



Synthesis, characterization and thermal studies of (Ni/Co) metal salts of hydrazine: potential initiatory compounds

J.S. Chhabra*, M.B. Talawar*, P.S. Makashir,
S.N. Asthana, Haridwar Singh

High Energy Materials Research Laboratory, Pune 411 021, India

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Abstract

Nickel hydrazinium nitrate (NiHN) and cobalt hydrazinium nitrate (CoHN) were prepared by reacting their respective metal nitrates with hydrazine hydrate at 25 and 65 °C. The compounds were characterized by metal content and infrared (IR) spectroscopy. Differential thermal analysis (DTA) results suggest that the nickel complex is relatively more stable than the cobalt complex. The activation energy determined by DTA and ignition delay measurements corresponds to an energy of activation (E_a) of 80 ± 4 kJ/mol for NiHN and that of 150 ± 8 kJ/mol for CoHN. Thermo gravimetry (TG) also revealed more rapid decomposition of NiHN than that of CoHN in the temperature region of 215–235 °C. High temperature Fourier transform-infrared (FT-IR) studies indicated rupture of the Ni–N/Co–N bond as the primary step in the thermolysis. As regards sensitivity to mechanical stimuli, NiHN was found to be less impact sensitive while CoHN exhibited less friction sensitivity. The study revealed that NiHN could be used alone as well as in combination with oxidizer/fuel as initiators depending upon the specific requirements. The effect of silver azide and glass on the sensitization of NiHN was also studied. CoHN appears to be an effective ballistic modifier in enhancing burning rates of composite propellants.

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1. Introduction

Lead azide is one of the foremost primary explosives, having gained prominence in military munitions as well as in civil applications. It has dominated the field of initiatory

* Corresponding authors. Tel.: +91-20-5869303x2220; fax: +91-20-5869316.
E-mail addresses: root@drerdl.ren.nic.in (J.S. Chhabra), sukeeru@yahoo.com (M.B. Talawar).

compounds for the last 70 years. However, despite being an excellent detonating agent, it suffers from certain inherent drawbacks such as hydrolytic instability, incompatibility with copper and its alloys commonly used for encapsulation of primary explosive formulations, and high friction sensitivity. Moreover, its high thermal stability up to 330 °C is undesirable from the point of view of effective initiation by thermal stimuli. The search is on for potential primary explosives with figures of insensitivity (F of I) >20, and which are less prone to initiation from potential mechanical shock during storage, transport or handling of the finished ammunition, and which are stable as well as compatible.

Lead-free co-ordination compounds are the choice of tomorrow in view of their additional advantage of being eco-friendly. Another desirable attribute of this class of compounds is the presence of almost stoichiometric fuel and oxidizer portions. These compounds may be applicable to the entire spectrum of explosives. Tomlinson et al. [1] and Joyner [2] have reported the relationships between co-ordination structure and explosive properties, whereas Sinditskii and Serushkin [3] co-related design and combustion behaviors of explosive co-ordination compounds. Although these co-ordination compounds [3,4] are well known for a long time, they have only recently [5,6] evinced interest as primary explosives. Patil and Vernekar Pai [7] reported transition metal complexes of nitrate/azide/perchlorate and proposed their application as initiators. The preparation of nickel hydrazinium nitrate (NiHN) as an initiatory compound has been recently reported by Shunguan et al. [8]. Hariharanath et al. [9] evaluated the potential use of NiHN as a component of squib composition required for igniting propellants and explosives.

In view of the above observations, coupled with the limited reported work on the application of transition metal complexes as initiatory compounds, the synthesis and characterization of NiHN and CoHN were undertaken with emphasis placed on understanding their decomposition behavior.

2. Experimental

2.1. Synthesis of hydrazinium nitrate complexes

Synthesis was undertaken along the lines of the method reported by Shunguan et al. [8].

2.1.1. At a reaction temperature of 65 °C

A volume of 50 cm³ aqueous solution of Ni(NO₃)₂ (8% w/w) was diluted to 100 cm³ and preheated to 65 °C in a steel reaction vessel with stirring. Another 50 cm³ of aqueous solution of Ni(NO₃)₂ (8% w/w) and 7 cm³ of hydrazine hydrate (>80% w/w) were simultaneously added slowly over a period of 30 min. A change in the color of the reaction mixture, from bluish to purple was observed during the reaction. The suspension was stirred for an additional 10 min at 65 °C. The purple-colored product was filtered under suction after cooling the contents and washed three times with distilled water (3 × 20 cm³). Finally, it was treated with alcohol and dried for 6 h at 60 °C. The yield was 11.2 g (~90%). A similar procedure was adopted for the preparation of CoHN and the yield obtained was 10 g (85%).

2.1.2. At a reaction temperature of 25 °C

An attempt was also made to synthesize the complexes at lower temperature (25 °C). To a solution of nickel nitrate (8% w/w), hydrazine hydrate (7 cm³ in 5 cm³ of water) was added slowly over a period of 15 min with vigorous stirring at 25 °C. The color of the reaction mixture changed from light blue to pink. The pH of the reaction mixture was maintained at 6.4–6.5 throughout the reaction. After the completion of the addition of hydrazine hydrate, the reaction mixture was further stirred for 5 min at 25 °C. The product obtained was filtered and washed with distilled water (3 × 50 cm³) followed by ethyl alcohol (50 cm³). The pink-colored compound was dried at 65 °C. The yield obtained was 11 g (~90%). CoHN was also prepared by the same procedure in ~90% yield (10.5 g).

The products obtained at 25 °C were found to be amorphous in nature whereas the materials prepared at 65 °C were in granular, free-flowing form with a bulk density of 0.88–0.90 g/cm³. The granular material was used for evaluation. Starting materials of AR grade were used in both the cases.

2.2. Characterization

An atomic absorption spectrophotometer (Chemito 2001) was used to determine the metal content of the complexes and their structural features were confirmed by Fourier transform-infrared spectrophotometry (FT-IR, Perkin-Elmer 1600). The experimentally determined metal content of NiHN and CoHN (Ni: 20.6% and Co: 20.2%) was found to be in close agreement with theoretical values (Ni: 21.06 and Co: 21.14). The FT-IR spectra revealed a stretching frequency due to NH₂, N–NO₂ and metal–hydrazine linkages (Table 1).

2.3. Thermal studies

The thermal decomposition pattern was determined by means of an in-house assembled differential thermal analyzer (DTA), a thermo gravimetric (TG) analyzer (Mettler Toledo Star system) and a differential scanning calorimeter (DSC) (Mettler Toledo Star system). The DTA was calibrated with indium metal. The DTA profiles were recorded using 5 mg sample material of NiHN and CoHN, and TG profiles with 1.1 mg each of NiHN and of CoHN. The DSC profile was recorded for NiHN only, with a sample weight of 0.5 mg at heating rate of 5 °C/min in N₂ atmosphere.

Table 1
Characterization data of NiHN and CoHN

Property	NiHN	CoHN
Metal content (%)	20.6	20.2
Bulk density (g/cm ³)	0.85–0.90	0.90
IR (cm ⁻¹)		
NH ₂	3238	3238
NH ₂	1626	1626
NO ₃	1356	1384
Ni–N	550	546 (Co–N)

The explosion temperatures and the explosion delay (σ) were measured by specially designed instruments. Decomposition was also monitored by observing changes in IR spectral features of samples heated to elevated temperatures (110–310 °C with an interval of 20 °C). Activation energies of the physico-chemical process which controls the decomposition were computed from DTA data obtained at different heating rates (5, 10, 15 and 20 °C/min) by applying Ozawa [10] and Kissinger [11] relationships ($\log \beta$ versus $1/T_m$ and $\log \beta/T_m^2$ plots, respectively, where β is the heating rate and T_m is the peak temperature). Similar data was obtained from ignition delays (σ) determined at different isothermal temperatures by plotting $\log \sigma$ against $1/T$ as per Arrhenius relationship [12,13]. Five experiments were carried out at each of the selected temperatures.

2.4. Sensitivity characterization

The sensitivity to impact of NiHN and CoHN was determined by using a 2 kg drop weight. The results are reported [14] in terms of height for 50% probability of explosion of the sample ($h_{50\%}$) determined by Bruceton analytical technique. Figure of insensitivity (F of I) was computed by using tetryl, commonly known as composition exploding (CE), as reference. The friction sensitivity of these compounds was determined using a Julius Peter apparatus, by increasing weights on the lever in the increments of 2 N, till there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction were within the uncertainty limits of ± 2.5 cm and ± 1 N, respectively

3. Results and discussion

3.1. Thermal decomposition

The explosion temperature obtained at the heating rate of 5 °C/min was 219 °C for NiHN and 188 °C for CoHN. These values are close to the T_m obtained by DTA at the same heating rate. The DTA profile indicates that NiHN is thermally more stable (up to 210 °C) compared to CoHN (175 °C) (Fig. 1). The stability of co-ordination complexes is not only decided by the nature of the co-coordinating agent, but also by the size and the charge on the central ion. On the basis of data generated for various complexes of divalent cations, it has been established that the co-ordinated complexes of nickel are more stable than those of cobalt [15]. Although the characteristic of the central ion contributing to this sequence is not readily apparent, the second ionization potential of these atoms follows the same order (Ni: 18.2 and Co: 17.3) [15]. Thus, the stability may depend on the relative acceptor properties of the central ion for the electrons of the co-ordinating group. The relative thermal stabilities of these complexes may also be correlated with the stability constants (Ni: 18.06 and Co: 13.82) [16] reported for [Ni(en)₃] and [Co(en)₃]. The IR absorption corresponding to the M–N bond (Ni–N: 550 cm⁻¹ and Co–N: 546 cm⁻¹) is also indicative of higher stability of the nickel complex.

The energy of activation (E_a) of 78 kJ/mol for NiHN and 162 kJ/mol for CoHN was determined from DTA data at the heating rates of 5, 10, 15, and 20 °C/min employing Ozawa [10] and Kissinger [11] relationship plots (Figs. 2 and 3). The activation energies

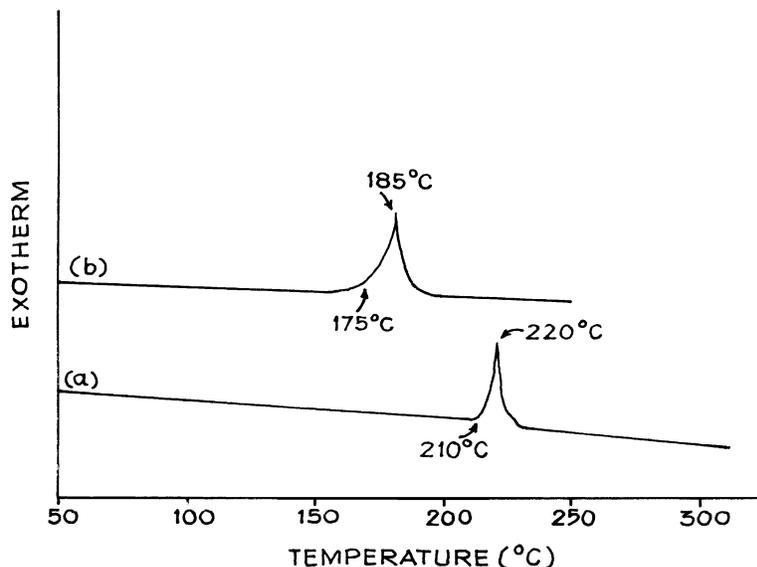


Fig. 1. Differential thermal analysis profile of (a) NiHN and (b) CoHN.

obtained from ignition delay experiment in the temperature range 210–260 °C by applying Arrhenius relationship (Fig. 4), correspond to 89 kJ/mol for NiHN and 135 kJ/mol for CoHN suggesting pattern similar to DTA. These results reveal that a relatively smaller energy barrier is encountered for decomposition in the case of NiHN than in CoHN. The TG of NiHN (Fig. 5) exhibited rapid change in weight at 215–235 °C amounting to 92.5% loss while in case of CoHN the decomposition amounting to the 36% weight loss occurred in the initial stage (Fig. 5). NiHN is reported to undergo rapid decomposition accompanied with ignition [9]. TG pattern suggests that CoHN gets converted into $\text{Co}(\text{NO}_3)_2$ and finally to Co_2O_3 .

Differential scanning calorimetry (DSC) of NiHN revealed a violent reaction at 220 °C followed by explosion, leading to abnormal curve (Fig. 6).

In order to obtain information on decomposition pathways, NiHN and CoHN were subjected to thermal stimuli at a constant temperature in the range of 110–310 °C (at the intervals of 20 °C) and the decomposition was monitored by FT-IR. It was observed that in case of NiHN, the intensity of the M–N bond does not change appreciably up to 190 °C, but subsequently a remarkable decrease in the intensity occurs (Fig. 7). The absorption band attributable to M–N bond disappears above 250 °C. As regards the N–N bond, it remains almost unaffected up to 210 °C. Other basic structural features do not exhibit major changes except merging of symmetric and asymmetric bands corresponding to N–H which may be due to influence of temperature on thermal motion.

Similar trends were observed in the case of CoHN, albeit at lower temperatures. Thus, a decrease in the intensity of absorption band corresponding to the Co–N bond commenced

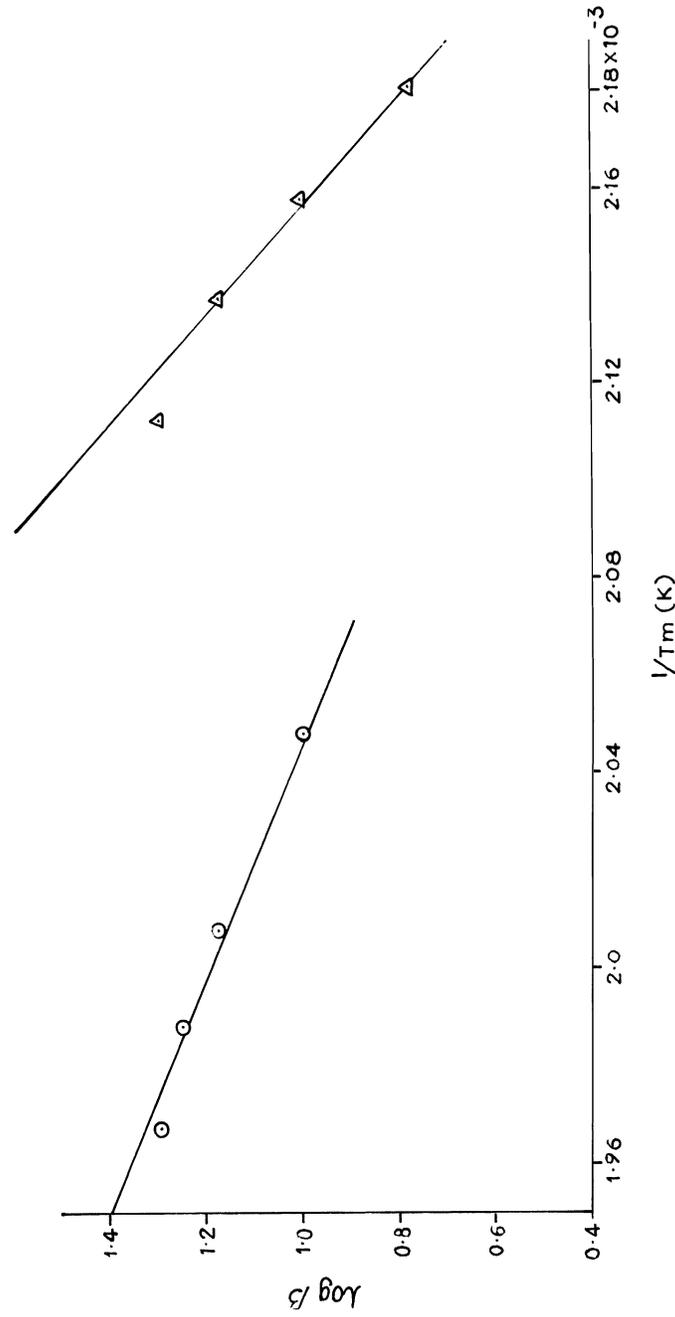


Fig. 2. Variation in $\log \beta$ with reciprocal of absolute temperature ($1/T$) for NiHN (○) and CoHN (△) (Ozawa relationship).

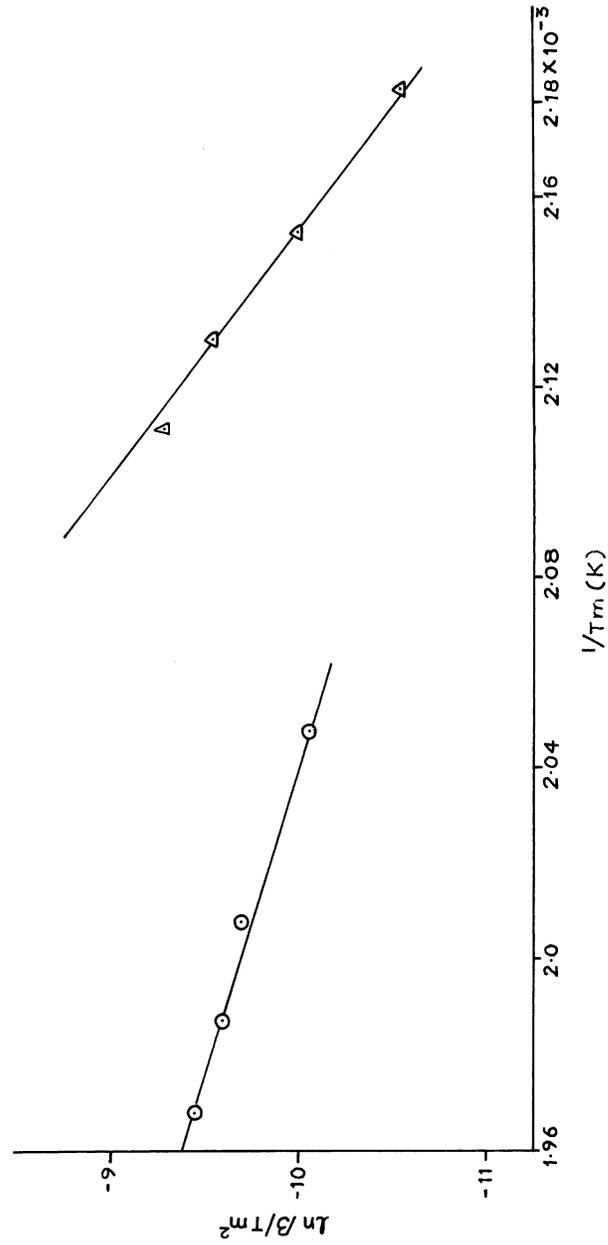


Fig. 3. Variation in $\log \beta/T_m^2$ with reciprocal of absolute temperature ($1/T$) for NiHN (○) and CoHN (△) (Kissinger relationship).

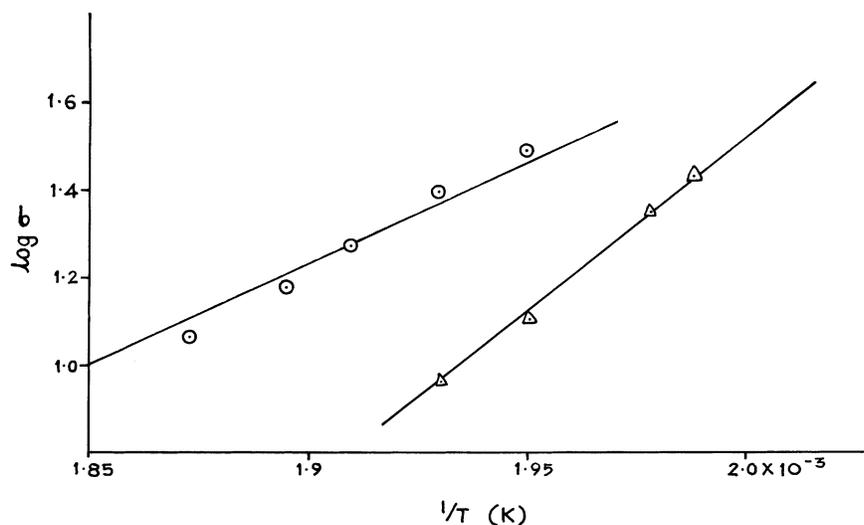


Fig. 4. Variation in $\log \sigma$ with reciprocal of absolute temperature ($1/T$) for NiHN (○) and CoHN (△) (Arrhenius relationship).

at 140 °C (Fig. 8). These studies reconfirm the higher thermal stability of NiHN and suggest preferential cleavage of M–N bond followed by that of N–N bond in both the cases. The rupture of the M–N linkage during first step of degradation may be correlated to the weak nature of these bonds formed by sharing lone pair of electrons from co-ordinating groups.

3.2. Sensitivity studies

In an impact sensitivity test, NiHN gave $h_{50\%}$ of 84 cm and in friction sensitivity test, it was found insensitive up to 10 N. On the other hand, CoHN exhibits higher impact sensitivity with $h_{50\%}$ of 59 cm but it was found to be less friction sensitive (insensitive up to 60 N).

The friction insensitive character of CoHN in comparison to NiHN may be co-related with their activation energies and auto ignition temperatures. However, the opposite trend is obtained for impact sensitivity. Similar observations have been made for some of the initiatory materials [17]. It is difficult to pin point the mechanism as the initiation of explosives by impact and friction stimuli is a complex phenomenon, which does not depend only on the molecular structure but also on several physical factors such as crystal hardness, shape and size as well as thermal conductivity [18].

3.3. Application

The results obtained during the present studies and those by other researchers [8,9] establish the potential of NiHN as an initiator. It is much safer than lead azide with respect to mechanical stimuli and offers a high velocity of detonation (VOD, 7000 m/s) in comparison

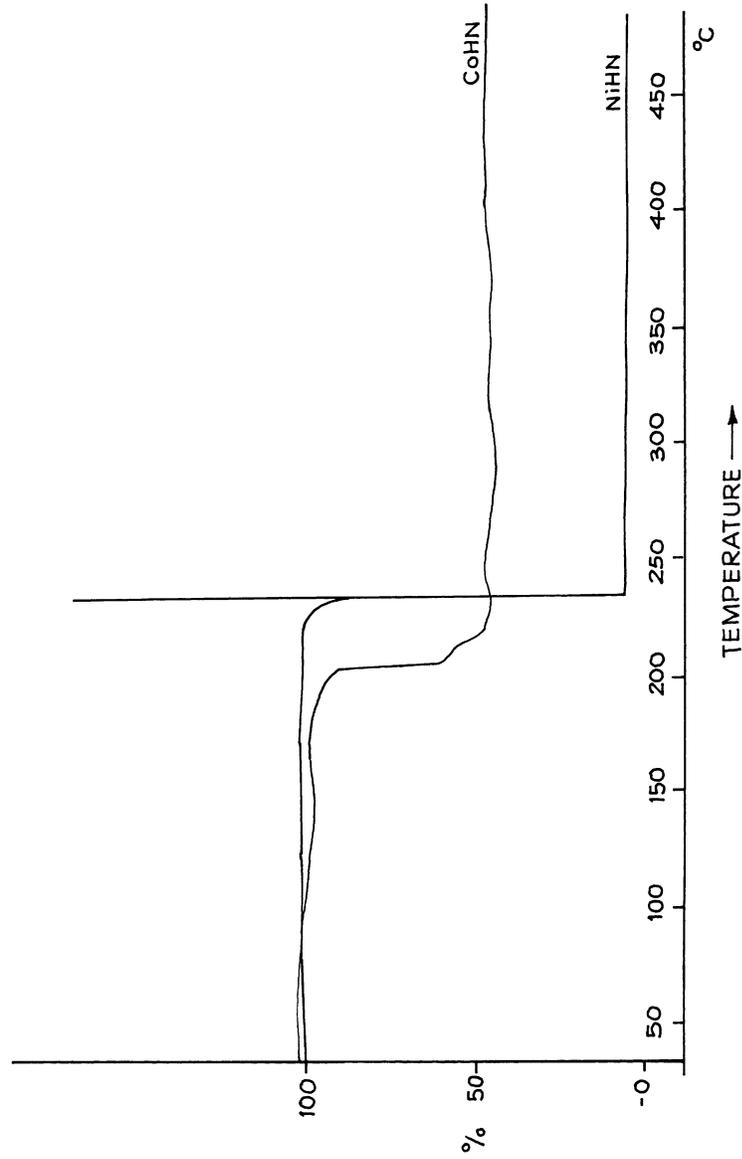


Fig. 5. Thermogravimetric profile for the decomposition of NiHN and CoHN.

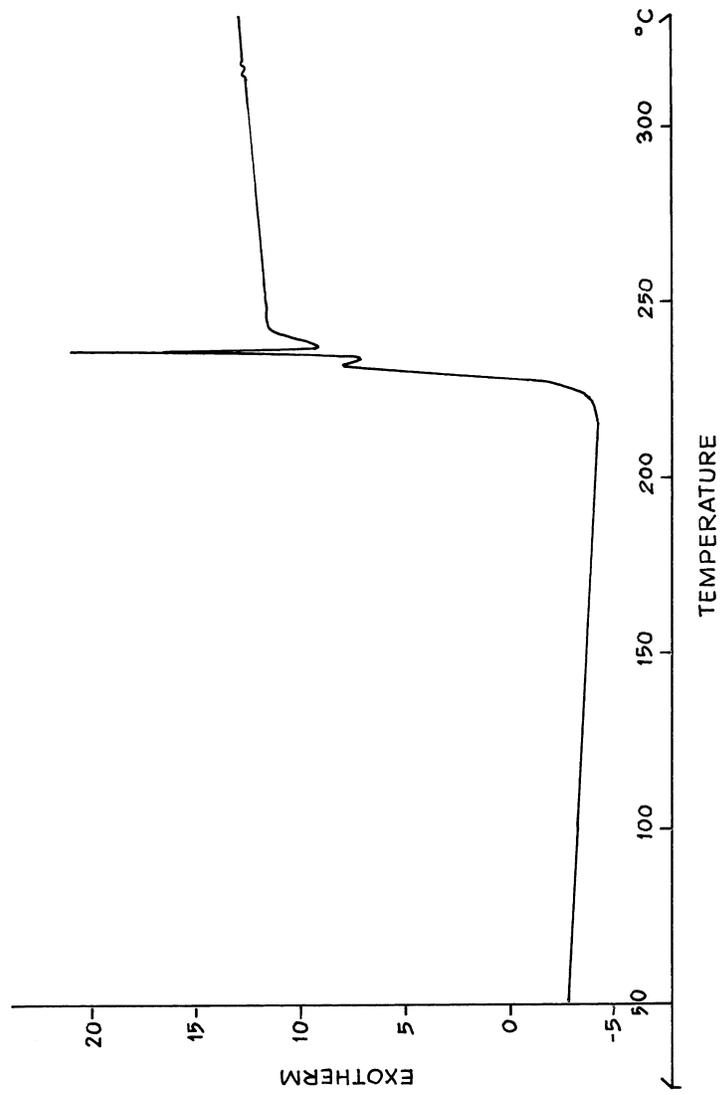


Fig. 6. Differential scanning calorimetric profile of NiHN (sample exploded).

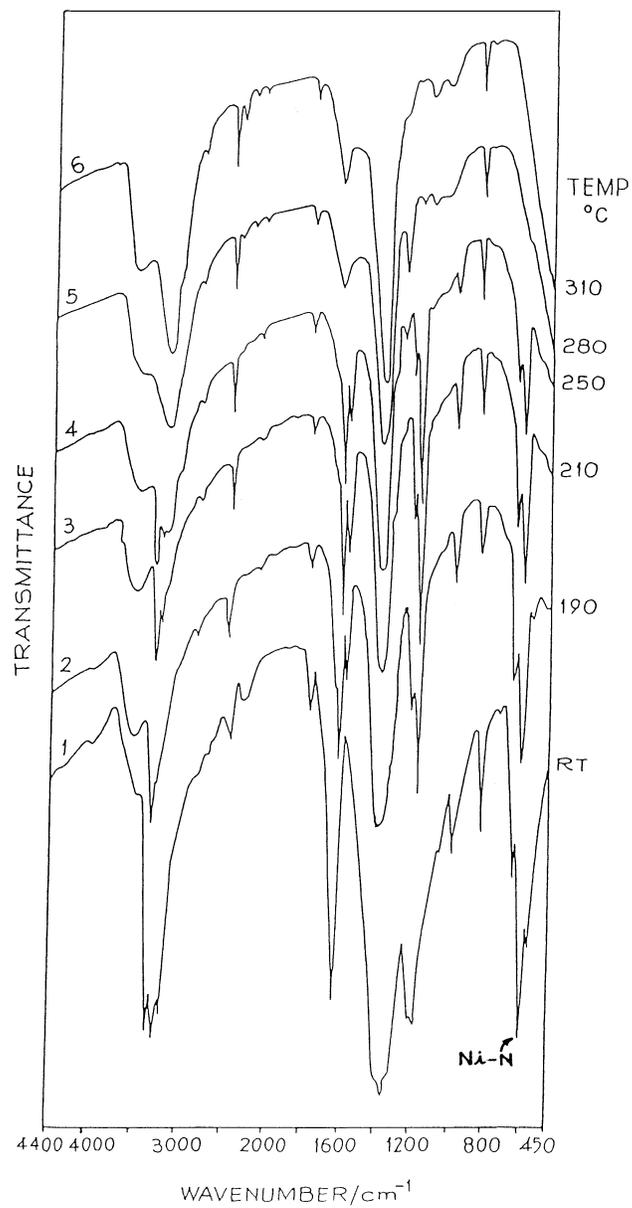


Fig. 7. Temperature dependency of FT-IR profile of NiHN.

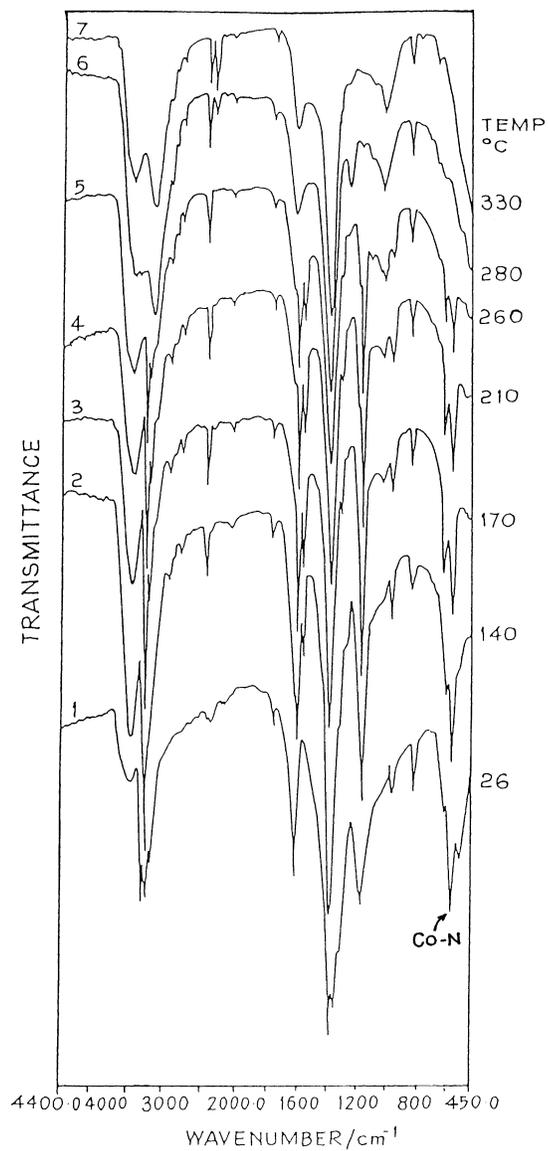


Fig. 8. Temperature dependency of FT-IR profile of CoHN.

Table 2
Effect of oxidizer/fuel on sensitivity of NiHN

Sample (ratio)	Impact sensitivity $h_{50\%}$ (cm)	Friction sensitivity (N)	Peak temperature T_m ($^{\circ}$ C)
NiHN:KClO ₃			
10:0	84	10	218
9:1	80	10	225
7:3	80	5	223
CoHN:KClO ₃			
10:0	59	60	188
9:1	60	40	185
7:3	59	16	185
NiHN: LFCN			
9:1	53	16	225
7:3	51	64	230
CoHN:LFCN			
9:1	59	40	185
7:3	58	64	185

to lead azide [8] (4360 m/s). The lower ignition temperature is advantageous from the point of view of ignitability by thermal stimuli.

Although the NiHN and CoHN are almost oxygen balanced, a study was undertaken on the mixtures of NiHN and CoHN with potassium chlorate and lead ferrocyanide (LFCN) in the ratio of 90:10 and 70:30 for possible optimization. Incorporation of potassium chlorate and LFCN did not have much effect on impact sensitivity except (NiHN+LFCN) combinations, which indicates increased sensitivity. However, addition of KClO₃ led to increase in friction sensitivity of both NiHN and CoHN while that of lead ferrocyanide rendered them more friction insensitive (Table 2). DTA results indicating meager changes in the T_m established the compatibility of the NiHN and CoHN with KClO₃ and LFCN.

Table 3
Effect of additives on sensitivities of NiHN

NiHN + additives	Impact sensitivity		Friction sensitivity (N)
	$h_{50\%}$ (cm)	F of I	
NiHN	96	80	10
NiHN + AgN ₃ (%)			
2.5	68	51	8
5.0	68	51	8
10.0	66	50	6
NiHN + glass (%)			
2.5	74	62	10
5.0	45	52	10
10.0	46	52	8

Table 4
Effect of CoHN on burning rates (mm/s) of AP- composite propellant

Chamber pressure (MPa)	Control	Control + Fe ₂ O ₃	Control + copper chromite (CC)	Control + <i>n</i> BF ^a	Control + CC + <i>n</i> BF	Control + CC + <i>n</i> BF + CoHN
1	8.1	10.8	10.8	12.9	13.9	13.4
2	8.5	11.7	11.5	14.0	15.1	15.6
3	10.2	14.1	14.9	15.2	16.0	16.6
4.9	12.3	17.0	17.1	17.4	17.5	22.0
6.9	15.5	20.7	20.9	20.0	22.2	27.4
8.8	16.1	22.4	22.3	22.1	23.6	33.0

^a *n*BF: *n*-butyl ferrocene.

In the next set of experiments, the effect of inclusion of silver azide and glass on sensitization of NiHN was studied. It was observed that silver azide sensitizes NHN to impact and friction stimuli, while glass reduces mainly, $h_{50\%}$ (Table 3). This result indicates that NiHN may find use in non-leaded cap compositions comprising a sensitizer, a fuel and an oxidizer.

CoHN being a highly friction insensitive compound may find application as an energetic additive in propellant/explosive compositions. During initial studies, it has been observed that incorporation of CoHN results in increase of burning rates as compared to control ammonium perchlorate (AP) composite propellants particularly in the pressure range >3 MPa (Table 4).

4. Conclusion

The preparation of the NiHN and CoHN has been accomplished at 25 and 65 °C from the respective metal nitrates and hydrazine hydrate in both amorphous and free-flowing granular forms, respectively. Thermal studies indicated that NiHN is stable at higher temperatures than CoHN. However, activation energy data establish that the decomposition of NiHN is more facile than that of CoHN. The data obtained during the work revealed that M–N bond cleavage is the primary step during decomposition. Relatively higher insensitivity to impact and friction confirm the safe nature of the complexes. The thermal and explosive characteristics of NiHN are indicative of its probable use as eco-friendly initiatory charge in detonators. Preliminary investigations bring out that NiHN can be used alone, as well as in combination with an oxidizer or fuel depending upon the specific requirements. Silver azide and glass appear to be effective as sensitizers. CoHN may find application in propellants as a ballistic modifier/additive.

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