

A study of the detonation parameters of bulk density nitroguanidine and aluminium powder mixtures

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Introduction

Nitroguanidine (NQ) was first prepared by Jouseline in 1877 and its properties investigated and described by Vielle in 1901. During the First World War, the mixture of nitroguanidine and nitrocellulose was used as a flashless propellant. However, it was difficult to maintain the stability of such a composition because nitroguanidine was reacting with nitrocellulose. The company Dynamit AG overcame that problem in 1937 by developing "Gudol Pulver" composition. At that time, it was used as a high explosive mixed with ammonium nitrate(V) to fill mortar ammunition. After the Second World War, nitroguanidine was used to produce triple-base propellants.

Nitroguanidine can be also used for solid rocket propellants, particularly propellants designed for the so called rocket engines, in which the steady and stable combustion takes place. Nowadays, the studies on developing the installation for the production of bulk density, spherical and cubical nitroguanidine are conducted in the USA. The aim of these works is to use nitroguanidine as a component of low sensitive explosive mixtures characterised by high detonation parameters.

Nitroguanidine can be potentially used in thermobaric explosive mixtures containing aluminium powder as one of their components. That is why the purpose of these investigations was to determine the effect of the aluminium powder additives on selected detonation parameters of nitroguanidine.

Experimental part

Formation and re-crystallisation of nitroguanidine

Nitroguanidine was obtained by dehydration in concentrated sulphuric acid (VI) at $35 \div 40^\circ\text{C}$ according to the method presented in the paper [1]. While nitroguanidine is synthesised and re-crystallised in water, it forms crystals in the shape of long needles characterised by low bulk density. This has a negative impact on the functional properties of nitroguanidine. Hence nitroguanidine was re-crystallised with various solvents. Four types of nitroguanidine crystal orientations from the available α and β crystalline forms are reported in the literature [2]. They are:

- LBDNQ (Low Bulk Density Nitroguanidine)
- CNQ (Cubical Nitroguanidine)
- LBDNQ (Low Bulk Density Nitroguanidine)
- SNQ (Spherical Nitroguanidine).

Such configurations can be obtained with various solvents and diverse parameters of the re-crystallisation process [3]. Dimethyl sulphoxide, N,N-dimethylformamide and 1-methyl-2-pyrrolidone were the solvents used in the experiments. In two cases, the nucleation of the crystallisation process was performed.

NQ crystallisation from DMSO

The mixture of nitroguanidine and dimethyl sulphoxide in a mass ratio of 1:2 was heated up to 90°C and simultaneously intensively stirred (approximately 1000 r/min). When the temperature reached 90°C , the mixture was cooled to the ambient temperature at a rate of ca. $5^\circ\text{C}/\text{min}$. The process of stirring and cooling was conducted for 1.5 h. After that time, the mixture was put into the refrigerator

($\sim 5^\circ\text{C}$) and left for 24 hours. Precipitated crystals were filtrated, washed with acetone and left until being dried. Shapes of polycrystals are presented in Figure 1a.

NQ crystallisation from N, N-dimethylformamide

Test 1

The mixture of nitroguanidine and DMF in a mass ratio of 1:4 was heated up to 85°C and simultaneously intensively stirred (approximately 1000 r/min). When the above temperature was reached, the mixture was cooled at a rate of ca. $20^\circ\text{C}/\text{min}$ reaching the temperature of ca. 5°C . Stirring at the temperature of 5°C was kept for 2 hours. After that time, precipitated crystals were filtrated, washed with acetone and left until being dried. The formed crystals are presented in Figure 1b.

Test 2

The course of the crystallisation process with DMF characterised by the prolonged precipitation time of crystals is described below. The mixture with the same ratio of components as in Test 1 was heated up to 85°C and stirred at the same rate as previously. When the temperature reached 85°C , the mixture was cooled at the modified rate of $5^\circ\text{C}/\text{min}$.

After initiating the cooling process, the spherical nuclei of NQ crystals obtained from NMP were thrown into the agitated vessel. The mixture was cooled to ca. 20°C and left in the refrigerator (ca. 5°C) for 24 hours.

After that time, precipitated crystals were filtrated, washed with acetone and left until being dried (Fig. 1c).

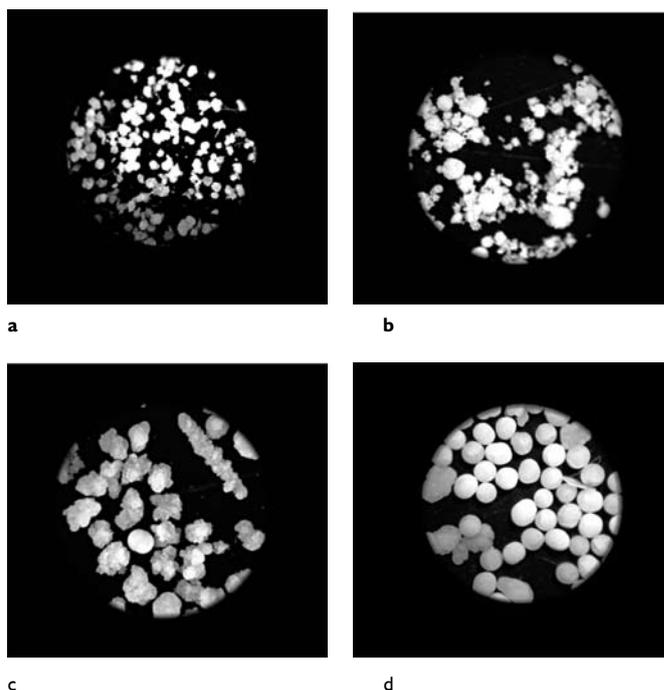


Fig. 1. Nitroguanidine grains after re-crystallisation: a – DMSO, b – DMF, c – DMF with crystal nuclei, d – NMP with crystal nuclei

Crystallisation from 1-methylo-2-pyrrolidone

Nitroguanidine and 1-methylo-2-pyrrolidone in a mass ratio of 1:3.5 were heated up to 85°C and simultaneously intensively stirred (approximately 1000 r/min). When the temperature reached 85°C, acetone was poured into the mixture. After adding the whole volume of acetone, the mixture was stirred for another 5 min. The mass ratio of nitroguanidine to acetone was 1:17. After initiating the cooling process, the spherical nuclei of NQ crystals were thrown into the agitated vessel. Precipitated crystals were filtrated, washed with acetone and left until being dried (Fig. 1d).

Then, the bulk density and tapped bulk density of obtained nitroguanidine grains and, for comparative purposes, nitroguanidine crystallised from water were measured. Table 1 presents the results of those tests.

Table 1

The density of received nitroguanidine grains

| Solvent | Bulk density g/cm ³ | Tapped bulk density, g/cm ³ |
|-----------------|-----------------------------------|---|
| Water | 0.40 | 0.48 |
| DMSO | 0.41 | 0.52 |
| DMF | 0.54 | 0.62 |
| DMF with nuclei | 0.59 | 0.67 |
| NMP with nuclei | 0.94 | 0.96 |

Preparation of samples of nitroguanidine and aluminium powder mixtures

Aluminium powder used in the research was manufactured by the company Benda-Lutz Skawina Spółka z o.o. and labelled with the serial number 7313. The parameters of aluminium powder specified by its producer are shown in Table 2.

Table 2

Aluminium powder parameters provided by the manufacturer

| Parameter | Value |
|--|--------|
| Purity of aluminium used for the production of aluminium powder, % | Min 97 |
| Bulk density, kg/dm ³ | 0.2 |
| Average size of particles, μm | 65 |
| Water coverage, cm ² /g | 5000 |
| Content of pure aluminium in powder, % | 93 |
| Quantity of powder residue on the sieve 125 μm mesh, % | Max. 1 |

During the experiments, three sets of compositions containing aluminium powder in quantities of 5%, 10%, and 15% and spherical nitroguanidine crystallised from DMF (Fig. 1c – SNQ) were tested. The measurements of detonation velocity were also conducted for the mixtures containing needle-shaped nitroguanidine of type LBDNQ crystallised from water and the constant quantity of aluminium powder. The samples were prepared by mixing the components until the homogeneity of the obtained composition could be visually observed. Compositions and densities of obtained mixtures are presented in Table 3.

Table 3

Compositions and bulk densities of NG-AI mixtures

| Mixture No. | Bulk density, g/cm ³ | Nitroguanidine content, % _{,type} | Aluminium powder content, % |
|-------------|------------------------------------|--|-----------------------------------|
| 1 | 0.69 | 95 _{,LBDNQ} | 5 |
| 2 | 0.67 | 90 _{,LBDNQ} | 10 |
| 3 | 0.66 | 85 _{,LBDNQ} | 15 |
| 4 | 0.83 | 95 _{,SNQ} | 5 |
| 5 | 0.82 | 90 _{,SNQ} | 10 |
| 6 | 0.79 | 85 _{,SNQ} | 15 |

Measurements of detonation parameters

The detonation velocity was measured by the ionisation probes technique. In the ionisation probes, the mechanical action of the pressure from the detonation wave closes or breaks the electrical circuit. Those experiments were carried out in PVC tubes having the following dimensions: length 120 mm, internal diameter 34 mm, wall thickness 1 mm. The measurement references had a length of 30 mm, and the impetus reference – 50 mm. Within that distance, the detonation wave parameters should become stabilised because a booster made of phlegmatized hexogen (10% of ceresin) of 10 g mass was used to initiate the explosive. The experimental results are illustrated in Figure 2.

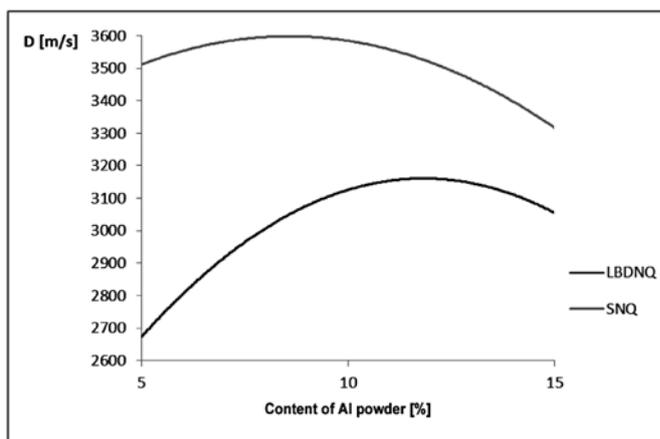


Fig. 2. Dependence of detonation velocity on the aluminium powder content in mixture with nitroguanidine

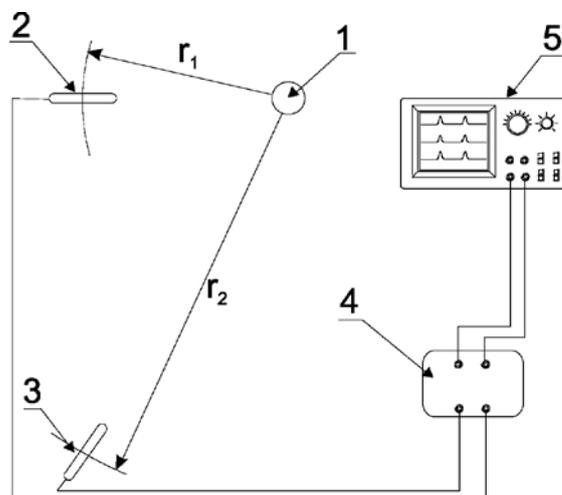


Fig. 3. Measurement diagram of blast wave parameters: 1 – explosive charge; 2, 3 – pressure sensors; 4 – signal conditioner; 5 – digital oscilloscope; r_x – the distance between explosive charge and pressure sensors

Considerably higher values of the detonation velocities were obtained for NQ-Al mixtures containing nitroguanidine grains of isometric shapes. Such values are connected with higher density of NQ-Al mixtures in comparison to mixtures containing nitroguanidine grains of type LBDNQ. The obtained relations $D=f(\text{Al})$ had a qualitative nature similar to analogous relations determined for the mixtures of ammonium nitrate(V) and guanidine nitrate(V) [4].

The overpressure of the blast wave was determined in the measurement system illustrated in Figure 3. The explosive charge was suspended in the air at a height of sensors, at a distance of 1 m from the first sensor and 1.5 m from the second one. High quartz pressure sensors of type I37A were applied in the experiment.

The pressure measurements were conducted with charges of 72 g mass placed in PVC tubes with an internal diameter of 34 mm. The measurement was registered by the voltage signal of one of the sensors, which was initiated when the blast wave reached the working surface of the sensor. Further, the signal was transmitted through RS interface to the oscilloscope plugged into the PC, where the results were saved in the form of text files. The mathematical processing in Excel spreadsheet was performed on produced results in order to get a set of measurement data for the function $\Delta p = f(t)$. The experiments were conducted for the mixtures of aluminium powder and guanidine of types SNQ and LBDNQ. Figure 4 illustrates a typical oscillogram of the overpressure changes, and the measurement results along with calculated pulses for the positive phase of overpressure are shown in Table 4.

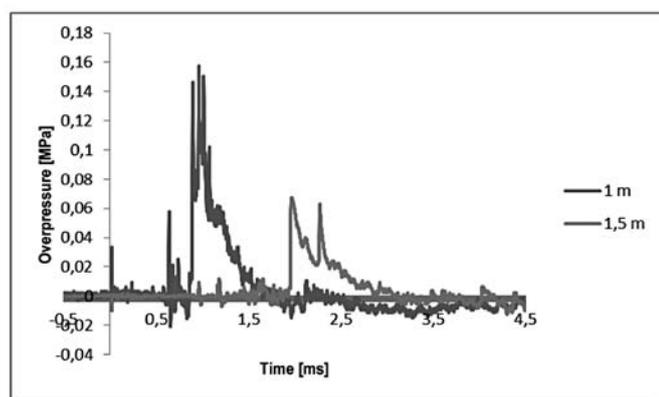


Fig. 4. Overpressure dependence of the time for SNQ/Al 85/15 sample

Table 4

The results of measurements and calculations of the intensity of blast wave generated by the detonation of mixtures of aluminium powder and nitroguanidine

| Composition, % NG/Al | Bulk density, g/cm ³ | Overpressure, kPa | | Pulse, Pa s | |
|-------------------------|------------------------------------|-------------------|-----|-------------|-----|
| | | Distance, m | | | |
| | | 1.0 | 1.5 | 1.0 | 1.5 |
| SNQ 90/10 | 0.82 | 122 | 66 | 22 | 17 |
| SNQ 85/15 | 0.83 | 143 | 93 | 31 | 18 |
| LBDNQ 95/5 | 0.69 | 105 | 52 | 24 | 18 |
| LBDNQ 85/15 | 0.66 | 120 | 62 | 29 | 22 |

The measurement data presented in Table 4 indicate that mixtures containing nitroguanidine of type SNQ and higher content of aluminium powder provide higher values of measured overpressure and calculated pulse.

Summary

Since R. Escalas and G. Roth developed explosive mixtures with aluminium powder, many papers considering the process of their detonation have been published, e.g. [4 ÷ 13].

Regarding aluminium powder, those papers indicate that it is added to explosives for two principal purposes. The first purpose is to increase the heat of explosion, and the second one is to make a particular composition more sensitive in some cases. The second purpose refers to the mixtures of aluminium powder and substances characterised by low explosive properties, such as ammonium nitrate (V) or guanidine nitrate (V). They belong to the group known as non-ideal explosives. By adding aluminium powder to ammonium nitrate (V) or guanidine nitrate (V), the dependence of the detonation velocity on the content of a metallic component reaches the maximum whose position depends on, among others, the degree of crystallinity of the explosive mixture components. By contrast, the detonation velocity decreases with the increase of aluminium powder content in case of aluminising mixtures containing high energy individual explosives (e.g. hexogen, TNT). The above also refers to emulsion explosives [14].

Nitroguanidine belongs to the group of individual explosives. That is why an attempt of obtaining the maximum from relation $D=f(\%Al)$ is untypical for this material and indicates that, under experimental conditions, nitroguanidine behaves like the non-ideal explosive. The achieved maximum can be connected with nitroguanidine low detonation ability – high critical diameter. The maximum has been obtained for the bulk density mixtures. That is the reason for conducting further series of tests for charges with higher densities.

Literature

- Cetner W.P., *Preparatyka materiałów wybuchowych i produktów pośrednich*, Wyd. WAT, Warszawa 1986.
- Sumrall S.T., Rector C.M., Graham W.H. *Improvements in the processing and performance of various crystalline forms of nitroguanidine*. <http://doc-00-94-docviewer.googleusercontent.com/viewer/securedownload>, accessed date
- Powala D., Orzechowski A., Maranda A., *Małowrażliwe materiały wybuchowe. Nitroguanidyna*. *Przemysł Chemiczny* 2005, **84**, 8.
- Maranda A., *Research on the process of detonation of explosive mixtures of the oxidizer fuel type containing aluminium powder*, *Propellants, Explosives, Pyrotechnics*, 1990, **15**, 4.
- Stromose E., Eriksen S., *Performance of high explosives in underwater application. Part 2: Alumised explosives*, *Propellants, Explosives, Pyrotechnics*, 1990, **15**, 2.
- Cook M.A., *The science of high explosives*, Reinhold PC, New York 1959.
- Cook M.A., Filler A.S., Keyes R.T., Partridge W.S., Ursenbach W.A., *Aluminized explosives*, *Journal of Physical Chemistry*, 1957, **61**, 2.
- Gogulya M.F., Makhov M.N., Dolgoborodov A.Yu., Brazhnikov M.A., Arkhipov V.I., Shchetinin V.G., *Mechanical sensitivity and detonation parameters of aluminized explosives*, *Combustion, Explosion, and Shock Waves*, 2004, **40**, 4.
- A. Maranda, *Wpływ reaktywności glinu na parametry detonacyjne mieszanin wybuchowych zawierających pył aluminiowy (MW-Al)*, *Wiadomości Chemiczne* 2001, **55**, 3-4.
- Apin A.Ya., Lebedev Yu.A., Khfedova O.I., *Reaktsi azota pri vzryve*, *Zhurnal Prikladnoy Khimii* 1958, **32**, 4.
- Maranda A., Włodarczyk E., *Analiza właściwości wybuchowych i procesu detonacji mieszanin zawierających pył aluminiowy*, *Biuletyn WAT*, 1992, **41**, 1-2.
- Smith K-T., *Pressable thermobaric explosives. Aluminium containing composition based on HMX and RDX*, Proc. 36th International ICT-Conference & 32nd International Pyrotechnic Seminar. Karlsruhe, June 28 – July 01. 2005.

13. Gogulia M.F., Makhov M.N., Dolgoborodov A.Yu., Brazhnikov M.A., Arkhinov V.I., Shchetinin A.G., *Mekhanicheskaya chustvitel'nost' i parametry detonatsii aluminizirovannykh vzryvchatykh veshchestv*, Fizika Goreniya i Vzryva, 2004, **40**, 4.
14. Maranda A., *Emulsyjne materiały wybuchowe*, Wyd. Naukowo-Techniczne, Warszawa 2008.

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International Symposium on Chromatography 2012 Toruń, 9 - 13 September 2012

The 29th international Symposium on Chromatography (the 29th ISC) will take place on 9 - 13 September 2012 in Toruń, Poland. For the first time the International Symposium of Chromatography Committee has made their decision to organize the event in a Central European country, in Poland. The theme of the 29th ISC is Chromatography & Separation Science. Past, Today, Future. The theme is of particular importance to us as the technique was developed in Warsaw, Poland by M.S. Tswett and the fundamentals of which were found by W. Nernst who was born in Wąbrzeźno, former Prussia. This significant meeting will be thoroughly devoted to the role modern separation methods play in scientific development. The co-organizers of the 29thISC are the European Society for Separation Science (EuSSS), Central European Group for Separation Sciences (CEGSS), and Nordic Separation Science Society (NoSSS). The Organizers, together with the Scientific Committee, have planned the program elements to inform and inspire, and to provide opportunities for increased collaboration among those involved in the separation techniques. The elements include plenary lectures, section lectures, oral and poster presentations or workshops. The Organizers will take full advantage of the opportunities for scholarly exchange and discussion on the latest achievements in the field of chromatography. With support from companies, we hope to reach the organizational success, from both, the scientific and social points of view.

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