The influence of small additions of diethylenetriamine on the detonation waves stability for nitromethane/acetone solution

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Abstract. Instability of detonation front in the nitromethane/acetone (NM/A) solution was observed in our previous work: at 10% of acetone the amplitude of heterogeneities was about 20 microns and at 20% of acetone this size was 50 microns. It is known that small additions of diethylenetriamine (DETA) considerably increase the initial rate of chemical reaction in detonation waves for NM. It was expected that DETA would influence the stability of detonation waves in the NM/A solution too. To investigate this phenomenon the laser interferometer VISAR was used for the recording of particle velocity profiles in detonation waves for NM/A. It was found that at the addition of 0.5% DETA to NM/A 90/10 the oscillations in the velocity profile decreased several times over. At the addition of 1% DETA the profile is smooth, i.e. the heterogeneities disappear and detonation wave becomes steady-state. In NM/A 80/20 at the addition of 5% DETA the heterogeneities size is reduced by the order. The increase of detonation wave velocity of NM/A grater than 1% was observed at small concentrations of DETA. Thus it was found that small additions of DETA to the NM/A solution with an unstable detonation front resulted not only in the decrease of heterogeneities size but in their disappearance and stabilization of detonation waves.

1. Introduction
In homogeneous High Explosives (HE) the detonation waves propagate both in steady-state and unstable, pulsatile conditions [1, 2]. The realization of these characters of flow is determined by the kinetics of chemical reaction. Experimentally the heterogeneity of detonation waves in homogeneous HE is mostly investigated in gases [1-3]. With the rise of amplitude of disturbances in gases the complex structure of flow is formed. The instability of detonation in liquid HE was not investigated thoroughly. After the classical works of A.N. Dremin with co-authors (for example, [4]) some notable success in this field was not achieved. At present time the use of techniques with high spatial and time resolution allows for the reliance on the opportunity of receiving of experimental results, which could concretize the conception about the structure of detonation waves in liquid HE.

It is known that small additions of amines can influence the detonation properties of nitromethane CH₃NO₂ (NM). This is especially shown in the change of critical values [5]. The addition of 2 mass % of diethylenetriamine (CH₂CH₂NH₂)₂NH (DETA) decreases the pressure of initiation of detonation by shock waves from 10 GPa to 7.5 GPa, and the failure diameter drops in 7 times in this case. In works by A. Ananin and S. Koldunov the influence of small DETA additions on the possibility of detonation for the nitromethane/diluent solution was investigated. They found that the value of the critical concentration of the solution, at exceeding of which the substance didn’t detonate, increased at almost 1.5 times at the addition of 2% DETA.
2. Experimental scheme
The scheme of experiments is shown in figure 1. NM with the initial density of 1.14 g/cm³ [4, 6], DETA with the initial density of 0.954 g/cm³ [7] and acetone with the initial density of 0.79 g/cm³ were used in the experiments. Mixtures were prepared directly before the experiments. HE charge was placed in the polyethylene or steel shell with 36 mm internal diameter (4). The charge length was 150 mm. The initiation of detonation was made by the pressed charge of RDX (1). A laser beam was reflected from 7-400 μm Al foil (3) which was placed between charge end and water window (2).

Figure 1. The scheme of experiments.

For evaluation of the heterogeneities amplitude and the character time of reaction the laser interferometer VISAR was used. As a result of the experiment we have the velocity profile of the foil – water border, which represents all details of the reaction zone structure in the detonation wave. The interferometer constant is equal to 305 m/s, it allows for the definition of the velocity with the accuracy of ±10 m/s. At the same time in each experiment, with the use of the ionization gauge (5), the detonation velocity D was measured. The second time point was the interferometer signal, which recorded the arrival of the detonation wave to the boundary with the window. The accuracy of the determination of the detonation velocity was not worse than 0.2%, it was about ±0.01 km/s.

3. Experimental results and discussion
In work [8] it is shown that small additions of DETA increase the initial rate of reaction of NM. Essential distinctions from the velocity profile of neat NM are seen at the addition of 0.02% DETA – after a shock jump the particle velocity continues to increase, in the vicinity of 10 ns reaches its maximum and then drops (figure 2).

Figure 2. Velocity profiles of the aluminum foil – water boundary for different concentrations of DETA: 0, 0.0125, 0.025 and 0.05%.
The amplitude of the Von Neumann spike noticeably decreases in comparison with neat NM. Such an unusual phenomenon is connected with the reaction of HE in the detonation front. The particle velocity profiles for the NM/DETA solution have a similar shape up to 15% DETA. The amines increase the rate of chemical reaction but with a thermodynamic viewpoint they are “inert” diluents. Therefore at the further increase of DETA concentration the part of HE, which reacts in the detonation front, decreases. At the addition of 30% DETA the velocity profile has shape, which corresponds to the classical detonation model: after a shock jump the velocity drops smoothly with the formation of the Von Neumann spike in the reaction zone (figure 3, profile 4).

![Figure 3. Velocity profiles for the NM/DETA solution: 1 – 95/5, 2 – 90/10, 3 – 85/15, 4 – 70/30.](image)

It is worth noting that the detonation front of the NM/DETA solution remains stable up to the concentration of 70/30, whereas in solutions NM/acetone and NM/methanol heterogeneity appears at several percentages of the diluent (figure 4). Instability of the detonation front arises due to additions of the inert diluent to NM, which decreases the chemical reaction rate. Instability is shown like oscillations in the registered velocity profiles.

![Figure 4. Velocity profiles for the NM/diluent solution 90/10: 1 – NM/methanol, 2 – NM/DETA, 3 – NM/acetone.](image)
The increase of the initial rate of reaction, caused by DETA additions, must influence not only the failure diameter, the pressure of the detonation initiation, critical concentration or the structure of the chemical reaction zone, but the stability of the detonation front in the NM/acetone solution, in which heterogeneities were observed by several authors [4]. The choice of the specific solution was determined by several conditions. Firstly, the detonation front must be unstable. Secondly, the size of heterogeneities must be an order of 10-50 µm so that they were visible at the use of the foil of the minimum thickness. Thirdly, the concentration of the inert diluent must be far from the critical one (for the NM/acetone solution it is equal to 27%) to provide the repeatability of the results. The NM/acetone solution with mass concentration of acetone from 10 to 20% satisfied all of these conditions.

At investigation of the NM/acetone (90/10) solution in a polyethylene shell with the internal diameter of 36 mm it turned out that this solution didn’t detonate. This is connected with the exceeding of the failure diameter in comparison with the diameter of the used shell. The addition to the solution of 0.1% of DETA in this shell results in a stable detonation wave, that is DETA decreases the failure diameter of the solution. At that the velocity profile is strongly oscillating. The replacement of the polyethylene tube by a steel one of the same diameter results in the propagation of the detonation wave in the NM/acetone (90/10) solution. Whereas disturbances of the detonation front don’t attenuate at the detonation wave propagation through 7 µm Al foil, it indicates that the size of the heterogeneities amplitude is comparable with the foil thickness, i.e. in the order of 10 µm (figure 5). The heterogeneities amplitude is smaller than the chemical reaction zone, the width of which exceeds 400 µm. At the addition of 0.5% DETA the amplitude of oscillations on the profile considerably decreases and at the concentration of 1% DETA the velocity profile is smooth (figure 5), i.e. the detonation front becomes stabilized. Therefore, the addition of 1% DETA to the NM/acetone (90/10) solution results in the rejection of the instability of detonation front.

![Figure 5. Velocity profiles for the NM/acetone solution 90/10 + DETA at different concentrations of DETA.](image)

In figure 6 the results of experiments for the NM/acetone (80/20) solution are shown. In the work [8] the results of the investigation of instability in this solution are conveyed. The heterogeneities size was determined in two ways: the laser interferometer VISAR (the longitudinal direction) and the photo camera CORDIN (the transverse size). The longitudinal size of the instabilities turned out about 50 µm and the transverse ~ 500 µm. The attempt to stabilize the detonation front by DETA additions resulted in a decrease of the heterogeneities size, but not a total absence – at 10% DETA their amplitude was about 10 µm (the gray profile in figure 6).
In each experiment for the NM/acetone with DETA solution, the detonation velocity was measured. In figure 7 the results of these experiments are shown. The gray line is the dependence of detonation velocity on the NM concentration for the NM/acetone solution from work by A. Ananin and S. Koldunov. The white points are the results of our experiments for this solution. The black points – the values of the detonation velocity for the NM/acetone + DETA solution. The numbers over the black points are the values of the DETA concentrations in the NM/acetone + DETA solution. It turned out that the additions of DETA to the NM/acetone solution resulted in a decrease of the detonation velocity by 1.5%.

**Figure 6.** Velocity profiles for the NM/acetone solution 80/20 and the NM/acetone solution 80/20 + 10% of DETA.

**Figure 7.** The dependence of the detonation velocity of the NM/acetone and the NM/acetone/DETA solutions on the NM concentration.

It was found that at the addition of 20% DETA to the NM/acetone (80/20) solution the detonation velocity remained almost the same as in the NM/acetone (80/20) solution without DETA additions,
although in the first case the concentration of NM was about 66%. It is surprising because in the NM/acetone solution the critical concentration of NM, at exceeding of which the solution doesn’t detonate, is about 73%. The heterogeneities size in the NM/acetone (80/20) + 20% DETA solution is about 20 µm, this is significantly smaller than in the NM/acetone (80/20) solution.

Thus, in our work it was shown that small additions of DETA not only influenced the critical parameters of detonation but resulted in the rejection of the instability of the detonation front in the NM/acetone solution with the size of the heterogeneities amplitude in the order of 10 µm. At higher acetone concentrations, when the size of heterogeneities was more than 50 µm, DETA didn’t reject the instability, but significantly decreased the amplitude of oscillations.

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