Central European Journal of Energetic Materials, **2014**, *11*(1), 115-127
ISSN 1733-7178

Explosive Properties of Mixtures of Ammonium Nitrate(V) and Materials of Plant Origin – Danger of Unintended Explosion

Daniel BUCZKOWSKI

Institute of Industrial Organic Chemistry,
6 Annopol St., 03-236, Warsaw, Poland
E-mail: buczkowski@ipo.waw.pl

Abstract: The addition of many organic substances decreases the thermal stability and increases the explosive properties of ammonium nitrate(V). In order to determine how very material of plant origin would increase the risk of decomposition and explosion of ammonium nitrate(V), tests using the DTA method and the detonation properties were performed. The materials tested were milled ammonium nitrate(V) mixed with wheat flour, hard coal, rape seeds or wood dust. It was found that all of the mixtures tested decompose at significantly lower temperatures than ammonium nitrate(V) and ANFO explosive. Some of them decompose close to the melting temperature of ammonium nitrate(V) and their decomposition is violent. All of the mixtures tested are cap sensitive and some of them have smaller critical diameters than ANFO. The detonation velocities of the mixtures are lower than the detonation velocity of ANFO, but significantly higher than that of ammonium nitrate(V).

Keywords: ammonium nitrate(V), materials of plant origin, decomposition, detonation properties

1 Introduction

Ammonium nitrate(V) (AN) has oxidizing and weakly explosive properties, but its mixtures with many fuels are typical explosives, *e.g*. ANFO or ammonals. AN is also an oxidizer towards majority of organic and combustible substances, including many materials of plant origin, *e.g*. starch or cellulose. A lot of these mixtures decompose at significantly lower temperatures and more violently than

AN [1-8]. Since the nineteenth century such mixtures have also sometimes been used as explosives [9-11]. The explosive properties of such types of materials have at times been tested for cognitive reasons [12, 13] or to acquire knowledge about possible criminal use [14].

The majority of regulations, *e.g.* transport regulations, treat AN as an oxidizer, but AN with the small addition of an organic substance is considered as an explosive [15, 16]. This is caused by the increase in its heat of explosion and of its explosive properties such as decreased critical diameter, increased sensitivity and the "force" of such the mixtures compared with AN.

The above mentioned factors: more violent, lower temperature decomposition and stronger explosive properties of these mixtures, compared with AN itself, increases the risk of unintended explosion. AN contaminated by materials of plant origin is more prone to decomposition and explosion than uncontaminated AN. Accidental explosions of AN, which still occur (Toulouse, France in 2001, Mihailesti, Romania in 2004, West, USA in 2013), indicate that AN is a dangerous material and the risk of explosion should not be underestimated. In order to understand better the hazards of such accidents, the explosive properties of AN and mixtures containing AN should be tested.

The aim of the present work was to examine the thermal stability and detonation properties, and to evaluate the danger of unintended explosion, of mixtures of AN and materials of plant origin. The thermal stability of these mixtures was tested by the DTA method and the detonation properties were determined by measurement of the critical diameter and detonation velocity. The thermodynamic parameters of mixtures of AN and fuels were also calculated.

2 Thermodynamic Parameters of Mixtures of AN and Fuels

The thermodynamic parameters of the explosion of mixtures of AN and fuels were calculated (heat of explosion and gas volume). The calculations were performed according to the EU standard, using program ZMWCyw [17, 18]. For comparative purposes data for TNT, AN and ANFO are also listed. The oxygen balance of all of the mixtures is zero. The results of these calculations are presented in Table 1.

As may be seen from Table 1, the heats of explosion of the mixtures of AN and materials of plant origin (carbon, cellulose and wood dust) are in the range of 3800-3900 kJ/kg. These values are only a few percent lower than the heat of explosion of ANFO and about 16% lower than the heat of explosion of TNT, but over twice the heat of explosion of AN. The volumes of the gases generated by

all of the materials containing AN are in the range 900-1000 dm^3/kg, significantly larger than the volume of gases evolved during the explosion of TNT.

Table 1. Thermodynamic parameters for the explosion of mixtures of AN and fuels (calculated)

Material (%)	Heat of explosion (kJ/kg)	Volume of gases (dm^3/kg)
TNT	4587	717
AN	1712	992
ANFO (AN 94.5 / mineral oil 5.5)	4018	986
AN 93 / carbon 7	3860	924
AN 86 / cellulose 14	3816	951
AN 88 / wood dust 12	3803	952

Taking into account the comparatively high values of the thermodynamic parameters of mixtures of AN and materials of plant origin, it seemed that such mixtures might have relatively strong explosive properties.

3 Tested Materials

The basic ingredient of the mixtures prepared was prilled fertiliser grade AN. AN contained about 1.2% of magnesium nitrate (used as a stabiliser), about 0.1% of anti-caking agent and 0.3% of water; the remainder of the fertiliser was essentially AN. In order to increase the explosive properties of the mixtures, AN was milled in a centrifugal mill, equipped with a sieve with trapezoid holes size 0.75 mm [10, 13, 19]. Photographs (made by SEM) of the milled fertiliser are presented below.

From the photographs presented in Figure 1, one may see that the grains of the fertiliser after milling have irregular shapes and rough surfaces. The dimensions of the grains are highly differentiated. There are many grains below a tenth of a millimetre, but some are several tenths of a millimetre.

As combustible ingredients were chosen: diesel oil (FO), wheat flour (WF), hard coal (HC), rape seeds (RS) and wood dust (WD).

Diesel oil and wheat flour were bought on the market and used with no additional preparation. Diesel oil has density 838 kg/m^3 (at 15 °C) and kinematic viscosity 2.93 mm^2/s (at 40 °C). Wheat flour was type 480 and characterised by a nutrition value of 14.5 MJ/kg.

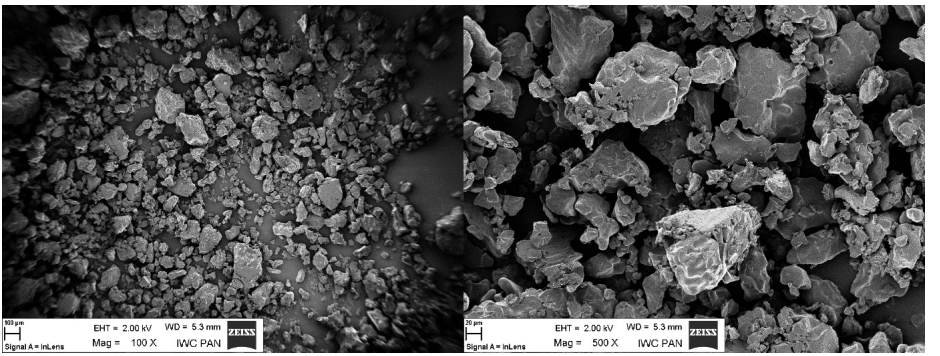


Figure 1. Photographs of milled fertiliser grade AN – magnification 100x (left) and 500x (right).

Hard coal and rape seeds were trade products. They were milled in the same manner as AN (see above).

Wood dust was delivered from industry and used with no additional preparation. It was a waste product obtained from wood treatment.

Photographs (made by optical microscopy) of the additives used are shown below.

Wheat flour Hard coal

Rape seeds Wood dust

Figure 2. Photographs of the additives used.

Milled AN was mixed with the above mentioned additives. Samples for the DTA tests were prepared in the same way, except that all solid components had been previously sieved with hole size 0.3 mm. The oxygen balance of all of the prepared mixtures was nominally zero; it was difficult to state the precise chemical compositions of the ingredients because they are natural products, so the oxygen balance may not be exactly zero. The compositions of the materials tested are shown in Table 2.

Table 2. Materials tested

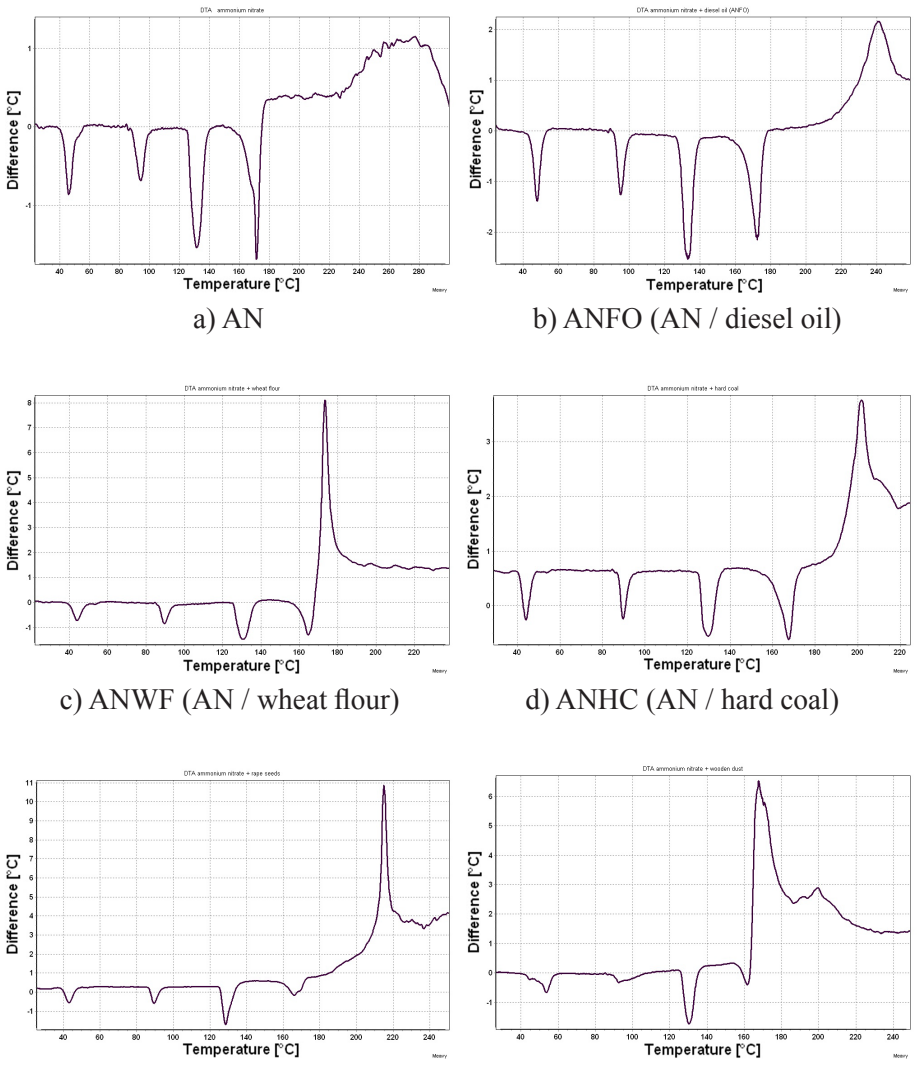
Symbol of material	Composition of material (%)
ANFO	AN 94.5 / diesel oil 5.5
ANWF	AN 85 / wheat flour 15
ANHC	AN 90 / hard coal 10
ANRS	AN 90 / rape seeds 10
ANWD	AN 88 / wood dust 12

4 Examination of the Mixtures by DTA

In order to examine the influence of the additives on the thermal stability of AN, the above mentioned mixtures and AN without additives were subjected to tests by the DTA method.

Differential thermal analysis (using DTA 551 Ex analyzer, manufactured by

OZM Research, The Czech Republic) was carried out by heating 30 mg samples at 5 °C/min. The samples to be analysed were placed in open test tubes and a thermocouple, protected by a glass sheath, was inserted directly into the sample. The data were evaluated using the analyzer and MEAVY 2.0.0.4 software. The DTA thermograms of the materials tested are presented below.



a) AN b) ANFO (AN / diesel oil)

c) ANWF (AN / wheat flour) d) ANHC (AN / hard coal)

e) ANRS (AN / rape seeds) f) ANWD (AN / wood dust)

Figure 3. DTA thermograms of the mixtures.

In all of the diagrams, from left to right:

- the first three "peaks" correspond to the polymorphic transitions of AN,
- the fourth "peak" corresponds to the melting of AN,
- commencement of decomposition.

During the analysis of the thermogram of AN, a problem occurred due to the irregularity of the run in the part of the diagram corresponding to the decomposition. For this reason only approximate temperatures for the decomposition of AN were determined.

Some "peaks" in the thermograms of the mixtures are not as sharp as in the case of AN alone. This was probably caused by a dilute influence of the additives. That influence is especially strong in the case of additives of low density such as wood dust.

From the diagrams presented in Figure 3 one may see that:

- AN – after melting there is a long plateau before slow decomposition commences,
- ANFO – after the melting of AN there is a short plateau and then more rapid decomposition commences,
- ANWF – violent decomposition commences close to the melting temperature of AN,
- ANHC – rapid decomposition commences immediately after the melting of AN,
- ANRS – the first stage of decomposition commences close to the melting temperature of AN, then, after a period of slow decomposition, a second stage of rapid decomposition commences,
- ANWD – violent decomposition commences close to the melting temperature of AN.

Table 3 shows the decomposition temperatures (start and onset) of the mixtures tested.

Table 3. Decomposition temperatures

Symbol of material	Decomposition temperature (°C)	
	start	onset
AN	approx. 230	approx. 250
ANFO	203	227
ANWF	165	170
ANHC	182	196
ANRS 1st / 2nd stage	166 / 182	169 / 212
ANWD	162	163

From data shown in the Table 3 one may observe that all of the mixtures tested decompose at lower temperatures than AN, whose onset temperature is

about 250 °C. The corresponding temperatures for mixtures of AN with the additives: mineral oil, hard coal, wheat flour, rape seeds and wood dust are 227, 196, 170, 169 (1st stage) and 163 °C, respectively. Also the start temperature is the highes for AN, lower for ANFO and still lower for the mixtures with the other additives.

5 Examination of Detonation Characteristics

The detonation properties of the mixtures of AN and materials of plant origin and AN without additives were determined by means of measurement of the critical diameter and the detonation velocity. The test methods are described below together with the results of the examinations.

5.1 Method for determining the critical diameter

The critical diameters were determined by initiating the tested mixtures contained in cylindrical, paper tubes. The tubes were positioned vertically standing on steel witness plates. The lengths of the charges were ten times their diameters ($L = 10 \times d$). Above the charge there was 50 mm of sand tamping. The diameters of the tubes were graded by 5 mm increments, starting from 15 mm, to 45 mm diameter were used. The charges were initiated by standard detonators; only charges of AN, due to its low sensitivity, were initiated by boosters consisting of 14 g of pressed RDX. The test results were assessed on the basis of the amount of charge remaining and the damage to the steel witness plate. If there was no remnant of the charge and the witness plate was holed, the result was considered as positive, *i.e*. detonation propagated through the whole charge. Any other result was considered as an extinction of detonation. The smallest diameter of the charge giving three positive results was taken to be the critical diameter.

5.2 Method for measuring the detonation velocity

The detonation velocities were measured by initiating charges of the mixtures placed in steel tubes of internal diameter 36 mm and wall thickness 3 mm. A charge consisting of 14 g of pressed RDX was used as a booster. The listed results are the average of at least two measurements; the difference between the measurements was not more than 90 m/s.

5.3 Results

The results for the measurement of the critical diameters and the detonation velocities are presented in Table 4.

Table 4. Critical diameters and detonation velocities

Symbol of material	Density (kg/m^3)	Critical diameter (mm)	Detonation velocity (km/s)
AN	826	over 45	1.65
ANFO	909	35	3.56
ANWF	873	45	3.14
ANHC	900	40	2.84
ANRS	865	30	2.28
ANWD	435	20	2.32

The experiments performed show that all of the mixtures tested exhibit distinct explosive properties and may detonate. They are cap sensitive, *i.e.* detonate if initiated only by a detonator. Taking into account the critical diameters, the results can be ordered from the smallest to the largest: ANWD, ANRS, ANFO, ANHC, ANWF and AN – 20, 30, 35, 40, 45 and >45 mm, respectively. Considering the detonation velocities, the materials may be listed from the highest to the lowest velocity: ANFO, ANWF, ANHC, ANWD, ANRS, AN – 3.56, 3.14, 2.84, 2.32, 2.28 and 1.65 km/s, respectively.

6 Discussion

The tests performed using the DTA method reveal that all of the mixtures of milled AN with materials of plant origin decompose at lower temperatures and more rapidly than AN and ANFO. Some of them *e.g.* containing wood dust or wheat flour, decompose close to the melting temperature of AN, and their decomposition is violent. Such runs to decomposition are caused by the oxidation of the organic components with the generation of a lot of heat.

For the decomposition of the mixture of AN and rape seeds, a two-stage process was observed. The first stage of the decomposition commences close to the melting temperature of AN and was similar to the decomposition of the mixture of AN and wheat flour. In order to determine if this phenomenon may be caused by a reaction between AN and carbohydrates, which are ingredients of rape seeds, an additional DTA test was performed. A mixture of AN, wheat flour and rape oil was prepared (proportions 91/4/5) and examined. The DTA thermogram and the decomposition temperatures of this mixture are shown below.

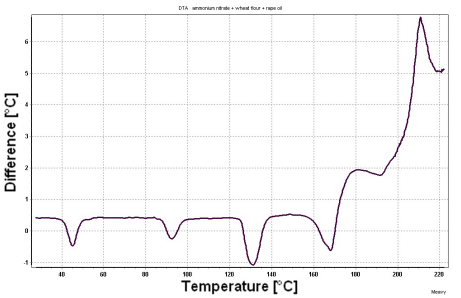


Figure 4. DTA thermogram of the mixture of AN, wheat flour and rape oil.

Table 5. Decomposition temperatures of the mixture of AN, wheat flour (WF) and rape oil (RO)

Decomposition temperatures of AN+WF+RO (°C)		
	start	onset
1st stage	168	169
2nd stage	191	203

From the thermogram presented in Figure 4 and the decomposition temperatures of the "peaks", one may say that the mixture of AN, wheat flour and rape oil decomposes in a similar manner to the mixture of AN and rape seeds, *i.e*. in two stages with the 1st stage commencing close to the melting temperature of AN. There were some differences between these two thermograms and the decomposition temperatures, but these may be explained by the presence of other ingredients, such as proteins, fibers *etc*., in the rape seeds. The similarities of the thermograms of the two mixtures seem to confirm that the 1st stage of the decomposition of the mixture of AN and rape seeds is connected with a reaction between AN and carbohydrates.

It may be stated that all of the mixtures of AN and materials of plant origin which have been tested have a smaller critical diameter than AN. Some of them, such as mixtures with wood dust or rape seeds, have a smaller critical diameter than ANFO, which is a typical explosive. The detonation velocities of the mixtures tested are lower than the detonation velocity of ANFO, but significantly higher than that of AN; some of the mixtures detonate with velocities over 3 km/s (AN and wheat flour).

There was no clear relation between the detonation properties of the mixtures. The mixture of AN and wheat flour exhibits the fastest detonation velocity (apart from ANFO) and the largest critical diameter. On the other hand the mixture of AN and rape seeds has the lowest detonation velocity and a small critical diameter.

Characterised with a very low density (below 500 kg/m^3), the mixture of AN and wood dust has a small detonation velocity and the lowest critical diameter. Such parameters may be explained by the way that many factors connected with materials of plant origin affect the detonation properties of the mixtures. It seems that the most important factors are:

- different physical properties (dimensions of particles, density, porosity, specific surface area *etc*.), and
- various chemical compositions (carbohydrates, fats, proteins, water *etc*.).

Due to the above mentioned factors, the interaction of chemical reactions and physical processes accompanying the detonation transformation is significantly different and is the reason for the variety of detonation properties in the mixtures examined.

7 Conclusions

Two kinds of tests – DTA and detonation properties − of mixtures of milled, fertiliser grade AN and materials of plant origin were performed. These tests are important from a safety point of view.

The tested mixtures of AN and materials of plant origin decompose at significantly lower temperatures than AN and ANFO, and the decomposition of some of them is violent. It is of concern that AN contaminated by materials of plant origin may decompose at a relatively low temperature.

The tests performed show that all of the mixtures of AN and materials of plant origin which have been tested have distinct explosive properties; they are cap sensitive and some of them have smaller critical diameters than that of ANFO. Their detonation velocities are lower than that of ANFO, but in the region of 2-3 km/s.

During all handling of AN, from the manufacturing process to spreading on fields, contamination of AN by materials of plant origin should be avoided.

Acknowledgements
These researches were partly supported by the Ministry of Science and Higher Education, Grant No. O N508 1192 33, and performed during 2007-2010.

8 References

[1] Urbański T., *Chemistry and Technology of Explosives*, Vol. II, Pergamon Press Oxford, **1965**.

[2] Fedoroff T.B., *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, Dover, New Jersey, USA, **1960**.

[3] Rubtsov Y.I., Kazakov A.I., Lempert D.B., Manelis G.B., Kinetic Regularities of the Heat Release for the Interaction of Some Organic Compounds with Ammonium Nitrate, *Propellants Explos. Pyrotech.*, **2006**, *31*(6), 421-434.

[4] Lurie B.A., Chang L.-S., Kinetics and Mechanism of Thermal Decomposition of Powdered Ammonium Nitrate Influenced by Soot (in Russian), *Fiz. Goreniya Vzryva*, **2000**, *36*(5), 63-73.

[5] Patil D.G., Jain S.R., Brill T.B., Decomposition of Energetic Materials 56. On the Fast Thermolysis Mechanism of Ammonium Nitrate and its Mixtures with Magnesium and Carbon, *Propellants Explos. Pyrotech.*, **1992**, *17*(3), 99-105.

[6] Izato Y., Miyake A., Date S., Combustion Characteristics of Ammonium Nitrate and Carbon Mixtures Based on a Thermal Decomposition Mechanism, *Propellants, Explos., Pyrotech.*, **2013**, *38*(1), 129-135.

[7] Biskupski A., Możeński C., Malinowski P., Miduch R., Grochowski L., Safety Hazard and Quality of Nitro-chalk Fertilizers in Relation to the Product Composition and the Granulation Method (in Polish), *Przem. Chem.*, **2013**, *92*(12), 2186-2191.

[8] Wrzesiński J., Popławska-Jach J., Kołaczkowski A., Liability of Ammonium Nitrate Emulsions to Spontaneous Decomposition, *New Trends Res. Energ. Mater.*, *Proc. Semin.*, *8th*, Pardubice, **2005**, 115-125.

[9] Ohlsson J.V., Norrbin J.H., *Improvements in the Preparation of Explosive Compounds*, British Patent 2766, **1867**.

[10] Kozevnikov V., Detonation of Ammonium Nitrate and Mixtures with Fuels Containing Inert Additives or Not (in Russian), *Fiz. Goreniya Vzryva*, **1999**, *35*(3), 114-119.

[11] Ye Z., Qian H., Lu C., Liu Z., Self-sensitizable Characteristics of Modified Ammonium Nitrate, *Cent. Eur. J. Energ. Mater*., **2005**, *2*(4), 55-62.

[12] Maranda A., Szymański R., Tests of Critical Diameter and Detonation Velocity of Mixtures of Ammonium Nitrate(V) and Selected Organic Substances, *Chemik*, **2013**, *67*(1), 13-18.

[13] 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.

[14] Kuzmin V., Kozak G., Mikheev D., Detonability of Ammonium Nitrate and Mixtures on its Base, *Centr. Eur. J. Energ. Mater*., **2010**, *7*(4), 335-343.

[15] Transport regulations by road *ADR (European Agreement Concerning the International Carriage of Dangerous Goods by Road)* or by train *RID* (*Reglement concernant le transport International ferroviare des merchandises Dangereuses par chemin de fer*), **2013**.

[16] Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October **2003** relating to Fertilisers, Annex III.
[17] European Standard EN 13631-15:**2005** *Explosives for Civil Uses – High Explosives – Part 15: Calculation of Thermodynamic Properties*.
[18] Grys S., Trzciński W.A., ZMWCyw – Program for Calculating Thermodynamic Properties of Explosives for Civil Uses (in Polish), *Scientific Works of Central Mining Institute*, No. 4/**2010**, Katowice.
[19] Zygmunt B., Buczkowski D., Influence of Ammonium Nitrate Prills Properties on Detonation Velocity of ANFO, *Propellants Explos. Pyrotech.*, **2007**, *32*(5), 411-414.