Ammonium nitrate – a treat of accidental explosion and terrorist attack

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Introduction

Ammonium nitrate (V) (AN) is produced globally in the quantity of more than twenty million tonnes annually. As the marketed product, nowadays it is almost exclusively manufactured in a granulated or prilled form providing its good friability that facilitates the work of both the manufacturers and the users. AN is mostly applied in two industrial branches:

- in the agriculture, it belongs to one of the most commonly used fertilisers
- in the industry, it is a component of explosives usually used for civilian purposes.

At the beginning of its mass production (during the First World War and shortly after it), AN was considered to be a completely safe product. Soon it turned out that fire or explosion risk during AN production, storage, transport or application was real, and the neglect of this risk factor was the cause for the biggest industrial accident of the time – the explosion in Oppau (Germany) in 1921 which left hundreds of people dead, thousands more injured and huge economic loss. Many serious accidents caused by the lack of knowledge on flammable and explosive properties of AN were reported within a period of nearly 100 years of its mass production. Despite significant technical progress and the accumulation of many dramatic experiences, the risk of accidental explosion or fire of AN during its production, storage, transport or application has still remained the crucial problem. This is confirmed by failures which have occurred in recent years in economically developed and technologically advanced countries, e.g. the explosion in Toulouse (France) in 2001 resulting in the death of 30 persons, injuries of thousands and widespread destruction of the industrial and urban area.

Fig. 1. A building destroyed in the terrorist attack in Oklahoma City
http://www.oklahomacitybombing.com/oklahoma-city-bombing-4.jpg
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In recent years, the problem of AN used as an elementary component in the production of explosives to launch bomb attacks has grown in particular importance. AN is the elementary component of explosives characterised by a very simple manufacturing technology. This knowledge is also possessed by the terrorists who for years have been producing the explosives with AN as their core component in order to launch bomb attacks. The most spectacular attack involving the application of AN was the bomb attack which took place in Oklahoma City (USA) in 1995. The explosion of the mixture of AN and liquid hydrocarbon caused the death of 169 persons, and an utter destruction of the massive tower block (Fig. 1). Also, the bomb attack in Oslo (Norway) in 2011 was carried out with the use of AN-based explosive.

The permanent threat posed by both the accidental explosions of AN and bomb attacks, in which AN-based explosives are used, results in expressing the deep concern for both technical and organisational issues which could reduce such danger [1÷4].

Explosive properties of ammonium nitrate and its mixtures

AN is a substance characterised by quite poor explosive properties, and it is not regarded as explosive according to the majority of classifications. However, serious accidents caused by explosions that occurred in the period of AN application indicate that such risk cannot be neglected. Explosive decomposition of ammonium nitrate can be caused by such factors as: the explosion of another material, thermal decomposition, blast wave, a contact with a material inducing a rapid chemical reaction (e.g. sodium nitrite).

AN is characterised by a very low level of sensitivity to mechanical stimuli. Heated or combusted in the form of an open charge, it decomposes smoothly. But heating AN in a closed vessel can result in the explosion [5, 6]. Thus, it is recommended not to store AN in durable and tightly closed containers.

AN detonates in the charges with large diameters, and a powerful booster has to be used to initiate the process. Grinding or porosity of AN and placing it in a massive, durable layer considerably facilitate the initiating and the course of detonation. Such AN can detonate in the charges with as a small diameter as just 5 mm (in the above layer), and the maximum measured detonation velocities are ca. 4 km/s [7, 8]. And this fact should be taken into consideration.

The mixtures of AN and flammable materials are the explosives mostly used by the civilian purposes. The most common flammable substances added to ammonium nitrate for this purpose are: mineral oils, powders of light metals, coal, etc. The below table presents the heats of explosion and volumes of post-explosion gases formed during the explosion of AN, and the mixtures of AN and flammable materials calculated in accordance with [9]; oxygen balance of all mixtures equals 0. For comparative purposes, the reference values for standard high explosives such as trinitrotoluene (TNT) and hexogen are also presented.

Table 1

Calculated explosion heat and volume of post-explosion gases for mixtures of ammonium nitrate and flammable materials

Composition of material	Heat of explosion, kJ/kg	Volume of gases, dm³/kg
Ammonium nitrate	1712	992
Ammonium nitrate and wooden dust	3803	952
Ammonium nitrate and coal	3860	924
Ammonium nitrate and mineral oil	4018	986
Ammonium nitrate and aluminium	6744	699
Trinitrotoluene	4587	717
Hexogen	5552	898

The analysis of the above table leads to the conclusion that the addition of flammable materials to AN considerably increases the heat of explosion. The mixtures of AN and wooden dust, coal and mineral oil are characterised by more than two-fold higher values of explosion heats than pure AN. And these values are lower than the explosion heat of TNT barely by between ten and twenty per cent. Even greater heat of explosion was observed for the mixture of AN and aluminium. This value is significantly higher than the heat of explosion of high explosives. The volume of gases formed during the explosion of AN and its mixtures with wooden dust, coal and mineral oil ranges from 900 to 1000 dm³/kg, and it is noticeably higher than the volume of gases formed during the explosion of TNT and hexogen. The volume of gases formed during the explosion of AN and aluminium mixture is slightly lower than the volume of gases formed during the explosion of TNT.

The calculations presented above confirm the facts known from the practice that the addition of flammable materials to AN improves its explosive properties: critical diameter of charges and the size of detonator are reduced with the automatic increase in its working abilities and the detonation velocity. Taking into account the first of the above mentioned parameters, the critical diameter of AN used in the agriculture ranges from 300 to 600 mm; ANFO (mixture of AN and mineral oil) obtained from highly porous AN detonates in the charges with the diameter smaller than 50 mm; ANFOs made from finely grinded AN have even a smaller critical diameter, and the mixture of much more grinded AN and aluminium (ammonal) detonates in the charges with the diameter of ca. 2 mm [10÷13].

Considering the above facts, it can be stated that the mixtures of AN and many flammable materials are relatively powerful explosives which can be easily manufactured. They can be often obtained incidentally, e.g. as the result of contamination.

A threat of accidental explosive of ammonium nitrate

The risk of accidental explosion or fire of AN during its production, storage, transport or application is a real problem confirmed by accidents which are continually happening. The following examples illustrate such incidents:

- Port Neal (USA) 1994 - the explosion of hot, concentrated solution of AN during the start-up of the production installation. This accident caused the death of four persons and huge economic loss. This industrial catastrophe was caused by the failure in complying with the technological regime, which resulted in the uncontrolled development of an exothermic reaction of the decomposition ending in the explosion
- Toulouse (France) 2001 - the explosion of AN stored in the storehouse caused the death of thirty persons and serious injuries of hundreds. The destruction covered the area within a radius of ca. 3 km, and the value of loss was estimated at about 2 billion Euro.

The circumstances of the catastrophe suggested that the thermal explosion had been the direct cause. The reasons for uncontrolled decomposition of AN should be explored in the interaction of additives which contaminated the stored AN
- Mihailesti (Romania) 2004 – a vehicle fire, and then the explosion of transported AN caused the death of 18 persons. The reasons for this accident were not thoroughly explained; however the explosion of high quantities of AN preceded by the long-term exposure to intense fire was repeatedly observed [14].

The destruction of the factory in Toulouse and the explosion effects in Mihailesti are presented in the figures below.

a) http://www.sache.org/files/2005/ChemReacHaz/images/1AZF_Toulouse_sept2001_full_000.jpg 20.01.2012

b) http://zomobo.net/mihailesti 20.01.2012

**Fig. 2. a. Destruction of the factory in Toulouse b) explosion effects in Mihailesti**

The above examples of serious catastrophes caused by the incidental explosions of AN indicate that such events can occur under various circumstances and due to various reasons. Therefore, it is crucial to comply with suitable technological regimes, provisions, instructions, etc on the safety, beginning from the manufacturing stage until the use of such a product.

AN contaminated with flammable materials can be one of possible reasons for the accidental explosion. Many of such mixtures decompose at lower temperatures, and their decomposition is far more rapid than in case of pure AN.

The results of studies on the behaviour of such mixtures during heating performed with the Differential Thermal Analysis (DTA) are presented below. The determinations were conducted with the device DTA 551-Ex of OZM company from the Czech Republic and MEAVY 2.0.0.4 software. The tests were performed under the air atmosphere, the samples were placed in glass crucibles, and silica was used as the reference material.

The materials were prepared by mixing adequate batches of grinded agriculture AN and a flammable component (oxygen balance

for all mixtures was 0) – diesel fuel, wheat flour and aluminium powder were used in the form purchased on the market, whereas hard coal had been previously grinded. The samples of 50 mg mass were investigated, and the rate of temperature increase was 5°C/min. Thermograms for tested materials are illustrated in figures below (the first three "peaks" correspond to consecutive polymorphic phase changes, the fourth peak presents the melting phase of AN and the fifth one presents the decomposition of mixtures); the determined temperatures are presented in Table 2.
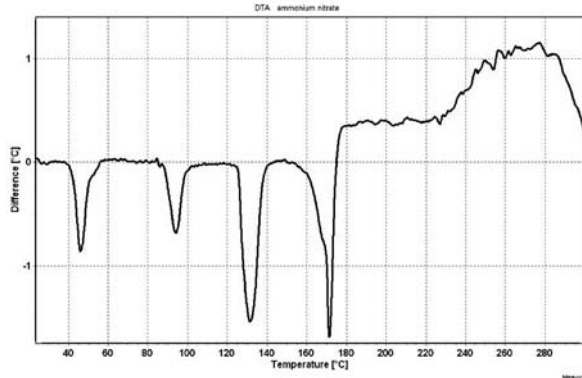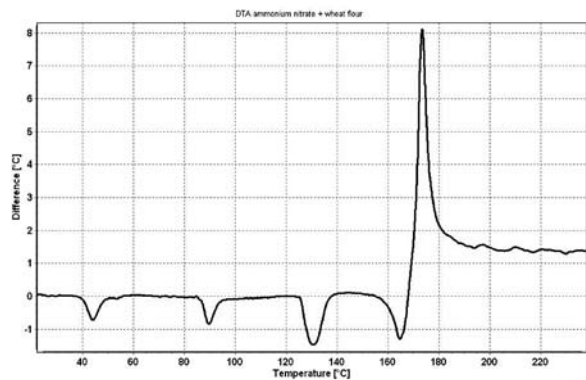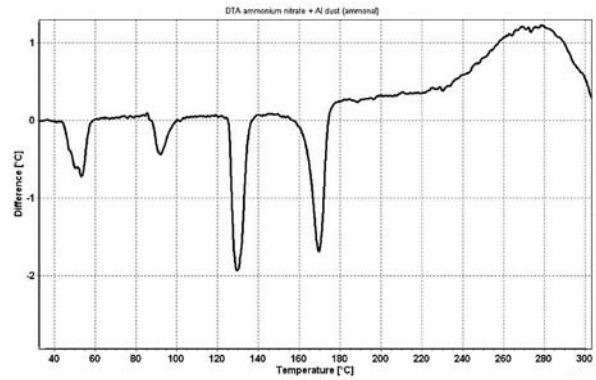

a)
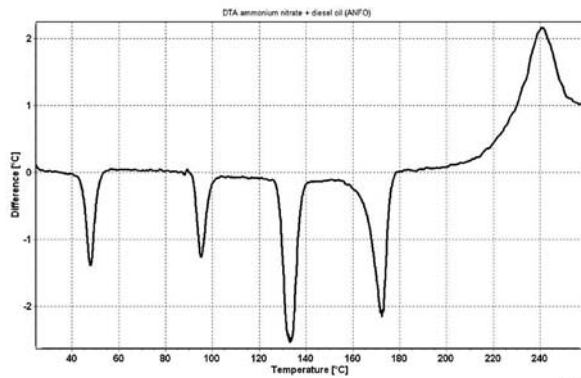
b)
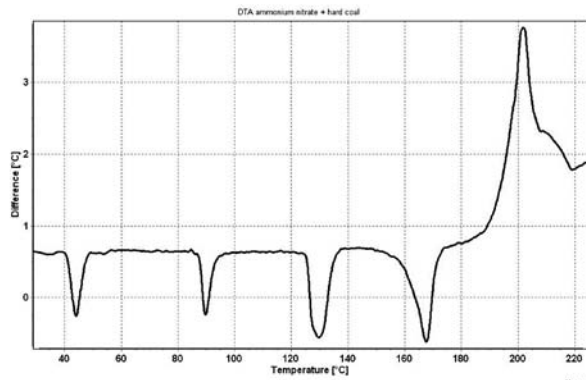
c)

d)

e)

Fig. 3. Thermograms of determinations with DTA technique a)AN, b) ANFO, c) AN and hard coal mixtures, d) AN and wheat flour mixtures, e) ammonal

The following observations can be made from the above graphs:
- AN and ammonal - after the melting phase, the long "plateau" phase takes place, and then the slow decomposition of AN begins
- ANFO – after AN melts, quite a short "plateau" phase takes place, and then faster decomposition of the mixture begins
- AN/hard coal – after AN melts, the fast decomposition of the mixture begins
- AN/wheat flour - the rapid decomposition of the mixture begins during the melting phase of AN.

Table 2

Determined temperatures of decomposition

Material	Decomposition temperature, °C	
	start	"onset"
AN and ammonal	approx. 230 *	approx. 250 *
ANFO	203	227
AN/hard coal	182	196
AN/wheat flour	165	170

* the approximate values of temperatures are presented due to the irregularity of graphs

On the basis of results from determinations in Table 2, it can be concluded that the additives of many flammable substances considerably reduce the temperature of AN decomposition, and the decomposition of such mixtures is faster than in case of pure AN. The determined onset temperature for AN and ammonal is ca. 250°C, for ANFO - 227°C, for AN and hard coal mixture - 196°C, and for AN and flour mixture – just 170°C. Also the start temperature of the decomposition was the highest for AN and ammonal (ca. 230°C), lower for ANFO and the mixture of AN and coal (203°C and 182°C respectively), and the lowest for the mixture of AN and flour - just 165°C.

Taking into account the above results of the calculations for thermodynamic properties (Tab. 1) and the results of tests conducted with DTA technique, it should be stated that the contamination of AN with flammable materials significantly increases the explosive properties and reduces its thermal stability. The contamination of production line with the above materials can lead to the uncontrolled decomposition of AN and consequently to the explosion. It is possible that some fires resulting in the explosion of AN were caused by such factors.

Tests on detonation properties

The detonation properties of the mixtures of AN and flammable materials were determined by investigating the critical diameter and the detonation velocity. The mixtures were prepared as the same way as materials tested by DTA method The applied methods and test results are presented below.

The method for determining the critical diameter

The critical diameter was determined by blasting tested mixtures placed in cylindrical paper tubes. The tubes were placed in a vertical position, on steel witness plates. The lengths of charges were 10 times greater than their diameters (L=10 × d). The sand tamp of 50 mm height was over the tested material. The gradation of tube diameters was about 5 mm, starting from 10 mm, i.e. the charges of 10, 15, 20, 25 mm, etc were tested. The tested materials were initiated with the standard detonators. The test results were evaluated on the basis of the damage level of the witness plate and the charge residues. The whole charge was considered to detonate and the test result was regarded to be positive if the witness plate were perforated and no residues of the charge could be observed. Any other test effect was regarded as negative, that is as the disappearance of the detonation.

The method for measuring the detonation velocity

The detonation velocity was determined while blasting the charges of tested materials placed in steel tubes with the internal diameter of 36 mm and wall thickness of 3 mm. The charges were initiated with a booster made from pressed hexogen of 14 g mass.

Test results

The results from measuring the critical diameter and detonation velocity are shown in the table below.

Table 3

Critical diameters and detonation velocities

Material	Density kg/m³	Critical diameter, mm	Detonation velocity, km/s
AN	826	exceeding 45*	1.65
ANFO	909	35	3.56
AN/hard coal	888	40	2.85
AN/wheat flour	873	45	3.14
Ammonal	670	15	2.95

*- initiation with boosters from pressed hexogen (see above)

The conducted determinations have demonstrated that all tested mixtures are characterised by clear explosion properties and they can detonate. Taking into account the critical diameters of tested materials, they can be arranged in an order from the largest to the smallest ones: AN, AN and wheat flour mixture, AN and hard coal mixture, ANFO and ammonal – their diameters are just more than 45, 45, 40, 35 and 15 mm respectively. Regarding the detonation velocity, AN detonated at the smallest velocity, and the mixture of AN and hard coal, ammonal, the mixture of AN and wheat flour and ANFO detonated at increasing velocities: 1.65, 2.85, 2.95, 3.14 and 3.56 km/s respectively.

The conducted tests indicate that the mixtures of AN and flammable materials have smaller critical diameters and higher detonation velocities than AN. They are sensitive to detonating caps that is they can detonate after being initiated with just a detonator.

The exceptionally high ability to detonate was observed for ammonal which detonated in the charges of 15 mm diameter.

Summary and conclusions

The tests conducted with Differential Thermal Analysis have revealed that the mixtures of AN and liquid hydrocarbons, coal, and cereal grains decompose at much lower temperatures than in case of AN, and some of them, e.g. the ones with cereal grain additives, decompose rapidly.

The performed tests on explosion properties have demonstrated that the tested mixtures of grinded AN and liquid hydrocarbons, coal and cereal grains are characterised by clear explosion properties. Such materials detonate after being initiated with the typical detonator, their critical diameters are within the range 35-45 mm, and the detonation velocities range from 2.8 to 3.6 km/s. The smallest critical diameter was observed for the mixtures of AN and grinded aluminium which detonated in the charges of only 15 mm diameter.

Considering the technical and public safety issues, the compliance with proper procedures related to both the work with AN and the access to it, are of crucial importance. The incidental contamination of AN with flammable materials (as well as many others) can be the reason for the uncontrolled decomposition of AN, and consequently the serious accident. Regarding the threat of terrorist attack, it should be emphasized that AN and many other commonly available products can be used to prepare relatively powerful explosives.

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