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SAFETY ASPECTS OF AMMONIUM NITRATE FERTILIZERS (a)

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1. Summary

This paper describes the potential hazards of ammonium nitrate and ammonium nitrate based fertilisers. It gives an historical perspective of the uses and development of safe process technologies and safe products. It reviews significant accidents of the past hundred years or so and their impact on industrial practices, bringing out main learning points. It describes some of the main safety related control systems, engineering design aspects and operational procedures, which can be applied or incorporated to control potential hazards of ammonium nitrate.

2. Introduction

Ammonium Nitrate (AN) is an important source of fertiliser nitrogen in Europe, North America and the former Soviet Union; with annual production in the region of 18 million tes. Ammonium nitrate is also an important base material for widely used explosive (blasting agent) ammonium nitrate fuel oil, ANFO. These two applications have been in practice for more than 50 years. Thus AN is an important chemical product. Over the last 100 years or so, significant developments have taken place in its process technology, product quality, safety related characteristics and uses. Unfortunately a number of accidents have happened during this period, some of which were major with much loss of life and property damage. This makes safety of ammonium nitrate a very important issue. This paper discusses the main uses of AN, its potential hazards, safety principles and the practical control measures to take.

3. Historical Perspective

Ammonium nitrate does not occur naturally in mineral form, it is produced synthetically. Although it was first chemically produced more than 300 years ago, its uses developed in a major way when its production technology took a step change in the period 1910-1920. Prior to this, it was produced from nitric acid derived from Chilean saltpetre (sodium nitrate) and aqueous ammonia solution, a by-product from gas/coke ovens. The successful development of the Haber-Bosch process for ammonia production and air-oxidation of ammonia for nitric acid made it possible to produce substantial quantities of AN of high purity at much reduced costs. This gave a major boost to its agricultural use [1].

The use of AN in the explosives industry in the early period was as a replacement for potassium nitrate as an oxidizer. Later dynamite type explosives based on AN were developed. After World War II its use in making ammonium nitrate fuel oil, ANFO, as a blasting agent in the mining industry developed in a major way. The on-site mixing of AN with fuel oil at the point of application removed the need to transport more sensitive and

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hazardous explosives; thus improving safety significantly. The introduction of ANFO had a major effect on the nature of the explosives industry.

In the agricultural field, AN had a similar impact. AN provides fertilizer nitrogen in two forms; quick acting nitrate and slow acting ammonium. In the northern European climatic and soil conditions it is considered to be more efficient and environmentally friendly than urea, which suffers significant losses of ammonia to atmosphere. In the 1910-20 period mixtures of AN with ammonium sulphate (AS) and AN with limestone were produced as commercial fertilizers. The AN/AS mixtures caked badly and explosives were used to break-up heaps; this practice resulted in the Oppau tragedy (see Table 1). When World War II was over, the AN plants in the US which were producing it for ammunition purposes, started applying wax to straight AN to prevent caking and selling the product for agricultural use; this practice led to the disastrous accident of Texas City in 1947 (see Table 1)[2].

The subsequent development of safe anti-caking treatment and prilling process, coupled with clearer guidance for safe practices helped to boost the large-scale production of high density AN as prills or granules and its use as a nitrogen fertiliser more than 50 years ago. The product has high resistance to detonation and its safety record has been excellent.

The main fertiliser products based on AN, which have been in use in modern times are:

Prilled or granulated AN, > 33.5% N.

CAN: AN mixed with limestone, typically 28% N maximum (i.e. 80% AN).

NPK fertiliser based on AN.

UAN solution – aqueous solution of AN and urea.

This prilling process also enables large-scale production of low density porous AN prills for making ANFO explosives. The porous nature facilitates oil absorption and enhances its sensitivity to detonation.

4. Properties and Potential Hazards

4.1 Physical Properties

AN possesses complex physical and chemical properties. Those, which have a bearing on safety, are briefly discussed below.

AN melts at 169°C, a relatively low temperature and is very hygroscopic. It cakes readily; particularly when handled in bulk and exposed to atmosphere. It needs an effective anti-caking treatment.

It exists in various crystalline forms depending on the temperature, as shown in Figure 1 [3]. The transition at 32°C is accompanied by a significant volume change; consequently repeated thermal cycling across this temperature causes physical breakdown of the prills/granules, unless they have been treated for thermal stability.

Suitable technologies have been developed to overcome the above problems, e.g. the addition of a small amount of magnesium nitrate and other proprietary agents such as sulphonates that can prevent caking and provide thermal stability.

In the manufacturing process, a hot concentrated solution of AN is produced and handled; this can give rise to the physical hazard of serious burns to operators if contacted, e.g. when cleaning a choked line or by solution leaking/spraying. Choked lines can also give rise to risk of uncontrolled decomposition as discussed later in section 3.5

4.2 Chemical Hazards

The three main potential hazards of relevance are: Fire.
Decomposition.
Explosion.

These are discussed below.

4.3 Fire Hazard

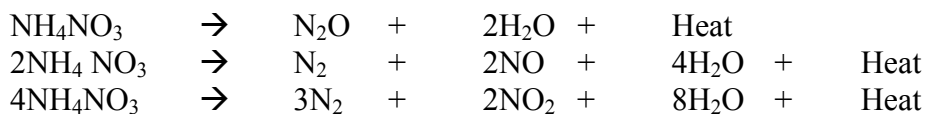
AN is an oxidiser; it can therefore support combustion even in the absence of air. It can help to initiate and intensify a fire. The important point to note is that AN itself is not combustible. Therefore, presence of a combustible substance and a source of heat are essential for the fire hazard to materialise. Toxic fumes containing NO_x are given off.

Hot AN solution as well as solid AN can present a fire hazard. Hot AN solution can initiate fire in rags, wooden articles etc. Clothing impregnated with AN and left on hot surfaces can also ignite given sufficient time.

Fires involving AN cannot be extinguished by the exclusion of air, because AN can provide the oxygen for combustion. Water has been found effective in fighting fires involving AN.

4.4 Decomposition Hazard

On heating beyond its melting point, AN decomposes in a number of different ways; giving off toxic fumes containing gases such as N₂O, NO, NO₂, N₂ and H₂O. The nature of reaction and the composition of product gases depend on temperature and other factors.



These reactions are exothermic and irreversible. AN also dissociates by the following reaction which is reversible, endothermic and dependent on vapour pressure.



The combined effect of the exothermic decomposition and endothermic dissociation can give rise to the so-called Steady State Reaction Temperature provided the product gases can escape freely [4]. At atmospheric pressure, this temperature has been found to be in the region of 292°C. Clearly, if the gases are not allowed to escape, the reversible dissociation stops, and with it the endothermic effect. The exothermic effect begins to dominate, which can cause a run-away decomposition to develop, leading to explosive behaviour. This phenomenon explains why heating AN in confinement can lead to an explosion.

A number of substances such as chloride, acids, chromates, zinc and copper have a strong catalytic effect on the decomposition [5, 6].

The decomposition of AN is suppressed or prevented by an alkaline condition. Thus, addition of ammonia offers a major safeguard against the decomposition hazard.

Certain compound (NPK) fertilizers based on AN and potash (a source of chloride) can present a self-sustaining type decomposition hazard. Once initiated by a hot source, the fertilizer continues to decompose with the reaction front moving at a characteristic speed or velocity depending on its composition, releasing relatively large amounts of toxic fumes. A special trough test has been developed to study this phenomenon and measure the speed. The results are normally plotted on a triangulation diagram showing the hazardous area.

4.5 Explosion Hazard

AN can present an explosion hazard by three different mechanisms:

By shock initiation by another explosive or mechanical impact, leading to detonation.

By heating under confinement.

By self-heating due to thermal decomposition leading to runaway.

Sensitivity to shock initiation increases with temperature, presence of combustible or reactive substances and presence of voids or bubbles. Low density AN being porous in nature is significantly more sensitive than the high density fertilizer grade AN [7]. Impact by falling objects is generally not energetic enough to initiate a detonation. Tragic accidents of Oppau and Tessenderloo are examples of initiation by high explosives, which were used to break up badly caked fertilizer – this unsafe practice has been abandoned.

Of the above-mentioned three mechanisms, heating under confinement is the most likely cause in an industrial environment. Actions such as welding on hollow sections containing AN, the application of steam to clear lines blocked by crystallised AN and the pumping of AN solution against blocked exits can lead to explosive decomposition/run-away. Conditions of pressure and temperature necessary to achieve detonation are severe [8] and not easily met by this mechanism.

Thermal decomposition in a bulk heap of AN or in AN solution, can in theory lead to self-heating and run-away. However, in practice, it is difficult to achieve this with pure AN. Presence of reactive contaminants or substances with strong catalytic effect can possibly lead to significant exothermic effect, developing into a run-away.

5. Past Accidents and their Impact

A number of reports have been produced, surveying the accidents, which have occurred over the past 100 years or so [9, 10]. A detailed analysis of accidents, which focus on production and industrial storage with points of learning has recently been published [11].

The history of accidents shows a break point around the beginning of the 1950^s. In the period 1910-1950 the production of AN-related products and their applications were increasing rapidly; but the necessary reliable technology for anti-caking treatment and detailed guidance for safe storage and transportation did not develop hand-in-hand. Consequently, some serious

accidents occurred with much loss of life. Useful research and investigation was then carried-out, which led to safer technology and effective guidance. Post 1950, we see a marked improvement in the accident record despite substantial increase in the tonnages produced. Some of the noteworthy accidents are listed in Table 1. The main safety lessons learnt from these accidents are summarised in the next section.

The recent major explosion in Toulouse (21 Sept. 2001) will impact on the AN industry. The factory produced fertilizer grade and low-density/porous explosive (ANFO) grade prilled products in two separate units. Reject/off-spec materials and fines from the two processes together with reject products returned by customers and other sub-standard AN materials were reportedly stored in a bulk heap. There have also been speculative press reports of presence of contamination. This heap containing about 300-400 tes of these mixed materials detonated, causing 30 fatalities (some off-site) and widespread damage to property on-site and in the surrounding area. The trigger mechanism, which caused the heap to detonate, is not known, although a number of possibilities are being investigated [12].

As a consequence of this tragedy, regulatory authorities are tightening up controls over the production and storage of AN. The industry via the European Fertilizers Manufacturers Association (EFMA) has produced a guidance for the safe handling and management of reject materials. It is also revising the existing (EFMA) guidance on storage and handling of AN fertilizers. The EU Commission has proposed to bring 'reject' AN material into the scope of the Seveso Directive at low thresholds. At national level, the authorities are seeking more effective compliance of the existing safety rules and guidance.

It is inevitable that the Toulouse tragedy will have an impact on the whole of the chemical industry in Europe.

6. Learning points and Safety Guidance

The past accidents, investigations and research have provided much useful information and learning points [11]. Some of the main safety points are summarised below; the coverage is not comprehensive.

6.1 Avoidance of Contamination

Precautions should be taken to avoid contaminating the process as well as product e.g. by oil in ammonia, oil/grease from equipment, cross-contamination with other stored products, recycling of product coated with organic agents; materials/tools left in vessels during overhauls etc.

6.2 Presence of Combustible Materials

Use of such materials should be avoided in the construction of plants and stores, and good housekeeping controls/standards should be maintained to prevent combustible materials coming into contact with AN.

6.3 Heating Under Confinement

This can arise in several ways e.g. pumping against dead-end, the friction heat in pump, steam input to clear an AN blockage in a line, injection of live steam into AN melt filters without adequate venting provision, removing bolts by burning, welding on hollow sections containing AN fertilizer etc.

Avoidance of the above requires the provision of correct procedures, good training and a high level of awareness.

6.4 Pumping Operation

External centrifugal type pumps handling hot AN or UAN solution deserve special attention. Unsafe conditions can arise due to the lack of flow, failure of the gland seal water causing overheating, mechanical failure leading to friction heat, ingress of contamination etc.

Protective systems can be provided such as alarm/trip based on high temperature of the pump casing, elimination of valves in lines, alarms for the failure of gland seal water, thrower plates on pump-shafts to prevent migration of oil from gearboxes, low flow alarms etc.

6.5 Control of Decomposition and Run-Away

Abnormal acid condition, the presence of contaminants and the input of heat raising temperature beyond design can potentially give rise to an uncontrolled decomposition. The control measures include the addition of ammonia to produce an alkaline condition, well instrumented control systems, reliable pH measurement, multipoint temperature measurement with high-temperature-based trip systems, automatic water drenching facility etc. Special care must be taken for plant start-ups, shutdowns and off-line situations, ensuring that process conditions continue to be monitored and protective systems remaining operable and live.

7. Concluding Remarks

The manufacture, distribution and use of ammonium nitrate based fertilizers and porous grade AN for the explosives industry is a mature industry, with much knowledge and understanding accumulated over many years. Following the introduction of better technology and safety related controls in the early 50^s the AN-based fertilizer industry has flourished over the last five decades with a very good safety record against an annual world production in excess of 20 million tes.

Concerning the Toulouse disaster it is important to note that the heap which exploded was not made up of fertiliser grade AN; it contained more sensitive porous grade AN, fines, reject and similar materials. Although the exact cause is not known; it has identified certain areas, where further safety controls are required. The industry has addressed these issues to prevent a similar accident happening again.

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Table 1: Summaries of some selected accidents [11]

Date Location	Description
1921 Oppau, Germany	Caked AN-AS fertiliser detonated when blasting explosive used to break it up. 509 fatalities.
1942 Tessenderloo, Belgium	Use of blasting explosive led to a detonation in AN pile. > 100 fatalities
1947 Texas City, Texas, USA	Wax-coated AN cargo in two ships exploded following a major fire > 600 fatalities.
Jan 1963 Finland	A violent explosion occurred in ca 8 te molten AN in a mixing tank. Likely causes include: uneven feeding of organic anti-caking agent (sodium dodecyl benzene sulphonate) to mixing tank and failure of steam control system leading to overheating. Plant extensively damaged. Ten people killed and sixteen injured.
Mar 1967 Holland	Welding work caused rupture of a hollow screw conveyor shaft. Fertiliser deposits suspected to be present in the screw. 2 killed.
Oct 1967 USA	A rail box-car, made of steel with a wooden interior and carrying 50 tes AN in paper bags caught fire. The fire was left to burn out. Large crusted mass of AN left. No explosion.
May 1972 France	Lagging on a road tanker carrying 20 te of hot AN solution (92.5%, 135-140°C) started decomposing and then exploded. Hot AN solution sprayed on the driver and another person who had come to help, both died later in hospital. Reaction of AN with organic contamination in lagging suspected.
Jan 1973 USA	A severe fire started in a store near plant holding about 14,000 te of high density AN prills and intensified, quickly assisted by wooden structure and possibly by release of propane from failed fuel tank on payloader under the influence of heat. An explosion followed, probably initiated by an explosion of crank case or the transmission or a conveyor roller filled with AN. A long but shallow crater was formed. The explosion caused some plant damage. Significant that the bulk heap did not detonate.
June 1975 Germany	Welding operation initiated self-sustaining decomposition in bulk NPK fertilisers in a store. Approximately 1,000 residents evacuated and 67 held for observation in hospital.
Dec 1976 Norway	Rapid decomposition occurred in a mixing vessel for potash and AN-AP melt (150°C) prior to prilling, when pump failed. Excess potash caused solid crust. Delay in stopping mixing device resulted in further heat input. Pressure build up caused deformation of mixing vessel.
Apr 1978 Canada	Rapid decomposition took place in a filter for hot conc (96%) AN melt when it was off-line and being steam cleaned. The gasket was blown off by pressure build up. Organic contamination from recycled AN suspected.
1979 UK	Bolts were being removed by burning from an NPK cooler when a bolt ejected with a loud bang. A small amount of fertiliser trapped between the shell and the bolt is believed to have undergone rapid thermal decomposition.
Oct 1982 UK	A major fire broke out in wooden furniture stored with AN fertilisers. It spread quickly, releasing dense cloud of smoke. Between 750 and 1,000 people were evacuated. No one was significantly affected by nitrous fumes. A series of low order explosions (deflagrations) took place, believed to be due to reactions between potassium nitrate and nearby stacks of charcoal.
Sep 1984 Canada	An AN melt line became blocked during a shut-down and was being freed using live steam when an explosion occurred in a 50 ft section of the steam jacketed line. Building damaged. No one injured.
1985 Canada	AN melt overflowing from a pumping tank initiated a fire in a scaffolding plank left above the tank.
Oct 1987 France	A major self-sustaining decomposition started in a bulk store holding 1,450 te NPK, 750 te AN and 150 te urea, probably caused by an electrical fault. Release of toxic fumes caused evacuation of more than 20,000 local residents. No one injured. Some pollution of the nearby river from the contaminated fire water run off.
Aug 1989UK	An NPK plant drier fan impeller was being stress relieved by heating in a furnace after welding repairs when an explosive decomposition took place. The hub section was distorted. AN fertiliser dust trapped in the confined volume in the hub may have entered through a 3 mm hole in the hub. No one was injured.
Dec 1994 USA	A major explosion occurred in an AN neutraliser and associated plant 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. The ammonia cloud caused evacuation of 2,500 people. Four employees were killed by the effects of the explosion.
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Figure 1
Crystalline Forms of Ammonium

