

Safety practice

Ammonium nitrate — decomposition, fire and explosive behaviour

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Introduction

Ammonium nitrate (AN) has been produced industrially in significant quantities since the beginning of the last century. A major boost to its production took place nearly a hundred years ago with the invention of the Haber-Bosch process in Germany for making ammonia from atmospheric air, guaranteeing a sustainable supply of low-cost nitrogen compounds like ammonia, nitric acid and urea. Ammonium nitrate has potentially hazardous properties and the associated reactions are complex. In the long history of production and application of AN, these properties have given rise to a number of accidents involving decomposition, fires and explosions^{1,2,3,4}. Some of these accidents unfortunately caused substantial numbers of fatalities —for example, Texas City (1947) which involved a cargo of wax-coated ammonium nitrate fertiliser aboard ships and resulted in uncontrolled fires and explosions. These accidents prompted much research and resulted in the development of safer products, processes, storage and handling practices.

This article explores the potential hazardous properties of ammonium nitrate, significant accidents that have occurred and the storage and handling practices that have been developed as a result.

Keywords: Ammonium nitrate, explosive

Main uses of ammonium nitrate

Tens of millions of tonnes of ammonium nitrate are produced annually worldwide synthetically from ammonia and nitric acid; it seldom occurs as a mineral. Its two main uses are for fertiliser application as a nitrogen (N) nutrient source (pure AN contains 35% N) and as a main raw material for making explosives e.g. AN-fuel oil (ANFO). The fertiliser products are mainly marketed in solid form as prills (spherical shape particles produced from melt by spraying) or granules, typically in 2 to 4 mm diameter size.

The main types of AN based fertilisers include the following range of products:

- AN prills or granules as a straight nitrogen fertiliser with around 34% N
- CAN, mixtures of AN and limestone/dolomite with less than 80% AN (typically 27%N)
- ASN, mixtures of AN with ammonium sulphate (typically 26% N)

- Compound fertilisers, which contain N and at least one other primary nutrient (P or K)
- UAN solution, solution of AN and urea containing typically 30 - 32% N.

The AN prills or granules for fertiliser application are of high density (bulk density in the approximate range of 0.9 to 1.0 g/ml) and low porosity; these characteristics enhance their resistance to detonation i.e. make them very difficult to detonate. It is pertinent to note that in the immediate post war period (1940s) it was practice to coat AN, often of relatively low bulk density, with approximately 0.8–1.0% wax and the product was called Fertiliser Grade AN. This type of product was involved in a few major accidents and is no longer produced; today's fertiliser grades AN (FGAN) are safe in this respect as any organic coating/additive and combustible substance is limited to 0.2% (calculated as carbon).

Ammonium nitrate has always been regarded and classified as an oxidising substance, as by itself it is not sufficiently sensitive to detonation to be classified as an explosive. On mixing with combustible substances, it can give rise to products which are more detonation sensitive and thus are suitable as commercial explosives. The explosive industry uses low density or porous grade AN (commonly known as explosive or industrial grade AN) for making AN-fuel oil (ANFO) explosives; the porous nature facilitates oil absorption, promoting intimate contact between the oil and AN. Porous AN prills can be safely transported to mines and quarries and are mixed on the spot with fuel oil just prior to the blasting operations. This avoids the more hazardous practice of transportation and storage of traditional (more sensitive) explosives and has substantially improved safety — saving many lives in addition to reducing the costs. The explosive grade AN does not generally satisfy the resistance to detonation criterion specified for transport in bulk by sea in the international sea transport regulations and therefore is not transported as a bulk cargo in ships.

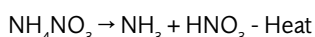
Key properties

AN and all ammonium nitrate-based fertilisers are stable materials under normal conditions, when properly produced, handled and stored; they in themselves present no risk. Under uncontrolled conditions they can give rise to certain hazards including thermal decomposition, fire and, under extreme conditions, explosion^{5,6,7}.

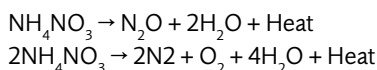
Decomposition

AN decomposes when heated to well above its melting point,

169°C, by way of two main types of reaction. Firstly, the dissociation reaction into its basic raw materials, ammonia and nitric acid vapours; this reaction is reversible, endothermic and vapour-pressure-dependent.



The second type includes a number of exothermic reactions which are irreversible and release gases containing water vapour, oxides of nitrogen and/or nitrogen. For example:



The combined effect of these sets of endothermic and exothermic reactions produces a self-limiting thermal effect up to a certain temperature, provided the gaseous products are able to freely escape. This phenomenon has been theoretically studied and experimentally verified; the studies show that under adiabatic conditions and free escape of gases the self-limiting temperature in pure AN is in the region of 290°C at atmospheric pressure^{8,9}. It is important to note that any adverse condition such as the presence of reactive or catalytic substances and/or confinement of product gases may reduce this temperature, making AN thermally less stable. Under extreme conditions, if the gases are not able to escape, the endothermic effect can become totally suppressed; this can lead to a rapid rise in temperature and explosive behaviour. It is, therefore, important to provide vent to permit reaction gases to escape in fire or uncontrolled heating situations.

Acid conditions and certain substances, notably chlorides and copper, enhance the rate of decomposition in AN.

AN-based fertilisers are thermally stable and are not prone to self-heat dangerously in normal conditions of storage. They require input of external heat to initiate decomposition. Consideration of the potential decomposition hazard is important for AN-based compound fertilisers, which contain chloride e.g. in the form of muriate of potash (MOP, mainly potassium chloride).

In many cases, the decomposition, initiated by an external heat source, will stop when the source is removed. With some fertilisers, however, the decomposition will continue and spread deep into the mass of material even when the heat source is removed. This phenomenon is known as self-sustaining decomposition (SSD), where the decomposition propagates through the mass of the material once initiated. The risk of SSD is therefore higher when the fertiliser is stored or transported in bulk in large quantities compared to bagged material and is affected by a source of heat.

Characteristics of self-sustaining decomposition such as speed of propagation, temperature in the decomposition zone and amount of gases produced, depend on the composition of the fertiliser and on the extent of melting at the decomposition temperature. The presence of compounds of trace elements such as copper can increase the decomposition rate. It is important, therefore, to be aware of this hazard and assess the product safety before and when adding micronutrients and other additives.

An official test, known as the Trough test¹⁰ is used to determine the SSD behaviour and to measure the speed of propagation.

Fire hazard

AN itself is not combustible, but as an oxidising substance, it can support combustion. Thus, it can intensify or sustain a fire in a combustible material even in the absence of atmospheric air/oxygen. AN reacts with many organic and combustible substances in exothermic ways.

The capability to intensify a fire depends not only on the AN content of, for example, a fertiliser but also on the nature of other components which may be present in such a fire and which may have a catalytic or thermal effect on the decomposition of AN.

Explosion hazard

AN can give rise to an explosion by way of rapid decomposition, causing pressure-build-up, or a detonation.

AN based fertiliser is difficult to detonate as it is manufactured to have a high resistance to detonation and thus requires very energetic shocks. In addition, its critical charge diameter is large, making it difficult to achieve a sustained detonation in practice. Neither flame, spark, nor friction can cause a detonation. If not properly handled, a number of factors can decrease this resistance — these include contamination with incompatible substances, reduced particle size, increase in temperature and thermal cycling (which increases the porosity and causes breakdown of the prill or granule structure). In practice, most products contain additives to give good anti-caking properties and thermal stability.

Based on the known causes of accidents with AN and related investigations, four main mechanisms for initiating an explosion or detonation in AN can be identified:

- i. Shock initiation by another explosive: An explosive detonating close to a large enough heap of AN could initiate a detonation or cause a sympathetic detonation in AN; the initiating energy required is very large and very unlikely to be available in normal industrial operations¹¹. Use of explosives to break-up badly caked fertiliser and storage of explosives near AN have been banned after some serious accidents several decades ago; most notable being the one in Oppau, Germany (1921) when caked fertiliser based on ammonium nitrate and ammonium sulphate detonated as blasting explosive was used to break it up.
- ii. Shock initiation by a high velocity projectile: Initiation by impact from a high velocity projectile is more difficult than shock initiation by another explosive; the fertiliser would need to be at significantly higher temperatures, molten or contaminated. Very high velocities (hundreds of m/s) may be necessary to initiate a detonation in foreseeable emergency situations.

High velocity projectiles can be generated in a fire when AN based fertiliser is confined, is heated and then violently decomposes inside hollow sections of equipment such as conveyor rollers, screw conveyors or components of loading equipment e.g. shovels. These projectiles would not have sufficient energy to initiate a detonation in normal solid products, but molten and/or contaminated fertiliser will be more susceptible. Investigations^{12,13} have shown that roof beams or building structures which may collapse in a severe fire are very unlikely to have sufficient impact energy to initiate a detonation even in molten decomposing fertiliser.

- iii. Deflagration-to-Detonation transition: This is popularly known as DDT. Deflagration is a rapid burning process whereas in a detonation a supersonic shock wave is generated. During a deflagration, the chemical reaction zone travels from one particle of the substance to another by thermal conduction and convection. In detonation the propagation is by a hydrodynamic shock, which when strong enough can preheat the material and cause a very fast reaction. Under certain conditions a rapid deflagration can become supersonic and thus can develop into a detonation. Investigations carried out by the US Bureau of Mines¹⁴ concluded that the conditions of pressure and temperature necessary to achieve DDT in free-flowing beds of uncontaminated AN or AN mixed with oil are extreme and are very unlikely to be met in practice in foreseeable emergency situations.
- iv. Heating under severe confinement: According to the work carried out at the US Bureau of Mines¹⁵ to trigger a detonation by heat and confinement of AN hot melt, the pressure needed is high, at least a few hundred psi. An explosion can, however, take place due to pressure build-up by the decomposition gases in the confined space causing a rupture of the equipment or vessel containing the material. Most accidental ruptures in equipment have been due to overpressure rather than the detonation.

An additional mechanism also exists — reactions with a highly reactive substance. In theory, certain substances can react very rapidly and energetically with AN on mixing, leading to the development of a detonation. It is very unlikely that in typical fertiliser production or storage operations any such material will find its way and cause an explosion.

Learning from accidents

Prior to around 1950, fertiliser products suffered from severe caking problems. The remedial measures then taken such as the use of explosives to break-up caked mass or application of wax-coating to AN prills/granules led to major accidents with hundreds of fatalities e.g. the Oppau tragedy in Germany (1921) and the ship disaster in Texas City (1947). In the former, explosives were used to break-up caked fertiliser and in the latter waxed coated fertiliser in paper bags was involved. Development of safer products and implementation of safer practices followed, which improved safety substantially and gave a major boost to the AN fertiliser industry, with production of more than a billion tonnes of AN as fertiliser in the years that followed. Unfortunately, during this period, several accidents with AN have happened — some major. Systematic reviews have been carried out for further learning^{4, 16, 17, 18}.

It is important to be aware that a fire incident involving AN does not readily escalate into an explosion. There have been many incidents of fire which have not developed into explosion; they either burnt out without escalation or were successfully controlled. Another important point to note is that in most explosions, much of the forensic evidence is destroyed, making reliable investigations into cause identification very difficult.

Some of the notable explosion incidents relating to modern production or storage operations are summarised below.

Terra Industries, Sioux City, USA (1994)

An explosion occurred in an AN neutraliser (reactor) as the plant was about to be restarted after being off-line for some days. The blast caused major damage to other plants on the site including ammonia tanks. Four employees were killed by the effects of the explosion. There has been controversy as to the basic causes.

Grande Paroisse, Toulouse, France (2001)

An explosion took place in a heap of reject material from two AN production plants, one for fertiliser grade AN and the other for technical (porous) grade. There were 30 fatalities, many injuries and substantial damage to the plants on the site and properties in the neighbourhood. No fire took place prior to the explosion and the AN involved was not a saleable product. The legal case relating to this incident is still on-going, where the likely cause remains under debate. Recognising a need, the fertiliser industry developed detailed guidance for safe management of reject material¹⁹.

West Fertilizer Company, West, USA (2013)

A substantial fire led to an explosion at a fertiliser blending plant and retail facility. The violent detonation fatally injured twelve emergency responders and three members of the public. It caused wide spread damage in the village. Fertiliser AN was stored in wooden bins. In its investigation report²⁰, the Chemical Safety Board of USA reported a number of key findings, including that the presence of combustible materials used for construction of the facility and the fertiliser grade ammonium nitrate (FGAN) storage bins, in addition to the practice of storing combustibles near the FGAN pile, contributed to the progression and intensity of the fire and likely resulted in the detonation. Further that the facility did not have a fire detection system to alert emergency responders or an automatic sprinkler system to extinguish the fire at an earlier stage of the incident. The legal case relating to this accident is still on-going as this article is prepared.

Cherokee Nitrogen, USA (1973)

A fire led to an explosion in the storage building on a production site. This incident is described in more detail below as it brings out a number of learning points. There were no fatalities or major injuries. It was investigated by a task force of experts and the following summary is based on their published findings²¹.

The Cherokee Nitrogen complex consisted of an anhydrous ammonia plant, a nitric acid plant, a high density AN fertiliser plant, a urea plant and storage facilities. The AN prills were delivered to the warehouse by a conveyor belt and were removed from the storage by another conveyor which was loaded by a propane-fuelled front-end loader in combination with a movable hopper. The main frames of the AN bulk storage building were constructed of laminated wood beams with wood purlins and steel attachments. The ends of the warehouse and the roof deck were sheathed with plywood and had an exterior covering of a layer of polyethylene film and aluminium sheeting. The floor was made of concrete.

A fire started in the bulk AN warehouse. When an alarm sounded in the control room two of the operators went first

to the bagging building to check and followed the product conveyor toward the bulk storage building. They saw flames coming from the direction of the bulk storage and noticed that the conveyor belt was slack suggesting belt failure or, more likely, burnt through. Fire hoses from water hydrants were applied but the water pressure was insufficient to get water to the roof line. The top of the building had burnt through and the fire was spreading to side walls. Fire-fighting efforts proved ineffective. About 25 minutes after the fire was discovered, an explosion occurred. Witnesses reported one small explosion followed by a major blast. Pieces of aluminium sheeting, partially burnt plywood and fragments of steel frame were scattered over the nearby area. A long and shallow trough (crater) was formed in the work aisle of the front-end loader. It is believed this area had compacted deposits of contaminated AN.

The likely source of ignition was believed to be either frictional heat from a roller setting the conveyor belt on fire, or leaking hydraulic oil coming into contact with the hot exhaust system on the front-end loader. The fire quickly spread to the wood and other combustible materials used in the construction. It is postulated that oil that leaked from the front loader on occasions, might have mixed with AN and formed compacted deposits on the floor near the front loader. With the heat of the fire this could produce molten contaminated AN.

Some rollers associated with the conveyors had shown signs of becoming filled with AN. These or other parts that become filled with AN, when heated in fire could violently rupture or explode due to pressure build up from gases resulting from the decomposition of AN. This could have become the booster for the fine, hot and contaminated AN on the floor in the area of the conveyor and the front-end loader.

From analyses of the damage caused, crude estimates of the amount of AN that detonated ranged around three to nine tonnes. It is important to note that the large bulk heap containing several thousand tons of AN nearby did not detonate — in this bulk heap AN had simply melted on the surface due to the fire.

Several recommendations were made, most of which are included in the following section.

Best practices for safe operations

Based on the knowledge and understanding of the properties of AN and learning from accidents, the fertiliser industry has developed several guidance documents for safe operations; these are free to download from Fertilizers Europe's website: www.fertilizerseurope.com

A number of guidance documents for storage have been published e.g. in UK, USA and Australia.

Examples of recommended best practices include:

- Keep fertilisers away from fire, flames or other heat and ignition sources.
- Do not store fertilisers near combustible materials.
- Prevent contamination by foreign matter of any kind but particularly combustible matter, (elemental) sulphur, farm chemicals such as weed-killers, organic materials, oils and greases, acids and alkalis. Bearing in mind that bulk material can be more prone to contamination than the

packaged product, special care should be taken with bulk AN. In the European Union regulations are in place to require the supply of high-N AN fertiliser to the final users in packaged form only.

- Do not store near explosives or other potential sources of strong shocks.
- Do not use explosives to break up caked fertiliser.
- Take special care in the selection, use and maintenance of front loaders, etc. when handling bulk AN to avoid contamination from oil leaks, etc.
- Avoid trapping of AN fertiliser in areas such as equipment, loading vehicles and plant/building structural elements.
- Observe fire precautions.
- Fire-fighting — if ammonium nitrate-based fertilisers are involved, do not use chemical extinguishers, foam or sand. Attempts to smother a fire are useless and potentially hazardous. In particular, never try to smother the fire with steam. Use plenty of water. Avoid breathing the fumes — they can be toxic. If the fire becomes uncontrollable and engulfs substantial quantities of AN, consider evacuation of all personnel.
- Prevent the combination of heat and severe confinement.
- Secure stores and associated vehicles against unauthorised access.
- Avoid moisture uptake.
- Adhere to good housekeeping practices.

Concluding remarks

This article describes the main properties of ammonium nitrate fertiliser and some of the main explosion incidents involving the modern product or process. It summarises current best practices which have been developed from the understanding of the potentially hazardous properties and the learning from accidents. Ammonium nitrate provides important plant nutrient in a very efficient way; ammonium nitrate based fertilisers, therefore, play an important role in agriculture. Handled correctly these are safe and effective products.

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