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Evaluation of a New Primary Explosive: Nickel Hydrazine Nitrate (NHN) Complex

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Bewertung eines neuen Initialsprengstoffs: Nickelhydrazinnitrat-Komplex (NHN)
Nickelhydrazinnitrat (NHN) ist ein thermisch und hydrolytisch stabiler Feststoff, leicht herzustellen aus zugänglichen Rohmaterialien. Die Restflüssigkeiten können wiederholt verwendet werden, d.h. bei der industriellen Produktion fällt kein Abwasser an. NHN ist unempfindlich gegen Schlag, Reibung oder elektrostatische Aufladung, aber empfindlicher gegenüber Flammeneinwirkung. Es wird gezeigt, daß NHN als Ersatz für Bleiazid bei Zündladungen für kommerzielle Zünder geeignet ist.

Evaluation d'un nouvel explosif initial: complexe nitrate d'hydrazine de nickel (NHN)
Le nitrate d'hydrazine de nickel (NHN) est une solide thermiquement et hydrolytiquement stable, facile à synthétiser à partir de matériaux bruts accessibles. Les liquides résiduels peuvent être utilisés à plusieurs reprises, c. à. d. qu'il n'y a pas formation d'eaux résiduaires lors de la production industrielle. NHN est insensible au choc, au frottement ou au chargement électrostatique, mais plus sensible à l'effet des flammes. On montre que NHN se prête à une utilisation en remplacement de l'azoture de plomb dans les charges d'amorçage destinées aux détonateurs du commerce.

Summary

NHN is a thermally and hydrolytically stable solid, easily prepared from available raw materials. Its preparation liquor can be used repeatedly, which means no waste-water pollution in industrial manufacture. NHN is not sensitive to impact, friction, or electrostatic charge, but is more sensitive to flame. It is demonstrated that NHN is suitable as a replacement for lead azide as an intermediate charge in commercial detonators.

1. Introduction

Lead azide (LA), as a main primary explosive, has become very important in civil or military purpose. It can be easily obtained by the reaction between sodium azide and aqueous lead salt. But the manufacture of sodium azide will cause inevitable harms to person because of its toxic gases. With the development of gas generator, sodium azide has been made shortage day by day.

Although NHN has been reported in the middle of this century, it has not as yet found application. In fact, some properties of NHN are much better than that of LA, e.g. its low mechanical sensitivity, good stability and no effect to light. The preparation of NHN is also very simple in laboratory. The reaction can be represented by the equation as follows:

$$Ni(NO_3)_2{\cdot}6H_2O + 3N_2H_4H_2O \rightarrow Ni(N_2H_4)_3(NO_3)_2 + 9H_2O$$

Controlling the reaction temperature will get more uniform spherical polycrystals. The size is at least not smaller than 80 μm. Its flowability is superior to other initiators.

The reaction liquor of NHN, unlike lead azide, does not contain any useless ions. This makes it possible to use the liquor repeatedly in the preparation of continuous batches. In order to maintain a constant amount of liquor, the strong solution of hydrazine hydrate must be used, the reaction temperature, hence, needs to be controlled reasonably.

2. Preparation

2.1 For First Batch

The $Ni(NO_3)_2$ (8% W/W) solution of 50 ml was diluted to 100 ml with pure water and preheated to about 65 °C in a beaker. Under stirring, another 50 ml solution of $Ni(NO_3)_2$ (8% W/W) and 7 ml $N_2H_4{\cdot}H_2O$ (> 80%W/W) were slowly added simultaneously about 30 min to the beaker. A visible change of colour in the liquor could be observed during the reaction. The suspension was stirred for 10 min at 65 °C, then followed by cooling. The product was suction-filtered on a 2-inch Buchner funnel and washed three times with water. Finally, it was alcoholized and dried over 6 hours at 60 °C inside the oil control thermostat. The dry chunks were easily converted to powder with a rubber spatula. The yield was 11.0 g ~ 11.5 g (92% ~ 96% of theory). IR(KBr) [cm^{-1}]: 3240 (NH_2 double peak)(s), 1630 (NH_2)(s), 1300–1400(NO_3).

2.2 For Following Batches

Stoichiometric amounts of nickel nitrate hexahydrate (14.0 g) were added to one-third of above liquor. Two-thirds of the liquor were heated to 65 °C in the beaker. Following operations were same as those described in 2.1. Nearly twenty runs, using the first batch of liquor, gave similar results.

It is critical to hold an adequate amount of initial solution in the beaker and to keep its pH 6–7 within the whole reacting process. The ratio of total liquor to the dry NHN

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for every batch is about 20 (liter):1 (kg). This value will be acceptable in actual manufacturing.

3. Physical and Thermochemical Properties

3.1 Density

Measurement by the pycnometric method in 95% ethanol gives a density of 2.129 g/ml (25 °C).

3.2 Free Density

Measurements by the volumetric method give the free density of 0.85 ~ 0.95 g/ml.

3.3 Solubility

Approximate solubility data for NHN at room temperature are summarized in Table 1.

3.4 Coloring Test

It is sure, through a lot of trials, that NHN cannot color cotton cloths or textile fibres and never penetrate the body's skin.

3.5 Heat of Explosion

The heat of explosion, Q, is 1014 cal/g in 1 atm of air. The value of specific volume is 529 ml/g.

4. Stability Test Data

4.1 Hydrolytic Stability

NHN was unaffected by stirring with distilled water for one week at 60 °C.

Table 1. NHN Solubility Data

Solvent	Gram/100 ml Solvent[g]
Water	< 0.0042
Ethanol	< 0.033
Acetone	< 0.039
Methanol	< 0.009
Ether	< 0.010

4.2 Action of Sulfuric Acid

NHN gets burning with the action of 96 % sulfuric acid at room temperature. Weak solution of acid only makes its decomposition gently.

4.3 Action of Sodium Hydroxide

NHN reacts mildly with 10% sodium hydroxide. This can be used as a method of disposal.

4.4 Effect of Light or X-Ray

Unlike other primary explosives, NHN does not change its characters on prolonged exposure to sunlight, neither to the X-ray.

4.5 Action of Laser Beam

A few milligrams of NHN would be ignited with the beam of a pulsed tunable CO_2 laser (1 pulse, 12 joule/1 cm^2, focussed).

4.6 Compatibility with Materials of Construction

NHN showed negligible reactivity at room temperature for a long time of 8 years in the presence of Al, iron, stainless steel or copper.

5. Explosive Performance Test Data

5.1 Explosion Temperature Tests

Data for NHN and other common primary explosives in the Five-Second Explosion Temperature Test are given in Table 2.

The Five-Second Explosion Temperature Test is run with 20 mg of NHN. At this dosage, NHN showed extensive disruption of the containing blasting cap and splashing of the Wood's metal from the test vessel.

Table 2. Five-Second Explosion Temperature

Compound	Temperature [°C]
LA	345
LTNR	282
DDNP	172
Tetrazene	160
NHN	167

Table 3. Detonation Velocity Data

Compound	Velocity[m/s]	Density[g/ml]
LA	4630	3.0
LTNR	4900	2.6
DDNP	6600	1.5
NHN	7000	1.7

Table 4. Relationship Between Pressure and Function

Pressure[MPa]	Detonation	Deflagration
< 50	5	0
60	5	0
70	3	2
80	2	3

5.2 Detonation Velocity

The detonation velocity of NHN in comparison with other explosives is given in Table 3.

5.3 Detonation Character under Different Pressure

Under different pressure, NHN will display different performances to the normal ignition of safety fuse. Table 4 gives the testing results of every five samples.

5.4 P–ρ Curve

The P–ρ curve of NHN is showed as Figure 1. A quickly rising of ρ between 40 MPa and 60 MPa may be caused by the break of polycrystal.

P [MPa]	0	20	40	60	80
$\bar{\rho}$ [g / cm^3]	0.9108	1.5464	1.5631	1.6984	1.7133
σ	0.0194	0.0054	0.0098	0.0077	0.0056

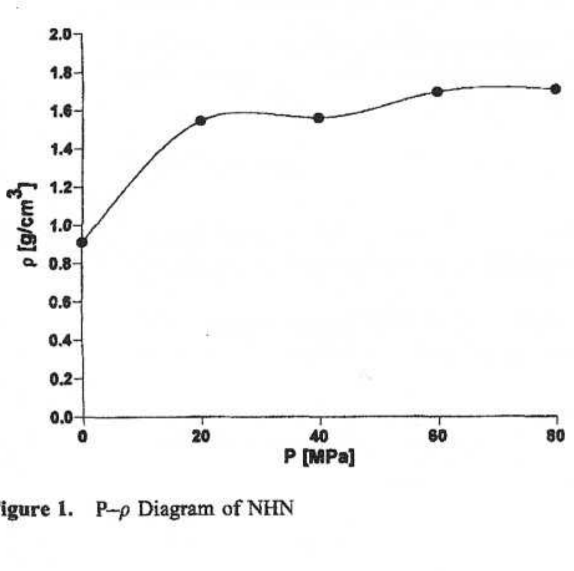

Figure 1. P–ρ Diagram of NHN

Table 5. Sensitivitiy Data of NHN

Compound	Electrostatic [joule] (a)	Friction [%] (b)	Impact [cm] (c)	
Lead azide	0.0070	—	—	—
Lead azide	0.003	100	24	10.5
LTNR (normal)$^{(d)}$	0.0009	70	36	11.5
LTNR (basic)	0.000341	—	—	—
Tetrazene	0.006	70	6.0	3.5
Diazodinitrophenol	0.012	25	40	17.5
NHN	0.02	12	26	21

(a) Minimum energy in joule.
(b) Explosion percentage of 25 samples under 588.40 kPa and 80° swinging angle.
(c) Drop-hammer test; height to give 100% fire and 100% no-fire, (400-gram hammer, 20 mg sample).
(d) LTNR: lead 2, 4, 6-trinitroresorcinate (normal or basic represents different crystal configuration).

5.5 Sensitivity to Electrostatic Charge, Friction and Impact

In the Approaching Electrostatic Test, NHN appears considerably less sensitive than other primary explosives. Its sensitivity to the mechanical actions is also very weak. The testing results are included in Table 5.

5.6 Minimum Priming Charge Test

This test was run by a same procedure as the detonator assembly. The pressures used are 30 MPa to the NHN and 15 MPa to the booster charge PETN. Then, different quantities of NHN will be chosen as the initial charge.

Such detonators must undergo the Lead-Plate Test for the examination of explosion power. The value of minimum priming charge to the PETN is 150 mg under the initiating of safety fuse and 120 mg of Nonel's tube.

6. Observation of Safety

6.1 When Anhydrous

The samples of NHN with different water ratios will be initiated directly with blasting caps. The results are given in Table 6.

6.2 NHN Suspension

The NHN suspension before suction-filtered cannot explode by the function of blasting cap and never be ignited with safety fuse.

Table 6. Explosion Performance of NHN

Water Ratio	Explosion
40%	0%
35%	20%
25%	80%

6.3 When Alcoholized

The NHN, after washed on the filter with ethanol and then sucked to dryness, could be ignited with safety fuse and deflagrated rapidly.

Even so, NHN as a kind of primary explosive, its preparation is much safer than other initiators, so does its handling. One of the critical factors is its crystal shape—polycrystal, which is similar to the diazodinitrophenol.

7. References

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