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Detonation Properties of Mixtures of Ammonium Nitrate Based Fertilizers and Fuels

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Abstract: Detonation properties of mixtures of milled ammonium nitrate based fertilizers and fuels – aluminium or mineral oil – have been determined. The fertilizers used were ammonium nitrate and its compositions with mineral meal; for some compositions additional amount of mineral meal was mixed with the fertilizer. Detonation velocity, Guerney's energy and limits of detonability of such mixtures have been measured. It was examined that mixtures of mineral oil and fertilizers containing over 20% of mineral meal detonated during the tests. Mixtures of aluminium and fertilizers detonated even if concentration of mineral meal in the fertilizers was 40%.

Keywords: ammonium nitrate based fertilizers, detonation properties, illicit use of explosives

Introduction

The main use of ammonium nitrate (AN) is soil fertilization. From the safety point of view explosive properties of AN are a disadvantage. The explosive properties of AN are relatively low, but its mixtures with many fuels are typical explosives. E.g. mixtures of AN and mineral oils, called ANFO explosives, are used mainly in mining; mixtures of AN and aluminium powder, named ammonals,

are used for some technical purposes.

Knowledge of preparing explosives from AN and common availability of ingredients are used by offenders and terrorists. In the past they used AN for running bomb attacks many times. Countermeasures against such events have been restrictions on access to AN and production of fertilizers with reduced explosive properties. A way of making more troublesome explosives preparation from fertilizers containing AN is manufacturing mixtures of AN and inert materials like: limestone, dolomite, anhydrite etc. – such fertilizers are called CAN. Nonetheless terrorists used even such mixtures for preparing explosives. Many works on AN based fertilizers useless for illegal applies were done in the USA after the Oklahoma bombing disaster. The general conclusion from performed tests was that there was not found substance which added to AN in a reasonable quantity would fully prevent the use AN based fertilizers for manufacturing explosives [1, 2].

Under the new EU regulations only fertilizers which contain less than 45% of AN (16% N) may be traded to the general public. Such fertilizers still may be used for preparing explosives, but require more preparation (milling, using large booster charge etc.) to achieve a full detonation and the blast have a significantly smaller effect [3, 4].

The aim of this work was to examine detonation properties of mixtures of AN based fertilizers and fuels (mineral oil or Al) and evaluation of a danger of illicit use such mixtures.

Tested materials

For preparing explosive mixtures commercially available AN based fertilizers were chosen. The fertilizers were AN and its mixtures with dolomite.

It is known that physical structure influences on explosives properties of materials significantly. This influence is especially important in the case of materials with low explosive properties like AN and its mixtures with non explosive ingredients. One of the factors that renders AN and mixtures containing AN more sensitive and improving their explosive characteristics are dimensions of prills, crystals, grains etc. [5-11]. In order to increase explosive properties of the tested mixtures the fertilizers were milled in a centrifugal mill equipped with a sieve of 0.75 mm trapezoid holes. Photos (made by SEM) of the three milled fertilizers are presented below.



Figure 1. Photos of the milled fertilizers – magnification 100 times.

From the photos presented in Figure 1 one may see that grains of the fertilizers after milling have irregular shapes and rough surfaces. Dimensions of the grains are highly diversified. There are many grains below tenth of a millimetre, but some are a few tenth of a millimetre.

Used diesel oil has density 838 kg/m³ (at 15 °C) and kinematic viscosity 2.93 mm²/s (at 40 °C). Flaked aluminium has specific surface area of 4500 cm²/g and contains about 89% of Al, 10% of Al₂O₃ and 1% of stearic acid.

The milled fertilizers were than stirred with diesel oil or flaked aluminium and so called modified ANFO explosives or modified ammonals were manufactured. In some trials additionally amount of dolomite was added to milled CAN. Oxygen balance of all prepared mixtures was zero.

Calculated parameters of the mixtures

For comparative purposes heat of the explosion and volume of gases evolving during the explosion have been calculated [12]. Calculations have been done for the mixtures of AN based fertilizers and fuels, ANFO explosive, AN and TNT. Oxygen balance of all the mixtures is zero. Results of calculations are presented in Table 1.

Material	Heat of explosion [kJ/kg]	Volume of gases [dm ³ /kg]	
TNT	4188	740	
AN	1592	980	
ANFO	3890	975	
AN / dolomite 90/10 + diesel oil	3234	902	
AN / dolomite 80/20 + diesel oil	2706	830	
AN / dolomite 70/30 + diesel oil	2163	758	
AN / dolomite 60/40 + diesel oil	1613	686	
AN / dolomite 50/50 + diesel oil	1071	609	
AN + Al	6712	691	
AN / dolomite 90/10 + Al	5954	655	
AN / dolomite 80/20 + Al	5269	612	
AN / dolomite 70/30 + Al	4505	570	
AN / dolomite 60/40 + Al	3713	526	
AN / dolomite 50/50 + Al	2891	481	

Table 1. Calculated parameters of the mixtures of AN based fertilizers and fuels

As may be seen from Table 1 the mixtures of AN based fertilizers and mineral oil have the medium heat of explosion. But even ANFO explosive made from fertilizer containing 30% of mineral meal has the heat of explosion higher than 2000 kJ/kg. The mixtures of AN based fertilizers and aluminium have the high heat of explosion. The mixture made from fertilizer containing 30% of mineral meal has the higher heat of explosion than TNT and the mixture prepared from fertilizer consisting equal amounts of AN and dolomite has the heat of explosion slightly below 3000 kJ/kg. These calculations show that the mixtures manufactured from AN based fertilizers and fuel may have strong explosive properties even if they contain significant amount of inert materials.

Methods of detonation properties research

Detonation properties of the mixtures of AN based fertilizer and fuels were determined by the means of measurement of detonation velocity and a cylindrical test [13, 14]. Detonation velocity was measured during shooting charges of the mixtures placed in a steel tube of internal diameter 36 mm and wall's thickness 3 mm. The cylindrical test was performed by using a copper tube about internal diameter 36 mm and wall's thickness 3.5 mm. The detonation velocity was measured and a X-rays (rtg) photo of the expanded tube was taken during the shot.

Analysing the photo and taking into account detonation velocity, the Guerney's energy (the sum of energies of expanding tube and detonation products) was then determined. A charge consists of 14 g pressed RDX was used as a booster in both the tests.

Results

Detonation velocities of modified ANFO explosives

The results of detonation velocity tests of the modified ANFO explosives are presented below. Modified ANFO explosives contained milled ammonium nitrate, dolomite meal and diesel oil. The number in brackets means the concentration of dolomite in the fertilizer.

Composition of explosive [%]		Density	Detonation
Fertilizer	Diesel oil	$[kg/m^3]$	velocity [km/s]
Pure AN (0) 94.5	5.5	909	3.560
AN / dolomite (7) 94.9	5.1	773	2.800
AN / dolomite (22) 95.6	4.4	808	2.370
AN / dolomite (30) 96.0	4.0	942	No detonation

Table 2. Detonation velocity of the mixtures of AN based fertilizers and diesel oil

Performed experiments show that even mixtures of milled fertilizers and mineral oil containing significant amount of inert substances can detonate. The highest detonation velocity, about 3.6 km/s, had explosive made of pure AN. As the amount of dolomite in the fertilizer increased, subsequently to 7 and 22%, detonation velocities of modified ANFO explosives fell to about 2.8 and 2.4 km/s. Only the mixture manufactured from fertilizer containing 30% of dolomite didn't detonate.

Detonation velocities of modified ammonals

The results of detonation velocity tests of the modified ammonals are presented below. Modified ammonals contained milled ammonium nitrate, dolomite meal and flaked aluminium. The number in brackets means the concentration of dolomite in the fertilizer.

Composition of explosive [%]		Density	Detonation	
Fertilizer	Aluminium	$[kg/m^3]$	velocity [km/s]	
Pure AN (0) 80.2	19.8	685	2.960	
AN / dolomite (7) 81.3	18.7	688	2.740	
AN / dolomite (14) 82.5	17.5	714	2.890	
AN / dolomite (22) 83.8	16.2	785	2.660	
AN / dolomite (30) 85.3	14.7	796	2.440	
AN / dolomite (40) 87.1	12.9	800	1.940	
AN / dolomite (50) 89.0	11.0	804	no detonation	

Table 3. Detonation velocity of the mixtures of AN based fertilizers and aluminium

Performed experiments show that even mixture of milled fertilizers containing 40% of dolomite and aluminium can detonate. Detonation extincted only in material manufactured from fertilizer consisting equal amounts of AN and dolomite. The highest detonation velocity, 3.0 km/s, had explosive made of pure AN. As the amount of dolomite in the fertilizer increased to 40%, detonation velocities of modified ammonals fell to about 1.9 km/s. These results are similar to those performed in Denmark [3] where ammonals manufactured from fertilizers containing even above 50% of inert substance detonated. Some differences may be explained by different test conditions – larger charges (25 kg), content 15% of Al were tested in Denmark; probably different kinds of Al powders and fertilizers were used.

Cylindrical test

The cylindrical test of some chosen mixtures were performed, in a way described in the previous paragraph. During the test detonation velocity and energetic characteristics expressed as Guerney's energy (E_G) were determined. Results of testing typical ANFO explosive made of porous AN are also presented as a reference material. The results are presented below.

Composition of explosive [%]		Density	Detonation	Fa
Fertilizer	Aluminium	[kg/m ³]	velocity [km/s]	[kJ/kg]
ANFO (porous AN 94.5/diesel oil 5.5)		820	3.300	1580
Pure AN (0) 80.2	19.8	820	3.190	1720
AN / dolomite (7) 81.3	18.7	820	2.910	1390
AN / dolomite (22) 83.8	16.2	830	2.620	1180

Table 4. Results of the cylindrical test

Performed experiments showed that all examined mixtures detonated during the tests. The highest detonation velocity had the ANFO explosive (about 3.3 km/s), but the largest Guerney's energy had the mixture of AN and aluminium (about 1720 kJ/kg). Mixtures made from fertilizers consisting of AN and dolomite detonated with lower velocities and their Gurney's energies were lower than explosives prepared from AN, but they were still relatively high. Detonation velocities of the mixtures manufactured from fertilizers containing 7% and 22% of dolomite were about 2.9 km/s and 2.6 km/s; Guerney's energies 1400 and 1200 kJ/kg, respectively.

Discussion and Conclusions

Obtained results may be interpreted in the following way. The inert substance added to AN and fuels acts as a diluent. With the decrease in concentration of explosive ingredients, i.e. AN and diesel oil/aluminium in such mixture the heat of explosion also decreases. Inert substance also plays a role of a medium absorbing heat from the reaction zone. Due to these phenomena detonation parameters such as: detonation velocity and energetic characteristics decrease. Finally, if an amount of the inert substance is high enough, detonation extincts.

Mixtures of AN based fertilizers, that contain even a significant amount of inert inorganic substances and fuels reveal noticeable explosive properties. Mixtures prepared from fertilizer containing 22% of mineral meal and diesel oil similar to the mixtures prepared from fertilizer containing 40% of mineral meal and flaked aluminium detonated during the tests. Such fertilizers may be used as a raw material for manufacturing explosives by non authorized persons. From the public safety point of view there is a danger that such prepared explosives may be used by offenders and terrorists to run bomb attacks.

At last, the mixtures of AN based fertilizers containing inert substances and fuels may be used for some technical applications like explosive working of metals.

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References

- [1] Editorial, Fact and Fantasy in Oklahoma, Nitrogen, May-June 1995.
- [2] Hands R., Ammonium nitrate on trial, Nitrogen, January-February 1996, 15-17.
- [3] Paper from Working Party on Technical Harmonisation (Dangerous Substances) on 10 April **2008**.
- [4] Regulation EU No 552/2009 published in Official Journal of EU No L 164/7 (Reach).
- [5] Zygmunt B., Buczkowski D., Influence of Ammonium Nitrate Prills Properties on Detonation Velocity of ANFO, *Propellants, Explos., Pyrotech.*, 2007, 32(5), 411-414.
- [6] Maranda A., Research on the Process of Detonation of Explosive Mixtures of the Oxidizer Fuel Type Containing Aluminium Powder, *Propellants, Explos., Pyrotech.*, 1990, 15(4), 161-165.
- [7] Zygmunt B., Initiation by Shock Wave Detonation of Water Containing Explosives about Various Structure of Grain, *Physics of Combustion and Explosion*, **1980**, *16*(4), 89-93 (in Russian).
- [8] Maranda A., Papliński A., Gałęzowski D, Investigation on Detonation and Thermochemical Parameters of Aluminized ANFO, J. Energetic Mater., 2003, 21(1), 1-13.
- [9] Buczkowski D., Zygmunt B., Influence of Ammonium Nitrate Prills' Porosity and Dimesions on Detonation Velocity of ANFO Explosives, *Vth Int. Seminar "New Trends in Research of Energetic Materials*", Pardubice, 21-23.04.2003, 45-51.
- [10] Miyake A., Kobayashi H., Echigoya H., Kubota S., Wada Y., Ogata Y., Arai H., Ogawa T., Detonation Characteristics of Ammonium Nitrate and Activated Carbon Mixtures, J. Loss Prev. Process Ind., 2007, 20, 584-588.
- [11] Kozevnikov V., Detonation of Ammonium Nitrate and Mixtures with Fuels Containing Inert Additives or not, *Physics of Combustion and Explosion*, **1999**, 35(3), 114-119 (in Russian).
- [12] Polish standard BN-80/6091-42.
- [13] Trzciński W.A., Cudziło S., The Application of the Cylinder Test to Determine the Energy Characteristics of Industrial Explosives, *Archives of Mining Sciences*, (2001), 46(3), 291-307.
- [14] Buczkowski D., Trzciński W. A., Zygmunt B., Examining of Energetic Properties of ANFO Explosive by Using Cylindrical Test, *Fifth Int. Armament Conf. , Scientific Aspects of Armament*", Waplewo, 9-11.10.2004, 74-82.