



Path to ϵ -HNIW with Reduced Impact Sensitivity

Ahmed ELBEIH*, Adela HUSAROVA and Svatopluk ZEMAN

*Institute of Energetic Materials, Faculty of Chemical Technology,
University of Pardubice,*

Studentska 95, CZ-532 10 Pardubice, Czech Republic

**E-mail: elbeih.czech@gmail.com*

Abstract: New purification method was applied to obtain epsilon HNIW (ϵ -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, ϵ -HNIW) which has low impact sensitivity. The method is based on removing the impurities from a solution of alpha HNIW (α -HNIW) by a chemical reaction to obtain pure epsilon form. For comparison, selected different published methods for recrystallization of HNIW to obtain the epsilon form were studied. All the selected methods are based on solvent-antisolvent technique. The optimum parameters, such as type of solvent and anti-solvent, volume ratio of solvent to anti-solvent, rate of addition, speed of stirring, etc., were applied to enhance the crystal size and shape of ϵ -HNIW. Checking the polymorphs of the obtained HNIW was done by Fourier transform infrared spectroscopy (FTIR). The thermal stability of the prepared samples was studied by using differential thermal analysis technique (DTA). Qualitative analysis of the crystal size and shape was done using scanning electron microscope (SEM) devise. Quantitative measurement of the crystals sizes for the studied samples was determined by Laser scattering particle size distribution analyzer. Impact sensitivity was measured by falling hammer test. The results indicate that all the applied methods of recrystallization give ϵ -HNIW. The impact sensitivity of HNIW decreases by obtaining small particles with regular shape. All the used published methods produce ϵ -HNIW with higher impact sensitivity than other nitramines. While the obtained crystals from the new method has regular smooth surface, with small particle size and its impact sensitivity is lower than RDX and HMX.

Keywords: HNIW, crystallization, thermal stability, impact sensitivity, SEM

Introduction

The sensitivity of explosives depends on properties of their crystals as well as their purity. Reduced sensitivity (RS) is desired to ensure safe load, assemble, and pack operations to meet safe handling requirements of the end user. 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20) is a high-energy material with a cage structure. Today it is considered as the most powerful explosive and displays the most promising performance data. It has four used structural isomers (α , β , γ and ϵ -form of crystal), the crystal of ϵ -form is thermodynamically and mechanically most stable due to its high symmetric configuration of molecules in the structure [1, 2]. ϵ -HNIW has high TMD ($>2 \text{ g cm}^{-3}$), positive heat of formation ($\sim 419 \text{ kJ mol}^{-1}$) and high performance [3, 4]. It is often obtained in the form of polycrystalline particles with sharp edges and microscopically visible defects while it is possible to control the particle size of HNIW by optimizing the crystallization process [5]. Many publications reported that ϵ -HNIW has high sensitivity to impact more than RDX and HMX [6, 7]. While Ou Yuxiang et al. [8] described pure ϵ -HNIW with impact sensitivity of 13.2 J and for the rest of pure polymorphs; α -HNIW of 10.1 J, β -HNIW of 11.9 J and γ -HNIW of 12.2 J. All these values are disregarded in literature yet.

Many publications were reported about the crystallization of HNIW to obtain ϵ -form with high purity, high yield, regular particle shape, and small particle size [9-12]. At the Institute of Energetic Materials (IEM), we have a new method (unpublished) to obtain HNIW with low sensitivity and good physical properties.

In this work, we studied the different published methods used for obtaining ϵ -HNIW with high quality and compared the results with our product obtained from the new method.

Crystallization of HNIW

HNIW was obtained in the α -form from the pilot plant of Explosia Company, Pardubice, Czech Republic. Different kinds of solvents (ethyl acetate, methyl ethyl ketone, acetone) and antisolvents (n-heptane, toluene, xylene, chloroform) were used for the crystallization process. The best result obtained from our study, regarding to the impact sensitivity and the crystal shape, was by using ethyl acetate as a solvent and n-heptane as antisolvent. Although n-heptane didn't give the highest yield of HNIW. Three published techniques were used to obtain ϵ -HNIW and compared with the product of our new method.

a) Crystallization by adding the anti-solvent to HNIW solution [9]

10 g of α -HNIW was dissolved in 30 ml ethyl acetate, and 10 ml solution of 5% K_2CO_3 was added during continuous stirring. Separation of the layers was done where the water layer washed twice with 10 ml ethyl acetate and separated each time. The ethyl acetate solution (50 ml) was placed in rotary evaporator to evaporate around 20 ml of eutectic mixture (ethyl acetate/water) then the rest of the solution (30 ml) was placed on 3 neck bottle under stirring by mechanical stirrer and 150 ml of n-heptane was added to the solution drop by drop during 4 hours, the stirring rate was 400 rpm. The sample obtained from this method has the symbol HNIW-1.

b) Crystallization by inverse precipitation technique [11]

10 g of α -HNIW was dissolved in 40 ml ethyl acetate, 2 g of silica gel was added to the solution and stirred for 30 min. The solution was filtrated and placed on rotary evaporator for evaporating the eutectic mixture (ethyl acetate/water) until the solution reached 20 ml. The solution was added drop by drop from dropping funnel to 100 ml of n-heptane with stirring. It takes around 2 hours under stirring rate 400 rpm. The sample obtained from this method has the symbol HNIW-2.

c) Crystallization by the assistant of ultrasound [12]

The same procedure as the inverse precipitation technique was applied, with the removing of the mechanical stirrer and placing the flask containing n-heptane on ultrasound device. The addition process takes around 20 min. After filtration, the sample was placed under vacuum for one day at 45 °C to get rid of any residual solvent present inside the crystal after the recrystallization process. The sample obtained from this method has the symbol HNIW-3.

d) HNIW from a new method

Our new method is based on removing the impurities and the water content from solution of HNIW by adding admixture in the solution. This admixture is able to make a non-bonding interaction with the molecules of this nitramine and react with the impurities in the solution. Then HNIW crystals were obtained by normal crystallization process. The details of the method are still unpublished. The obtained sample has the symbol HNIW-4.

Spectral studies

Nicolet protege 460 FTIR spectrometer was used to record the IR spectra of the samples using transmittance technique in KBr matrix. FTIR spectra for

α -HNIW shows absorption at $3600\text{--}3700\text{ cm}^{-1}$; also it has different absorptions at $3000\text{--}3100\text{ cm}^{-1}$, $1550\text{--}1650$ and $1200\text{--}1350\text{ cm}^{-1}$ compared with ϵ -HNIW as shown in Figure 1. The IR absorption stretching of CL-20 at $3000\text{--}3100\text{ cm}^{-1}$ is due to six cage (C–H) and around both 1600 and 1300 cm^{-1} are attributable to asymmetric and symmetric stretching of NO_2 groups [13]. FTIR spectra for all the prepared samples showed the same characteristic peaks as that for standard ϵ -HNIW.

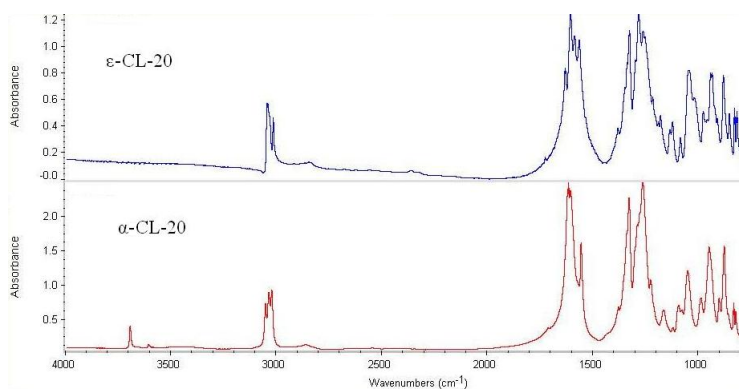


Figure 1. IR spectra of HNIW samples.

Thermal studies

A DTA 550 Ex apparatus was used for thermal analysis of the samples [14]. The measurements were carried out at atmospheric pressure, with the tested sample in a direct contact with the air. The tested sample (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminum oxide. A linear heating rate of 5 °C min^{-1} was used. The results are reported in Table 1. Figure 2 shows the exothermic peaks of the thermal decomposition of the samples. α -HNIW showed a maximum peak at 222 °C while the other samples showed maximum peaks at temperatures higher than α -HNIW. The exothermic peaks temperature of all the prepared samples is close to each other with nearly the same shape. This proves that the method of crystallization hasn't significant effect on the thermal stability. Figure 3 shows the endothermic peaks of changing the polymorph of HNIW. The α -HNIW didn't show any endothermic peak while the other samples have endothermic peaks in the range between $167\text{--}172\text{ °C}$ maximum peaks temperatures.

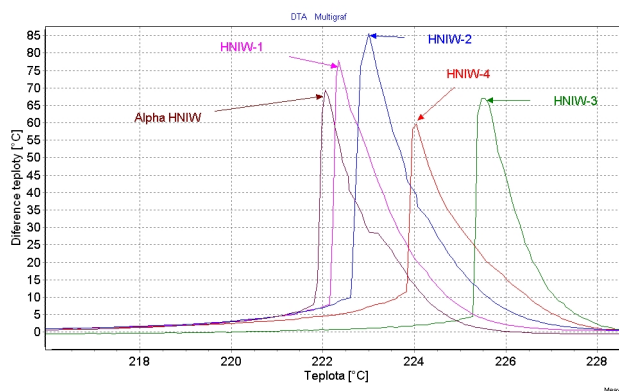


Figure 2. Exothermic peaks of samples measured by DTA.

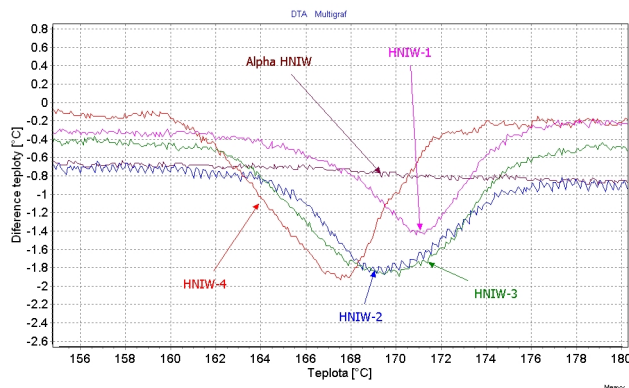


Figure 3. Endothermic peaks of samples measured by DTA.

Analysis of particle size distribution

The obtained samples were measured using particle size distribution analyzer Partica LA-950. The particle size of CL-20 was determined on the principle based on laser light scattering. It uses Mie Scattering Theory (laser diffraction) to measure particle size over the range of 0.01-3000 μm . Figure 4 shows the particle size distribution of all the prepared samples. The particles size of HNIW-1 is in the range of 27-76 μm , with mean size of 50 μm . HNIW-2 has particles size in the range of 13-54 μm with mean size of 28 μm . The crystals of HNIW-3 obtained by the sonication process are smaller in size with 13 μm mean size of the particles and falls in a narrow range of 7-22 μm . While the particles size of

the HNIW-4 obtained by the new method is in the range of 2-16 μm and has mean size of 8 μm with few quantity on the nano-scale. This study reveals that HNIW particles obtained from both the sonication process and the new method have a narrow range of particle size. In the case of normal re-precipitation and the inverse precipitation, the particles fall in wider range.

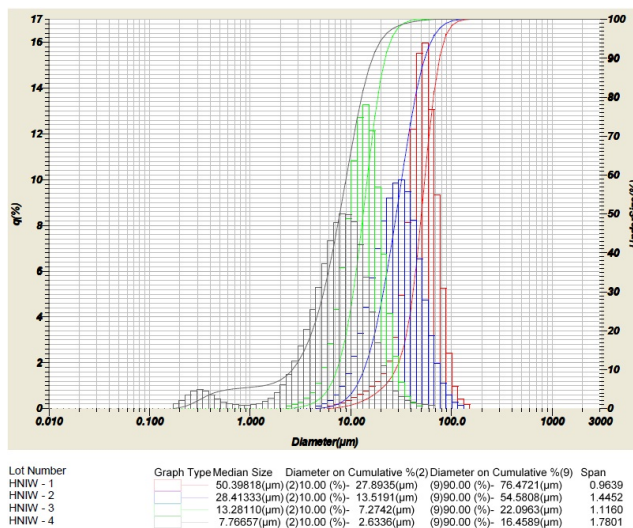


Figure 4. The particles size distribution of the samples.

Scanning electron microscope (SEM) studies

The crystal morphology has been studied by scanning electron microscope (SEM) JEOL JSM-5500LV. SEM photographs of the alpha-HNIW at Figure 5 showed random crystals have different shapes and sizes, full of cracks and porosities with high degree of agglomeration. After the recrystallization, the sample HNIW-1 showed also random crystals with a high degree of agglomeration. It has irregular shape of crystals with different particles size as well as full of cracks but much lower porosity than α -HNIW (Figure 6). HNIW-2 has also irregular crystal shape and different particle size with cracks but slightly lower crystal size than HNIW-1 (Figure 7). HNIW-3 precipitated in the presence of ultrasound showed regular crystal shapes and small size. Further, the particles are in a good distribution but still there are cracks at the surface of the crystals (Figure 8). HNIW-4 has regular uniform shape of crystals; it has very small particle size without sharp edges (Figure 9). Also it is clear that HNIW-4

has a good smooth crystal surface which is the main advantage compared with crystals of HNIW-3.

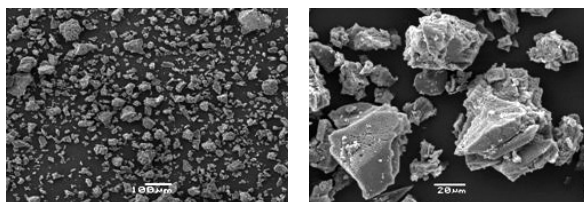


Figure 5. SEM photos of α -HNIW.

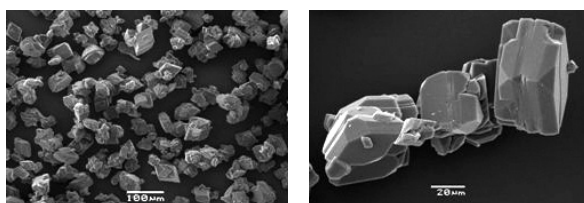


Figure 6. SEM photos of HNIW-1.

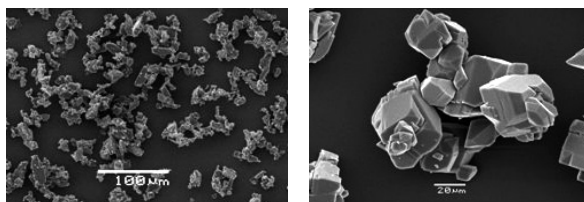


Figure 7. SEM photos of HNIW-2.

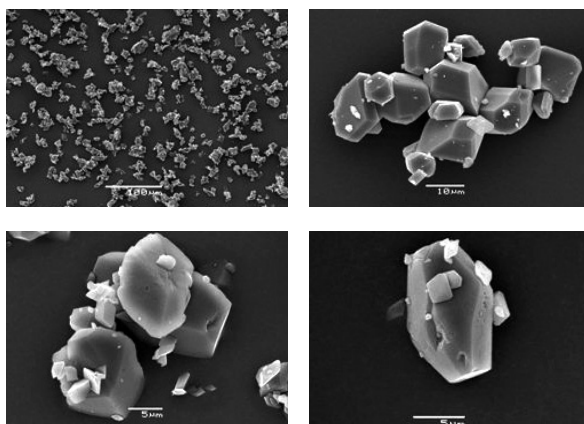


Figure 8. SEM photos of HNIW-3.

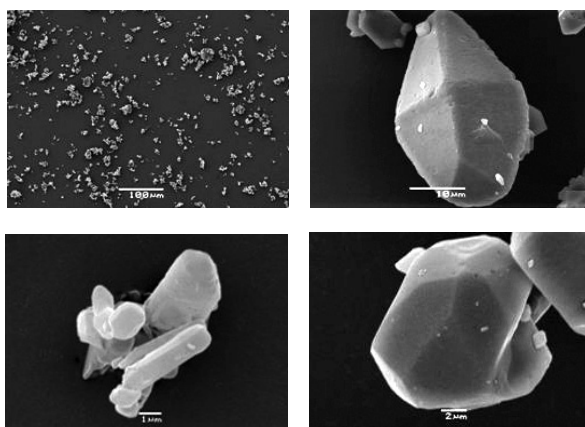


Figure 9. SEM photos of HNIW-4.

Impact sensitivity measurements

The standard impact tester (Julius Peter [15]) was used with exchangeable anvil, the amount of tested substance being 40 mm³, 2 and 5 kg weight drop hammers were used. The probit analysis [16] was used to determine the probability levels of the initiation. The obtained sensitivity was expressed as the drop energy (E_d) versus percentage of initiation. Only the 50% probability of initiation is used in this article and is reported in Table 1.

Table 1. Measured data of the prepared samples

| Sample | DTA exothermic peak (°C) | Mean particle size (μm) | Impact energy (J) |
|--------|--------------------------|-------------------------|-------------------|
| HNIW-1 | 222.4 | 51.7 | 1.86 |
| HNIW-2 | 223 | 31.8 | 2.34 |
| HNIW-3 | 225.4 | 14.2 | 4.12 |
| HNIW-4 | 224 | 9.1 | 10.83 |

The samples obtained by the normal recrystallization and the reverse methods show high sensitivity to impact, while the sample obtained by the sonication process gives better impact sensitivity 4.1 J. This might be due to partial elimination of the crystal defects, enhancing the particle shape as well as decreasing its size. Another reason might be due to the removing of any residual solvent inside the crystal. HNIW-4 obtained by the new method showed lower impact sensitivity (10.8 J) than all the other samples. This fact mostly

due to the enhancement of the physical characteristics of the crystals (regular smooth particles without cracks and having a small size) as well as the highly purified technique used in this method based on removing the impurities by chemical reactions.

Conclusion

It was concluded that HNIW sample obtained by the new method is ϵ -HNIW. It has small particle size with smooth surface and regular shape without cracks. The impact sensitivity of the sample is lower than RDX and HMX (our measurements are 5.6 and 6.4 J, respectively). The published methods of obtaining pure epsilon HNIW based on the solvent-antisolvent technique aren't suitable for obtaining low sensitive HNIW. The new method used based on removing the impurities and the water content by chemical reactions showed better influence on the impact sensitivity of HNIW.

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References

- [1] Russel T.P., Miller P.J., Piermarini G.J., Black S., High Pressure Phase Transition in Hexanitrohexaazaisowurtzitane, *J. Phys. Chem.*, **1992**, 96(13), 5509-5512.
- [2] Foltz M.F., Coon C.L., Garcia F., Nichols A.L., III, The Thermal Stability of the Polymorphs of Hexanitrohexaazaisowurtzitane, Part II, *Propellants, Explos., Pyrotech.*, **1994**, 19, 133-144.
- [3] Latypov N.V., Wellmar U., Goede P., Bellamy A.J., Synthesis and Scale-Up of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane from 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20), *J. Org. Process Res. Dev.*, **2000**, 4(3), 156-158.
- [4] Samudre S.S., Nair U.R., Gore G.M., Sinha R.K., Studies on an Improved Plastic Bonded Explosive (PBX) for Shaped Charges, *Propellants, Explos., Pyrotech.*, **2009**, 34(2), 145-150.
- [5] Nair U.R., Sivabalan R., Gore G.M. et al., Hexanitrohexaazaisowurtzitane (CL-20) and CL-20-Based Formulations, *Combust., Explos. Shock Waves*, **2005**, 41(2), 121-132.
- [6] Ostmark H., Bergman H., Sjoberg P., Sensitivity and Spectroscopic Properties of the β and ϵ -Polymorphs of HNIW, *Proc. Energ. Mater. Technology*, Phoenix, **1995**,

- 75-81.
- [7] Sider A., Sikder N., Gandhe B., Agrawal J., Singh H., Hexanitro-hexaazaisowurtzitane or CL-20 in India: Synthesis and Characterisation, *Defence Science Journal*, **2002**, 52(2), 135-146.
- [8] Yuxiang O., Cai W., Zelin P., Boren C., Sensitivity of Hexanitrohexaazaisowurtzitane, *Chin. J. Energet. Materials (HenNeng CaiLiao)*, **1999**, 7, 100.
- [9] Thome V., Kempa P.B., Herrman M., Solvent Effects on the Morphology of CL-20 Crystals, *Proc. 32nd Int. Ann. Conf. ICT*, Karlsruhe, **2001**, 157/1-157/7.
- [10] Johnston E.H., Eugene R.W., Use of Chlorine-Free Non-Solvents in Solvent Crystallization of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12,-hexaazatetracyclo [5.5.0.05,903,11]-dodecane (CL-20) Explosive, *US Patent 5874574 A*, **1999**.
- [11] Hamilton R., Crystallization of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12, hexaazatetracyclo [5.5.0.05,903,11]-dodecane, *US Patent 0130503 A1*, **2003**.
- [12] Sivabalan R., Gore G.M., Nair U.R., Saikia A., Venugopalan S., Gandhe B.R., Study on Ultrasound Assisted Precipitation of CL-20 and Its Effect on Morphology and Sensitivity, *J. Hazard. Mater.*, **2007**, A139, 199-203.
- [13] Li J., Brill T., Kinetics of Solid Polymorphic Phase Transitions of CL-20, *Propellants, Explo., Pyrotech.*, **2007**, 32(4), 326-330.
- [14] Krupka M., Devices and Equipments for Testing of Energetic Materials, *Proc. 4th Int. Seminar "New Trends in Research of Energetic Materials"*, Univ. Pardubice, **2001**, 222.
- [15] Sućeska M., *Test methods for Explosives*, Springer, Heideleberg, **1995**.
- [16] Šelešovský J., Pachman J., Probit Analysis – a Promising Tool for Evaluation of Explosive's Sensitivity, *Cent. Eur. J. Energ. Mater.*, **2010**, 7(3), 269-278.