The Behavior of Ammonium Nitrate in a Fire, Recent Events, and Resulting Changes in Fire Code

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Abstract

Ammonium nitrate is used as a fertilizer and as a primary feedstock for commercial explosives. Recent events have shown that ammonium nitrate can mass explode when involved in a fire. This paper will highlight the chemical behavior of AN in the context of recent events with a focus on the explosion at the West Fertilizer Company, and the resulting actions being taken to update relevant Fire Codes and industry Codes of Practice.

Key Words: Ammonium nitrate, fire, explosion,

1. Introduction

Ammonium nitrate (AN) is a synthetic chemical that is used primarily in agriculture as a nitrogen source for plants, as a precursor for commercial blasting explosives, and in other industrial applications such as the generation of nitrous oxide gas.

The synthesis of ammonium nitrate is through the neutralization of nitric acid with ammonia. The resulting ammonium nitrate solution is concentrated to 99.5% for agricultural use as a fertilizer (fertilizer grade AN, FGAN) and 97.5% for use in the explosives industry, as technical grade AN, TGAN. The primary difference in the two grades of AN is that the TGAN has a lower density than FGAN due to the particle having a porosity.

A schematic of the process for manufacturing AN is shown in Figure 1.

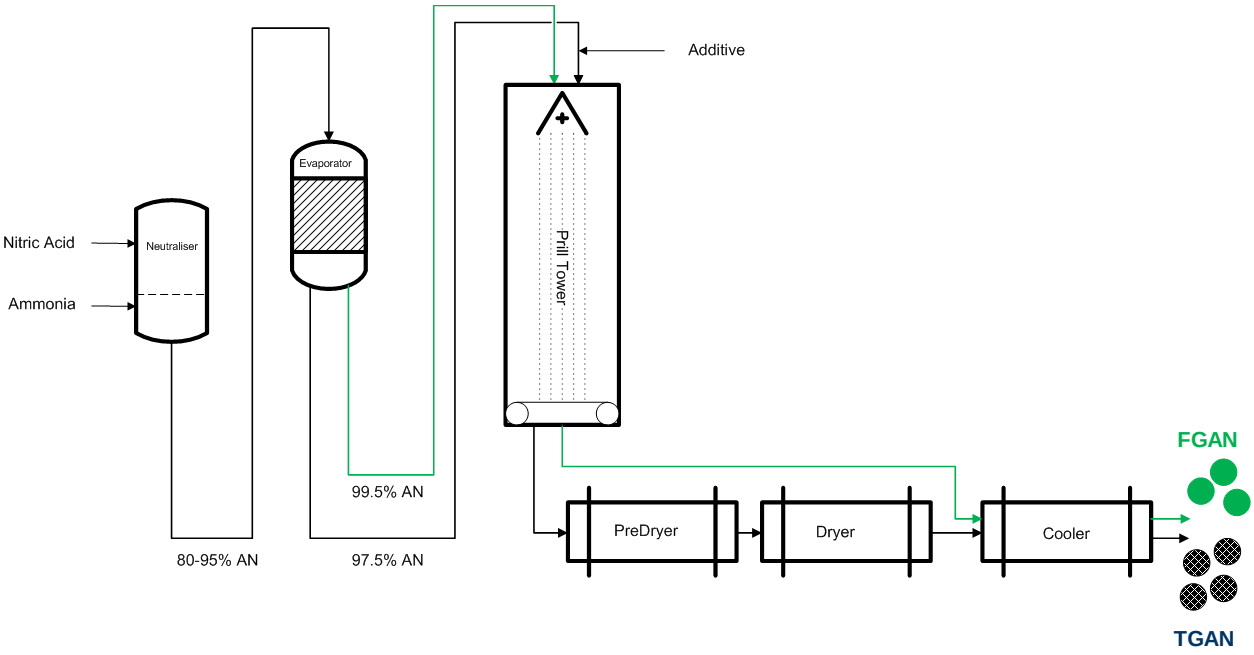

Figure 1. Schematic for the Manufacture of Ammonium Nitrate

Since the AN solution entering the prill tower for FGAN manufacture is almost a pure melt (99.5% AN), the solids only undergo cooling. In contrast, the TGAN prill requires an AN solution of 97.5% and once the prill is formed in the tower it then undergoes drying to remove the residual moisture and subsequent cooling. The AN prills can be coated with a waxy substance to prevent caking. Most TGAN prills have this coating applied after the cooling step.

Ammonium nitrate plants have capacities that range from 200,000 tonnes to over one million tonnes per annum. Transport and the resulting storage of AN is therefore a necessity since the product needs to be distributed to the end-users.

The annual global production of ammonium nitrate is approximately 60 MTe, of which almost 75% goes into agricultural use and 25% for use in commercial explosives formulations (Informa 2018).

This paper will mainly deal with the events related to the storage of ammonium nitrate.

2. Chemistry of AN

Ammonium nitrate is susceptible to initiation by shock, reaction with other chemicals, and decomposition when subjected to heat (SAFEX 2014). This paper focuses on the exposure of AN to heat.

The melting point of AN is 169.1±0.5°C (Honti 1976). As described earlier, the difference between FGAN and TGAN is the final physical form, but once exposed to sufficient heat to cause it to melt, the melt will be the same for both forms of AN prill. On continued heating AN will begin to decompose. The decomposition of AN is complex, and the reaction pathways are shown below (Keleti 1985):

1. $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ ΔH +44.6 (kcal/mol)
2. $NH_4NO_3 \rightarrow N_2O + 2H_2O$ ΔH -8.8
3. $2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O$ ΔH -28.2
4. $2NH_4NO_3 \rightarrow N_2 + 2NO + 4H_2O$ ΔH -6.6
5. $3NH_4NO_3 \rightarrow 2N_2 + N_2O_3 + 6H2O$ -
6. $4NH_4NO_3 \rightarrow 3N_2 + 2NO_2 + 8H_2O$ ΔH -22.2
7. $5NH_4NO_3 \rightarrow 4N_2 + 2HNO_3 + 9H_2O$ ΔH -29.4

Reaction (1) is reversible and endothermic, while all the others are irreversible and exothermic. The industrial generation of nitrous oxide is by the controlled decomposition of AN holding the temperature below 250°C during which reaction (2) is the prevalent reaction. Reactions (3) to (6) occur above 300°C and *are usually associated with explosive and detonative behavior of ammonium nitrate* (Keleti 1985). According to Keleti, reaction (3), which generates three times the heat of reaction of reaction (2), is believed to be the reaction of greatest importance in a detonation.

3. Recent Accidents with Ammonium Nitrate involving fire

The incidents described below are those involving ammonium nitrate where the product has decomposed or reacted, and the result was an explosion. There are numerous events in which AN has been involved in a fire but there has not been an explosion.

Farmhouse in France

On October 2, 2003 there was a fire in a barn in the town of Saint Romain-en-Jarez, in the Loire region of France (ARIA 2010). Around 15:00 a fire broke out inside the barn at the mezzanine level, which also had bales of straw and hay stored. The farmer tried to put out the fire using an extinguisher but was unsuccessful.

Fire-fighters arrived at the scene at 16:23 and began to fight the fire. The captain called for a water supply backup at 16:38. At 17:12, with a large portion of the roof already collapsed, there was a hissing sound heard followed by an explosion. There were 26 people injured, with fire-fighters accounting for 18, nine of whom were seriously injured.

The exact cause of the initiation of the fire was not determined, but the possibilities cited were: electrical source, fermentation of stored hay, or a lit cigarette. The presence of significant amount of combustibles facilitated the spread of the fire. The AN bags were stored within 10 cm of 3,000 wooden and plastic crates.

Among the lessons learnt and measures implemented was that fertilizer storage in a barn must not contain the following:

- *products capable of igniting during a fire: straw, hay, cereals, livestock feed, sawdust, wooden crates, pallets, sulphur, etc.*
- *products capable of contaminating fertilizers: organic materials, fuel, fuel oil, gasoline, gas, phytosanitary products, and a number of incompatible products (chlorates, copper salts, etc.)*

West Fertilizer Company, West Texas

On April 17, 2013 the West Fertilizer Company (WFC) in West, Texas, was involved in a fire and subsequent explosion. WFC was a fertilizer blending, retail and distribution facility (CSB 2016). The Chemical Safety Board in 2016 issued a comprehensive report based on their investigation.

At the time of the incident the stockpile of AN was estimated to be between 40 to 60 tons of FGAN. In addition to FGAN, the storage facility also had potash, diammonium phosphate, ammonium sulfate and zinc sulfate. These solids would be blended to meet the various fertilizer needs of nearby farmlands. The site also stored anhydrous ammonia, which is also used by farmers who inject it directly into the soil as a source of nitrogen. A seed room was located at the North end of the building. On the day of the fire, the seed room had about 3,000 bags of out-of-season seeds, and also 700 bags of zinc sulfate. The seeds and zinc sulfate were stored in bags on pallets, with about 40 to 50 bags per pallet.

The bins holding the fertilizer solids were made of plywood, and the building was of a wood-frame construction with a concrete floor.

The fire was first seen and reported at approximately 19:29. Responders to the scene included the volunteer fire department of West, Texas, and the West Police Department. After 20 minutes of the fire being reported, there was an explosion that fatally injured 12 emergency responders and three members of the public.

Based on the blast damage, the mass of FGAN involved in the explosion was estimated to be about 30 tons.

As was the case with the fire in the farmhouse in France, the precursor event in WFC was a fire. There was an investigation carried out by the Texas State Fire Marshall Office as well. In the executive summary of that report, it is stated that “As the building became more involved the roof collapsed and an explosion occurred. (SFMO 2013).”

Tianjin Port

There was a series of explosions at the container storage Port of Tianjin on the night of August 12, 2015. The explosions resulted in 173 fatalities and several hundred injuries. The first two explosions occurred within 30 seconds of each other. The second explosion was the larger of the two and involved the detonation of about 800 tonnes of ammonium nitrate (Wikipedia 2018).

The first report of a fire was at ~22:50. The first explosion occurred around 23:30, about 40 minutes after the first fire reports. The second more powerful explosion, which was 30 seconds later, caused most of the damage and injuries. This explosion registered a magnitude 2.9 earthquake and generated seismic shock-waves. The investigation concluded that the first explosion was that of an overheated container of dry nitrocellulose.

4. Actions taken by Regulatory Bodies and Industry Associations

In the months immediately following the event in the West Fertilizer Company, there were a series of actions taken by both governmental agencies and industry bodies.

On June 27, 2013, the Chairperson of the U.S. Chemical Safety Board (CSB), Rafael Moure-Eraso testified before the U.S. Senate Committee on Environment and Public Works (Chemical Safety Board 2013). The testimony covered the explosions at West Fertilizer as well as Williams Olefins.

In the testimony, Chairperson Moure-Eraso cited that the CSB has determined that “ammonium nitrate fertilizer storage falls under a patchwork of U.S. safety standards and guidance – a patchwork that has many large holes.” These holes were the use of combustible materials of construction for buildings and storage bins, no requirement for sprinklers, and no zoning requirements for large quantities of AN.

Institute of Makers of Explosives

On July 30, 2013, the Institute of Makers of Explosives (IME) issued "Safety and Security Guidelines for Ammonium Nitrate" which was endorsed by the International Association of Fire Chiefs, the National Sand, Stone and Gravel Association, and the International Society of Explosives Engineers (IME, Safety and Secutiry Guidelines for Ammonium Nitrate 2013).

IME is the safety and security institute of the commercial explosives industry in the United States. IME is a non-profit, incorporated association, founded in 1913, to provide technical information and recommendations concerning explosive materials their precursors, and to serve as a source of reliable data about their use. The primary concern of IME is the safety and security of commercial explosives products and their precursors, and the protection of employees, users, the public and the environment in the manufacture, transportation, storage, handling, use and disposal of these materials.

In the Guidelines, IME advocates the use of non-combustible materials of construction for the storage of ammonium nitrate. This is industry best practice and is commonplace in the commercial explosives industry. This practice however differs from both 29 CFR 1910.109(i)(4)(ii)(a) and the 2013 revision of NFPA 40, both of which permit the use of wooden and aluminum bins. The Guidelines state that "owners/operators of storage facilities should develop a written plan responding to emergencies as defined by 29CFR 1919.120(a)(3) and provide training to employees implementing the emergency plans…" These plans should be provided to local emergency responders, with guidance that the appropriate fire response is "DO NOT FIGHT AMMONIUM NITRATE FIRES", a statement which should be posted on the storage facility access points where it is visible to fire responders and police.

In April 2017, IME issued a Safety Library Publication (SLP-30) on the Safe Handling of Solid Ammonium Nitrate (IME, Safety Library Publications 2018). This SLP is a comprehensive document on AN outlining its classification, properties, hazards, management guidelines, and emergency response. The emergency response specifies an evacuation distance of at least one mile in all directions for fires involving AN.

Executive Order 13650

On August 1, 2013 the President of the United States issued Executive Order 13650 which aimed at improving chemical facility safety and security (USA 2013). Within this EO was identified, among other directives, Policy, Regulation and Standards Modernization, with directives to develop options for improved chemical facility safety and security. There was a 90-day limit for the Administrator of the Environmental Protection Agency (EPA) and the Secretary of Labor (Occupational Safety and Health Administration), to review the chemical hazards covered by EPA's Risk Management Program (RMP) and the Process Safety Management (PSM) Standard administered by OSHA and determine if the RMP or PSM should be expanded to address additional regulated substances and hazards.

As a consequence of this EO, OSHA and EPA issued Requests for Information related to PSM and RMP respectively on December 9, 2013 and July 31, 2014.

Since then, the EPA has determined that AN will not be added to the RMP. As of July 2018, OSHA has not yet made a decision on AN with respect to the PSM[1].

Chemical Advisory

Shortly after EO13650 was issued in late August 2013 EPA, OSHA and the ATF issued a joint advisory entitled "Chemical Advisory: Safe Storage, Handling and Management of Ammonium Nitrate". The Advisory was updated in June 2015.

The hazard information contained in the Advisory highlights the hazards of AN, with an inset that states: ""Pure" solid ammonium nitrate is fairly stable and will explode only under extreme conditions. However, the addition of combustible contaminants, even in low percentages, creates a dangerous combination and the ammonium nitrate mixture becomes far more susceptible to detonation…" (EPA 2015). Guidance is provided in the Advisory on

[1] IME has advocated that AN not be covered under PSM, and that the OSHA blasting standards under 1910.109(i) be amended to include the recommendations in IME's SLP-30.

chemicals that should not be stored with AN, and reference is made to the NFPA Code 400 document in which the materials to avoid are listed.

The Fertilizer Institute (TFI)

In February 2014 TFI issued the "Safety and Security Guidelines for the Storage and Transportation of Fertilizer Grade Ammonium Nitrate at Fertilizer Retail Facilities" (TFI 2018). Guidance is provided on incompatible materials and chemicals, and the need for special coatings to protect steel and wooden bins and other structural materials that are in contact with AN.

Guidance on AN Storage Requirements (OSHA)

On December 3, 2014 OSHA issued a memorandum to its regional administrators (OSHA 2014). In it was guidance on the Ammonium Nitrate Storage Requirements in 29CFR 1910.109(i) to assist OSHA officials in enforcing that regulation.

To date, the use of wood is permitted in 1910.109(i). Section (4)(ii)(b) reads: *Due to the corrosive and reactive properties of ammonium nitrate, and to avoid contamination, galvanized iron, copper, lead, and zinc shall not be used in a bin construction unless suitably protected. Aluminum bins and wooden bins protected against impregnation by ammonium nitrate are permissible. The partitions dividing the ammonium nitrate storage from other products which would contaminate the ammonium nitrate shall be of tight construction.* The Compliance Guidance provided cites three situations that may be encountered, namely, (i) wooden bins that are not and never have been coated or treated to prevent AN impregnation, (ii) Wooden bins that are coated but have not been maintained, and (iii) wooden bins treated with a material claimed to be chemically compatible with and impregnable to AN, and the citation approach to be taken for each situation.

National Fire Protection Association (NFPA)

The current OSHA regulation for AN, 1910.109(i) was derived from the NFPA Code for AN. In June 2015, NFPA issued the 2016 Edition of Code 400 Hazardous Materials Code (NFPA 2016), in which Chapter 11 deals exclusively with AN. The key changes from the 2016 Edition over the 2013 Edition with respect to the hazards of AN are:

- Removal of the 2,500 tons threshold for sprinkler requirements. 400-13 only required sprinklers if this threshold was met. Code 400-16 now requires sprinklers with no threshold requirement.
- All new buildings for storage and handling of AN shall be of non-combustible construction
- A public notification/alert system shall be provided notifying individuals located within 1 mile of the facility of the need to evacuate
- Specification of separation requirements for AN with a comprehensive list of materials/chemicals
- Signage must be posted that states: DO NOT FIGHT FIRE. EXPLOSION HAZARD.

The Technical Committee is presently working on the 2019 Edition of Code 400.

A timeline of the described activities is shown in Figure 2.

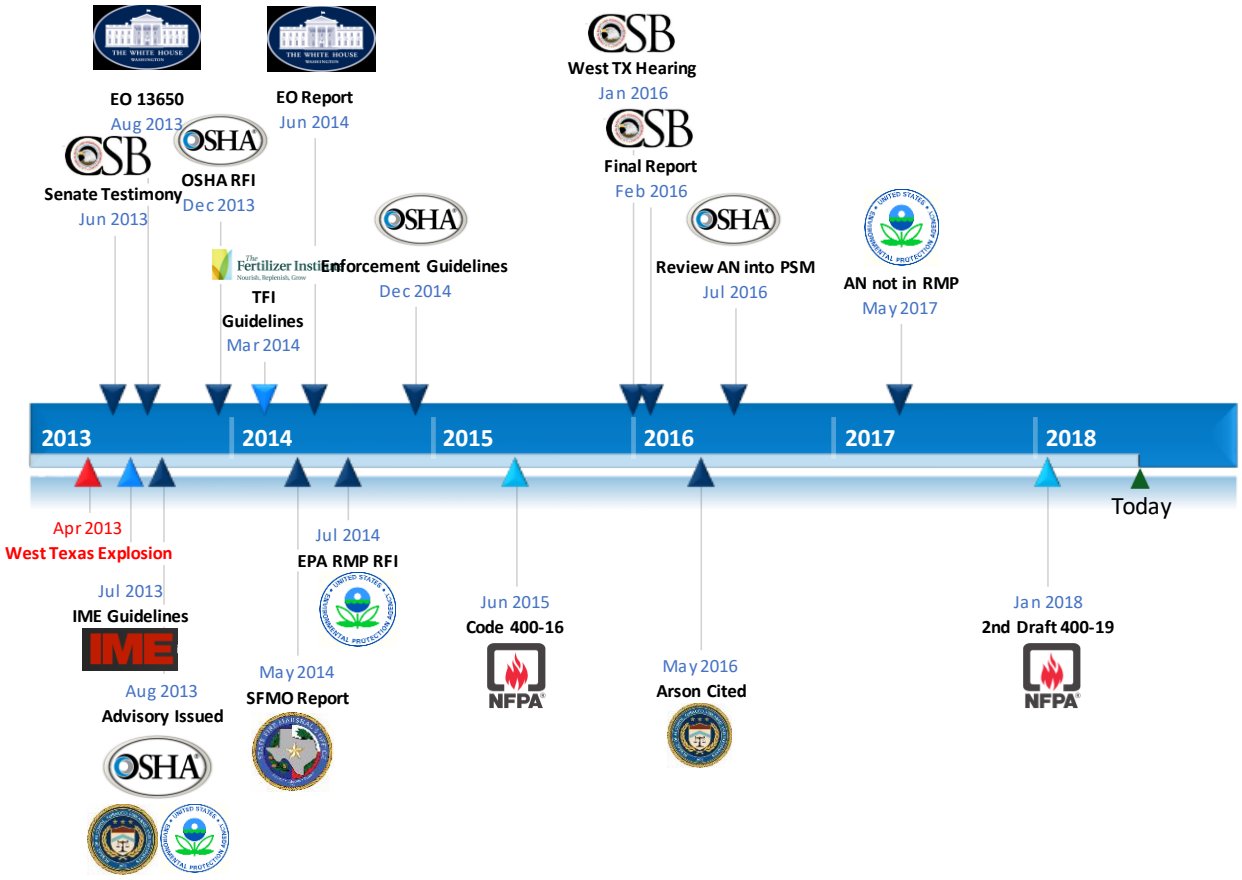

Figure 2. Timeline of Activities Post WFC Explosion

5. Summary

Ammonium nitrate, in both the fertilizer and technical grades, has been manufactured, stored, transported and used for several decades. The hazards of this chemical are well known, and although the exact mechanism of how fires involving AN lead to an explosion is not fully understood, the safety management systems focus on preventing exposure of AN to fires.

In all three accidents described above, the precursor event to the explosion was a fire. Exposure of AN, in either FGAN or TGAN form, to heat will result in the product first melting and then decomposing. On prolonged heating, as was the case in all three accidents, the AN decomposition can runaway, leading to a thermal explosion. In the case of Tianjin, the confinement of the AN in containers would have exacerbated the event.

The guidelines and codes from regulatory agencies, consensus organisations and industry bodies provide guidance on both prevention of fires as well as the required emergency response in the event that the fire involving AN is out of control.

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