AMMONIUM NITRATE AND MIXED FERTILIZERS CONTAINING AMMONIUM NITRATE

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1.0 SCOPE

This data sheet provides guidance for the manufacturing, storage, and handling of ammonium nitrate (AN) products in solid and liquid forms, as well as mixed fertilizers. This data sheet applies to the following:

A. Manufacturing of AN (liquid and solid)

B. Storage and handling of the following:

1. Solid ammonium nitrate products or fertilizers with a concentration of 60% or more by weight
2. Mixed fertilizers with nitrogen concentration of 28% or more by weight
3. Mixed fertilizers at any concentration when the mix is capable of self-sustaining decomposition (SSD)

C. Storage areas storing a minimum of 1,000 lb (450 kg) of ammonium nitrate products or mixed fertilizers

This data sheet does not cover blasting agents, ammonium nitrate emulsions (ANE), or commercial explosives. For those, see Data Sheet 7-28, *Energetic Materials*.

1.1 Hazards

Ammonium nitrate is a noncombustible oxidizer capable of supporting the combustion of combustible materials. It is considered a stable material under normal conditions. However, when heated or contaminated, exothermic decompositions and explosions can occur.

Ammonium nitrate must be considered detonable when confined and exposed to elevated temperatures, boosted by high explosives, low pH conditions during processing, or under the presence of incompatible materials, such as organic materials, oils, acids, sulfur, powdered metals, chlorates, and copper salts, that can initiate a decomposition.

1.2 Changes

January 2021. This document has been completely revised. The following significant changes were made:

A. Reorganized the document to provide a format that is consistent with other data sheets.

B. Revised recommendations to align with current codes, standards, and industry practices.

C. Updated loss history.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

2.1.1 Use FM Approved equipment, materials, and services whenever they are applicable and available. For a list of products and services that are FM Approved, see the *Approval Guide*, an online resource of FM Approvals.

2.2 Construction and Location

2.2.1 General

2.2.1.1 Perform a facility siting study to determine adequate separation between storage and process areas, and other important buildings or structures.

2.2.2 Process Areas

2.2.2.1 Locate manufacturing equipment in the open or in steel-frame buildings of damage-limiting construction.

2.2.2.2 Use only compatible materials that will resist the environment and process conditions for the construction of equipment and piping.

2.2.2.3 Design piping to minimize the probability of valving off sections of high temperature or high concentration of ammonium nitrate.

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2.2.3 Storage Areas

2.2.3.1 Construct storage areas with noncombustible materials. Ensure all materials and fittings used during construction and that may come in contact with the stored materials under normal operation, or in the event of spillage, are compatible or protected (suitable robust coating).

2.2.3.2 Use beams and partitions made of only noncombustible construction of compatible materials in the storage areas. Do not use wood, galvanized steel/iron, copper, lead, or zinc.

2.2.3.3. Design floors of the storage areas with noncombustible and nonporous materials with no open drains, traps, tunnels, pits, or pockets where ammonium nitrate can collect and be confined.

2.2.3.4 Provide storage buildings with ventilation means (e.g., vent fans, ridge vents, roof-lines louvered vents) to adequately remove products of combustion and decomposition in the event of a fire. Consider the following activation options in the design:

A. Manual. Ensure the fire can be detected at early stages using a reliable detection system (i.e., smoke or heat detection) and vents that can be activated from a constantly-attended location.

B. Automatic. Smoke, heat or other reliable detection systems can be used to activate the vents.

2.2.3.5 Provide storage areas with temperature and humidity controls to prevent AN changes or crystallization that could increase the AN sensitivity.

2.3 Process Safety

2.3.1 Establish a formal process safety program in accordance with Data Sheet 7-43, *Process Safety*. Include a detailed evaluation of all process and storage areas, and ensure a thorough process is followed for implementation.

2.4 Occupancy

2.4.1 General

2.4.1.1 Store and handle ammonium nitrate and products containing ammonium nitrate in dry areas, free of water spots or leakages.

2.4.1.2 Keep areas clean and free of any combustible materials or contaminants. Immediately clean any spills and dispose of materials in accordance with local regulations.

2.4.1.3 Immediately remove any damaged container or waste from the storage area to a safe location.

2.4.1.4 Use only clean tools and equipment for manufacturing and handling operations to prevent any ammonium nitrate contamination. Ensure the tools do not present signs of corrosion, AN crystals, or other contaminants such as grease or oil.

2.4.1.5 For bagged storage, use only pallets that are clean and free of any oil or combustible substances or materials. Keep all packaging clean and free of all contamination.

2.4.1.6 Provide stock rotation procedures (“first-in, first-out”) for storage areas to prevent material decomposition due to long storage periods. Consider storage periods no longer than one year.

2.4.1.7 Dedicate the storage area to only compatible materials.

2.4.1.8 Never loosen caked storage by blasting. Never store ammonium nitrate with explosives or blasting agents.

2.4.1.9 Separate bulk storage from other materials stored in the area. Provide separation by noncombustible walls to prevent mixing and contamination. Include curbs, drains, or liquid-tight walls to prevent incompatible materials from flowing into the AN storage area.

2.4.1.10 Store off-spec AN in separated and designated areas. Ensure no other material that could contaminate or produce a decomposition reaction in the off-spec AN is stored in the same area.

2.4.1.11 Immediately remove any contaminated material from the storage area following specific procedures for safe removal and disposal. Perform an incident investigation, and establish the necessary actions to prevent recurrence. See Data Sheet 7-43, *Process Safety*, for additional information.

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2.4.1.12 Apply the following for bagged storage of fertilizer-grade AN (FGAN), palletized or solid piled:

A. Limit the height of bagged storage to 20 ft (6.1 m).

B. Arrange palletized storage so that any point on a line through the pallet channels, running at right angles to the aisles, is no further than 10 ft (3 m) from the aisles to limit spread of fire through pallet channels and to facilitate firefighting. Overall distance along the channels should not exceed 20 ft (6 m).

C. Arrange unpalletized storage so that no point within a pile is more than 10 ft (3 m) from an aisle.

D. Limit the quantity of bagged storage in a single building to 5,000 tons (4,500 tonnes) maximum, arranged in 1,000 tons (900 tonnes) piles separated by 20 ft (6.1 m) aisles.

E. Keep the length of the pile for both palletized and solid-pile bagged storages limited by the other dimensions of the pile and the 1,000 ton (900 tonnes) storage limitation. Pile sizes for bulk storage are not limited.

F. Keep bagged storage at least 30 in. (0.75 m) from any walls of the storage building.

2.4.1.13 Apply the following for bagged storage of technical-grade AN (TGAN), palletized or solid piled:

A. Limit the height and width of bagged storage to 12 ft (3.7 m).

B. Keep the length of the pile for both palletized and solid-pile bagged storages limited by the other dimensions of the pile and the 1,000-ton (900 tonnes) storage limitation. Limit the quantity of bagged storage in a single building to 5,000 tons.

C. For pile arrangements provide aisles with a minimum of 65 ft (20 m).

D. Keep bagged storage at least 30 in. (0.75 m) from any walls of the storage building.

2.4.2 Indoor Storage

2.4.2.1 Maintain the height of AN bulk storage piles at least 3 ft (0.91 m) below overhead equipment and structures.

2.4.3 Outdoor Storage

2.4.3.1 Provide outdoor storage with weather protection to prevent direct sunlight and rainwater coming into contact with AN piles.

2.4.3.2 Maintain AN piles with a minimum separation distance of 30 ft (9 m) from any combustible building or materials.

2.5 Protection

2.5.1 Protect conveyers located in storage, process areas, or in between those areas, in accordance with Data Sheet 7-11, *Conveyers*.

2.5.2 Provide automatic sprinkler protection for AN manufacturing if combustible building materials are present, and packaging areas in accordance with Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*, using hazard category HC-2.

2.5.3 Protect all areas occupied by support operations, NOT handling or storing AN, in accordance with the applicable FM data sheets.

2.6 Equipment and Processes

2.6.1 General

2.6.1.1 Provide process pumps with safety controls and interlocks to automatically shut down the process upon low flow or high temperature detection.

2.6.1.2 Perform a process hazard analysis (PHA) to determine the necessary safety controls and interlocks to prevent the following process conditions:

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- Low solution density.
- Bubble formation (solution aeration).
- High acid concentration: typical operating range pH is 3 to 5.
- High temperature: typical operating range is 260-290°F (127-143°C).
- Liquid confinement without circulation during idle periods.
- Lack of or poor circulation of solution.
- Formation of nitrous oxides or the presence of contaminants.

2.6.2 Neutralizer

2.6.2.1 Provide safety controls and interlocks for temperature and acid concentration in the neutralization reactors and attached process equipment. Determine set points based on the specific manufacturing process and plant design. Locate alarms at a constantly-attended control room or area.

2.7 Operation and Maintenance

2.7.1 Operation

2.7.1.1 Establish operational procedures for all operation modes, including normal startup and shutdown, emergency shutdown and restart, process upsets, and prolonged temporary stoppages that include activities to prevent conditions such as the following:

- Confinement without circulation during idle periods
- High acid concentration
- Temperature increase
- Crystal formation
- Maximum hold time in the neutralizer to be no longer than 8 hours or 1 shift

2.7.1.2 Develop emergency procedures for the neutralization reactor and include clear instructions for when safe operating conditions are exceeded.

2.7.1.3 Provide operators with full authority to stop a reaction and emergency dump or water flood the contents of a reactor system when safe boundary conditions are exceeded. See Data Sheet 10-8, *Operators*, for additional information.

2.7.1.4 Perform routine contaminant testing for water systems or any material that needs to be returned to the neutralizer during processing.

2.7.1.5 Promptly rework any uncontaminated off-spec material, or dispose of it in accordance with local regulations if reworking is not possible.

2.7.1.6 Arrange the process to deliver ammonium nitrate to the storage area at temperatures below 130°F (55°C).

2.7.2 Maintenance

2.7.2.1 Establish an asset integrity monitoring program in accordance with Data Sheet 9-0, *Asset Integrity*.

2.7.2.2 Inspect, test, and maintain safety controls, alarms, and interlocks in accordance with Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks*.

2.7.2.3 Use only substances compatible with ammonium nitrate during inspection, testing, and maintenance (ITM) activities. If this is not practical, ensure a thorough cleaning operation is performed to eliminate any substance that could present a contamination source to the process before operations are restarted.

2.7.2.4 Ensure the management of change (MOC) program is implemented for every non-in-kind replacement of equipment, parts, and any substance used during ITM activities.

2.8 Training

2.8.1 Train operators on the functions and required actions associated with the storage, processing, and handling of ammonium nitrate in accordance with Data Sheet 10-8, *Operators*. At a minimum, include the following in the training:

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A. Specific hazards associated with AN, and conditions that could result in product decomposition or detonation

B. Manufacturing, storage, and handling procedures

C. Normal and emergency procedures, including shutdown and startup

2.9 Ignition Source Control

2.9.1 Control or eliminate ignition sources within the storage building. Keep all storage away from steam lines, radiators, light bulbs, or other heat sources.

2.9.2 Provide coverings for high-intensity lighting. For additional information, see Data Sheet 5-21, *Metal Halide High-Intensity Discharge Lighting*.

2.9.3 Provide direct-strike lightning protection for all buildings that store or handle ammonium nitrate.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

Since 1916, at least 31 explosions have occurred worldwide involving AN (see Table 1). Among these events, three were caused by blasting performed to disaggregate caked material, one explosion was most probably due to material incompatibility (contamination), and one event was related to unsafe operation. In all of the remaining 26 events, fire preceding the explosion was identified as the most probable cause.

Table 1. Ammonium Nitrate Explosion Events Worldwide, 1916 - 2020

Location	*Country*	*Date*	*Category*	*Cause*
Faversham, Kent	UK	4/2/1916	Storage	Fire
Kriewald	DE (PL)	7/26/1921	Train	Blasting
Oppau	DE	9/21/1921	Storage	Blasting
Nixon, NJ	US	3/1/1924	Storage	Fire
Muscle Shoals, AL	US	4/4/1925	Train	Fire
Miramas	FR	8/5/1940	Train	Fire
Tessenderlo	BE	4/29/1942	Storage	Blasting
Texas City, TX	US	4/16/1947	Ship	Fire
Brest	FR	7/28/1947	ShipF	ire
Red Sea		1/23/1953	Ship	Fire
	US	1957	Truck	Fire
Roseburg, OR	US	8/7/1959	Truck	Fire
Traskwood, AR	US	12/17/1960	Train	Fire
Norton, VA	US	12/27/1961	Storage	Fire
Mount Vernon, MO	US	11/9/1966	Storage	Fire
Taroom	AU	1972	Truck	Fire
Pryor Creek, OK	US	1/17/1973	Storage	FirePo
Port Neal, IA	US	12/19/1994	Process (LAN)	Unsafe operation
	BR	1997	Truck	Fire
Toulouse	FR	9/21/2001	Storage	Material incompatibility
St. Romain en Jarez	FR	10/2/2013	Storage	Fire
Neyshabur	IR	2/18/2004	Train	Fire
Barracas	ES	3/9/2004	Truck	Fire
Mihăileşti, Buzău	RO	5/24/2004	Truck	Fire
Ryongchõn	KP	2004	Train	Fire
Pernik	BG	3/6/2007	Truck	Fire
Monclova	MX	9/4/2007	Truck	Fire
West, TX	US	4/17/2013	Storage	Fire
Charleville	AU	9/5/2014	Truck	Fire
Tianjin Port	CN	8/12/2015	Storage	Fire
Beirut	LB	8/4/2020	Storage	Fire

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3.2 Illustrative Losses

3.2.1 Solid Ammonium Nitrate Explosions

3.2.1.1 Explosive Charges Used to Break up Caked Ammonium Nitrate/Sulfate Blend Cause Pile to Detonate

In Oppau, 1921, a pile consisting of 4,500 tons (4,000 tonnes) of a blend of ammonium nitrate with ammonium sulfate exploded during blasting to break up caked material. About 16,000 explosive charges were fired into this mixture without incident, but this time a more powerful explosive was used. The plant was demolished and 600 people were killed. (Oppau, Germany, 1921.)

3.2.1.2 Detonation of AN Destroys Steamships Grandcamp and High Flyer at Texas City

In 1947, the steamship Grandcamp exploded about one hour after fire was discovered in a hold containing 2,300 tons (2,090 tonnes) of AN fertilizer (wax-coated) in paper bags. About 40 hours later, the steamship High Flyer, which was docked near the Grandcamp and also loaded with about 900 tons (815 tonnes) of bagged AN, exploded. Brands from the Grandcamp fire/explosion apparently ignited storage in the hold of the High Flyer. Five hundred and eighty-one people were killed and more than 4,000 injured. (Texas City, Texas, USA, 1947.)

3.2.1.3 Detonation of Off-Spec AN at Fertilizer Plant

In Toulouse, 2001, a detonation occurred at a plant producing agricultural and industrial nitrates, as well as chlorine-containing compounds. Off-spec nitrates were stored in a dedicated building and detonated shortly after a mixture of AN and sodium dichlorocyanurate, a pool chemical, was brought to the building. Investigations confirmed that AN and sodium dichlorocyanurate are strongly incompatible and can detonate when mixed. The explosive yield was estimated at 22-44 tons (20-40 tonnes) TNT, which indicates that about 10%-30% of the material present detonated. Thirty people were killed and more than 2,500 injured. (Toulouse, France, 2001.)

3.2.1.4 Detonation of AN Following Fire in Combustible Construction

In West, Texas, 2013, fire broke out at a facility that was used to blend, store, and distribute fertilizers. About 20-30 tons (18-27 tonnes) of AN were stored in a main plywood bin in an unsprinklered building with combustible construction. The fire burned for about 20 minutes and engulfed the main storage bin before the explosion occurred. The explosive yield was estimated at 5.0-12.6 tons (4.5-11.4 tonnes) TNT, suggesting that nearly all AN in the main storage bin detonated. Fifteen people were killed and more than 260 injured. (West, Texas, USA, 2013.)

3.2.1.5 Detonation of AN Stored in Containers Following Nitrocellulose Fire

At Tianjin Port, 2015, about 880 tons (800 tonnes) of AN were stored in bags and sacks inside containers at the site of a logistics company. The site also stored a number of other chemicals and hazardous materials in close quarters, including nitrocellulose. A fire occurred in the nitrocellulose storage and subjected the AN containers to intense heat. The first explosion occurred about 42 minutes after the fire was reported, and a second, major explosion followed about 30 seconds later. The explosive yield of the main explosion was estimated at about 470 tons (430 tonnes) TNT, suggesting that all AN detonated at a high efficiency. Container storage provides confinement, low ventilation, and heat retention, which are negative factors increasing the chance and severity of AN detonation when exposed to fire. About one hundred and seventy people were killed and more than 800 injured. (Tianjin Port, China, 2015.)

3.2.1.6 Detonation of AN in a Port Warehouse Following Fire

At the Port of Beirut, 2020, fire broke out at a warehouse storing about 3,030 tons (2,750 tonnes) of AN. Reports indicate that the fire was caused by welding performed at the building and involved several combustibles also stored in the warehouse. After about 14 minutes of fire, a smaller first explosion occurred, which was attributed to fireworks, and a main explosion of AN followed about 35 seconds later. The AN had been stored in the warehouse for about 6 years prior to the explosion, leaving the material exposed to thermal cycling and potential contamination. About 220 people were killed, more than 6,500 injured, and more than 300,000 left homeless. (Beirut, Lebanon, 2020.)

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3.2.2 Fertilizer Decomposition

3.2.2.1 Water Ineffective in Controlling Decomposition of Bulk Fertilizer Storage

Decomposition started in the bulk storage of 47,000 tons (42000 tonnes) of 12-12-12 fertilizer. Water was immediately sprayed on the decomposing mass with hose streams, but had no apparent effect in controlling decomposition. Several thousand gpm of water were applied for approximately 10 hours before bringing decomposition under control. The fertilizer was almost completely consumed, and the building severely damaged. Total property damage exceeded US$1 million. (South Point, Ohio, 1957.)

3.2.2.2 Overheated Electric Cord Starts Decomposition in Silo Holding 1500 Tons of Fertilizer

An imported 12-12-12 fertilizer was stored in a 114 ft (35 m) x 44 ft (13 m) high, steel storage silo. An overheated electrical cord apparently started self-sustaining decomposition in the 1500 tons (1300 tonnes) of fertilizer. The decomposition continued for 14-½ hours, until the fertilizer was washed out of the silo using 800,000 gal (3000 m^3) of water.

3.2.2.3 Dynamite Used to Break Up Bulk Fertilizer Pile Cause Decomposition that Consumed 1/3 of the Pile

A 170 ton (150 tonnes) pile of 12-12-12 fertilizer was dynamited to break up the mass for handling. After several tons had been removed, employees noted fumes coming from the remaining material. The decomposing material was removed from the building and the decomposition was allowed to go to completion. The loss involved 50 tons (45 tonnes) of material.

3.2.2.4 Three Hundred Tons of Bulk Fertilizer Pile Destroyed by Slow Decomposition

A new granular composition of 12-8-4 fertilizer was blended containing cottonseed meal and ammonium nitrate. Since this was a new product, samples were taken almost daily to check thermal stability and graining. No heating was noted in samples taken from near the surface of a 20-ft (6 m) high pile. The plant was shut down for a long weekend with employees making periodic visits. The last visit was made at 11:00 p.m. and nothing unusual was reported. At 1:30 a.m., neighbors called the fire service upon seeing fumes coming from the storage building. Small hose was used to wet down the material, but proved ineffective. The material was removed to the yard, and decomposition was halted by the application of water. 300 tons (270 tonnes) were involved.

3.2.3 Liquid Ammonium Nitrate Explosions

Several low-order detonations involving liquid AN have occurred. These all caused very localized damage within plant boundaries.

In 1964, a small explosion occurred at a plant in Tennessee, USA, involving a fertilizer solution. A pipe connected to a pump detonated, causing shock damage to tanks and equipment. The cause was never determined. A recommendation was made to avoid confinement of solutions, especially where steam heating potential exists.

In 1966, two explosions occurred in a plant in Kansas, USA. Both involved liquid nitrate solutions. Both incidents involved pipes or pumps and only caused local damage.

The only known significant incident involving liquid AN occurred in 1994 in the United States. Widespread damage occurred both on- and off-site. Many details of this incident are not available. The following abstract is taken from various news media and the official Chemical Accident Report by the US Environmental Protection Agency (EPA). The loss is estimated to be in excess of US$300 million.

The plant produced various grades of liquid AN and urea-ammonia nitrate (UAN) solutions as well as ammonia and solid urea fertilizer products. Solid (prilled) AN had not been produced for many years, nor was any solid AN stored on site.

An 83% solution of liquid AN was produced by reacting nitric acid with ammonia in a neutralizer reactor. The 83% solution was not further concentrated at this plant. The reactor featured an off-gas scrubbing system and a rundown (surge) tank for collection of product prior to bulk storage and shipping. Approximately 60 tons (55 tonnes) of 83% liquid AN was present in the process system.

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During an unplanned shutdown, the liquid AN plant experienced a large explosion. The explosion destroyed the AN plant and severely damaged the urea and ammonia plants, including the main control room located over 700 ft (200 m) from the epicenter. Overpressures from the event were felt off site. Two large craters were formed at the explosion epicenter and process structures were fragmentized, indicating one or more detonations occurred. No significant fires ensued due to lack of combustible or flammable materials in the process.

The initial detonation may have occurred in a confined pipe within the process system. The EPA report shows evidence of a scrubber pump deadheading into a pipe. The initiating pipe explosion likely shocked part of the larger mass of the neutralizer and rundown tanks. Of the 60-ton (55-tonnes) mass of 83% AN, it is postulated that up to 10% or 6 tons (5.5 tonnes) of liquid AN contributed to detonation energy. Suspected factors contributing to the explosion were:

- Unplanned shutdown during extremely cold weather.
- The process did not have an ability to recirculate solution.
- Solution was confined and stagnant within vessels for many hours.
- Cold weather caused concern with freezing of the AN solution.
- Steam was added directly to the neutralizer to prevent freezing (this was a change from normal procedure).
- Acid concentration was higher than normal, possibly caused by a leaking acid valve.
- Chlorinated water leaked into nitric acid solution inside a condenser (possibly sensitizing the solution with chlorides).
- Steam could have concentrated the solution above the normal 83%.
- Steam could have caused bubble formation that caused highly sensitive low-density pockets.
- Steam could have caused higher than normal temperatures.

The root cause can be attributed to a failure of process safety management as changes in the process were made without commensurate understanding of the potential hazard presented by the changes. According to the EPA report, no process hazard analysis had been conducted nor was there a process safety oversight program in place for this part of the plant.

3.3 Ammonium Nitrate

Ammonium nitrate (NH_4NO_3) is a white crystalline or granular solid that readily absorbs moisture, is highly soluble in water, and has a melting point of 336°F (169°C). Below its melting point, five crystalline states of AN exist, and each transition between states is accompanied by a change in material density. The solid density of AN at room temperature is 108 lb/ft^3 (1,725 kg/m^3); at a temperature just below its melting point, the density decreases to 96.8 lb/ft^3 (1,550 kg/m^3). Solid AN is typically produced in prills, granules, or flakes. Liquid products are also available.

The two major uses of ammonium nitrate are in fertilizer, either by itself or as a major ingredient, and as an ingredient in the manufacture of blasting agents (TGAN). While fertilizer-grade AN (FGAN) and technical-grade AN (TGAN) are chemically identical, TGAN features a higher porosity (lower density) than FGAN, which allows TGAN to better retain additives, such as fuel oils to produce ammonium-nitrate fuel-oil (ANFO). Several grades and mixtures of FGAN are available, with different blending substances, coatings, or additives to control moisture absorption or to reduce detonation sensitivity.

FGAN production facilities are usually on the site of a larger fertilizer complex that manufactures ammonia and other fertilizers such as solid urea and urea ammonia nitrate (UAN) solution mixtures. In the past, most plants produced solid (prilled) AN. However, in recent years liquid products have become more prevalent. UAN solutions do not appear to be subject to detonation and create a limited hazard.

3.3.1 Solid Ammonium Nitrate

3.3.1.1 Hazards

Ammonium nitrate (AN) is a noncombustible oxidizer capable of supporting the combustion of combustible materials. It is considered a stable material under normal conditions. However, when heated or contaminated, exothermic decompositions and explosions can occur. AN undergoes a variety of decomposition reactions, varying from endothermic breakdown into ammonia and nitric acid, to detonation yielding water, nitrogen, and nitrogen oxides.

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Conditions for detonation can be promoted by heating under confinement, contamination, or severe shock. The shock-sensitivity of AN increases as density decreases, which can occur due to crystalline state changes following temperature rise through repeated cycles at about 90°F (32°C).

Available data shows that AN as prepared today (post-1945) is insensitive to explosive decomposition under normal storage conditions as long as it is not contaminated with incompatible materials, such as ignitable liquids, greases, oils, sulfur, hydrocarbons, acids, fibers, sawdust, charcoal, and most organic materials. In the presence of moisture, copper reacts with ammonium nitrate to form tetramine cupric nitrate, which is very sensitive to impact and can trigger an explosion. Acids tend to promote ammonium nitrate decomposition.

The addition of inert material, such as other fertilizer ingredients or limestone, tend to reduce the tendency for detonation. Concentrations below 60% ammonium nitrate should not detonate, but a mixture of ammonium nitrate and ammonium sulfate is hazardous down to 40% ammonium nitrate.

Explosion losses of note in the past were due to the presence of substantial amounts of organic materials in the coating, on the order of 1%-2%, or other organic contamination (e.g., lift truck oils, fuel spills, rubber belt conveyor debris). The newer manufacturing methods and coating materials have significantly reduced the hazard. There have not been any significant explosions with uncontaminated materials in recent history.

3.3.1.2 Manufacturing Process

AN is produced by reacting 55%-56% nitric acid with ammonia in a continuous neutralization process. The nitric acid is usually produced onsite from ammonia, and the ammonia is also produced onsite by steam reforming of natural gas. Occasionally, ammonia and nitric acid will be purchased and stored for production at a stand-alone AN plant.

The manufacture of ammonium nitrate (see Figure 1) essentially follows four steps:

- Neutralization
- Evaporation
- Prilling/granulation
- Conditioning

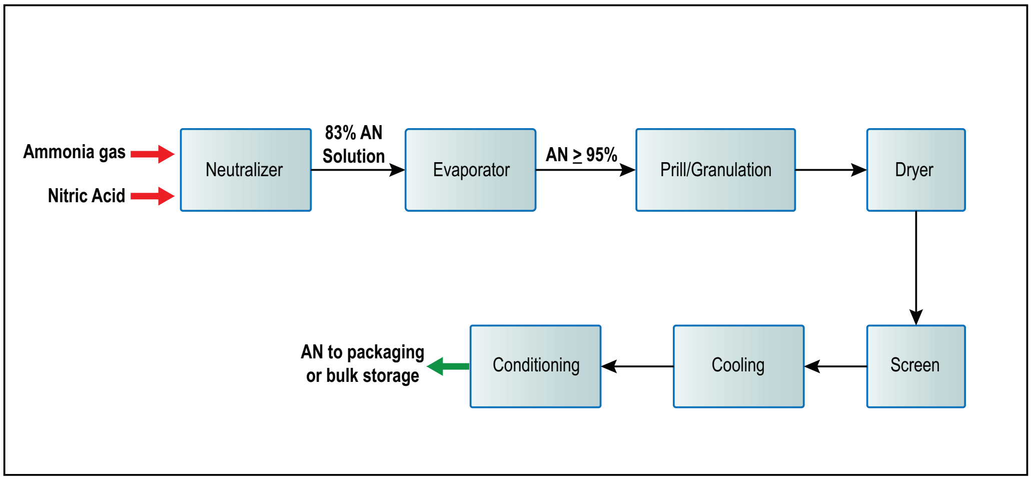

Fig. 1. Ammonium nitrate manufacturing process

Neutralization. The reaction between ammonia and nitric acid is highly exothermic and takes place in a neutralization reactor to produce 83% AN in a water solution. Process conditions are typically 260°F-290°F (127°C-143°C) and pH from 3 to 5. Stoichiometric reaction of the feed materials would result in a solution having a pH of about 4. Control temperature in the reactor is normally achieved by regulating the addition of feeds and by removal of heat. The heat removed can be recovered for acid preheating, ammonia evaporation, or evaporation of additional water.

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The outflow from the reactor usually enters a surge tank (also called a rundown tank) and then is stored in large bulk tanks for shipment as 83% AN or for mixing with urea solutions.

Several AN manufacturing processes exist worldwide, where neutralizers can operate below, exactly at, or above the atmospheric boiling point of the ammonium nitrate solution.

Evaporation. The AN solution store at the surge tanks is pumped to the evaporators to produce AN with a concentration of 95% or greater by weight. Efficient vacuum evaporators, falling film units, or second stage evaporators can be used. This last type of evaporator is commonly used for concentrations of 99% or more and are designed for small volume of melt retention with short residence times.

Prilling/granulation. These final steps will provide a uniformly sized product with abrasion and crush-resistant properties as well as some other properties required for the safe storage and handling of the product.

Prilling is the process of forming solid rounded and granular ammonium nitrate products. Different tower heights are used, depending on the characteristics and product density desired. For instance, low-density and porous products, usually made for the manufacture of explosives, are produced in towers of 110-200 ft (33-60 m) in height using AN solution with a 96%-97% concentration. For the manufacture of fertilizers, for which high-density AN product is required, towers only 66-98 ft (20-30 m) in height and solutions with a 99.7%-99.8% concentration are used.

The prilling process consists of spraying the ammonium nitrate concentrate solution at the top of the tower with an upward air flow for droplet cooling, which solidifies the AN droplets into spherical prills that are collected at the bottom of the tower.

For the granulation process, the ammonium nitrate is layered in onion-skin fashion on small seed particles by spraying a 99+% solution on a dense cascading curtain of granules. This process is carried out in a 11-15 ft (3.5-4.5 m) diameter by 46-59 ft (14-18 m) long rotating drum having specially designed flights. The well-rounded particles are screened and cooled, producing granules having moisture content of about 0.1%; they do not require a conditioner. These granules also have a higher crushing strength than prills and are less subject to breakdown in storage and handling.

Conditioning. After prills are formed, they are dried, screened, and cooled, before a conditioning coating is applied. Usually clay, diatomaceous earth, or very small amounts (less than 0.2%) of liquid fat or oil to control moisture absorption are used. A common practice in Europe is to mix ammonium nitrate with limestone, which makes it less sensitive to detonation. Such mixtures are known as cal-nitro, nitrochalk, ammonium nitrate lime (ANL), or ammonium nitrate dolomite (AND).

Once prills are conditioned, they are either packed in bags or stored in bulk form, ready for shipment. Ammonium nitrate is available in various grades and mixtures. Pure ammonium nitrate is rarely used because of its hygroscopicity.

3.3.2 Liquid Ammonium Nitrate

The potential for explosions in solid AN has long been recognized, but until recently the potential for an explosion in liquid AN has not been of great concern. However, research and loss history now demonstrate that explosions can occur in liquid materials if certain conditions of sensitization, confinement, and concentration exist in combination.

In addition, production of solid AN for fertilizer use has gradually been replaced by liquid solutions. Many facilities no longer make solid products, or now make a combination of solid and liquid products. However, all facilities that produce AN, whether solid or solution, have a liquid phase step in the process.

Given the very large number of operating ammonium nitrate plants worldwide and the many years of operation without significant explosion events, it can be assumed that the potential for an explosion in AN solutions is very low.

3.3.2.1 Research

Imperial Chemicals Industries (ICI) conducted tests on nitrate/water solutions between 80% and 100% concentration in temperature ranges between 230°F and 365°F (110°C and 185°C). The tests were carried out in containers with only moderate confinement. The primary conclusions were as follows:

- Only a powerful initiator, such as RDX explosive, produced detonation initiation in AN solutions.

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- There appeared to be minimum critical levels of temperature and concentration below which initiation did not take place. At atmospheric pressure, ICI concluded that these levels are 90% concentration and 302°F (150°C) temperature.

The US Bureau of Mines carried out tests on molten AN (100% concentration) in steel tubes and glass beakers at temperatures of 356°F, 392°F, 428°F (180°C, 200°C, and 220°C). Only at the highest temperature could the AN be detonated.

TNO (Netherland Organization for Applied Scientific Research), under contract to the Dutch government, conducted research on AN solutions to determine the hazards of transporting these solutions in road and rail tankers. The tests were carried out under strong confinement in steel pipes. Tests were conducted on solutions varying from 80% AN in water to 99.9% solutions, and at temperatures ranging from 259°F to 446°F (126°C to 230°C). The solutions were all pure; that is, there was no purposeful contamination (sensitization) of the solution. The explosion was initiated by an explosive charge. The conclusions of these tests were as follows:

- 99% solutions of AN produce high-speed detonations (velocity = 4,500 mph [2000 m/sec]) at temperatures above 401°F (205°C) when strongly confined. Fragmentation of the tube was evidence of a high order detonation.

- Solutions as low as 80% produced lower order explosions (2,600 mph [1150 m/sec]) at temperatures as low as 259°F (126°C). The tube containment did not fragment at these levels, indicating no detonation occurred.

- Low-velocity detonations are possible in AN solutions confined in pipes, but not in large vessels such as tanks (due to the absence of wall effects).

- During transport in tanks, no detonation can occur in AN concentrations below approximately 95% or below solution temperatures of approximately 302°F (150°C).

Over a five-year period ending in 1982, the Department of Mining Engineering at Queen's University, Kingston, Ontario, Canada, conducted a series of tests on solid and liquid AN to better understand its propensity to detonate under accidental conditions. This study was under contract to the Canadian Fertilizer Institute and others.

The principal conclusion was that the shock sensitivity of ammonia nitrate, whether liquid or solid, is a function of density, which is a direct function of temperature. The higher the temperature, the lower the density and the greater the potential for shock detonation. AN solutions and molten AN both have lower densities than solid materials. Further, aerated (bubbling) solutions are further decreased in density and sensitized. Finally, AN solutions or molten AN are most sensitive when contaminated by copper.

Other testing showed a combination of aluminum and zinc with molten AN caused a violent decomposition, whereas aluminum or zinc alone had no similar effect.

3.4 Ammonium Nitrate Mixed Fertilizers

Ammonium nitrate fertilizer is regulated as a Division 5.1 oxidizer by the US Department of Transportation (Title 49 Code of Federal Regulations). This tracks the UN Recommendations on the Transport of Dangerous Goods, a code that many nations are adopting in whole or in part. In NFPA 400, *Hazardous Materials Code*, ammonium nitrate is considered a Class 2 oxidizer.

The main nutrients in mixed fertilizers are nitrogen, phosphorus, and potassium. Mixed fertilizers are available in various grades, usually designated by three numbers (e.g., 8-6-4, 12-12-12, 20-10-5). The numbers express percentage of available nitrogen (N_2), phosphorus as phosphate (P_2O_5), and potassium as potash (K_2O), in that order.

Note: The percentage of available nitrogen is not the same as the percentage of ammonium nitrate. For example, 100% ammonium nitrate is 34-0-0 fertilizer.

These main nutrients are obtained from various components in the mix:

- Nitrogen: ammonia, ammonium nitrate, ammonium sulfate, urea, sodium nitrate, ammonium chloride, or ammonium phosphate
- Phosphorus: calcium phosphate or ammonium phosphate
- Potassium: potassium chloride or potassium sulfate

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Fertilizers containing 60% or more ammonium nitrate or 40% or more ammonium nitrate mixed with ammonium sulfate have the same potential detonation hazard as described in Section 3.3.1.1 for ammonium nitrate.

Lower concentrations of ammonium nitrate in mixed fertilizers have shown a tendency for self-sustaining decomposition, which gradually spreads through a pile of fertilizer. This is not burning, as such. No flames are produced unless paper, oil, or other organic material is present. The decomposing material does not usually get hot enough to glow. Hot, toxic gases are given off, and any combustible material present may become ignited.

The tendency of a mixed fertilizer for self-sustaining decomposition is promoted by the following:

A. Ammonium nitrate must be present to decompose and provide the heat and gases.

B. Chloride tends to act as a catalyst.

C. There must be a rigid porous matrix which withstands the high temperatures produced. (A higher concentration of ammonium nitrate tends to melt, which stops the decomposition reaction).

The reaction can be initiated by heat, which results in the endothermic decomposition:

$$NH_4NO_3 \xrightarrow{\text{heat}} NH_3 + HNO_3$$

The more volatile ammonia is driven off. The nitric acid remaining increases the acidity of the mixture in the area. Together with the chloride present, this tends to promote exothermic decomposition reactions such as:

$$NH_4NO_3 \xrightarrow{H+} N_2O + H_2O + \text{heat and } 5NH_3 + 3HNO_3 \xrightarrow[Cl-]{H+} 4N_2 + 9H_2O + \text{heat.}$$

The heat produced causes decomposition of adjacent ammonium nitrate making it acid, and the reaction progresses gradually through the pile at a rate of a few feet per hour, generating temperatures of 500-1000°F (260-540°C).

The composition of a given fertilizer mix which will undergo self-sustaining decomposition can be determined experimentally. Figure 2 and Figure 3 show the area of decomposition for ammonium nitrate-ammonium phosphate-potassium chloride and ammonium nitrate-ammonium sulfate-potassium chloride mixes, respectively. The ammonium sulfate mix appears to be more subject to self-sustaining decomposition because it has a lower pH (more acidic) than the phosphate mix.

The decomposition can start from localized heating, such as a hot light bulb, a blasting attempt, or an external fire. If the whole pile is at a high temperature, it can undergo a spontaneous decomposition reaction or fume-off. This hazard exists mainly in storage bins or driers in process areas.

A standardized test for determining the potential for self-sustaining exothermic decomposition is the UN Test S.1 (Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Part III, Subsection 38.2.4, United Nations).

A 6 x 6 x 20 in. (150 x 150 x 500 mm) trough of stainless steel wire gauze is filled with fertilizer and heated at one end with two laboratory burners or a 250 W electric heating element. Heating is applied until decomposition of the fertilizer is well established and propagation of the front is observed. Heating is discontinued. After about 20 minutes the distance the decomposition has progressed is measured; if it has traveled the length of the trough, the fertilizer is considered as subject to self-sustaining decomposition.

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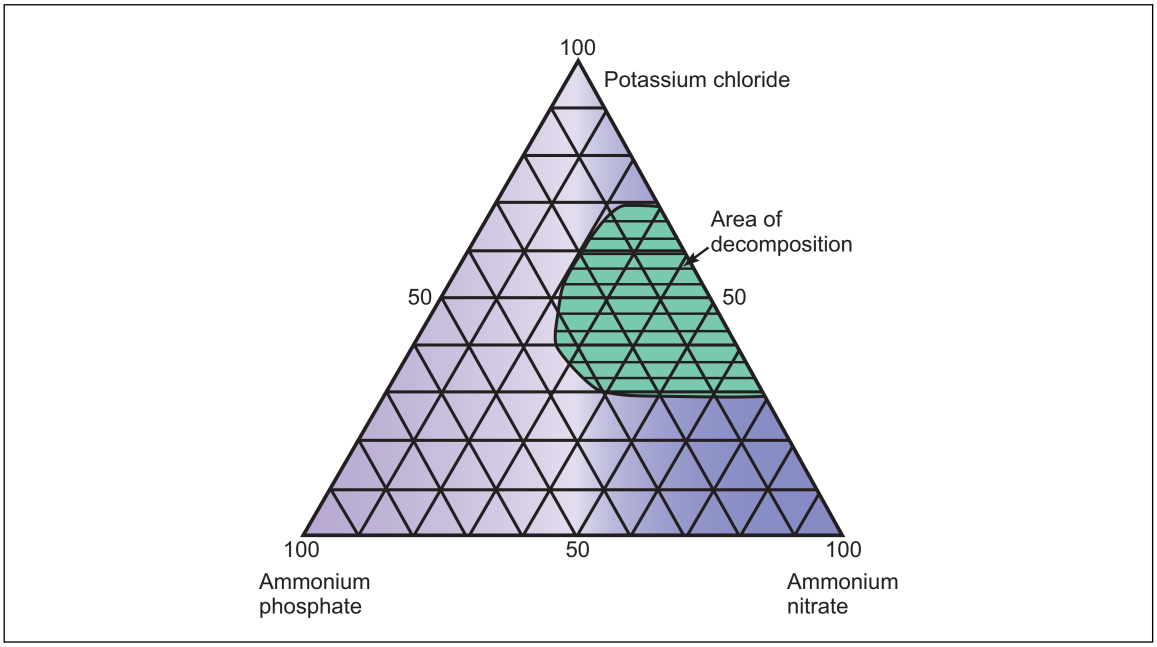

Fig. 2. Area of self-sustaining decomposition in mixtures of ammonium nitrate, ammonium phosphate and potassium chloride

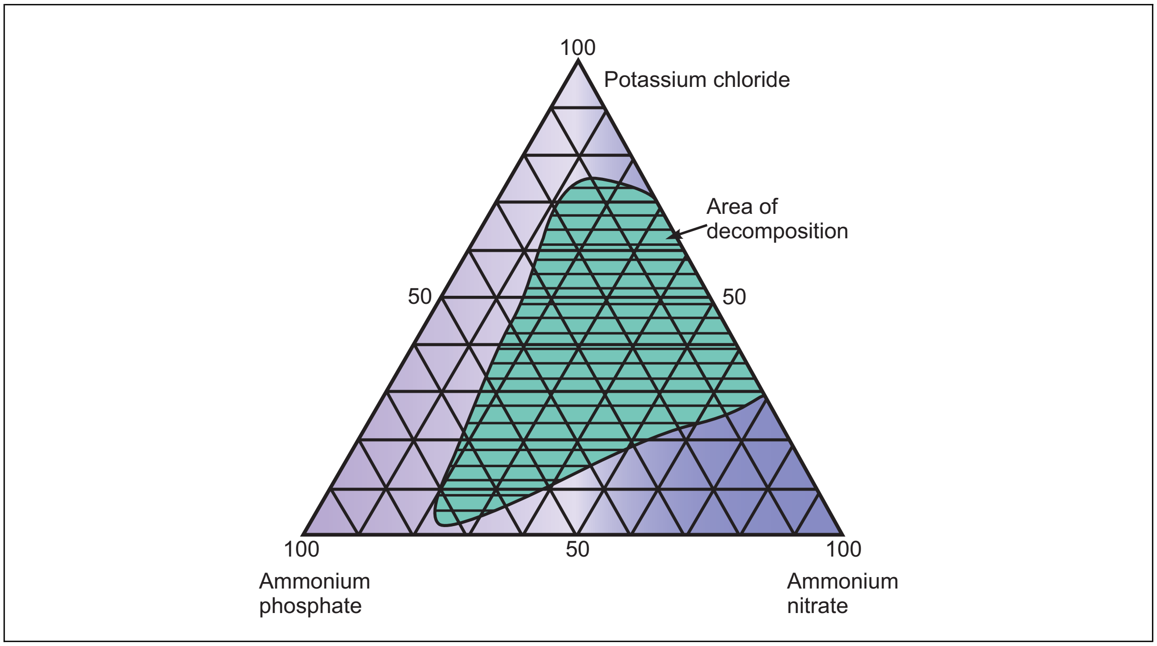

Fig. 3. Area of self-sustaining decomposition in mixtures of ammonium nitrate, ammonium sulfate, and potassium chloride

4.0 REFERENCES

4.1 FM

Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*
Data Sheet 5-21, *Metal Halide High-Intensity Discharge Lighting*
Data Sheet 7-11, *Conveyors*
Data Sheet 7-28, *Energetic Materials*
Data Sheet 7-43, *Process Safety*

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Data Sheet 7-45, *Safety Controls, Alarms and Interlocks*
Data Sheet 9-0, *Asset Integrity*
Data Sheet 10-8, *Operators*

4.2 Other

Center for Chemical Process Safety (CCPS). *Plant Guidelines for Technical Management of Chemical Process Safety*.

The Department of Mining Engineering, Queen's University. *The Explosion Hazards of Ammonium Nitrate and Ammonium Nitrate Based Fertilizer Composition*. Kingston, Ontario, November 1982.

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APPENDIX A GLOSSARY OF TERMS

Fertilizer-grade ammonium nitrate (FGAN): Ammonium Nitrate commonly used to formulate fertilizer products with a typical density of 62 lb/ft^3 (100 kg/m^3). This can also be known as a high density AN.

Self-sustaining decomposition (SSD): Is the phenomenon in which a fertilizer is capable of decomposition initiated by spontaneous heating or an external heat source, at a localized area that will spread throughout the mass.

T**echnical-grade ammonium nitrate (TGAN):** Ammonium Nitrate generally presented in the form of porous prills with a typical density of 50 lb/ft^3 (800 kg/m^3) or lower, which is commonly used in the manufacture of explosives. This can also be known as low density AN.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

January 2021. This document has been completely revised. The following significant changes were made:

A. Reorganized the document to provide a format that is consistent with other data sheets.

B. Revised recommendations to align with current codes, standards, and industry practices.

C. Updated loss history.

October 2013. Editorial corrections, the correction of the NFPA code references on ammonium nitrate and updating the information on hazard testing of fertilizer blends of ammonium nitrate with other components (fuse decomposition).

April 2013. Changed references from Data Sheet 7-42 to 7-0 reflecting the use of a non-TNT model for vapor cloud explosion evaluations.

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

January 2000. This revision of the document was to provide a consistent format.

September 1998. Document was revised to incorporate new information on liquid ammonium nitrate hazards.

March 1977. Document was updated from information provided in the *Handbook of Industrial Loss Prevention*. This data sheet was revised to incorporate material on mixed fertilizers containing ammonium nitrate. Other important changes were: a) the establishment of 60% ammonium nitrate as the concentration above which detonation is considered possible (40% if mixed with ammonium Sulphate); b) the addition of sprinkler system design and water supply specifications; and c) the explanation in more detail of fuse-type decomposition of mixed fertilizers.

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