AMMONIUM NITRATE EXPLOSIONS: LESSONS LEARNED



Ammonium nitrate (AN) is a chemical compound with the power to feed billions but also the potential to devastate. AN is the most potent, economical, and convenient fertilizer on the market; thus, AN continues to be stored in large quantities in ports and other places around the world. However, the recent catastrophic explosion in Beirut is a reminder of the hazards associated with the improper storage and use of AN, as well as the need for diligent enforcement of its regulations. Unless everyone working with AN—manufacturers, sellers, users, first responders, and regulators—is more aware of the hazards of AN and diligently implements safety rules, then future accidents with AN will be inevitable.

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EXECUTIVE SUMMARY

The catastrophic explosion in Beirut was one of the worst accidents caused by ammonium nitrate (AN) in history. Since the explosion, there has been a dramatic increase in interest concerning the safety aspects of AN. Herein, we review the history of accidents involving AN around the world, most of which happened during storage or transportation, showing a general lack of awareness of safe handling and storage of AN. We then discuss safer formulations of AN and strategies for preventing accidents and misuse found in the patent literature. The explosive nature of AN is then evaluated.

In addition, we review potential environmental and health consequences of toxic gases and chemicals released during the AN explosion. We then explore the regulations from many countries and international agencies related to AN with important safety rules highlighted. **This report serves as an introduction to the physical and chemical properties of AN, its hazards and safety rules, and provides a useful resource to scientists in the AN research field, as well as business leaders in the fertilizer and related chemical industries.**

SINCE 1901, THERE HAVE BEEN NEARLY 40 ACCIDENTS INVOLVING AMMONIUM NITRATE

NOTABLE HIGHLIGHTS:

- Since the beginning of the 20th century, there have been nearly 40 accidents involving AN, most in storage or transportation.
- The catastrophic explosion in Beirut was one of the worst accidents in history based on lives lost and property damaged caused by AN, comparable only to explosions of large amounts of AN in Texas City, United States (1947); Toulouse, France (2001); and Tianjin, China (2015).
- AN is made by reaction of ammonia with nitric acid in water followed by careful evaporation of the water.
- Additives for AN have been used to control its form and reduce the hazards of its storage and handling.
- Strategies for preventing misuse of AN-based fertilizers found in recent patent literature are provided.
- AN is an explosive hazard, as it is both a fuel and an oxidizer. It decomposes into gases which are more stable than AN and take up much more volume; the reaction also generates large amounts of heat.
- AN explosions generate large amounts of toxic gases and carcinogens.
- Safe storage of AN requires ventilation, isolation from combustible materials, temperature control, control of the amount in storage, fire protection, and avoidance of combustible contaminants.

CHAPTER 1. MAJOR EXPLOSIVE ACCIDENTS INVOLVING AMMONIUM NITRATE

1.1 THE BEIRUT DISASTER: EXPLOSION OF A SIGNIFICANT QUANTITY OF AMMONIUM NITRATE.

The catastrophic explosion in Beirut was one of the worst accidents caused by ammonium nitrate (AN) in history.

On August 4, 2020, a large amount of AN in a storage hangar at the Port of Beirut exploded, causing nearly 300 deaths, 6,000 injuries, and enormous property damage, leaving an estimated 300,000 people homeless.^{1, 2}

Lebanese authorities confirmed that the explosion was caused by 2,750 tonnes (metric tons) of AN; it was detected by the United States Geological Survey as a seismic event of magnitude 3.3, and is considered one of the most powerful non-nuclear explosions in history.² **The Beirut explosion was comparable to explosions of large amounts of AN in Texas City, United States (3,000 tonnes, 1947); in Toulouse, France (200-300 tonnes, 2001); and in Tianjin, China (800 tonnes, 2015).**

On the afternoon of August 4, 2020, a fire broke out in Warehouse 12, followed shortly thereafter

by an explosion that sent up a cloud of smoke and flashes of light from the stored fireworks. Half a minute later, a second, stronger explosion rocked central Beirut, sending a reddish-brown cloud surrounded by a white condensation cloud into the air. The reddish-brown color of the smoke was caused by nitrogen dioxide (NO_2), a byproduct of AN decomposition, present in a mixture with other nitrogen oxides (NO_x). The white cloud was likely water vapor forced into the air by the shock wave of the explosion.³

By studying the blast's effect on nearby buildings, video of the Beirut accident shows that in the eighth of a second after the explosion occurred, its spherical shockwave grew to roughly 240 meters in diameter. It was estimated that the blast was roughly equivalent to that of several hundred tons of TNT.⁴ For comparison, the atomic bomb dropped on Hiroshima, Japan, in 1945 had a yield of at least 13,000 tons of TNT and damaged and destroyed buildings within 1.5 miles of the site of the explosion.^{4,5}

The crisis created by the explosion, which included the destruction of 85% of the grain silos in Beirut, comes on top of an already crippled economy, the coronavirus pandemic, and regional tensions.



1.2 HISTORICAL REVIEW OF AMMONIUM NITRATE EXPLOSIVE ACCIDENTS

Since the beginning of the 20th century, there have been nearly 40 large accidents involving AN worldwide. Details of each of these accidents are shown in Figure 1 and Appendix 1. Eight of these accidents involved deaths of more than 100 people. In nearly all of these accidents, material damage was extensive. Most of these accidents occurred during the storage or transportation of AN. Indeed, **17 accidents** occurred in storage facilities alone due to unsafe operating procedures and conditions, such as storage with highly flammable materials. An additional 15 accidents took place during transportation, while a further 7 occurred while evaporating AN solutions during manufacturing or from attempts to break up aggregated AN with industrial explosives (Figure 2). It is also worth mentioning that among all the major accidents, about half of them occurred in the last 20 years during storage or transportation. Analysis of these incidents shows that AN explosions are almost always preceded by fires or other ignition sources.



Figure 1. Accidents of ammonium nitrate around the globe. Major accidents are those that involved more than 1,000 tonnes of AN or caused more than 30 deaths during the explosion (Five of the minor accidents are not shown in the figure).

NUMBER OF ACCIDENTS



Figure 2: Distribution of AN accidents that happened during storage, transportation, or manufacturing / processing, shown as percentage with actual number in parenthesis.

CHAPTER 2. AMMONIUM NITRATE SYNTHESIS, FORMULATIONS, AND RELATED PATENTS

2.1 HOW AMMONIUM NITRATE IS MADE. CAN IT BE MADE MORE STABLE?

Ammonium nitrate (AN) is made by reaction of ammonia with nitric acid in water followed by careful evaporation of the water: $NH_3 + HNO_3 \rightarrow NH_4NO_3$

Ammonia is most often prepared by the Haber-Bosch process from atmospheric nitrogen, while nitric acid is prepared from the combustion of ammonia.^{6,7} This method uses starting materials that are thus most commonly made together or near one another. The reaction gives off significant amounts of heat, so the AN is made in aqueous solution. The water must be removed to yield the solid AN, most often by evaporation.

In the early 20th century, there were at least four instances of explosions caused during the evaporation process.⁸ While AN is stable at the usual temperatures of its manufacture and purification, **impurities may lower the stability of AN** or provide fuel for combustion or explosion. At least one AN explosion was caused by the use of contaminated nitric acid in its production; in another case, an explosion was triggered by air sprayed with oil from machinery into cooling AN. What's more, temperature variations within a facility can lead to AN mixtures being heated above their decomposition temperatures during evaporation, causing fires or explosions.

AN can absorb water or change crystal forms, leading to undesirable masses (agglomerates) that are unusable. The most important change in crystal form of AN occurs at 32 °C. This transition in crystal form is associated with a large volume change, which causes cracks in particles, making them more susceptible to water absorption and agglomeration.⁷ For these reasons, **temperature control is essential during the manufacture and storage of AN.** To avoid the formation of agglomerates, AN is formed into prills or granules. Prills, resembling grains of rice, are formed by forcing molten AN through nozzles. Granules are formed by clumping smaller particles with binding agents.⁹

Additives have also been used to make AN safer to handle and store for use as a fertilizer with varying degrees of success. For example, potassium compounds have been used to increase the stability of AN to phase transition and sensitivity to explosion or detonation; nitrogen-potassium and nitrogen-phosphorus-potassium (NPK) fertilizers have improved stability.

Potassium nitrate has been added to AN to increase its physical stability, but because of the added nitrate, the mixtures with AN are still strong oxidants. Additionally, calcium and magnesium nitrate have been added to AN in small amounts to improve its physical stability, but the mixtures more easily absorb water from the atmosphere.

Calcium ammonium nitrate (CAN), prepared from AN and calcium carbonate, is used in some cases as an alternative to AN. In Finland, a commercial product ("FinnCAN") was prepared from AN and the mineral phlogopite.⁷ FinnCAN contains 27% nitrogen (versus 34% nitrogen in fertilizer-grade AN) and has improved stability to temperature changes over unstabilized or ammonium sulfate-stabilized CAN.⁷

Aluminum sulfate has also been used as a drying additive for AN. Clays and inorganic compounds have been used as nucleating agents to improve the stability of AN granules or prills by reducing their size and thus the strains caused by temperature changes.

Other additives have also been tried, such as surfactants, but some of them act as fuels for the AN, while others are either incompatible with the use of the stabilized AN as fertilizer or decrease its stability, increasing the risk of explosion or detonation. As a result, alternatives to AN have been tried, such as urea and ammonium sulfate; however, these alternatives are less suitable. For example, urea evaporates, leading to rapid nitrogen loss after application to fields.¹⁰

2.2 PREVENTING MISUSE OF AMMONIUM NITRATE-BASED FERTILIZERS

Although the millions of tonnes of AN produced worldwide are mainly used as fertilizer, **AN is widely used in explosives for peaceful means.** In fact, the second most common use is as a component—the oxidizer—of industrial explosives.

The mixtures of AN with fuel oil (ANFO) and AN with nitromethane (ANNM) form powerful explosives that are commonly used in mining,

CONTROL OF THE FORM OF AMMONIUM NITRATE IS IMPORTANT TO REDUCE ITS POTENTIAL HAZARDS quarrying, and construction. Unfortunately, as the components are relatively easy to obtain and inexpensive, ANFO and ANNM are also favorites of terrorists. AN therefore has the dubious distinction of being involved in not just the most deadly industrial accidents as discussed in Section 1.2, but also in some of the most deadly terrorist attacks, such as the bombing of the Alfred P. Murrah Federal Building in Oklahoma City in 1995, which killed 168 people.

Afghanistan banned the import and storage of AN in 2009 due to its use in improvised explosive devices (IEDs). In 2010, Afghanistan also banned CAN, a form of AN valued for its stability toward accidental explosion. However, AN or CAN are produced in large quantities and can still be easily smuggled for use in explosives. As a result, **in 2012, 60% of IEDs in Afghanistan were made with AN derived from the fertilizer CAN.¹¹** IEDs were deployed often in Afghanistan (~14,500 events in 2012) and there were approximately 6,000 IED events around that time annually outside of Afghanistan.¹²

Consider CAN, which has been used for decades precisely because it is much less likely than AN to accidentally explode. CAN is a mixture of AN and calcium carbonate, which comes from limestone or dolomite. The calcium component acts as a stabilizer—a diluent—making a product in which an explosive reaction is difficult to sustain: it is not likely to explode by accident.¹³⁻¹⁶ Unfortunately, there are easy ways to convert CAN into something that can explode on command: separating the soluble AN from the insoluble calcium carbonate (the wet method) or grinding the CAN into a fine powder (the dry

method).¹⁷⁻¹⁸ Therefore, **it is not enough to make fertilizers that do not accidentally explode; it is also important to make ones that cannot be easily made to explode.**

A sampling of documents describing efforts to prevent accidental explosion or misuse are summarized in Table 1. Entries 2 and 3 describe coatings to make AN safer: the coating in entry 2 purports to make AN safer by preventing fuel oil from entering the pores of AN (although no mention is made of what happens when it is crushed), while entry 3 explicitly notes that the coal combustion-byproduct coating remains effective after crushing or attempts to separate AN by wet chemical means. Entries 4-11 describe blends to make AN less explosive.

Physical countermeasures to prevent misuse include adding a coloring agent to prevent separation of AN and diluents by color screening (entry 6), and ensuring that prills (or grains) of AN and the diluents are the same size to prevent separation by a sized sieve (entry 10). Entries 9 and 10 use a well-known property of AN—its hygroscopicity, or tendency to absorb water from the air—to help complicate separation.

In entry 9, urea double salts are added that form stable, non-hygroscopic fertilizers with AN, but, when crushed or added to water in an attempt at misuse, form hygroscopic urea-AN mixtures; the inclusion of a foaming agent in the blend then makes a mess of any attempts to boil off the water. Entry 10 adds an organic polymer-encapsulated urea that forms a hydrogel with added or absorbed water if wet or dry methods of separation are attempted.



TABLE 1. SAFER AMMONIUM NITRATE FORMULATIONS.

	Patent	Description
1	WO200240427 ¹⁹	An ammonium sulfate nitrate composite fertilizer that is non-explosive. The material is made in such a way that it is mainly a 1:2 double salt of ammonium sulfate and AN (i.e., (NH4)SO4.2(NH4NO3)), with very little of the more hazardous 1:3 double salt or residual AN. Tests show that it is not an oxidizer.
2	WO2003106377 ²⁰	A coating for a fertilizer that prevents the infiltration of hydrocarbons (such as fuel oil) into the pores of fertilizer, thereby reducing its efficacy as an oxidizer in the production of an incendiary device.
3	US20080223098 ²¹	A method of reducing the explosion potential of AN fertilizer by coating the fertilizer with a coal combustion by-product such as Class C fly ash, Class F fly ash, flue gas desulfurization waste, or atmospheric fluidized-bed combustion waste, and perhaps a binder.
4	WO2010053604 ²²	A method to create stable AN composites by blending AN with substantially non-oxidizing compounds such as ammonium sulfate, ammonium phosphate, ammonium molybdate, ammonium hexafluorosilicate, calcium nitrate, calcium carbonate, magnesium nitrate, potassium nitrate, and potassium phosphate.
5	for humanitarian reasons, the inventors chose not to patent the formulation ²³	A non-detonable fertilizer obtained by mixing iron sulfate with AN. The inventor (Fleming, then at Sandia National Laboratory) notes that iron prefers the nitrate, and ammonium prefers the sulfate, so that if fuel oil is added to attempt to make an explosive, the ions swap, and no explosion occurs. The mixture has an advantage for use in Afghanistan with its high pH soil because it acidifies the soil, unlike CAN, which makes soil more alkaline.
6	WO2014033159 ²⁴	A method to make solid blends of urea-based particles either mixed with, or coated with, ammonium sulfate, and AN-based particles mixed with salts able to bind crystallization water such as magnesium nitrate, magnesium sulfate, or aluminum sulfate. The desiccant limits the formation of the liquid phase, and the ammonium sulfate avoids the formation of an unwanted urea AN double salt. The resulting blend is difficult to reprocess for explosive use. It also includes a coloring agent to make separation based on color screening impossible.
7	WO2015073561 ²⁵	An AN-based fertilizer that includes stabilizers to prevent its use in ANFO-type explosives. The stabilizers included a layered double hydroxide, hydrocalumite, hydrotalcite, and hydroxyapatite, added in sufficient quantity to give a product with low specific impulse, when measured in a blast propagation test.
8	WO2015102544 ²⁶	A non-explosive and non-flammable AN-based fertilizer made by mixing AN, urea, and formaldehyde in water, and then adding an acid to catalyze the polymerization of urea and formaldehyde, followed by drying.
9	US20150218058 ²⁷	Uses the hygroscopicity of AN-based fertilizers to prevent misuse: if the fertilizer is crushed it will turn muddy, and if it is dissolved it will be harder to concentrate. The inventors claim an AN-based fertilizer composition that is non-hygroscopic under normal conditions, but becomes hygroscopic after contact with water, e.g. by dissolving or grinding for potential misuse. The key ingredient is a urea double salt—for example, urea calcium nitrate—which forms a stable (non-hygroscopic) fertilizer with AN, but when dissolved forms a hygroscopic composition that is a challenge to dry. A foaming agent is included in the composition to complicate attempts to boil away the moisture for misuse.
10	US9296663 ¹⁸	Another patent that uses hygroscopicity to advantage. A method is described to prevent the removal of calcium carbonate from CAN by adding an organic polymer to CAN that forms a hydrogel if water is added, making it impossible to remove the calcium carbonate, or a mixture that also includes encapsulated urea, so that if it is ground to a fine powder, the urea will absorb water, liquefying the mixture, and forming a hydrogel that preserves the non-detonable nature of CAN. The particles are the same size to prevent separation of the CAN using a sized sieve.
11	CN105622252 ²⁸	A composite fertilizer having AN and a phosphate, also containing an explosion-proof agent that includes a fire retardant, anti-explosion agents, hygroscopic agents, emulsifiers, dispersants, and anti-sticking agents.

In addition, there is the broad class of NPK fertilizers (Section 5.3), which are three-component fertilizers providing nitrogen, phosphorus, and potassium and that contain relatively small amounts of AN; although non-explosive, they are subject to self-sustaining decomposition.^{29,30}

2.3 PATENTS RELATED TO AMMONIUM NITRATE AS FERTILIZERS

The number of patent publications relating to AN fertilizers by country and year was extracted

from the CAS content collection to establish an overview of the worldwide research efforts on AN as a fertilizer (Figure 3). China published significantly higher numbers of such patents in the years from 2001 to 2019, followed by the United States, the Russian Federation, and Germany.

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
*: China	27	13	26	19	30	24	47	56	65	122	124	192	307	284	471	580	1038	855	558
USA	7	10	12	8	3	8	11	8	13	11	16	13	14	16	10	20	18	11	22
Russian	8	9	7	28	8	8	5	11	10	11	8	8	12	14	7	11	14	7	6
Germany	2	2	0	1	1	2	1	3	0	1	3	3	1	2	6	6	4	9	12

Figure 3. Number of patent publications yearly on ammonium nitrate fertilizers from the top four countries.



CHAPTER 3. THE EXPLOSIVE NATURE OF AMMONIUM NITRATE

3.1 PROPOSED MECHANISMS OF AMMONIUM NITRATE DECOMPOSITION AND EXPLOSION

Although the reactions of ammonium nitrate (AN) have been studied since the 1880s,³¹ a complete understanding of the exact mechanisms that take place during its thermal decomposition or combustion have yet to be realized. The challenge of the study of AN lies in its inherent physical and chemical complexity as well as the dependence of its reactivity on ambient conditions, such as temperature, pressure, and water content. The presence of contaminants, which can decrease the stability of AN, further complicates the study of AN reactions.

Keeping these limitations in mind, the first step in the thermal decomposition of AN is the proton transfer between the ammonium cation and nitrate anion, as shown below (eq 1).^{32,33}

reactions will give off heat and thus accelerate the decomposition of AN.

ionic pathway.³⁴⁻³⁶ Upon reaction with a proton source (NH₄⁺, H₃O⁺, or HNO₃), nitric acid (HNO₃) affords the nitronium ion (NO₂⁺) (eq 2), which subsequently oxidizes ammonia, giving N₂O and H₃O⁺ (eq 3).

Above 290 °C, radical mechanisms predominate following the dissociation of AN.^{37,38} Homolysis of the N—O bond in nitric acid gives the hydroxyl radical as well as NO₂, a toxic gas responsible for the reddish-brown plume sometimes seen in AN explosions.

Both radical and ionic pathways account for N_2O as the major gaseous product in the thermal decomposition of AN. However, N_2 and O_2 are

also produced. Although the exact mechanism is not known, the following equation is believed by some to be the main detonation reaction:

$$2NH_4NO_3$$

► 2N, + O, + 4H,O

3.2 WHY AMMONIUM NITRATE EXPLODES

Explosives require fuel (something that can be burned or oxidized) and an oxidant (something that can add oxygen to or remove electrons from other molecules) in confinement.

AN contains both a fuel and an oxidizer in the same place: ammonia, which is generated by deprotonation of the ammonium ion, is a fuel, while nitrate is a strong oxidant. Their co-presence means that the fuel does not have to wait for oxygen or some other oxidant to cause combustion ("Any intimate mixture of a fuel and an oxidizer is a potential explosive"³⁹). As the decomposition of AN is exothermic, once some of the AN breaks down, the released heat can initiate explosions or detonations; for example, the combination of AN and fuel oil (ANFO) is used as an explosive.

Compounds susceptible to explosion generally need to contain much more energy in their bonds than in the products they generate: the products of their reaction should be much more stable than the starting materials. This is seen in AN, where the products of AN decomposition are much more stable than AN itself. Nitrate contains nitrogen-oxygen bonds; nitrogen and oxygen both have non-bonded electron pairs that repel each other and thus make the bonds between them weaker. The weaker bonds in nitrate make it easier to initiate reactions because breaking those bonds costs less energy.

Decomposition and detonation of AN give off nitrogen oxides, nitrogen, oxygen, water, and large amounts of heat.⁴⁰ Molecular nitrogen has a very stable triple bond, so reactions that can form nitrogen are highly exothermic, and the formation of water also emits large amounts of energy. The energy heats the surrounding material, easing the movement of atoms to accelerate the decomposition, and expands the surrounding air, converting chemical energy to kinetic energy.

Explosions also require that the products take up more volume than the reactants, either by generating so much heat that the products expand to a much larger volume than the volumes of the reactants or by creating gaseous products from solid or liquid starting materials. AN takes up a small volume (as solid or liquid) and produces gases (nitrous oxide, nitrogen, oxygen, water vapor) that take up a much larger volume. In the decomposition of AN, between 2.5 and 3.5 moles of gases are formed for each mole of AN;⁴⁰ at 200 °C, **the volume of the** products is likely to be more than 1,000 times the initial volume of AN. The change in volume from solid to gas generates kinetic energy which, together with heat released by the decomposition, will damage the surroundings.

CHAPTER 4. HAZARDS DURING THE RECOVERY PHASE AFTER AMMONIUM NITRATE EXPLOSIONS

4.1 POLLUTANT GASES

An ammonium nitrate (AN) explosion produces massive amounts of pollutant gases, such as nitrogen oxides (NO_x), nitrogen dioxide (NO_2), nitrous oxide (N_2O), ammonia (NH_3), and others, which are harmful to the health of humans and other living beings, and also cause environmental damage.

Nitrogen oxides (NO_x), comprising NO and NO₂, are common air pollutants and can irritate the respiratory system. Elevated levels of these pollutants caused by AN explosions are particularly concerning for people with respiratory conditions.

Nitrogen dioxide (NO₂), the gas that provides the characteristic reddish-brown color of smog as well as the cloud seen in the Beirut explosion, is extremely toxic and harmful to human health. Acute exposure to NO₂ at a concentration of about 100 ppm can irritate skin and lungs; at higher concentrations, it can cause lung damage, edema, and death due to asphyxiation.⁴¹ Chronic exposure to NO₂ may lead to respiratory complications such as airway inflammation and can exacerbate asthma.⁴²⁻⁴⁴ Furthermore, reactions of NO₂ and NO_x with water, oxygen, and other chemicals in the atmosphere form acid rain, leading to severe environmental damage.⁴⁵

 $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

Nitrous oxide (N₂O), which is commonly known

as "laughing gas" and is used as an anesthetic in surgery and dentistry, is another main product of AN decomposition. Nitrous oxide is a potent greenhouse gas: it has about 300 times the global warming potential of carbon dioxide $(CO_2)^{46}$ and has been implicated in damage to the ozone layer.⁴⁷

Ammonia (NH₃) has a pungent odor, and readily dissolves in water. Humans can detect ammonia by odor at concentrations as low as 5 ppm, and detoxify ammonia in the liver at low concentrations.⁴⁸ However, ammonia is irritating to the moist mucous membranes of the eyes, mouth, and respiratory tract of humans.⁴⁹ U.S. OSHA (Occupational Safety and Health Administration) set an exposure limit stating that at concentrations of 25 ppm in the air, exposure time should be limited to under 8 hours; at concentrations of 35 ppm, the exposure time should be limited to within 15 minutes.⁵⁰ Exposure to extremely high concentrations (500 ppm) of gaseous ammonia can result in lung damage or death.⁵¹

4.2 CARCINOGENS SUCH AS POLYCYCLIC AROMATIC HYDROCARBONS, SILICA AND ASBESTOS

In addition to the toxic gases discussed above, airborne chemicals produced by the explosion can cause serious health problems. Some of the accidents discussed in this report were known to produce polycyclic aromatic hydrocarbons (PAHs) (produced from combustion), asbestos, and silica from fragmented building materials, which are carcinogens and can cause lung damage and exacerbate asthma.

Polycyclic aromatic hydrocarbons (PAHs) are

a large group of organic compounds with two or more fused aromatic rings. They are combustion products of organic materials, mixtures of which contain multiple human carcinogens. Human exposure to PAHs takes place mainly by inhalation, ingestion, and topical absorption. When the PAHs are metabolized, the metabolites formed bind to DNA. Formation of the PAH-DNA adducts is considered a necessary step in PAH-initiated carcinogenesis, as studied in experimental models and detected in human tissues.⁵²

According to the United States Environmental Protection Agency (EPA), 16 PAHs are catalogued as "priority pollutants" because of their toxicity, potential for human exposure, and frequency of occurrence in hazardous waste sites.⁵³ They are also found at high concentrations at National Priorities List (NPL) hazardous waste sites.^{54,55}

Following the explosion in Beirut, monitoring equipment at the American University of Beirut registered a sharp rise in **particulate matter**. The most worrisome constituents of the particulate matter are **respirable crystalline silica (RCS) and asbestos.**

Silica and asbestos, which are still common building materials in many places, are inorganic substances composed largely of silicon and oxygen. Small fibers or particles can be generated during an explosion and remain in the air for an extended period, causing inhalation risks. The role of asbestos exposure in mesothelioma and lung cancer is well documented, but the dangers of exposure to RCS are less well recognized. Although only minimal exposure to asbestos is enough to cause harm, RCS requires greater exposure to cause conditions such as silicosis, lung cancer, and chronic obstructive pulmonary disease (COPD).^{56,57} Unfortunately, such high levels of exposure can easily occur because RCS is invisible and exposure causes no immediate symptoms. According to the International Agency for Research on Cancer (IARC), asbestos and silica are established human lung carcinogens (Group 1).^{58,59}

Silica exists in many different crystalline and non-crystalline (amorphous) forms. Quartz, the most common form of crystalline silica, is the second most common mineral on the planet. **RCS** is fine enough to inhale deep into the bronchioles and alveoli causing serious harm. Silica causes progressive granulomatous and fibrotic lung disease.

The strong immunological response in the lung induced by silica particles and their toxicity to macrophages may promote not only fibrosis but also cancer. The mechanism by which silica induces lung cancer is not clear, whether directly through effects on DNA or indirectly by promoting growth of already initiated tumor cells. Silica can cause chromosomal abnormalities in mammalian cells. There is recent evidence that lung tumors arise in areas adjacent to areas of fibrosis and that cytokines may play a role in carcinogenesis.⁶⁰

Asbestos refers to a variety of hydroxylated silicate minerals. Asbestos minerals are divided into two broad groups: serpentine and amphibole. Serpentine asbestos is called chrysotile, and the amphibole family includes crocidolite, anthophyllite, amosite, actinolite, and tremolite. Numerous studies have demonstrated that all types of asbestos have the potential to induce lung tumors and mesothelioma.⁶⁰ Figure 4 shows the number of published articles per year according to the CAS content collection

related to PAH, asbestos, or silica hazards.

Figure 4. Number of published articles per year related to the hazards of polycyclic aromatic hydrocarbons, silica, or asbestos, according to the CAS content collection.

Recent official legal documents and guidance may explain the increased interest in PAH hazards. In 2000, the EPA established ambient water quality criteria to protect humans from the carcinogenic effects of PAH exposure. Similarly, in 2003, WHO published guidance that set the unit risk of lung cancer of benzo[a] pyrene (BaP) and other PAHs. On the other hand, because of the recognized hazards of asbestos exposure and its reduced use in commerce, publications discussing it have declined in recent decades.

CHAPTER 5. REGULATIONS ON AMMONIUM NITRATE STORAGE AND TRANSPORTATION

5.1 WHY LARGE AMOUNTS OF AMMONIUM NITRATE ARE STORED

Ammonium nitrate (AN) is widely used in fertilizers and mine explosives. As a nitrogen source, it has an NPK rating of 34-0-0, where the three numbers provide a measure of the relative content of nitrogen, phosphorus, and potassium. It is also a commonly used oxidant in many types of mining explosives. The total AN production worldwide was estimated to be 22 million tonnes in 2017, according to the data published by the Food and Agriculture Organization of the United Nations. Figure 5 shows the top six AN producers in 2015, 2016 and 2017.

Figure 5. The top six countries in ammonium nitrate production. Data source: Food and Agriculture Organization of the United Nations <u>http://www.fao.org/faostat/en/#data/RFB</u>

In addition, data with the import and export AN amount were analyzed, results shown in Figure 6. The overall worldwide import amount seems to be stable, with the top six AN importing countries being Brazil, Ukraine, United States, Peru, Australia and United Kingdom, and the top six exporting countries being the Russian Federation, Georgia, Lithuania, Bulgaria, United States and Sweden. These data give an estimate of how much AN is transported between countries, but do not include AN transportation within countries.

Figure 6. Worldwide import amount of ammonium nitrate from 2002 to 2018 and top six countries in ammonium nitrate import or export. Data source: Food and Agriculture Organization of the United Nations <u>http://www.fao.org/faostat/en/#data/RFB</u>

AN has often been stored in large amounts in warehouses, because it was considered safe and does not easily burn when pure.

However, it is a stronger oxidant than air and can accelerate combustion of other materials. When mixed with fuels, as in ANFO, explosions can readily occur. Once heated, AN decomposes to release large amounts of heat and gases. As discussed in Section 1.2, there have been nearly 40 AN disasters reported globally, causing more than 2,500 deaths. These tragedies highlight the dangers of AN, and justify the need for diligent implementation of regulations worldwide, as well as increasing public awareness.

5.2 REGULATIONS AND RULES FOR AMMONIUM NITRATE

Previous disasters (Appendix 1) have heightened public awareness of the explosive nature of AN, and the consequences of its unsafe storage and use. In response, many regulations, rules, and guidelines for AN, especially regarding its storage and handling, have emerged in different countries and areas in a bid to improve safety, as shown in Table 2.

TABLE 2. REGULATIONS AND GUIDELINES FOR STORAGE AND HANDLING OF AMMONIUM NITRATE.

Country /Area	Title	Description
European Union	Directive 82/501/EC (Seveso Directive I, 1982), Directive 96/82/EC (Seveso Directive II, 1996), DIRECTIVE 2003/105/EC (amending Seveso Directive II), Directive 2012/18/EU (Seveso Directive III)	The European Parliament and the Council of the European Union
European Union	Selected Tests Concerning the Safety Aspects of Fertilizers (1992)	EFMA, IFA
European Union	Handbook for the Safe Storage of Ammonium Nitrate Based Fertilizers (1992)	EFMA, IFA
European Union	Best Available Technique Series for production of ammonium nitrate products (2000)	EFMA, IFA
Russian Federation	GOST 2-2013 - Ammonium nitrate. Specifications	GOST
United States	OSHA 29 CFR 1910.109(i) – Storage of Ammonium Nitrate (2001)	OSHA
Canada	Ammonium Nitrate Storage Facilities Regulations (C.R.C., c. 1145) (2006, amended in 2015)	стс
United Kingdom	Ammonium Nitrate Materials (High Nitrogen Content) Safety Regulations 2003	HSE
United Kingdom	Storing and handling ammonium nitrate (2001)	HSE
Australia	Safe storage of solid ammonium nitrate (3rd ed.) (2013)	W.A. Govt., Dept. of Mines and Petroleum Resources Safety***
Australia	Storage requirements for security sensitive ammonium nitrate (SSAN) (2020)	Queensland Govt., Dept. of Natural Resources, Mines and Energy
Australia	High consequence dangerous goods (HCDG): Safety basics (2020)	WorkSafe Victoria
China	GB 2945-1989 GB/T 2945-2017 Ammonium nitrate	AQSIQ SAC
China	**GBF[2020] 52 Notice of Further Strengthening Safety Management of Civil Explosives	China State Council

* Abbreviation of Organizations:

EFMA: European Fertilizer Manufacturers Association, Brussels IFA: International Fertilizer Industry Association. Paris

OSHA: Occupational Safety and Health Administration

CTC: Canadian Transport Commission

HSE: Health and Safety Executive

AQSIQ: General Administration of Quality Supervision, Inspection and Quarantine

SAC: Standardization Administration of China

GOST: Russian Governmental Standard

** GBF: Document issued by the general office of the State Council, China

***Superseded by Dept. of Mines, Industry Regulations and Safety (DMIRS) in 2017

The United States is one of the largest producers and consumers of AN and has suffered many tragedies involving AN (15 accidents listed in Appendix 1). As a result, a variety of regulations, rules, and guidelines have been published by the U.S. government, as listed in Figure 7 and Table 3. In addition, some local governments or agencies also have guidelines related to AN.

Figure 7. Timeline for ammonium nitrate-related accidents and regulations in the United States.

TABLE 3. REGULATIONS/GUIDANCE ABOUT AMMONIUM NITRATE IN THE UNITED STATES.

Title	Organization*	Year
NFPA 490 (Hazardous Materials Code)	NFPA	1974
NFPA 400 (The National Fire Protection Association Hazardous Materials Code) Chapter 11 on ammonium nitrate	NFPA	2016
OSHA 29 CFR 1910.109(i) et seq Storage of Ammonium Nitrate	OSHA	2001
Chemical Advisory: Safe Storage, Handling, and Management of Solid Ammonium Nitrate Prills	EPA-OSHA-ATF	2013**, 2015
Safety and Security Guidelines for Ammonium Nitrate	IAFC-IME- ISEE-NSSGA	2013
Regulation of Fertilizers: Ammonium Nitrate and Anhydrous Ammonia	CRS	2013
Safety and Security Guidelines for the Storage and Transportation of Fertilizer Grade Ammonium Nitrate at Fertilizer Retail Facilities	TFI ARA	2014
Safety and Security Guidelines for the Storage and Transportation of Fertilizer Grade Ammonium Nitrate at Fertilizer Retail and Distribution Facilities	TFI ARA ResponsibleAg Inc.	2018
Chemical Facility Anti-terrorism Standards (CFATS)	CISA	2007
Ammonium Nitrate Security Program (ANSP)	CISA	proposed

* Abbreviation of Organizations: NFPA: National Fire Protection Association OSHA: Occupational Safety and Health Administration EPA: Environmental Protection Agency ATF: Bureau of Alcohol, Tobacco, Firearms, and Explosives IME: Institute of Makers of Explosives IAFC: The International Association of Fire Chiefs ISEE: The International Society of Explosives Engineers

The primary U.S. regulations for AN are "OSHA 29 CFR 1910.109(i) – Storage of Ammonium Nitrate", and the Memorandum of "Guidance on the Ammonium Nitrate Storage Requirements in 29 CFR 1910.109(i)" published in 2014 after the Adair Grain (DBA West Fertilizer) Company explosion (Appendix 1). In combination with other documents, the regulations may be summarized as follows:

Ventilation is the first requirement for safe storage of AN, because it can (1) prevent the accumulation of highly toxic off-gas products, such as ammonia and nitrogen oxides, and (2) remove hot gases from the structure to limit NSSGA: National Stone, Sand, and Gravel Association CRS: Congressional Research Service TFI: The Fertilizer Institute ARA: Agricultural Retailers Association CISA: Cybersecurity and Infrastructure Security Agency

**Initially published in 2013 and republished in 2015

heating of the AN and reduce the risk of an explosion. For example, OSHA requires that "Storage buildings shall have adequate ventilation or be of a construction that will be self-ventilating in the event of fire." [1910.109(i)(2)(iii)(b)], and "Warehouses shall have adequate ventilation or be capable of adequate ventilation in case of fire." [1910.109(i)(4)(i)(a)] for bulk storage.

Ventilation also helps prevent AN agglomeration. AN is an extremely hygroscopic chemical and prills or grains will stick together after absorbing moisture. The powerful 1921 explosion in Oppau, Germany, was caused in part because AN and ammonium sulfate had agglomerated in a storage silo and formed a huge solid mass. Similarly, the 1942 Belgium explosion was also caused in part by an attempt to disaggregate an agglomerated pile of 150 tonnes of AN with industrial explosives (Appendix 1). Therefore, OSHA requires that *"Height or depth of piles shall be limited by the pressure-setting tendency of the product. However, in no case shall the ammonium nitrate be piled higher at any point than 36 inches below the roof or supporting and spreader beams overhead." [1910.109(i)(4)(iii)(b)]. Reduced humidity and temperature can also inhibit AN agglomeration.*

Noncombustible and AN-resistant materials are required for use in storage and

handling areas, as stated in OSHA regulations 1910.109(i)(2)(iii)(d) and 1910.109(i)(4)(ii)(b). Galvanized iron, copper, lead, zinc, aluminum, and wood cannot be used due to either their combustibility or susceptibility to corrosion and reaction with AN. However, these materials can be used for storage bins if the bins are protected by an impermeable coating or cladding, such as two-part epoxy coatings, steel sheet cladding, or sodium silicate.

Low temperature is required for safe storage of AN. OSHA requires that "Containers of ammonium nitrate shall not be accepted for storage when the temperature of the ammonium nitrate exceeds **130** °F." [1910.109(i)(3)(ii)(a)] (~54 °C).

Limits on the amount of AN stored are important for preventing tragic explosions.

In the United States, the limit of bagged AN stored in a building or structure not equipped with an automatic sprinkler system is 2,270 tonnes (2,500 tons) [1910.109(i)(7)(i)]. Many disasters involved amounts exceeding 2,270 tonnes (the 1947 Brest explosion, the 2020 Beirut explosion), but others involved only tens or hundreds of tonnes (the 2001 Toulouse explosion, the 2013 West Fertilizer Company explosion, and the 2015 Tianjin Port explosion). Meanwhile, in Europe, though the European Union does not mandate limits on the amounts of AN stored, the stringency of regulations in the Seveso Directive acts to limit the amount of dangerous substances present within an establishment.

Fire protection is essential for AN storage.

Fire has played a significant role in many accidents involving AN. Accordingly, strict fire protection measures are necessary for AN storage. The requirements for water sprinkler systems and fire control devices (such as fire hoses, portable fire extinguishers, water supplies, and fire hydrants) are clearly stated in OSHA regulations 910.109(i)(7)(i) and 1910.109(i) (7)(ii)(a) & (b).

In summary, safe AN storage requires ventilation, isolation from combustible materials, temperature control, control of the amount in storage, fire protection, and avoidance of combustible contaminants (Figure 8).

Figure 8: Ammonium nitrate safe storage guidelines.

5.3 ALTERNATIVE NITROGEN FERTILIZERS

Although AN is an important fertilizer because of its high nitrogen content, its explosive hazards limit its applications and it is even banned in some areas. Reducing the concentration of AN, finding alternative compounds, and developing safer forms may help to increase the safety of nitrogen fertilizers. Table 4 lists alternative nitrogenous fertilizers with their NPK ratings (defined above in comparison to AN). Unfortunately, the alternative with the highest nitrogen content is anhydrous ammonia, which is a gas at ambient temperature and is toxic. Other alternatives with high nitrogen content, such as ammonium hydroxide solutions and urea, are volatile. Mixing high nitrogen content fertilizers with other macronutrients to form NPK mixtures reduces the explosive risk while still meeting plant nutritional requirements (Table 5).

TABLE 4. COMPARISON OF AMMONIUM NITRATE WITH ALTERNATIVE NITROGENOUS FERTILIZERS

Fertilizer	Formula (CAS Registry Number)	NPK rating* ¹⁰⁸	Comment
Ammonium nitrate	NH ₄ NO ₃ (6484-52-2)	34-0-0	High nitrogen content with explosive risk
Anhydrous ammonia	NH ₃ (7664-41-7)	82-0-0	Pressurized gas, RMP**-regulated substance with a threshold of 10,000 lbs, ¹⁰⁹ regulated as Dangerous Goods for transportation. ¹¹⁰
Aqua ammonia	NH₄OH (1336-21-6)	(16-25)-0-0	Volatile, RMP-regulated substance with a threshold of 20,000 lbs. ¹⁰⁹
Urea	CO(NH ₂) ₂ (57-13-6)	46-0-0	High nitrogen content, volatile
Ammonium sulfate	(NH ₄) ₂ SO ₄ (7783-20-2)	21-0-0	Non-volatile, low nitrogen content
Diammonium phosphate	(NH ₄) ₂ HPO ₄ (7783-28-0)	18-46-0	Contains phosphorus
Monoammonium phosphate	NH ₄ H ₂ PO ₄ (7722-76-1)	11-48-0	Contains phosphorus
Potassium nitrate	КNO ₃ (7757-79-1)	13-0-44	Contains potassium, stable
Sodium nitrate	NaNO ₃ (7631-99-4)	16-0-0	Stable
Calcium cyanamide	CaCN ₂ (156-62-7)	21-0-0	Contains calcium
Calcium nitrate	Ca(NO ₃) ₂ ·4H ₂ O (13477-34-4)	15-0-0	Contains calcium

*NPK rating: relative content of nitrogen, phosphorus, and potassium **RMP: Risk Management Plan⁶²

TABLE 5. FERTILIZER MIXTURES CONTAINING NITROGEN

Fertilizer	Formula (CAS Registry Number)	NPK rating*61	Comment
Calcium nitrate/urea (Cal-Urea)	Ca(NO ₃) ₂ + 4CO(NH ₂) ₂ (5124-41-4)	34-0-0	Contains calcium; urea volatilizes from the soil before it is all used by the plants.
Ammonium nitrate sulfate	NH ₄ NO ₃ + x(NH ₄) ₂ SO ₄ (1628327-53-6)	N.A.	Reduced explosive risk compared to AN
Urea/ammonium nitrate (N-SOL or UAN solutions)	CO(NH ₂)₂ + NH₄NO₃ (15978-77-5)	(19-32)-0-0	50% nitrogen is volatile
Ammoniated superphosphate	N.A.	(12-17)-(22-35)-0	Contains phosphorus
Ammonium phosphate nitrate	NH ₄ H ₂ PO ₄ + xNH4NO3 (57608-40-9)	N.A.	Contains phosphorus
Ammonium phosphate sulfate	NH ₄ H ₂ PO ₄ + x(NH ₄) ₂ SO ₄ (86438-07-5)	N.A.	Contains phosphorus
Ammonium polyphosphate	N.A. (68333-79-9)	N.A.	Contains phosphorus, liquid
Nitric phosphate	N.A.	(12-17)-(22-35)-0	Contains phosphorus

Urea has been explored as another alternative as its high nitrogen content and low cost make it an attractive candidate. However, urea fertilizers are volatile, so many slowrelease formulations have been developed.⁶¹⁻⁶⁴ Other slow-release nitrogen fertilizers, such as modified lignins⁶⁵ and hydrogels,⁶⁶ have also been developed.

CHAPTER 6. SUMMARY AND PERSPECTIVES

Despite associated safety concerns, ammonium nitrate (AN) remains an important fertilizer worldwide as it is effective, inexpensive, and easy to manufacture. However, as has been highlighted once more by the Beirut incident, AN's susceptibility to fire and explosion when contained, contaminated, or located near flammable substances present significant risks.

The development of improved AN formulations, better management of the handling of AN, diligence in isolation and fire prevention in the storage of AN, and better general awareness of the associated risks of AN are crucial in preventing further disasters.

The associated risks of AN are significantly increased when large quantities are stored in populated areas for an extended period of time. The recent explosion in Beirut triggered a dramatic increase in interest concerning the safety aspects of AN. A review of the historical accidents involving AN around the world showed that they mostly occurred during storage or transportation.

A lack of awareness of how to safely handle and store AN is one of the common factors that cause these tragic accidents. Therefore, the need for safer formulations of AN and better strategies and training for preventing accidents and misuse is clear. As analysis of patent literature shows, better formulations are in development; however, there is yet to be a suitable, accessible alternative. The market for AN is expected to grow at 4.90% annually over the next seven years.⁶⁷ There is therefore a clear commercial opportunity to develop a safe, affordable alternative for AN.

However, the development of a suitable alternative is likely to take several years, putting pressure on governing bodies worldwide to implement and enforce adequate AN safety regulations. In addition, improved enforcement and regulation of AN handling by governments in combination with stewardship of AN by its manufacturers will likely be necessary. Improved management of the AN supply chain can also reduce the use of AN in improvised explosives. Further enforcement needs to be focused on longer time scales, and consistently applied worldwide.

Overall, this report may serve to educate the public for promoting the awareness of AN safety. It may also provide a useful resource to scientists in the AN research field, as well as business leaders in the AN industry, for their efforts to further improve the safety of AN.

APPENDIX 1. LIST OF AMMONIUM NITRATE DISASTERS.⁶⁻⁹

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence							
ACCIDENTS DURING STORAGE												
1916 2-Apr	United Kingdom	Faversham, Kent	115	630	Storage	A fire spread to 25 tons of TNT and 700 tons of AN stored at a factory in Uplees, Faversham which then exploded. ⁷²						
1924 1-Mar	United States	Nixon, New Jersey	20	2	Storage	A warehouse containing 4,800 pounds of AN at the Nixon Nitration Works was destroyed by a fire and several large ex- plosions. The explosiveness of the product may have been enhanced by impurities present in the nitric acid which had been used previously for producing TNT. ⁷³						
1940 5-Aug	France	Miramas	0	240	Storage (warehouse)	240 tonnes of AN exploded from the impact of a shell thrown from a fire in a nearby munitions train. ⁷⁴						
1947 26-Aug	United States	Presque Isle, Maine	0	220	Storage	Spontaneous heating in a stack of mixed fertilizer destroyed 240 tons of AN stored at a plant of the A.W. Higgins Company. ⁷⁵						
1947	Canada	St. Stephen, New Brunswick	0	360	Storage (plant)	Fire at the Summers Fertilizer Company (St. Stephen, New Brunswick) burned 400 tons of stored AN; no explosion occurred. ⁷⁵						
1963 9-Jan	Finland	Oulu	10	10	Storage	AN used for fertilizer and explosives at the Typpi Oy industrial site in Oulu caught fire and exploded. ⁷⁶						
1988 29-Nov	United States	Kansas City, Missouri	6	23 (ANFO**)	Storage (trailer)	More than 25 tons of AN with fuel oil (ANFO) (to be used for blasting) exploded at a construction site in Kansas City, Missouri. Five people were convicted of arson for the explosions. ⁷⁷						
1994 2-Aug	Papua New Guinea	Porgera Gold Mine	11	80 (ANE)	Storage (plant)	Two explosions occurred at a sensitized AN emulsion (ANE) plant near the Porgera Gold Mine in Papua New Guinea. The initial explosion involved a few tonnes of explosive; the subsequent fire ignited about 80 tonnes of the ANE causing a larger explosion with a mushroom cloud. ⁷⁸						
1994 13-Dec	United States	Port Neal, Iowa	4	N.A.	Storage (plant)	Two explosions at the Port Neal, Iowa, AN processing plant operated by Terra Industries caused the release of 5,700 tons of anhydrous ammonia that continued for 6 days after the explosions. Nearby groundwater was contaminated. ^{79,80}						

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details							
	ACCIDENTS DURING STORAGE												
1998 6-Jan	China	Xingping, Shanxi	22	25	Storage (plant)	An accident caused the explosion of 27.6 tons of AN liquor contained at the Xinghua Fertilizer Company. ^{81,82}							
2001 21-Sep	France	Toulouse	31	200-300	Storage	A warehouse at the AZF (Azote de France) fertilizer factory (Toulouse, France) exploded. The warehouse contained off-specification granular AN which was stored flat and separated by partitions. The cause of the explosion was not determined. ⁸³							
2003 1-Jan	Spain	Cartagena, Murcia	0	N.A.	Storage (warehouse)	AN fertilizer in the storage facility of Fertiberia (Cartagena, Spain) underwent self-sustained decomposition and caught fire. Mechanical removal of unburned AN controlled the fire. ⁷⁴							
2003 2-Oct	France	Saint-Romain- en-Jarez	0	3-5	Storage	A barn in Saint-Romain-en-Jarez (Loire) containing 3-5 tonnes of bagged AN caught fire. ⁸⁴							
2009 30-Jul	United States	Bryan, Texas	0	N.A.	Storage (warehouse)	The El Dorado Chemical Company in Bryan, Texas, a company processing AN into fertilizer, caught fire. ⁸⁵							
2013 17-Apr	United States	West, Texas	15	240	Storage	A fire (determined to be arson) at a fertilizer company in West, Texas, caused AN stored there to explode. The explosion destroyed roughly 80 homes and a middle school. ^{86,87}							
2015 12-Aug	China	Port of Tianjin	173	800	Storage (warehouse)	Nitrocellulose stored at a Port of Tianjin hazardous goods warehouse spontaneously combusted, igniting a fire which triggered the detonation of AN stored nearby. ^{88,89}							
2020 4-Aug	Lebanon	Beirut	200-300	2,750	Storage (plant)	Fire broke out in a Port of Beirut (Lebanon) warehouse containing 2,750 tonnes of AN seized from an abandoned ship impounded in 2014. At least 6,000 people were injured and nearly 300 people died. ^{90,91}							

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details
		AC	CIDENTS	DURING TR	ANSPORTATIO	ON
1920 14-April	United States	Brooklyn, New York	0	1,919 / 882	Transportation (cargo ship)	Fire broke out on the steamer Hallfried while discharging cargo, which included 1,919 tonnes of AN in casks. Although the fire was intense and 882 tonnes of the AN were destroyed, no explosion occurred. ⁷⁵

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details					
ACCIDENTS DURING TRANSPORTATION											
1925 3-May	United States	Muscle Shoals, Alabama	0		Transportation	440 barrels of AN caught fire and exploded during shipping from a warehouse in Muscle Shoals, Alabama. The barrels had been stored in a warehouse with varying humidity for 6 years, and were likely ignited by friction of the barrels with their nitrate-impregnated paper linings. ⁹²					
1947 16-Apr	United States	Texas City	581	2,100+ 870	Transportation (cargo ship)	The cargo ship Grandcamp was being loaded when a fire was detected in the hold: 2,300 tons of AN in sacks were already aboard. The ship exploded, setting fire to another vessel, 250 m away, which contained 1,050 tons of sulfur and 960 tons of AN. ^{93,94}					
1947 28-Jul	France	Brest	29	1,700-3,309	Transportation (cargo ship)	The Norwegian cargo ship Ocean Liberty was loaded with 3,309 tonnes of AN and various flammable products when it caught fire. Pumping pressured steam into the sealed hold did not stop the fire; the ship exploded while being towed from the harbor. ^{95,96}					
1953 23-Jan	-	Red Sea	0	N.A.	Transportation (cargo ship)	The Finnish cargo ship Tirrenia caught fire while carrying AN. The fire could not be extinguished with steam, and the ship was abandoned before it exploded. ⁹⁷					
1959 7-Aug	United States	Roseburg, Oregon	14	4.1	Transportation (truck)	A truck carrying dynamite and 4.5 tons of AN caught fire and exploded. A number of blocks of downtown Roseburg, Oregon, were destroyed by the explosion. ^{98,99}					
1960 17-Dec	United States	Traskwood, Arkansas	0	140-180	Transportation (train)	A train carrying AN, fuel oil, and nitric acid derailed. The AN did not explode, but reac- tion of the nitric acid with fuel oil caused an explosion which scattered the AN at the crash site. ¹⁰⁰					
1972 30-Aug	Australia	Taroom, Queensland	3	11	Transportation (truck)	An electrical fault in a truck carrying 11 tonnes of AN caused a fire and explosion north of the Queensland town of Ta- room. ¹⁰¹					
2004 18-Feb	Iran	Neyshabur	300	399	Transportation (train)	A train carrying sulfur, AN, cotton, and oil derailed and exploded, killing 300 people. ^{102,103}					

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details						
ACCIDENTS DURING TRANSPORTATION												
2004 9-Mar	Spain	Barracas	2	25	Transportation (truck)	A truck carrying 25 tonnes of AN fertilizer exploded after a traffic accident. ¹⁰⁴						
2004 24-May	Romania	Mihăileşti, Buzău	18	20	Transportation (truck)	A truck carrying 20 tonnes of AN over- turned and caught fire. The explosion left a crater 6.5 m deep and 42 m in diameter. ¹⁰⁵						
2004 22-Apr	North Korea	Ryongchŏn	162		Transportation (train)	A freight train carrying AN exploded,in Ryongchon, destroying the train station and nearly 8,000 homes in the city; most buildings within 500 m of the explosion site were damaged. ¹⁰⁶						
2007	Spain	Estaca de Bares	0	400	Transportation (cargo ship)	2,600 tonnes of NPK fertilizer *** (of 6,000 tonnes) carried on the ship Ostedijk underwent self-sustained decomposition and burned for 11 days. NPK fertilizer contains about 15% AN. ¹⁰⁷						
2007 9-Sep	Mexico	Monclova, Coahuila	28	22 (ANFO)	Transportation (truck)	A pickup truck crashed into a trailer containing 22 tonnes of ANFO, causing a fire in the trailer and a large explosion. ¹⁰⁸						
2014 5-Sep	Australia	Wyandra, Queensland	0	56	Transportation (truck)	A truck carrying 56 tonnes of AN exploded due to a traffic accident. The explosions sent debris up to 2 km from the crash site. ¹⁰⁹						

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details				
ACCIDENTS DURING MANUFACTURING / PROCESSING										
1916 14-Jan	United States	Gibbstown, New Jersey	1	1.81	Manufacturing	4,000 pounds of AN exploded in an evaporating pan of the Repauno works of the du Pont Co. The explosion may have been caused by overheating of the AN by a clogged air lance. ¹¹⁰				
1916 15-Sep	United States	Oakdale, Pennsylvania	6	1.36	Manufacturing	At Aetna Chemical Co., 3,000 pounds of AN exploded while being concentrated by evaporation. Impurities in the nitric acid used to produce the AN were proposed as the cause. ¹¹¹				

Date	Country	Location	Deaths	AN (tonnes*)	Occurrence	Details					
ACCIDENTS DURING MANUFACTURING / PROCESSING											
1921 26-Jul	Germany	Kriewald	19	30	Processing	Mining explosives were used in an attempt to dislodge 30 tonnes of AN that had aggregated in two wagons, exploding the wagons instead.					
1921 21-Sep	Germany	Oppau	561	450	Processing	Attempted disaggregation of a 50:50 mixture of AN and ammonium sulfate stored at a BASF plant in Oppau caused a massive explosion. Only 450 tonnes of the AN exploded, out of 4,500 tonnes of fertilizer in the pile. ^{112,113}					
1925	United States	Emporium, Pennsylvania	N.A	0.2	Manufacturing	500 pounds of AN exploded during evaporation. ⁸					
1942 29-Apr	Belgium	Tessenderlo	189	150	Processing	Attempted disaggregation of a pile containing 150 tonnes of AN with industrial explosives caused an explosion. ¹¹⁴					
1944	United States	Milan, Tennes- see	4	N.A.	Manufacturing	Explosion during evaporation (AN contami- nated with oil and further sprayed with oil-air mixture from a broken compressor). ⁸					

*One tonne, sometimes called a metric ton, is equal to 1,000 kg, as opposed to one ton, which is 2,000 lb. ** ANFO: ammonium nitrate mixture with fuel oil *** NPK fertilizer: Nitrogen-phosphorus-potassium fertilizer

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