Ammonium Nitrate – An overview for its safe storage and handling

By

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Ammonium nitrate (AN) is a naturally occurring chemical compound that was extracted from the earth in the past. It was successfully synthesized in the lab by Glauber in 1659 and not until the first industrial scale manufacture of ammonia in 1913 was its industrial synthesis enabled. Today the chemical is industrially manufactured and used primarily in agriculture (~75-80%) as a source of nitrogen and industrially for the manufacture of commercial-grade explosives (~15-20%); the remaining 2-5% is used in specialised technical applications, such as the generation of nitrous oxide gas. Globally approximately 85 million te AN are produced with more than half of it sold as pure or nearly pure (+90%) AN in the product.

This article is about the safety related to ammonium nitrate in handling and storage, focusing on technical grade ammonium nitrate (TGAN), which in this context is any ammonium nitrate not used in agriculture. The SAFEX Good Practice Guide (GPG) on technical grade ammonium nitrate storage details the necessary steps and controls for the safe storage of this product.

Manufacture

AN is manufactured by the neutralization of nitric acid with ammonia. AN plants typically have their own nitric acid plants. The principal raw material is ammonia, which is either produced locally or imported. Ammonia is commonly produced out of natural gas, air and water. Ammonia is commonly produced out of natural gas (coal and naphtha are also used in some countries)[1], air and water. AN is made by the neutralization of nitric acid and ammonia, with nitric acid itself being produced out of ammonia and air. The neutralized solution containing AN and water is concentrated before being converted into solids through a prilling tower or granulation process. The solid AN is further processed, depending on the plant and the intended grade, through different steps such as drying, screening, cooling, coating. TGAN (technical grade AN) is normally a prilled product, and FGAN (fertilizer grade AN) is normally either prilled (1 to 4mm diameter) or granulated, granules being slightly larger (2 to 5mm diameter).

AN is produced in large plants or industrial sites, typically 100 to 2,000 tonnes/day for TGAN, and typically 500 to 5,000 tonnes/day for FGAN and require warehouses in accordance with these scales. FGAN storages are typically larger than TGAN because of the scale of production and the seasonal demand of agriculture.

Properties

Pure AN is a stable compound with a melting point of 170°C. It is classified as an oxidizer, Division 5.1 substance, for transport provided it meets the requirements of the testing regime of the UN Manual of Tests and Criteria. Although it does not burn it will readily support combustion. It is a hygroscopic compound. The solid has five crystalline phases (Figure 1.) that are temperature dependent (Keleti). These

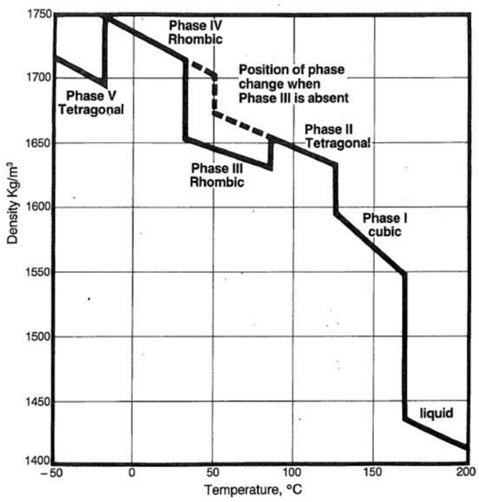

Fig. 1 Density changes in phase transitions of ammonium nitrate.

[1] There are several projects to manufacture ¨green ammonia¨ where hydroge
hydrocarbons´ reforming is not required. In such a process, especially if electri
ammonia synthesis does not emit any CO_2.

crystalline phases pose unique challenges to the storage of AN. At 32°C, a temperature reached in many parts of the globe, the AN that transitions through this temperature undergoes a 3.7% volume change, and on cycling through this temperature results in degradation of the structure of this prill.

Temperature cycling coupled with the hygroscopic nature of AN results in caking of the product when stored over extended periods. Hence on storage, even prolonged storage, the AN remains unchanged chemically, but its physical form may be altered depending on the temperature and humidity conditions.

Manufacturers use various internal additives and coating agents, at levels of ten to hundred parts per million, to mitigate these deleterious effects and, combined with good storage practices preserve the physical quality of the product.

Hazards

AN is a stable compound under normal storage and handling conditions. However, if involved in a fire, large amounts of toxic gases will be generated, and the fire will be enhanced by the AN because it is an oxidizer. Ultimately explosion is its worst-case hazard. AN is a dangerous good and the controls for its safe storage must be strictly in place.

Contaminated AN or off-spec AN cannot be considered as AN and must be handled specifically, as their inherent risks can be disproportionally high compared to pure AN. For example, AN spillage on the ground soiled with fuel traces can become a Class 1 substance – an explosive – which highlights the importance of proper handling and good housekeeping standards.

The most common threat is fire and its uncontrolled consequences, in particular if AN is co-stored with incompatible goods such as flammable or combustible materials. Exposed to fire, solid AN will melt at 170°C and support combustion even in the absence of atmospheric oxygen. Contamination with incompatible material such as chlorine compounds, acids or some metal salts may lower the decomposition temperature of molten AN significantly and support a potential run-away reaction. On prolonged exposure to fire AN will start decomposing becoming a shock-sensitive mixture. The decomposing melt can also progress to a thermal explosion if confined; or form explosives mixtures with incompatible materials in proximity, such as fuels, organics, metal powder, molten aluminum, etc.

AN is classified as a dangerous good, specifically a Division 5.1 substance i.e. an oxidizer. In normal storage, transport, handling and use AN is very stable: it is insensitive to friction, impact, and static discharges. When exposed to major insults and under very abnormal conditions such as shock, heat, and contamination it can however explode and hence the institution of controls, as specified in the GPG will prevent such an event from occurring.

Since AN can be shock-initiated, it needs be included in estimating the Net Explosives Quantity when it is stored next to Class 1 products. Due to its relative low sensitivity, some competent authorities require it is included as an acceptor only.

Manufacturers must ensure sound product stewardship is in place to prevent people forgetting the hazards of AN throughout its lifecycle: from manufacture, storage, transport, use, and where necessary disposal, and to develop and maintain safe practices.

The industrial accidents described below highlight the effect of these threats on AN.

I. Oppau (Shock initiation)

One of the most cited industrial accidents involving AN is that at the BASF plant in Oppau, Germany in 1921 (Wikipedia, 2020). The practice of breaking up masses of caked fertilizers using dynamite was common, and prior to the mass explosion on September 21 was estimated to have taken place approximately 20,000 times. The product manufactured was a mixture of ammonium sulphate and ammonium nitrate, nominally a 50:50 mix. It is possible that the composition was not uniform and that some areas in the pile were more concentrated in AN (Medard, 1987). The initiation was clearly by shock. The explosion destroyed the plant, with a fatality count of 500-600 people with about 2,000 more injured. The use of explosives to disaggregate caked fertilizers and AN was strictly forbidden although a similar event occurred in 1942 in Tessenderloo where disaggregation with explosives resulted in an explosion that killed 189 people (Wikipedia, 2020).

II. Toulouse (Chemical contamination)

The only known industrial accident where chemical contamination was a root cause took place at the AZF fertilizer plant in Toulouse France on September 21, 2001(Wikipedia, 2020). The explosion occurred in a warehouse which was used as a temporary storage for off-spec AN. These materials were intended to be recycled in AN-based binary or ternary fertilizer processes (Nicolas Dechy, 2004). The mass involved was approximately 400 tons. INERIS estimated that the TNT equivalent of the explosion was in the range 20 to 40 tons. There were 30 fatalities and over 2,000 people injured. While the original cause of the accident is not agreed between the investigators and the parties involved, it was judged that the most likely cause was identified as a reaction between AN and sodium dichloroisocyanurate or AN and thrichloroisocyanurate acid, both compounds which are incompatible with AN and on reaction release tricloramine (NCl_3), a sensitive and explosible compound.

III. Tianjin (Fire)

A large fire was reported at a warehouse in the Tianjin port area in the evening (about 22:50 local time) on August 12, 2015. The fire was in the area where dangerous goods were stored. First responders and firefighters were on the scene but unable to contain the fire. Around 23:30 a first explosion occurred that was equivalent to 2.9 tonnes TNT equivalent based on the seismic waves generated (2015 Tianjin explosions, 2020). After 30 seconds, a subsequent more powerful explosion occurred equivalent to 21.9 tonnes TNT. There were 173 fatalities and 797 people injured. Of the fatalities 93 were firefighters. The cause of the explosions was not immediately known, but an investigation concluded in February 2016 that an overheated container of dry nitrocellulose was the cause of the initial explosion.

IV. Beirut (Fire and possibly Shock)

On August 04, 2020 there was an explosion involving AN at the Beirut port. The mass involved was significantly higher – 2,750 tonnes, and the explosion resulted in over 190 fatalities, injuring 6,000 and causing billions of dollars in damage. There was a preliminary explosion that was followed about 30 seconds later with the larger explosion that involved the AN stored in the port. According to the news and the official statements of the Lebanese authorities soon after the explosions, these 2750 tons of ammonium nitrate had been stored for six years in that warehouse.

The Lebanese authorities are leading the investigation and are being supported with foreign experts including the FBI and French experts. From the information released to date, the most likely cause of ignition of the fire that preceded the first explosion was welding that was carried out that day (New York Times, 2020). The article also stated that in the same warehouse there were 15 tons of fireworks, five miles of fuse on wooden spools, jugs of oil and kerosene, and hydrochloric acid.

Maritime transport and storage at Ports

Ammonium nitrate is internationally traded, and volumes moved by sea are in million tonnes per year. TGAN sea vessels will typically transport ~1,000 to ~10,000 tonnes while FGAN are commonly transported20,000 tonnes in a vessel.

Over the decades this mode of transport has been carried out safely by following strict controls. Nevertheless, during its transport or intransient storage, if the controls are not in place the product may be exposed to threats that can result in a catastrophic event.

Published information on the explosions at the Tianjin and Beirut ports indicate that there were failures of controls for the safe storage of AN. In both events there were flammable, combustible, or pyrotechnic substances in proximity to the AN. These substances did accidentally ignite leading to a thermal insult to the AN. Since there were fireworks (New York Times, 2020), which are classified as Class 1 goods, co-located with the AN in the warehouse at the Beirut port, there may have been a shock insult as well.

Reminders and Lessons from the Recent Events

Ammonium nitrate manufacture and use has a long history, and as mentioned in a previous SAFEX newsletter, certain well-known accidents had practices from the past that are not comparable to those of today. Learnings and knowledge were gainedand practices improved. The AN manufactured post-WW I or shortly after WW II is not the same product as today. Many of these products would be classified as explosives under today's UN safety regulations.

The following are reminders from the Beirut Port event:

(i) Prohibition on the Co-storage of Flammable/Combustible, Explosible and Incompatible Materials

One of the principal controls when storing AN is that there should not be any flammable/combustible, explosible or incompatible materials in proximity to it. This becomes even more important when the product is entrusted to the carrier or stored under the jurisdiction of a third party, as was the case in the Beirut port.

(ii) Clear accountability and ownership

The Beirut event highlights the responsibility of care of all stakeholders: the supplier (AN manufacturers, who are aware of the product and its hazards), the buyer (explosive manufacturer, also aware of the product and its hazards) and the authorities. The supply chain actors will normally be less knowledgeable on the product, but they should not be less aware of the product and its safe handling. The supply chain must not be overlooked as it is of utmost importance with respect to transferring hazards knowledge to all stakeholders.

(iii) Compliance Checks

Auditing of operations against the SAFEX GPG or internal standards should be carried out to ensure strict compliance with segregation, safeguards, etc. This should also include assurance that the risk controls on the whole product lifecycle, product ownership and/or stewardship are in place.

In summary, when storage conditions are neglected and AN characteristics are forgotten the AN storage can become unsafe. The subsequent probability of an event can be orders of magnitude higher and the TNT equivalent can be higher as well since the product may be degraded, contaminated, incorrectly co-stored, etc. In the case of the Beirut Port explosion, the newsfeeds indicate that hot work may have initiated the fireworks and other combustible materials stored in the same warehouse as AN.

When storage conditions are in conformance to either the GPG or appropriate internal standards, AN storage is safe.

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