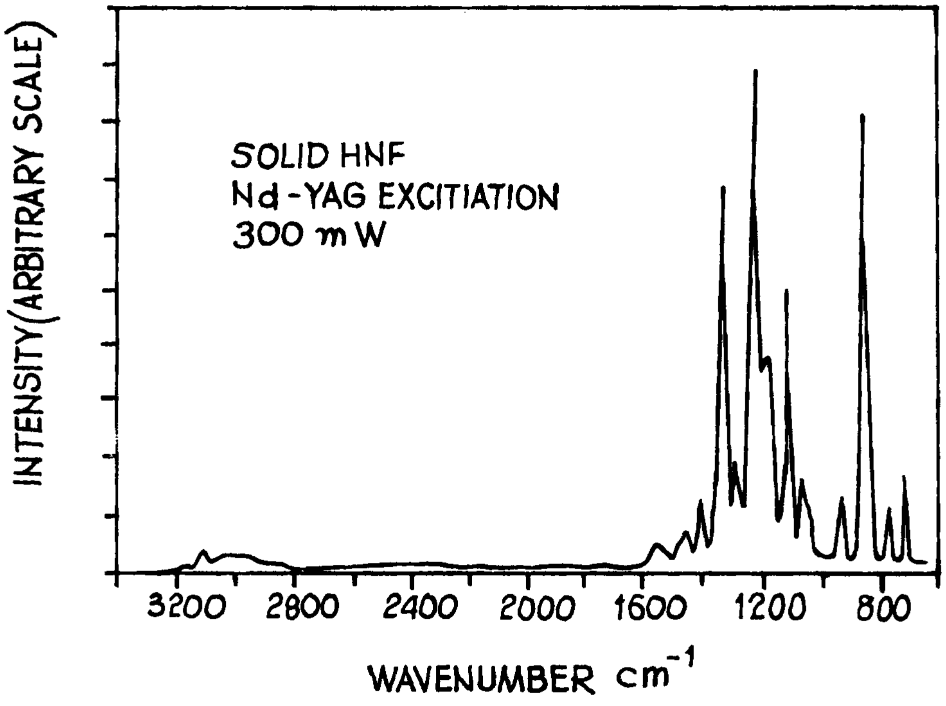

FIG.5 - FT-RAMAN SPECTRUM OF DRY SOLID HNF
(REF. 33)

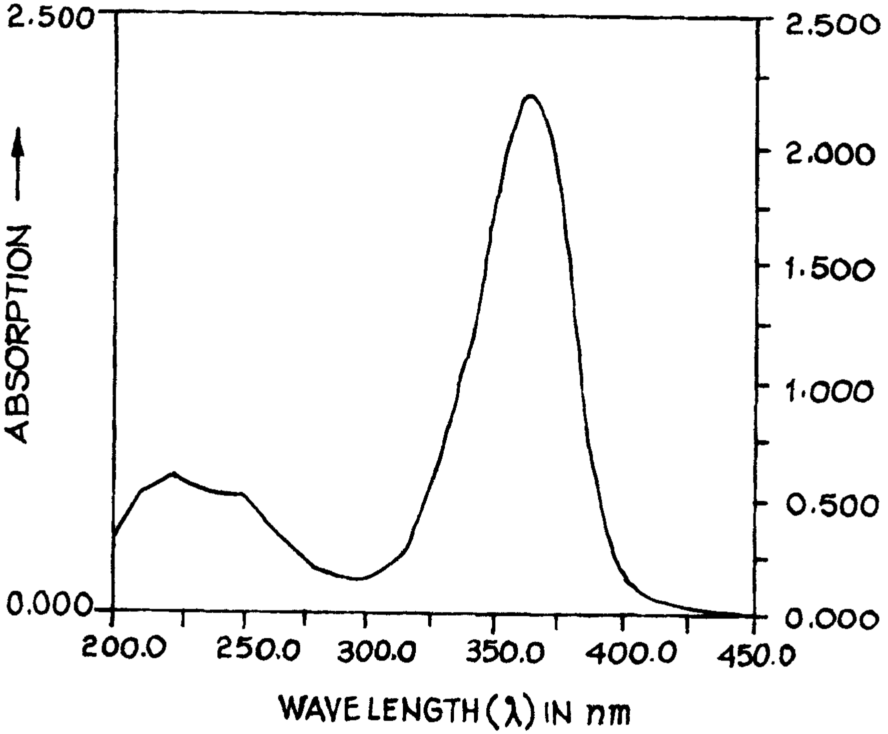

FIG. 6 - ULTRAVIOLET SPECTRUM OF HNF (REF. 17)

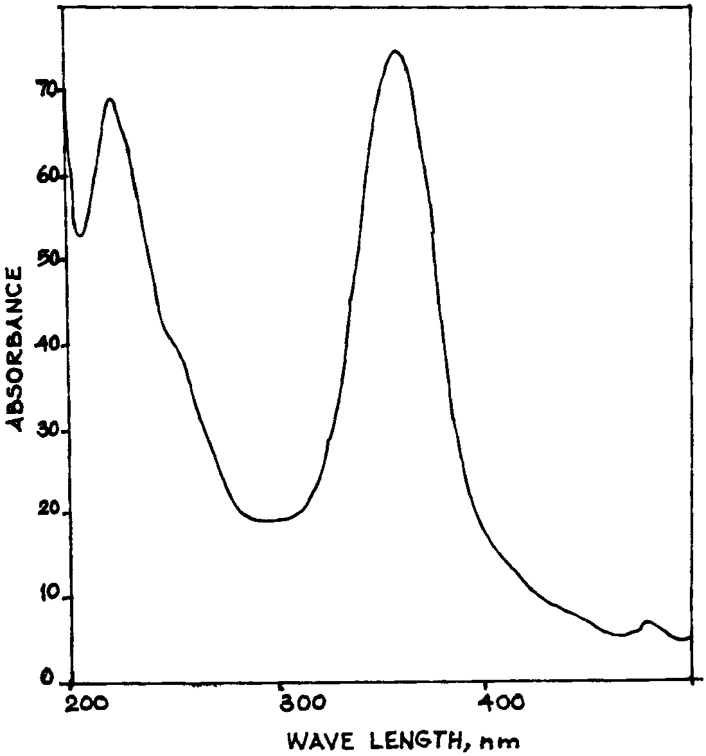

FIG 7 : UV SPECTRUM OF HNF

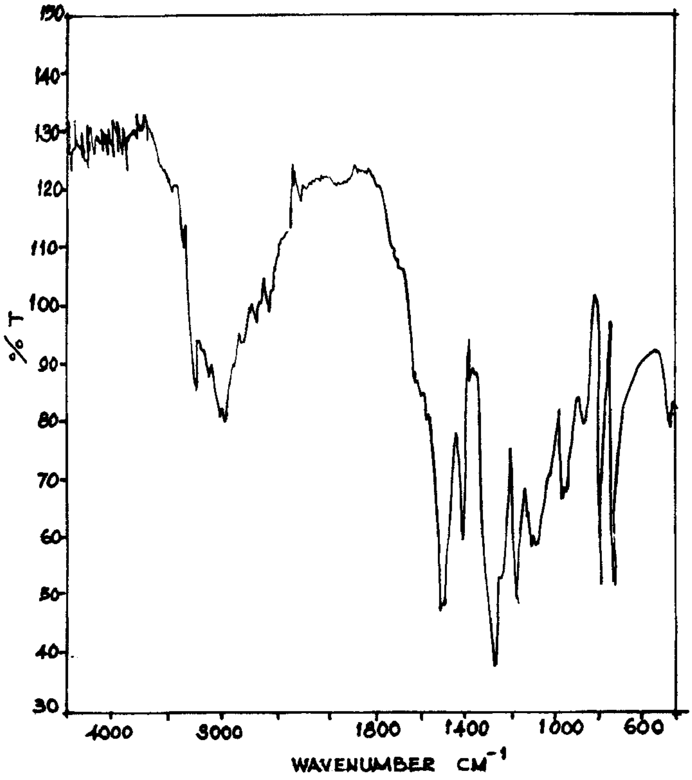

FIG 8 : IR SPECTRUM OF HNF

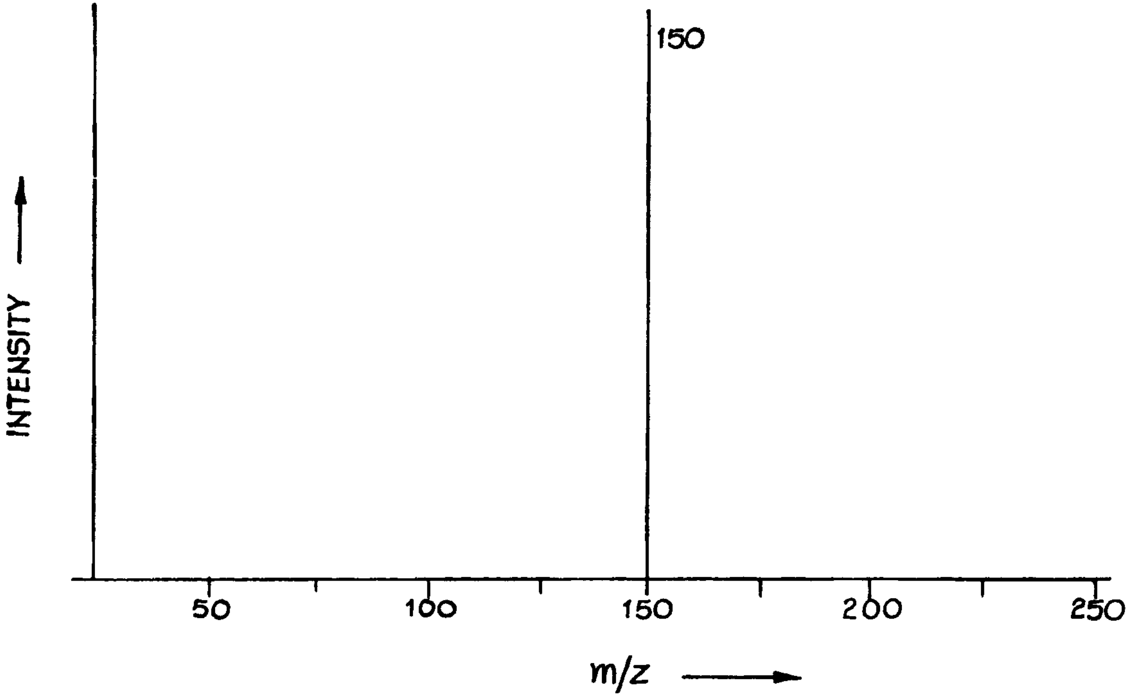

FIG. 9 - NEGATIVE ION SPECTRUM OF PURIFIED HNF
(REF. 17)

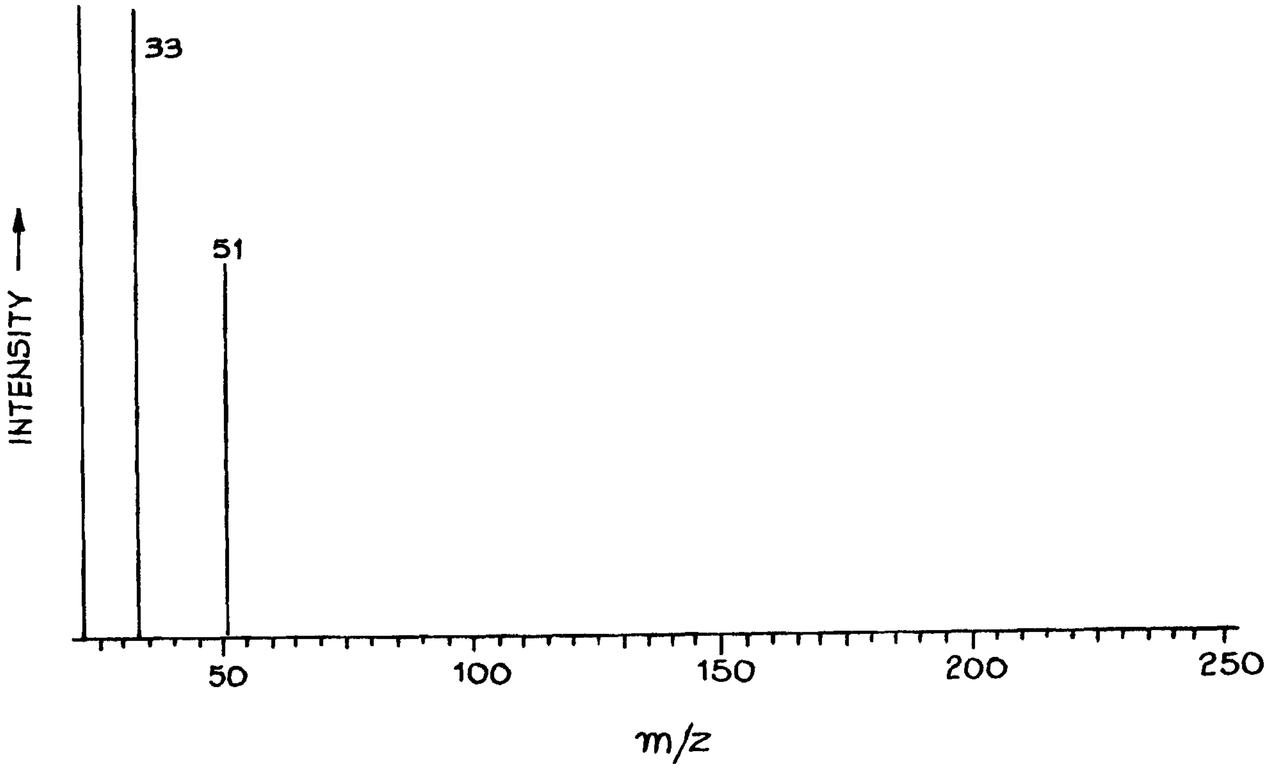

FIG.10- POSITIVE ION SPECTRUM OF PURIFIED HNF
(REF. 17)

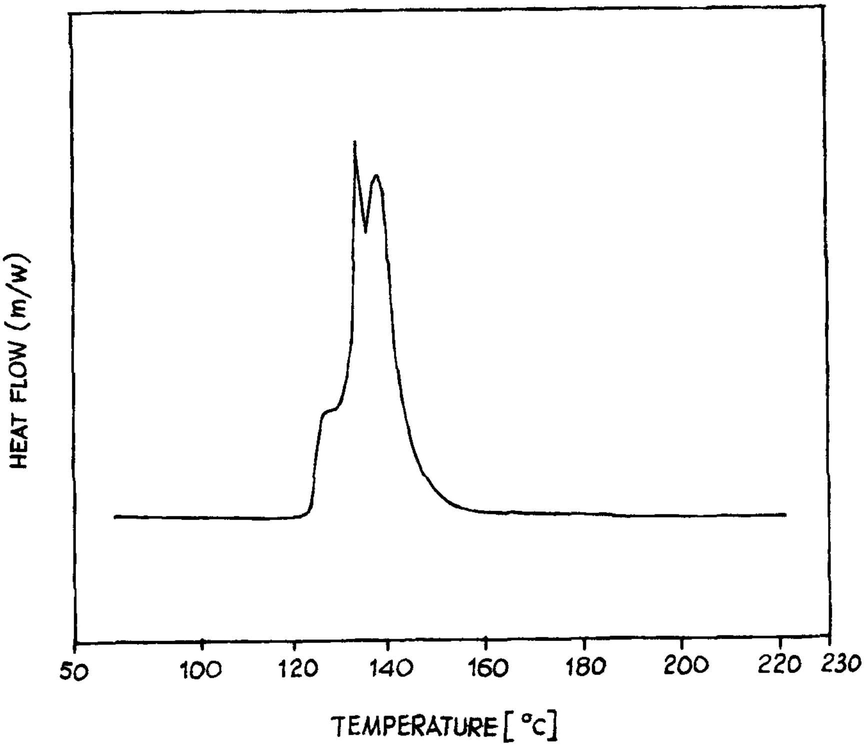

FIG.11 - TYPICAL DSC CURVE OF HNF
(REF. 17)

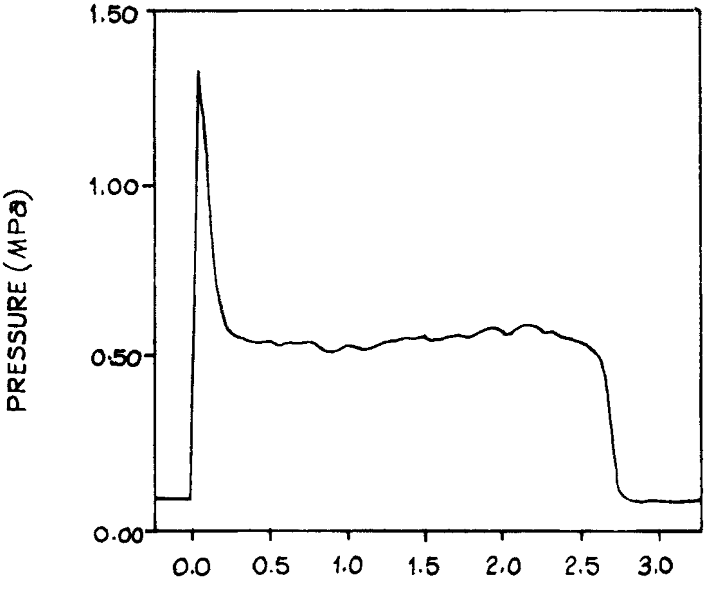

FIG.12- TYPICAL PRESSURE HISTORY OF PRESSED HNF/Al/GAP PROPELLANT AT LOW PRESSURE (REF. 1)

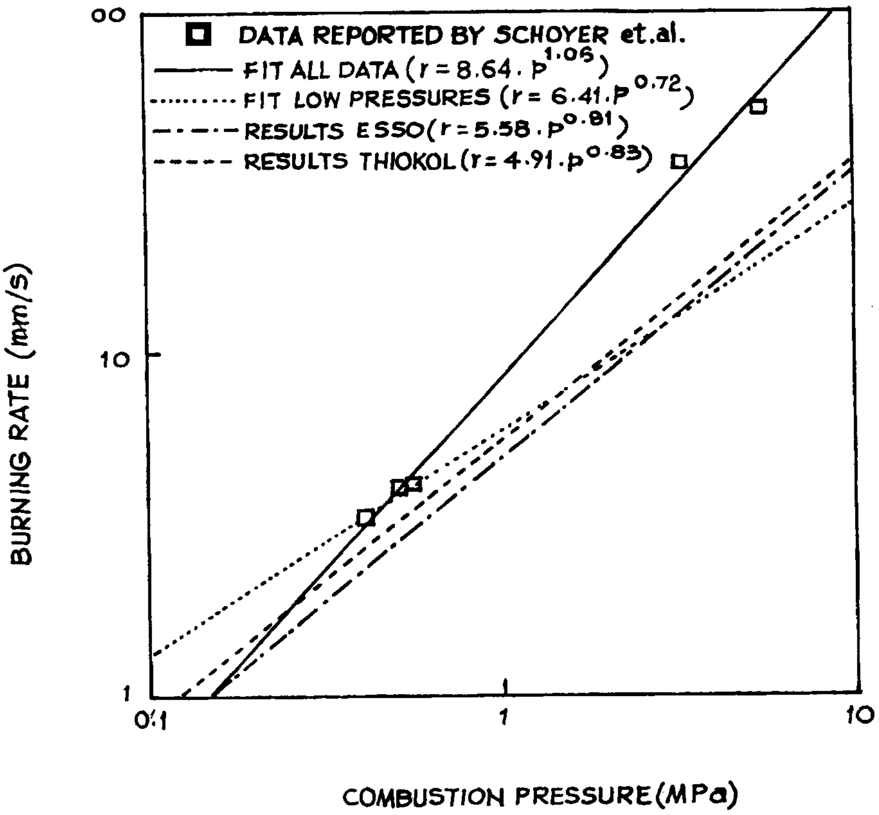

FIG.13 - BURNING RATE OF HNF PROPELLANTS
(REF. 1)