Variables Associated with the Classification of Ammonium Nitrate – A Literature Review

FINAL REPORT BY:

Sean Gillis
Sreenivasan Ranganathan
Fire Protection Research Foundation, Quincy, MA

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Ammonium Nitrate (AN) “is a chemical compound produced in both solid and liquid forms that is commonly used in fertilizers”. The burning rate of technical-grade AN prill falls within the Class 2 oxidizer criteria in Annex G of NFPA 400, 2016. The loss history of AN also indicates potential for unstable reactive hazard properties, uncontrolled decomposition and/or detonation under circumstances that are not fully understood. In the most recent revision of NFPA 400, Hazardous Materials Code, the Technical Committee (TC) classified Ammonium Nitrate as a Class 2 Oxidizer. However recent hazardous material incidents involving AN have resulted in differing views regarding the reactivity of the compound and whether or not it should be considered an unstable reactive in NFPA 400. The different behaviors of AN in different fire situations make it difficult to determine the appropriate safe practices for AN storage and handling. There are also discrepancies between the NFPA and International Fire Code (IFC) classifications of Ammonium Nitrate. As a result there is a need for additional data to assist in the proper classification/treatment of AN. An examination of existing data involving the reactivity of AN will assist the NFPA 400 TC in determining the appropriate classification of Ammonium Nitrate, and perhaps point to a need for future Ammonium Nitrate testing.

The purpose of this project is to summarize the available information on the different forms of Ammonium Nitrate and how they are classified. This will be accomplished through a two-step literature review: summarizing the available information on AN classification from chemistry and code-based documentation, and identifying the variables which led to AN instability from existing test data and results.

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Keywords: Ammonium Nitrate, Classification, Critical variables, NFPA 400, Fertilizer grade, TGAN, FGAN.

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PROJECT TECHNICAL PANEL

Elizabeth Buc, Fire & Materials Research Laboratory, MI

Jonathan Butta, Jensen Hughes, MD

Henry Febo, FM Global, MA

Martin Gresho, FP2Fire Inc., CO

Noel Hsu, The Fertilizer Institute, CO (Alt. Donald Thomas)

Lynne Kilpatrick, Sunnyvale Public Safety, CA

James Lay, OSHA, DC

Tod Ossmann, Willis Towers Watson, NY

Nancy Pearce, NFPA, MA

Ronald Thomas, Institute of Makers of Explosives, UT

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1. Background Information

1.1. Project Background

Ammonium Nitrate (AN) “is a chemical compound produced in both solid and liquid forms that is commonly used in fertilizers”. The burning rate of technical-grade AN prill falls within the Class 2 oxidizer criteria in Annex G of NFPA 400, 2016. The loss history of AN also indicates potential for unstable reactive hazard properties, uncontrolled decomposition and/or detonation under circumstances that are not fully understood. In the most recent revision of NFPA 400, Hazardous Materials Code, the Technical Committee (TC) classified Ammonium Nitrate as a Class 2 Oxidizer. However recent hazardous material incidents involving AN have resulted in differing views regarding the reactivity of the compound and whether or not it should be considered an unstable reactive in NFPA 400.

In 2013, a fire broke out at an ammonium nitrate plant in West, Texas that ultimately caused a massive explosion culminating in the deaths of 15 people, mostly first responders. On the other hand a similar fire at an Ammonium Nitrate storage facility in Athens, Texas simply burned itself out without detonation and without the help of firefighters. The different behaviors of AN in different fire situations make it difficult to determine the appropriate safe practices for AN storage and handling. There are also discrepancies between the NFPA and International Fire Code (IFC) classifications of Ammonium Nitrate. As a result there is a need for additional data to assist in the proper classification/treatment of AN. An examination of existing data involving the reactivity of AN will assist the NFPA 400 TC in determining the appropriate classification of Ammonium Nitrate, and perhaps point to a need for future Ammonium Nitrate testing.

The purpose of this project is to summarize the available information on the different forms of Ammonium Nitrate and how they are classified. This will be accomplished through a two-step literature review: summarizing the available information on AN classification from chemistry and code-based documentation, and identifying critical variables which led to AN instability from existing test data and results. The following tasks are carried out for this project:

- **Task 1: Literature Review** – A review of relevant literature related to previous and current classifications of Ammonium Nitrate, and a brief summary of recent Ammonium Nitrate explosion events.
- **Task 2: Identify the critical variables** – Identifying the critical variables associated with Ammonium Nitrate instability from previous test data and results. Provide baseline recommendations for future Ammonium Nitrate testing, if necessary.
- **Task 3: Final Report** – Produce a final report based on the gathered information from Tasks 1 and 2.

### 1.2. Ammonium Nitrate

Ammonium Nitrate (AN) is a crystal salt which can be synthesized through the reaction between nitric acid and pure ammonia\(^1\). The chemical configuration commonly synthesized of Ammonium Nitrate is \(\text{NH}_4\text{NO}_3\) and the main application of this chemical compound is for plant fertilizer, although it can also be used in the mining industry for controlled explosions. According to Kiiski\(^2\) in the report titled *Properties of Ammonium Nitrate Based Fertilizers*, it accounted for 20% of world consumption of nitrogen fertilizers in 2005 and “about 132 million tons of Nitrogen (N) is annually fixed from the air of which Ammonium Nitrate (AN) accounts for 13%”\(^2\), which makes it one of the most popular uses for nitrogen and one of the most abundant fertilizers available on the market.

There are two main grades of Ammonium Nitrate, Fertilizer Grade (FGAN) and Technical Grade (TGAN). Both are chemically identical. TGAN formulations are more porous than FGAN to facilitate the absorption of fuel for use in explosives (e.g., ANFO). As the name suggests, Fertilizer Grade is the type that is used for fertilizer application in the agriculture industry, and most commonly in prill/granule form. FGAN can include pure ammonium nitrate, which is found to have “relatively weak explosive properties and is not considered an explosive in many classifications”\(^3\).

However since the chemical compound contains a significant amount of oxygen, Ammonium Nitrate (including FGAN) is inherently a strong oxidizer. Technical Grade AN puts the oxidizing properties of AN to

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use, and is typically combined with some sort of combustible material (which is often fuel oil at about 6% concentration) and designated as ANFO which is used for controlled explosions in the mining industry. TGAN prills used for explosive applications are physically different from FGAN prills having a lower bulk density being more porous than FGAN\(^3\). ANFO is DOT classified 1.5D, Blasting Agent.

Although not typically considered to be explosive, under certain conditions including confinement, heating, and/or the presence of contaminants, both FGAN and TGAN have the ability to detonate. For this reason, as well as the dangers associated with the misuse of ammonium nitrate (such as the 1995 Oklahoma City bombing), the storage and handling of any type of ammonium nitrate is heavily regulated around the world.

### 1.3. NFPA 400\(^4\)

In the United States, the most widely used standard for the regulation of ammonium nitrate is NFPA 400, *Hazardous Materials Code*. The purpose of this code is “to provide fundamental safeguards for the storage, use and handling of hazardous materials”\(^4\). Several previous NFPA codes were combined to be included in the first edition of NFPA 400, which was published in 2010. These documents include NFPA 430 *Code for the Storage of Liquid and Solid Oxidizers*, NFPA 432 *Code for the Storage of Organic Peroxide Formulations*, NFPA 434 *Code for the Storage of Pesticides*, and NFPA 490 *Code for the Storage of Ammonium Nitrate*\(^4\). Significant changes were made to NFPA 400 in both the 2013 and 2016 editions. Most recently and of interest to this project, the 2016 edition of NFPA 400 incorporated a number of changes to Chapter 11 of the document, which details the requirements for the storage and handling of Ammonium Nitrate\(^4\).

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2. Historical Incidents

This section tabulates a list of historical incidents involving Ammonium Nitrate and some pertinent information identified from these incidents.

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<tr>
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<th>Mass (tons)</th>
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<tbody>
<tr>
<td>01/14/1916</td>
<td>Gibbstown, NJ</td>
<td>USA</td>
<td>3</td>
<td>AN was evaporating in a boiler around 187 deg C. An explosion occurred which created a 1.8 m deep crater. 1 person was killed and 12 injured. AN adjacent to boiler did not detonate.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation(^5)</td>
</tr>
<tr>
<td>09/15/1916</td>
<td>Oakdale, PA</td>
<td>USA</td>
<td>3</td>
<td>AN was recovered from TNT residuary acid, and it exploded in the pan. A 173-lb fragment was found 3/4 miles away, and the explosion was heard 15 miles away. 6 people died, 8 were injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation(^5)</td>
</tr>
<tr>
<td>10/04/1918</td>
<td>Morgan, NJ</td>
<td>USA</td>
<td>1000</td>
<td>Fire occurred in an ammunition factory, where 4000 tons of AN. One AN drum burned and explosions occurred in AN sheds. The drums contained molten AN. AN at other places in the fire and explosion area remained intact. 64 killed, 100 injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation(^5)</td>
</tr>
<tr>
<td>04/12/1920</td>
<td>Stolberg, Germany</td>
<td>Germany</td>
<td>-</td>
<td>Crushed AN (in a railway car) was being crushed through blasting, which resulted in an explosion.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation(^5)</td>
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<tr>
<td>07/26</td>
<td>Kriewald</td>
<td>Germany</td>
<td>ca. 25</td>
<td>Two piles of crushed AN (in a railway car) were being loosened through blasting, which resulted in an explosion. 19 people were killed, 23 more were injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>09/21</td>
<td>Oppau</td>
<td>Germany</td>
<td>-</td>
<td>De-aggregate or breakup a pile of AN mixed with Ammonium Sulfate through blasting led to a massive explosion. Damages spread over 6km from the blast site, where 561 people were killed and 1997 injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>05/07</td>
<td>Emporium, PA</td>
<td>USA</td>
<td>0.25</td>
<td>AN was evaporating in a boiler at 136 deg C. It was contaminated with organic surface coating and an explosion occurred.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>04/29</td>
<td>Tessenderloo</td>
<td>Belgium</td>
<td>150</td>
<td>Blasting was being done on a pile of crushed AN. An explosion occurred and more than 100 people died.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>02/01</td>
<td>Milan, TN</td>
<td>USA</td>
<td>-</td>
<td>AN in a pan at 175 deg C was agitated with a pressurized air stirrer. Due to the presence of oil in the air an explosion occurred. 4 were killed and 17 injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
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<tr>
<td>04/16/1947</td>
<td>Texas City, TX</td>
<td>USA</td>
<td></td>
<td>A fire occurred onboard a cargo ship that was carrying AN. Suppression was called off in hopes of saving the precious cargo onboard, but a massive explosion occurred. Around 600 killed and 3500 injured.</td>
<td><em>Ship Explosion Ignites 3-Day Rain of Fire and Death</em>&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>07/28/1947</td>
<td>Brest, France</td>
<td>France</td>
<td>ca. 3000</td>
<td>A cargo ship docked in the port of Brest, France caught fire. The load of 3000 tons of AN exploded, 30 people were killed and thousands were injured.</td>
<td><em>Tragedies sparked by fertiliser explosions around the world</em>&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>01/23/1954</td>
<td>Red Sea</td>
<td>-</td>
<td></td>
<td>A fire occurred onboard the cargo ship Tirrenia which contained 4000 tons of AN. The ship was abandoned and exploded in the middle of the night.</td>
<td>Lessons learned from Toulouse and Buncefield Disasters: From Risk Analysis Failures to the Identification of Atypical Scenarios Through a Better Knowledge Management&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
<tr>
<td>04/16/1972</td>
<td>Harrison, TN</td>
<td>USA</td>
<td>-</td>
<td>Decomposition of AN and associated exothermic oxidation of an ion-exchanger resin caused an explosion in a water-preparation plant.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation&lt;sup&gt;5&lt;/sup&gt;</td>
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<tr>
<td>01/17/1973</td>
<td>Pryor, OK</td>
<td>USA</td>
<td>7000 - 20000</td>
<td>A fire caused explosion of a propane tank, which resulted in the explosion of a nearby AN stored in bags.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
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<tr>
<td>05/12/1988</td>
<td>Pawlograd</td>
<td>Ukraine</td>
<td>12</td>
<td>Ammonite (ca. 90% AN) was being loaded when an explosion occurred. 3 people died.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>11/29/1988</td>
<td>Kansas City, MS</td>
<td>USA</td>
<td>25</td>
<td>Several fires began due to suspected arson, which resulted in several explosions of trailers loaded with ANFO. Minor explosions continued and ultimately 6 firefighters were killed.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>01/14/1991</td>
<td>Hanau, Germany</td>
<td>Germany</td>
<td>-</td>
<td>AN Solution in a washer resulted in an explosion at a Nuclear factory. The nuclear plant had the highest level of safety, but the safety organization was not aware of the risks of AN in solution.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>12/13/1994</td>
<td>Port Neal, IA</td>
<td>USA</td>
<td>74</td>
<td>This accident was during the neutralization reaction of ammonia with nitric acid. All others cited are with the finished product. A highly acidic solution of AN (83% AN) was contaminated by chlorides. Steam and air were compressed through the nitric acid line for several hours after the shutdown of the process, when the solution exploded. Two explosions within less than 1 second, 1st in the neutralizer, 2nd in the rundown tank. 4 fatalities and 18 injuries,</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
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<tr>
<td>09/21/2001</td>
<td>Toulouse</td>
<td>France</td>
<td>300</td>
<td>A pile of declassified AN exploded, causing 31 fatalities, more than 1,000 injured.</td>
<td>Assessment of Safety and Risk with a microscopic model of detonation⁵</td>
</tr>
<tr>
<td>10/02/2003</td>
<td>Saint-Romain-en-Jarez</td>
<td>France</td>
<td>3-5</td>
<td>A fire began in a barn where wooden crates containing apples were stored. Ammonium nitrate fertilizer was also being stored in the same building. The fire source lost intensity when a hissing sound was heard, which resulted in the explosion of the ammonium nitrate.</td>
<td>Fire inside a barn and explosion of fertiliser – 2 October 2003: Saint Romain-en-Jarez (Loire) France⁹</td>
</tr>
<tr>
<td>02/18/2004</td>
<td>Neyshabur</td>
<td>Iran</td>
<td>ca. 420</td>
<td>51 run-away train cars derailed, 7 of which contained 420 tons of AN fertilizer in bags. The AN exploded after catching fire from 10 Sulphur and petroleum products. 300 were killed.</td>
<td>Safety of Ammonium Nitrate¹⁰</td>
</tr>
<tr>
<td>03/09/2004</td>
<td>Castellon</td>
<td>Spain</td>
<td>ca. 25</td>
<td>An open truck carrying AN in bulk collided with a car and rolled over on its back, causing a spill and subsequent fire. An explosion occurred killing 2 people, 5 people injured.</td>
<td>Safety of Ammonium Nitrate¹⁰</td>
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<tr>
<td>04/22/2004</td>
<td>Ryongchon</td>
<td>North Korea</td>
<td>-</td>
<td>An oil road tanker collided with two railcars loaded with AN. Electric sparks from a downed electric pole sparked a fire and caused the AN to explode. 161 died and 1300 injured. Size of the crater has led military officials to question whether military explosives were involved.</td>
<td>Safety of Ammonium Nitrate¹⁰</td>
</tr>
<tr>
<td>05/24/2004</td>
<td>Mihailesti, Buzau</td>
<td>Romania</td>
<td>23</td>
<td>A truck carrying AN in bags turned over and the cabin began burning. An explosion occurred an hour later, 20 people were killed and houses nearby were damaged.</td>
<td>Safety of Ammonium Nitrate¹⁰</td>
</tr>
<tr>
<td>09/12/2005</td>
<td>Shengangzhai</td>
<td>China</td>
<td>18</td>
<td>Truck loaded with 18 tons of ammonium nitrate exploded, killing at least 11 and injuring 43.</td>
<td>Safety of Ammonium Nitrate¹⁰</td>
</tr>
<tr>
<td>07/30/2009</td>
<td>Bryan, TX</td>
<td>USA</td>
<td>-</td>
<td>A fire began at a chemical plant that blends and packages fertilizer and other chemicals, including AN. Thousands were evacuated but no explosion occurred.</td>
<td>Chemical Plant Fire Evacuates Thousands¹¹</td>
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<tbody>
<tr>
<td>04/17/2013</td>
<td>West, TX</td>
<td>USA</td>
<td>-</td>
<td>A fire began in a fertilizer plant that contained 40 – 60 tons of fertilizer grade AN (FGAN). The fertilizer came into contact with the flames and an explosion occurred within 20 minutes of the initial fire. 15 people were killed and more than 260 injured.</td>
<td>Investigation Report: West Fertilizer Company Fire and Explosion12</td>
</tr>
<tr>
<td>08/12/2015</td>
<td>Tianjin Port</td>
<td>China</td>
<td>-</td>
<td>Incident occurred in a warehouse at the port which contained hazardous/flammable chemicals – calcium carbide, sodium cyanide, potassium nitrate, ammonium nitrate and sodium nitrate. The immediate cause of the fire was traced to the spontaneous ignition of dry nitrocellulose.</td>
<td>China explosions: What we know about what happened in Tianjin13</td>
</tr>
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3. Classifications

It is rather difficult to identify the exact classifications of Ammonium Nitrate put forth by code-making bodies or other scientific outlets. Some of the classifications do not explicitly state why they were decided upon, and some resources don’t provide exact classifications but rather give explanations and information regarding what the classification might be. The resources identified that provide explicitly stated classifications of Ammonium Nitrate include the United Nations and HMEx (Hazardous Materials Expert Assistant). Other resources such as the International Fire Code provide information on possible classifications, but do not state what they believe Ammonium Nitrate can be classified as. These resources have still been identified and researched as they may provide information useful to the Technical Committee on Hazardous Chemicals. First, it is important to understand how NFPA 400 *Hazardous Materials Code*\(^4\) classifies Ammonium Nitrate.

3.1. Classification of Ammonium Nitrate in NFPA 400 – Summary

NFPA 400, *Hazardous Materials Code*\(^4\), is a standard developed by the National Fire Protection Association that applies to the storage and handling of a number of classifications of materials that are deemed, in one way or another as hazardous.

Ammonium nitrate was unique in its incorporation into NFPA 400. While other materials were incorporated as classes of hazardous materials, ammonium nitrate was a specific material that had its own requirements within a specific chapter of NFPA 400. The first two editions of NFPA 400 did not provide a classification of Ammonium Nitrate, rather they gave guidance as to how it should be classified “based on information found in safety data sheets”\(^{14}\). The documents noted that Ammonium Nitrate may be considered as an oxidizer (due to its ability to facilitate the combustion process of combustion materials) or as an unstable reactive (due to its ability to undergo chemical change under high pressure or temperature). Once classified, the document user would then refer to the chapter requirements for that class of material. For the 2016 edition of NFPA 400, rather than providing a classification of Ammonium Nitrate, the Technical Committee on Hazardous Chemicals believed that it was more important to develop safe storage, handling and protection requirements that anyone dealing with Ammonium Nitrate must adhere to\(^{14}\). The difficulty of directly classifying Ammonium Nitrate as either an

Oxidizer or an Unstable (reactive) comes from the nature of Ammonium Nitrate to behave differently under different storage and handling conditions.

Since Ammonium Nitrate is not classified in NFPA 400, it is important to determine how NFPA 400 defines an Oxidizer and an Unstable (reactive). In the 2016 edition of NFPA 400, there are four different types of oxidizers: Class 1, 2, 3 and 4. Along with a general definition of the term “oxidizer”, NFPA 400 also provides a specific definition for the four classes of oxidizers. Additionally the Hazardous Materials Code provides annex material associated with the oxidizer definitions. The definitions and annex material are provided below.

**Oxidizer** – Any solid or liquid material that readily yields oxygen or other oxidizing gas or that readily reacts to promote or initiate combustion of combustible materials and that can, under some circumstances, undergo a vigorous self-sustained decomposition due to contamination or heat exposure.

**Oxidizer Class 1** – An oxidizer that does not moderately increase the burning rate of combustible materials with which it comes into contact or a solid oxidizer classified as Class 1 when tested in accordance with test protocol set forth in G.1.

**Oxidizer Class 2** – An oxidizer that causes a moderate increase in the burning rate of combustible materials with which it comes into contact or a solid oxidizer classified as Class 2 when tested in accordance with the test protocol set forth in G.1.

**Oxidizer Class 3** – An oxidizer that causes a severe increase in the burning rate of combustible materials with which it comes into contact or a solid oxidizer classified as Class 3 when tested in accordance with the test protocol set forth in G.1.

**Oxidizer Class 4** – An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock and that causes a severe increase in the burning rate of combustible materials with which it comes into contact.


The definitions for Class 1, 2, 3 and 4 oxidizers make reference to G.1, which is a section in Annex G, Oxidizers (in NFPA 400[^4]). Annex G has extensive explanatory material that provides significant information related to how the Technical Committee on Hazardous Chemicals views and defines Oxidizers. Section G.1 of Annex G, among other explanatory material, provides a rubric of a test protocol which materials are tested to in order to determine which class of oxidizer the material is.
The test protocol consists of two separate “reaction-to-fire tests”, a bench-scale test and an intermediate-scale test. The bench-scale test consists of 30 g mixtures of oxidizer and dried cellulose (which acts as a combustible material), and the mixture is ignited by a glowing wire. The intermediate-scale test consists of 10.9 kg of oxidizer in combustible test packaging and is ignited by an external fire source. According to NFPA 400, “either of these tests can be used to classify a solid oxidizer. If both of these tests are conducted and the results differ, then the results from the intermediate-scale fire exposure test data should be used as the basis for the classification.” The metrics which define the severity of an oxidizer are the Mass Loss Rate, Active burning time, and Peak Convective Heat Release Rate. These metrics can be considered the critical variables that the NFPA 400 Technical Committee on Hazardous Chemicals believe define an oxidizer.

Similar to oxidizers, the 2016 edition of NFPA 400 *Hazardous Materials Code* provides one general definition of an unstable (reactive) material, and also breaks unstable reactive into four different classifications. These five definitions are provided below.

*Unstable (Reactive) Material* – A material that, in the pure state or as commercially produced, will vigorously polymerize, decompose, or condense, become self-reactive, or otherwise undergo a violent chemical change under conditions of shock, pressure, or temperature.

*Class 1 Unstable (Reactive)* – Materials that in themselves are normally stable, but can become unstable at elevated temperatures and pressures.

*Class 2 Unstable (Reactive)* – Materials that readily undergo violent chemical change at elevated temperatures and pressures.

*Class 3 Unstable (Reactive)* – Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction, but that require a strong initiating source or that must be heated under confinement before initiation.

*Class 4 Unstable (Reactive)* – Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures.

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Accompanying these definitions are the explanatory annex material pertaining to unstable (reactive) material. The explanatory material provides extra clarification as to what separates the different classes of an unstable (reactive) material. The explanatory material can be seen below.
• **Class 1 unstable (reactive) materials** are those that, in themselves, are normally stable, but that can become unstable at elevated temperatures and pressures and include among others, materials that change or decompose on exposure to air, light, or moisture and that exhibit an exotherm at temperatures greater than 30 °F (-1 °C), but less than or equal to 57 °F (14 °C), when tested by differential scanning calorimetry.

• **Class 2 unstable (reactive) materials** are those that readily undergo violent chemical change at elevated temperatures and pressures and include, among others, materials that exhibit an exotherm at temperatures less than or equal to 30 °F (-1 °C) when tested by differential scanning calorimetry.

• **Class 3 unstable (reactive) materials** are those that, in themselves, are capable of detonation, explosive decomposition, or explosive reaction, but that require a strong initiating source or that must be heated under confinement before initiation, and include, among others, materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures.

• **Class 4 unstable (reactive) materials** are those that, in themselves, are readily capable of detonation, explosive decomposition, or explosive reaction at normal temperatures and pressures and include, among others, materials that are sensitive to localized thermal or mechanical shock at normal temperatures and pressures.

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From the previous definitions along with the additional explanatory information found in the annex, we can develop a set of critical variables that help define a material as an unstable reactive, as well as the material’s specific class (1-4) of unstable reactive. According to NFPA 400, all classes of unstable reactive require some form of **sensitivity to temperature, pressure, or shock**. Reactive such as class 4 unstable (reactive) material have the ability to detonate at normal temperatures. Unstable reactive, as their name implies, exhibit reactions as they become unstable due to increased temperature or pressure scenarios. In terms of ammonium nitrate, if one were to question whether or not it can be classified as an unstable (reactive) material, it would be important to determine its level of reactivity at normal temperatures and pressures, and then again as temperatures and pressures are increased. If no contaminants are present, will ammonium nitrate become unstable and react explosively or exhibit exothermal at normal or elevated temperature and/or pressure? It is clear that the critical variables of NFPA 400’s classification of a material as an unstable (reactive) is the sensitivity of the material to temperature and pressure increase.
The exact classification of Ammonium Nitrate has implications on the storage, handling and usage of the material. In the 2016 edition of the Hazardous Materials Code, Chapter 11 details the storage and handling requirements of Ammonium Nitrate over 1,000 lbs. Quantities under 1,000 lbs. may divert the storage and handling requirements to a different chapter of the code, such as Chapter 15 (oxidizers) or Chapter 19 (unstable reactive materials). Since these chapters have different requirements, determining the classification of Ammonium Nitrate is critical to maintaining safe storage of the material.

3.2. Classification of Ammonium Nitrate in HMEx – Summary

HMEx stands for Hazardous Materials Expert Assistant. This is a software product developed by the International Code Council, which is the code making body that is responsible for documents such as the International Fire Code, International Building Code, and the International Mechanical Code. According to the HMEx product listing on the International Code Council Website, the software tool can be used to identify classifications of chemicals, determine physical and chemical properties and determine threshold limits for listed chemicals. By simply typing in the name of a chemical, the software will access its database and search for that chemical’s data sheet. The software recognizes that some chemicals have multiple names and nicknames, so it includes 9,000 names and synonyms for roughly 3,500 chemicals.

Using the HMEx software and searching for Ammonium Nitrate results in the software producing a material data sheet.

The data sheet provides properties of ammonium nitrate along with relevant classifications and a description of the material. HMEx provides classifications of ammonium nitrate based on information found in the 2009 edition of the International Fire Code and International Building Code. Other classifications in the data sheet come from United Nations (UN). Both of these resources will be expanded on later in this document. Based on the International Fire Code, HMEx gives Ammonium Nitrate a classification of Oxidizer Solid/Liquid Class 1, and Unstable Reactive Class 3D. Based on the United Nations transportation guidelines, HMEx gives Ammonium Nitrate is a hazard Division 5.1 Oxidizer. In order to attempt to understand why HMEx classified AN as an Oxidizer Solid/Liquid Class 1 and an Unstable


Reactive Class 3D based on the 2009 IFC and IBC, we must first define what criteria both of these physical hazards encompass. In other words, what critical variables help us determine that a chemical or material is an Oxidizer Class 1 and Unstable Reactive Class 3D according to the IFC and IBC?

3.3. Classification of Ammonium Nitrate in the International Fire and Building Codes – Summary

The International Fire Code “establishes regulations affecting or relating to structures, processes, premises, and safeguards regarding” various fire and life safety hazards. The International Building Code establishes provisions for “the construction, alteration, movement, enlargement, replacement, repair, equipment, use and occupancy, location, maintenance, removal and demolition of every building or structure or any appurtenances connected or attached to such buildings or structures.” Some of the IFC contains the same language as the IBC, which is why HMEx references both of these documents when detailing the proper ammonium nitrate classification. For instance, definitions for unstable reactive materials and oxidizers are the same between the IFC and IBC. For this reason, the definitions will be taken from the 2009 IFC and further explanatory material will be gathered from the commentary of the 2009 IBC. International Fire Code definitions and International Building Code commentary for both oxidizers and unstable reactive are presented below.

**Oxidizer** – A material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials and, if heated or contaminated, can result in vigorous self-sustained decomposition.

**Class 1 Oxidizer** – An oxidizer that does not moderately increase the burning rate of combustible materials.

**Class 2 Oxidizer** – An oxidizer that will cause a moderate increase in the burning rate of combustible materials with which it comes in contact.

**Class 3 Oxidizer** – An oxidizer that causes a severe increase in the burning rate of combustible materials with which it comes in contact.

**Class 4 Oxidizer** – An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock and that causes a severe increase in the burning rate of combustible materials with which it comes into contact. Additionally, the oxidizer causes a severe increase in the burning rate and can cause spontaneous ignition of combustibles.

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Accompanying these definitions in the International Building Code commentary are the details regarding where the definitions come from. The commentary states that “the classification of oxidizers is based on the provisions of NFPA 430. Oxidizers, whether a solid, liquid or gas, yield oxygen or another oxidizing gas during a chemical reaction or readily react to oxidize combustibles...Specific classification of oxidizers is important because of the varying degree of hazard”\(^{18}\). NFPA 430 is the *Code for the Storage of Liquid and Solid Oxidizers*\(^{19}\). As was previously mentioned, this document has been withdrawn and included in NFPA 400, *Hazardous Materials Code*\(^{4}\). Since the 2009 IBC and IFC were developed prior to the development of NFPA 400, we will look to NFPA 430 for supplementary information to the IBC definitions of Oxidizers.

The definitions of oxidizer class 1 – 4 in NFPA 430 are almost identical to those found in the IBC and IFC. There isn’t significant reasoning provided in NFPA 430 that substantiates their definitions of the different type of oxidizers. Rather, explanatory material in the Annex of NFPA 430 states that “The classification of oxidizers is based on the technical committee’s evaluation of available scientific and technical data, actual experience, and its considered opinion...Gross contamination can cause oxidizers of all classes to undergo exothermic or explosive reaction, particularly if they also are subjected to confinement and heating”\(^{19}\). There isn’t any substantial scientific information available in NFPA 430 such as a test method that helps to differentiate between class 1 – 4 oxidizers. Therefore, we can assume that the developers of HMEx used their best judgement when classifying ammonium nitrate as a Class 1 Oxidizer. Regardless, it is evident that the critical variables associated with classifying ammonium nitrate as an oxidizer by the International Fire Code (and ultimately HMEx as well) are the severity with which the material increases the *burning rate* of the combustibles which it comes in contact with. This is seen in the definitions provided by the International Fire Code which all mention the level of increase in the burning rate of the combustible materials due to the presence of the oxidizer\(^{16}\).

Unstable reactive are also defined by the International Fire Code. These definitions can be seen below.

*UNSTABLE (REACTIVE) MATERIAL.* A material, other than an explosive, which in the pure state or as commercially produced, will vigorously polymerize, decompose, condense or become self-reactive and undergo other violent chemical changes, including explosion, when exposed to heat, friction or shock, or in the absence of an inhibitor, or in the presence of contaminants, or in contact with incompatible materials.

**Class 4.** Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures. This class includes materials that are sensitive to mechanical or localized thermal shock at normal temperatures and pressures.

**Class 3.** Materials that in themselves are capable of detonation or of explosive decomposition or explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. This class includes materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures.

**Class 2.** Materials that in themselves are normally unstable and readily undergo violent chemical change but do not detonate. This class includes materials that can undergo chemical change with rapid release of energy at normal temperatures and pressures, and that can undergo violent chemical change at elevated temperatures and pressures.

**Class 1.** Materials that in themselves are normally stable but which can become unstable at elevated temperatures and pressure.

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Accompanying these definitions in the International Building Code is commentary that details where the definitions of unstable reactive are derived from. The commentary states that “The classification of unstable (reactive) materials is based on provisions in NFPA 704. The different classes of unstable (reactive) materials reflect the degree of susceptibility of the materials to release energy”\(^\text{18}\). Since we are examining the 2009 editions of the International Building and Fire Codes, it is assumed that the version of NFPA 704 that was used as a reference was the 2007 edition. NFPA 704 is titled *Standard System for the Identification of the Hazards of Materials for Emergency Response*\(^\text{20}\). The 2007 edition of NFPA 704 does not provide definitions of the different classes of unstable (reactive) materials. Rather it provides a general definition of an unstable material as well as a table detailing the different levels of instability hazards\(^\text{20}\). This table, seen below, appears to be the basis for the unstable (reactive) material definitions found in the International Fire Code. These definitions were used as the basis of the HMEx classification of ammonium nitrate as an unstable reactive 3D. The “D” in 3D stands for detonable, as seen beneath table F101.2 in the International Fire Code\(^\text{16}\). The information from NFPA 704 that substantiated the definitions for different classes of unstable (reactive) materials in the International Fire and Building Codes is provided below.

### 3.3.5.2 Unstable Materials

A material that, in the pure state or as commercially produced, will vigorously polymerize, decompose or condense, become self-reactive, or otherwise undergo a violent chemical change under conditions of shock, pressure, or temperature.

<table>
<thead>
<tr>
<th>Degree of Hazard</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures.</td>
</tr>
<tr>
<td></td>
<td>Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) of 1000 watts per milliliter or greater</td>
</tr>
<tr>
<td>3</td>
<td>Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but that require a strong initiating source or must be heated under confinement before initiation</td>
</tr>
<tr>
<td></td>
<td>Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 100 W/mL and below 1000 W/mL</td>
</tr>
<tr>
<td>2</td>
<td>Materials that readily undergo violent chemical change at elevated temperatures and pressures</td>
</tr>
<tr>
<td></td>
<td>Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 10 W/mL and below 100 W/mL</td>
</tr>
<tr>
<td>1</td>
<td>Materials that in themselves are normally stable but that can become unstable at elevated temperatures and pressures</td>
</tr>
<tr>
<td></td>
<td>Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 0.01 W/mL and below 10 W/mL</td>
</tr>
<tr>
<td>0</td>
<td>Materials that in themselves are normally stable, even under fire conditions</td>
</tr>
<tr>
<td></td>
<td>Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) below 0.01 W/mL</td>
</tr>
<tr>
<td></td>
<td>Materials that do not exhibit exotherm at temperatures less than or equal to 500°C (932°F) when tested by differential scanning calorimetry</td>
</tr>
</tbody>
</table>

The above table has been recreated from NFPA 704 Table 7.2. **All definitions from the NFPA 704 Standard System for the Identification of the Hazards of Materials for Emergency Response** are copyrighted by the National Fire Protection Association, 2007.

The degrees of instability from Table 7.2 in NFPA 704 correlate directly with the International Fire Code and International Building Code definitions of class 1 – 4 unstable (reactive) materials. Examining Table 7.2, we can see that their basis for differentiating between levels of instability is the material’s
“instantaneous power density”\textsuperscript{20}. This property is the product of the heat of reaction of the material and the reaction rate, specifically at 250 °C (482 °F)\textsuperscript{20}. Other measures of instability from NFPA 704 are the materials sensitivity to thermal or mechanical shock at normal or elevated temperatures\textsuperscript{20}. Both of these measures (instantaneous power density and sensitivity to thermal or mechanical shock) help to provide classifications of unstable materials. Since HMEx classification of ammonium nitrate is based off of the International Fire Code, and the International Fire Code’s definitions of unstable (reactive) materials are derived from NFPA 704, HMEx classifications are inherently based off of NFPA 704. Being that HMEx classified ammonium nitrate as an unstable reactive 3D (as well as an oxidizer 1), we can determine that the critical variables associated with the unstable reactive 3D classification are Ammonium Nitrate’s instantaneous \textit{power density and sensitivity to thermal or mechanical shock}.

### 3.4. Classification of Ammonium Nitrate in the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) – Summary

As was mentioned previously, the United Nations (UN) provide their own classification of Ammonium Nitrate. This classification is found in the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR)\textsuperscript{17}. The UN classifies many types of Ammonium Nitrate, however since this project is investigating classifications related to ammonium nitrate in terms of fertilizers, we will consider the classification of UN No. 2067, Ammonium Nitrate Based Fertilizer\textsuperscript{17}. ADR considers UN No. 2067 as ammonium nitrate as defined by special provisions 186, 306 & 307 with a range of concentrations including mixtures out of the scope of NFPA 400 chapter 11\textsuperscript{17}. These concentrations from special provisions include uniform mixtures containing ammonium nitrate as the main ingredient with these limits:

- With 90% or more ammonium nitrate with not more than 0.2% total combustible/organic material calculated as carbon and with added matter (inorganic and inert towards AN)
- With greater than or equal to 70% but less than 90% ammonium nitrate with inorganic materials. OR “more than 80% but less than 90% ammonium nitrate mixed with calcium carbonate and/or dolomite and/or mineral calcium sulphate and not more than 0.4% total combustible/organic material calculated as carbon”.
- “Nitrogen type” AN based fertilizers with “more than 45% but less than 70% ammonium nitrate” but lower than 0.4% combustible material.
The UN classifies Ammonium Nitrate as a Division 5.1 solid oxidizer. This information is found in Table A of Chapter 3.2 in the ADR\textsuperscript{17}. According to this document, the types of materials considered to be included in Division 5.1 are “\textit{substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause or contribute to the combustion of other material, and articles containing such substances}”\textsuperscript{17}.

This definition is similar to those provided by NFPA and the International Code Council. While NFPA and IFC/IBC breakdown oxidizers into separate classes (1-4), the UN separates oxidizers by packing group. The UN considers Ammonium Nitrate Based Fertilizers (UN 2067) as a Division 5.1 Oxidizer Packing Group III\textsuperscript{17}. The method for determining if a substance is a Division 5.1 oxidizer and the packing group involves a detailed test method. In the ADR, this test is titled Test O.1: Test for oxidizing solids\textsuperscript{17}. This test method is found in the Manual of Tests and Criteria\textsuperscript{21}. The test is conducted similar to NFPA 400 Oxidizer classification test. Test O.1 involves creating a mixture with the test substance and cellulose, and then applying a hot wire to the mixture\textsuperscript{21}. The results are assessed by examining “the mean burning time with those of the reference mixtures” as well as “whether the mixture of substance and cellulose ignites and burns”\textsuperscript{21}. Results from Test O.1 are compared to reference results when potassium bromate and cellulose are the mixture being tested. Different ratios of potassium bromate and cellulose have different results from the test, and are considered a reference for determining which packing group the oxidizer belongs to\textsuperscript{21}. Since Ammonium Nitrate (UN 2067) is part of packing group III, it can be seen that the mixture of ammonium nitrate and cellulose “exhibits a mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose”\textsuperscript{21}. Also, as the particle size has a significant effect on the result, the particle size of the substance tested also should be stated in the test report. Narrating the entire test procedure is beyond the scope of this report.

The UN, through the ADR and the Manual of Tests and Criteria, have classified Ammonium Nitrate Based Fertilizers (UN 2067) as a Division 5.1 Oxidizer Packing Group III\textsuperscript{17}. This is a result of Test O.1, Test for Oxidizing Solids. This test compares the burning rate of a mixture of the substance and cellulose to the burning rate of a mixture of potassium bromate and cellulose\textsuperscript{21}. The critical variable of this classification is the \textbf{burning rate} of an ammonium nitrate and cellulose mixture.

Figure 10.2 (in p. 16) in UN Manual of Test and Criteria\textsuperscript{21} provides a flow chart for the procedure for provisional acceptance of a substance or article in Class 1. For the substance classification purpose, it is to be noted that Test series 2 is conducted first. Test series 2 needs to be carried out to demonstrate that the substance is not Class 1, before being transported as UN 2067. It also determines if a substance is too insensitive for inclusion in Class 1. This requirement is stated in the Dangerous Goods List as Special Provision 306. For brevity, they are not reproduced in this report.
4. Testing and Additional Literature

This section discuss information gathered from additional literature reports and articles with a focus on testing related information.


This article examined the likelihood of an explosion of ammonium nitrate when exposed to fire scenarios. The mechanism of an explosion of ammonium nitrate under fire conditions was unclear and this article discuss two types of tests that gives more insight into the same. The first was a set of experiments using an Advanced Reactive System Screening Tool (ARSST) in order to examine the reactivity of ammonium nitrate at high temperature conditions. The second was a set of experiments intended to analyze “the effect of contamination” on ammonium nitrate reactivity on a larger scale. The article also provided some discussion regarding historical ammonium nitrate incidents.

Two methods of ammonium nitrate explosions were identified, which the authors base off from recent ammonium nitrate explosion events. The first group of explosion include the ones that were caused by a shock to detonation transition (SDT). These could be the result of “an explosive mass going off in the material or by the detonation of a shell thrown into the mass, or by the detonation of an explosive mixture in contact with ammonium nitrate.” The second group of ammonium nitrate explosions are those that occur when the ammonium nitrate comes into contact with a fire that started outside of the ammonium nitrate storage area. The authors make it clear that although there are enough examples of outside fires causing ammonium nitrate to explode to be considered their own group, there are also many instances where a fire did not cause an ammonium nitrate stockpile to explode. An important takeaway from this discussion is that “some level of confinement” is found to be an important boundary condition for the transition of a fire to an explosion. Further, contamination is also identified to be an important parameter for causing AN explosion by the action of heat alone. Under exposure to fire contaminants Charcoal from paper and wood, organic fuels such as diesel oil, plastics, chlorine, polyethylene from bags,

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aluminium from conduit or wiring and copper from wiring results in increasing the shock sensitivity of AN as these contaminants results in the formation of deflagration mixtures with AN.

The Advanced Reactive System Screening Tool (ARSST) was used in experiments to determine the reactivity of ammonium nitrate when exposed to elevated temperatures (greater than 250 °C)\textsuperscript{22}. Part of these experiments included an assessment of the effects of several types of contamination and differing pressure on the ammonium nitrate reactions\textsuperscript{22}. The following are a summary of the results of the experiment. In each test, materials exhibited a release of energy around 250 °C, with varying “occurrence and violence” based on the heating rate\textsuperscript{22}. Also noted was that when tests were conducted at normal atmospheric pressure, there was no evidence of a reaction. The researchers also found through their tests that Ammonium Nitrate reactions were much more violent under high pressure (10 bar) conditions\textsuperscript{22}. Therefore variables such as the pressure and temperature of the reactions were much higher at the high pressure test conditions than those at the low pressure conditions (such as 1 bar). Finally, it was also observed that the copper and diesel oil only have a small effect on the violence of the reaction, whereas the material polyethylene seriously affected the intensity of the reaction\textsuperscript{22}. Some important takeaways from these results include the exothermic reactivity of ammonium nitrate at temperatures around 250 °C, that the heating rate directly affects the violence of an exothermic reaction, and no reactions occur at atmospheric pressures\textsuperscript{22}. These results show the effect of elevated temperatures on ammonium nitrate, and they show the lack of effect from normal pressures on the reactivity of ammonium nitrate.

Additional experiments were conducted on a larger scale than those that used the ARSST. These experiments involved a steel tube with a diameter greater than the critical diameter of molten AN. The tube was filled with AN and eventually polyethylene was included after the temperature had been raised significantly\textsuperscript{22}. No explosion occurred and the conclusion from these experiments was that molten AN cannot detonate due to heat without confinement, even with contamination added in\textsuperscript{22}. The same set up was used to determine the critical initiation pressure for molten AN. It was concluded that the critical initiation pressure was between 3.5 G Pa and 5.1 G Pa (35,000 to 51,000 bar)\textsuperscript{22}. 

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b. **Summary of the article Ammonium Nitrate Fertilizers: Analysis and Appraisal of Classification Categories**\(^{23}\) by H. Kiiski (2008)

The author investigated several types of ammonium nitrate and their relative safety, summarizes the safe composition of fertilizer mixtures\(^{23}\). Major findings confirm the significance of density as a safety parameter. Article also summarized the recent and historical research efforts in the field of ammonium nitrate, similar to the nature of this report. Presented in the article is compiled test data from a research project completed by researchers (Bauer and King, 1977) from Queens University in Ontario, Canada\(^{24}\). The researchers tested ammonium nitrate products that were available on the North American market. The actual article detailing the Queens University project was not reviewed since a copy of the document could not be obtained. The data from the detonation tests shows that the prills with density values 0.76 to 0.78 kg/dm\(^3\) failed to detonate\(^{23}\). However, the failure to detonate will be under the conditions they studied. Further, failure to detonate was assumed to be as a result of the limiting diameter. Hence **critical diameter** contribute significantly to whether AN prill will detonate or not. Although the exact test procedure and quantities of ammonium nitrate is not known, this information is important because it clearly shows a relationship between the **bulk density** of an ammonium nitrate product and its ability to withstand detonation. Kiiski also developed a benchmark bulk density that can be considered relatively safe in terms of withstanding detonation. Even though a threshold density value to withstand detonation was proposed Bauer and King\(^2\) concludes that failure to detonate, detonation rate and shock initiation are all dependent on size of the particle, confinement, temperature and energy of charge and apparent density\(^{23}\).


Contents of the report included a discussion of the historical Ammonium Nitrate behavior and hazards research that’s been completed. The first research project that the authors identify was completed by the


U.S. Bureau of Mines between 1947 and 1966. This work was initiated due to the Texas City disaster and a few other high-scale accidents. The final reports produced as a deliverable of this research project include discussion of “the effect of heating and confinement, behavior of AN under fire conditions, investigating the various aspects such as the effects of contamination (e.g. oil, urea), impact of projectiles, impact of explosives-derived shocks, and conditions for deflagration-to-detonation (DDT) transition”\textsuperscript{25}.

Another research reviewed the Ammonium Nitrate products’ resistance to detonation\textsuperscript{25}. The most important take away from this research is the identification of bulk density as a very important parameter in relation to detonation behavior, and further it is observed that molten AN is much more detonation sensitive than solid dense AN prills\textsuperscript{25}. Another study reviewed by Shah and Balken discuss the sensitivity of molten Ammonium Nitrate to shock as opposed to its prilled counterpart. It is seen that molten Ammonium Nitrate can be significantly more sensitive to shock than its prilled counterpart. In order to test this, TNO dropped objects from certain heights into collections of molten AN. Take away from this study, as Shah and Balken point out include: “a detonation of molten AN is unlikely to result from the impact forces of collapsing buildings”\textsuperscript{25}. This specific report is expanded upon further within this document.

The last relevant work that the authors Shah and Balken summarized was initiated due to the Toulouse explosion, and new consideration of “the risk and consequences of a major explosion in AN store”\textsuperscript{25}. Results from the large scale Ammonium Nitrate detonation testing concludes that prills or granules of ammonium nitrate is typically insensitive to detonation and a separation distance of 1 meter is sufficient for protection from “sympathetic detonation in fertilizer grade AN”\textsuperscript{25}. The final report for this TNO research project is reviewed further in this document.

d. Summary of the article Explosions of Ammonium Nitrate Fertilizer in Storage or Transportation are Preventable Accidents\textsuperscript{26} by Vytenis Babrauskas (2015)

Explosion of ammonium nitrate fertilizer in any storage or transportation capacity can be prevented with sound scientific judgement and risk management. It is identified that, for explosions in storage or transportation, an uncontrollable fire is the single causative factor. Thus, such disasters can be eliminated by eliminating the potential for an uncontrolled fire\textsuperscript{26}. The author tabulated a list of every historical

\textsuperscript{26} Babrauskas, V. (2016). Explosion Hazards of Ammonium Nitrate Fertilizer in Storage or Transportation are Preventable Accidents. Journal of Hazardous Materials, 304, 134-149.
ammonium nitrate incident (excluding “ANFO or additional explosives apart from AN”) involving storage or transportation, and lists whether a fire or an explosion occurred. Although not every incident that Babrauskas identified involved an explosion, it was proved with references that each AN incident was caused by an uncontrollable fire. This is an interesting take on an issue that has been obviously recurring throughout the past century. From 1920 to 2014, Babrauskas identified 58 separate Ammonium Nitrate incidents that were caused by an uncontrollable fire, and from those 58 uncontrollable fires, 17 explosions occurred.

Babrauskas then looked into why those incidents occur and what was learned from the disasters, as well as how we can prevent disasters from occurring in the future. Since every incident was unique, a risk management philosophy need to be followed while examining past incidents. Further it is important to identify the common factors from the incidents. The argument being made in the report is that if code-making bodies and policymakers are able to develop regulations that eliminate the possibility of an uncontrollable fire occurring where Ammonium Nitrate is stored, then history tells us that an Ammonium Nitrate incident will not occur.

A critique of various Ammonium Nitrate regulations, including NFPA 400 Hazardous Materials Code was presented in this article. It was mentioned that the primary safety needs were not addressed in various codes and guidance documents which provide provisions regarding storage of AN. Some of the critical points (or lack thereof) about the NFPA 400 (2013 edition) that are an issue related to Ammonium Nitrate include:

- The length of the document makes it unreasonable for someone to be able to understand the requirements for safe Ammonium nitrate storage
- The nature of the document allows for subjectivity on the side of the Authority Having Jurisdiction, which “creates a lack of rigor and objectivity”.
- The document doesn’t include language that requires storage bins for Ammonium nitrate to be made of non-combustible materials. (2013 edition)
- The document allows for buildings storing Ammonium nitrate to be constructed of combustible materials.
- The document doesn’t require an alarm system to be installed in every location where ammonium nitrate is stored.
• Although the document includes requirements for sprinkler systems to be installed (Section 11.2.6 and 6.2.1.1), such systems are only required for protection level 1 through 4 chemicals. Ammonium nitrate is not considered a protection level 1 through 4 chemical.

The recurring explosions caused by uncontrollable fires is alarming. Although this article does not assist with identifying critical variables of Ammonium Nitrate classifications, it does offer a unique and critical view of the state of Ammonium Nitrate regulation and perhaps how future Ammonium Nitrate incidents can be indefinitely prevented.

e. Summary of the article Investigations into the Initiation of a Detonation of Molten Ammonium Nitrate by Falling Objects by Th. M. Grouthuizen, and A.H. Heemskerk (1988)

The intent of this research project was to investigate the effect of large building components becoming unstable during a fire and falling into a pool of molten Ammonium Nitrate. Previous testing raised concern that this type of situation could result in a large explosion due to the shock sensitivity of Ammonium Nitrate. This work was conducted at the TNO Prins Maurits Laboratory, in Netherlands. A drop tower was constructed by the researchers at a height of 14 m, and a beaker of Ammonium Nitrate was positioned below with a diameter of 200 mm. As such, it was necessary to maximize the accuracy of the dropping items. Therefore the weights being dropped into the Ammonium Nitrate are guided by a PVC pipe into the beaker. The researchers used about 3 to 3.3 kg of molten Ammonium Nitrate, which is heated through the use of an electric wire. The 3.3 kg of Ammonium Nitrate is not entirely representative of a real world incident, as there would most likely be larger concentrations of AN in a fire at a fertilizer facility. Detonation was to be observed through the use of blast gauges. The researchers also used multiple diameter discs placed atop the liquid that were intended to simulate the effects of confinement.

The researchers conducted a total of 47 drop tests with varying temperatures and densities of Ammonium Nitrate, as well as both pure and contaminated (sand, other minor additives) AN. The results from each experimental test were observed and recorded. The researchers found that no detonations occurred in

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all of the 47 tests, including those with contaminated AN\textsuperscript{27}. In conclusion, it has been observed that “it is unlikely that a detonation of molten AN may result from the impact forces of collapsing buildings”\textsuperscript{27}. This information is very relative to the NFPA 400 Technical Committee, as it shed light on the shock sensitivity of Ammonium Nitrate. Materials labeled by NFPA 400 as an unstable reactive are typically going to be very sensitive to shock. However it has been observed that in some instances, small-scale Ammonium Nitrate experiments are not entirely representative of real-life incidents.


This article presents a thorough review and discussion of the hazards associated with ammonium nitrate based fertilizers\textsuperscript{28}, a review of various ammonium nitrate regulations and the actual safety achieved with such regulations, and discuss the economical, technical and organizational factors that could lead to some underestimation of the risk compared to large scale storage facilities\textsuperscript{29}. This work differs from most other articles reviewed in this report because it addresses the possibility for explosions or other related ammonium nitrate incidents in low capacity storage rather than in large facilities.

Ammonium nitrate storage becomes more dangerous as it progresses from the “producers” stage eventually to the “end-users” stage\textsuperscript{28}. The authors discuss that although regulation may be present for the storage of AN on the side of AN producers, distributors, and even retailers. However it is tough to enforce proper regulations on the end-users side since AHJs either don’t know every location where AN is stored, or AHJs don’t even exist at all. Another issue may lie in the ignorance of farmers to the hazards associated with storing certain materials in proximity with Ammonium Nitrate\textsuperscript{28}. A graphic developed by Marlair and Kordek shows the factors affecting the storage of ammonium nitrate and different types of stakeholders who, at some point, will have ammonium nitrate stored as it progresses from producers to end-users\textsuperscript{28}. It was shown that as the product moves from the producers down to the end-users, the following variables also occur that contribute to the decrease in ammonium nitrate storage safety\textsuperscript{28}:

- The number of storage facilities increases
- The amount of Ammonium Nitrate in storage decreases
- Regulation by AHJs decreases

• Awareness of the dangers of Ammonium Nitrate becomes less and less
• Easier access to the product by outsiders

Although this article doesn’t present any critical variables such as separation distance, critical diameter or critical density, etc., it does bring up the idea that low-capacity storage of Ammonium nitrate is a serious issue that needs to be addressed. The NFPA 400 Technical Committee might want to consider the effect that their code has on low-capacity storage of AN which is part of the “end-users” demographic, and how NFPA 400 can better protect AN storage in low-capacity facilities such as rural farms. Perhaps the answer doesn’t lie in actual fire or explosion protection, but more the side of regulating what types of AN can be used in such locations (for instance a form of AN less susceptible to detonation).

g. Summary of the article Safety Testing of Ammonium Nitrate Products\textsuperscript{29} by R.J.A. Kersten, E.I.V. van den Hengel, and A.C. van der Steen (2006)

This research effort was established by the European Fertilizer Manufacturers Association (EFMA) and carried out by TNO. The project consisted of a number of large scale detonation tests on different forms of Ammonium Nitrate, such as fertilizer grade AN, technical grade AN, AN with gypsum, and Calcium Ammonium Nitrate (CAN/nitro-limestone)\textsuperscript{29}. The results from these tests were used to examine the safety properties of the products and to validate the parameters used in advanced detonation simulation\textsuperscript{29}. The following is a recreation of Table 1 of the report, which shows the list of chemicals used during the testing\textsuperscript{29}:

<table>
<thead>
<tr>
<th></th>
<th>FGAN (0.92)</th>
<th>FGAN (0.97)</th>
<th>CAN</th>
<th>AN + Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Total Nitrogen</td>
<td>33.4</td>
<td>33.4</td>
<td>27.3</td>
<td>26.8</td>
</tr>
<tr>
<td>% Total Ammonium Nitrate</td>
<td>95</td>
<td>95</td>
<td>78</td>
<td>77</td>
</tr>
<tr>
<td>% Ammonium Nitrogen</td>
<td>16.7</td>
<td>16.6</td>
<td>13.7</td>
<td>13.7</td>
</tr>
<tr>
<td>% Nitrate Nitrogen</td>
<td>16.7</td>
<td>16.9</td>
<td>13.8</td>
<td>13.1</td>
</tr>
<tr>
<td>% Moisture Content</td>
<td>0.17</td>
<td>0.42</td>
<td>0.19</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The four types of tests were conducted: denting tests, medium scale tests, gap tests, and full scale tests\textsuperscript{29}. Results from the medium scale tests were intended to determine the critical diameter of the test materials, results from the gap tests were intended to determine the critical separation distance of two

of the test materials and the results from the full scale tests were intended to validate the detonation parameters that were recorded in the medium scale tests and the separation distances found in the gap tests\(^{29}\). The critical separation distance as defined in the report is the minimum distance at which a sympathetic detonation between donor and acceptor is no longer possible. In the gap tests, **critical separation distances observed ranged from 0.35 m to 0.75 m**. The researchers suggested 1 m as a benchmark to be “sufficient to prevent a sympathetic detonation”\(^{29}\) in FGAN with a 0.92 g/cm\(^3\). Medium scale tests results showed the researchers that an increase in the bulk density results in an increase in critical diameter\(^{29}\). The large scale tests were able to provide TNT equivalences for the various Ammonium Nitrate products used. All in all, the key takeaways from this research project include the identification of 1 meter as a sufficient separation distance for FGAN storage of densities close to 0.92 g/cm\(^3\). Additionally, the researchers confirm the idea that Ammonium Nitrate has a strong resistance to detonation, unless large boosters are present\(^{29}\).

### h. Detonation Test Methods - Summary:

As mentioned earlier Ammonium Nitrate can detonate although it is very difficult to initiate a non-contaminated and high density substance\(^{30}\). Lower the product density and higher the porosity, the more chance for AN product to detonate\(^{31}\). Hence for usage as fertilizer AN is typically manufactured as a non-porous high density prill. Various test methods for determining the explosiveness/detonability of AN are summarized by Kiiski\(^2\). Some of the test methods described are summarized below:

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trauizl test</td>
<td>To measure explosiveness; 10 g of sample is placed into a cylindrical hole drilled into a lead block with specific dimensions and detonated electrically; The increase in the hole volume is related to the explosiveness.</td>
</tr>
<tr>
<td>Ballistic mortar test</td>
<td>Using a laboratory instrument used to measure relative weight strength of a material as compared to picric acid.</td>
</tr>
<tr>
<td>Small scale explosivity device (SSED)</td>
<td>To obtain the relative ranking of materials</td>
</tr>
<tr>
<td>Denting test</td>
<td>To determine the detonative behavior of substance under the influence of shockwave</td>
</tr>
<tr>
<td>Cook-Talbot lead block test</td>
<td>To determine the detonation sensitivities of AN mixtures</td>
</tr>
<tr>
<td>Steel tube test</td>
<td>Material is filled into a tube that can have various diameters and subjected to a shock from a booster consisting of high explosives.</td>
</tr>
</tbody>
</table>


\(^{31}\) Eck, G., Machacek, O., and Tallent, K., Detonation characteristics of commercial ammonium nitrate prills, UTeC Corporation, LLC, USA.
AN is a compound with complex hazardous properties. Certain variables identified include physical properties like particle size, porosity and density; chemical properties like moisture, contamination, stabilizers; environmental factors including confinement, temperature and pressure\textsuperscript{30}.

4.1. Takeaways from Testing and Additional Literature Review

In summary, the review of testing and additional literature material provided a few results and discussion points that can be considered as the “critical variables” that affect ammonium nitrate and its properties, which ultimately lead to its classification. As pointed out in much of the research that has been reviewed, ammonium nitrate testing has been completed extensively in the past century. Some of the research articles reviewed above provide numerical and scientific parameters that can be considered as critical to the performance of ammonium nitrate in various scenarios. In the report titled Ammonium Nitrate Fertilizers: Analysis and Appraisal of Classification Categories\textsuperscript{23}, Kiiski summarizes a 1970’s research project\textsuperscript{24} where the tests included a variety of different brands of ammonium nitrate at densities ranging from 0.74 kg/dm\textsuperscript{3} to 0.93 kg/dm\textsuperscript{3}. Within the ranges of 0.76 kg/dm\textsuperscript{3} to 0.93 kg/dm\textsuperscript{3}, all but one of the tests failed to detonate. This information suggests that at increasing densities, specifically 0.76 kg/dm\textsuperscript{3} and above, Ammonium Nitrate becomes more stable and less likely to detonate, even in confinement. Kiiski then goes on to form his own hypothesis and states that “The effect of density is so important that it is perhaps surprising that it has not been regulated or controlled. A threshold value of around 0.85 kg/dm\textsuperscript{3} could be considered”\textsuperscript{23}. 

Along with bulk density, separation distance was discussed and in terms of this report can be considered a critical variable of an ammonium nitrate classification. For instance, the unstable reactive classification might be given to ammonium nitrate if it is to be stored in piles within a certain distance from each other, and an oxidizer classification might be given if it is stored in piles at a minimum certain distance from each other. This is because ammonium nitrate is more likely to experience a sympathetic detonation if it is very close to a nearby explosion\textsuperscript{29}. The researchers suggested that 1 meter be used as a benchmark to prevent sympathetic detonation of ammonium nitrate at high densities\textsuperscript{29}. Article Ammonium Nitrate Behavior in a Fire\textsuperscript{22} discussed a variety of tests, one of which was intended to determine the critical initiation pressure of Ammonium Nitrate. The values they received were between 35,000 and 51,000 bar, which is a very large amount of pressure. The authors concluded that “these pressures are still too high for initiation in practical situations”\textsuperscript{22}, therefore it would be difficult to attempt to recreate Ammonium Nitrate explosion due to such pressures. However it is worth knowing these results as they provide insight into the critical behavior of ammonium nitrate. In addition to the actual numerical and scientific parameters (i.e. some of
the critical variables of ammonium nitrate) that were found in the reviewed research articles, there was good discussion about the overall nature of ammonium nitrate in certain defined conditions. Insights into the reactivity of the molten version of the AN was also studied\textsuperscript{27}. 
5. Summary

This report is based on a literature review of documents that provide classification for Ammonium Nitrate, specifically Fertilizer Grade Ammonium Nitrate (FGAN), as well as a review of ammonium nitrate testing and similar research that has been conducted over the years. The intent of the project was to identify any critical variables associated with Ammonium Nitrate classifications and behavior in order to provide insight to assist in eventual classification of the chemical compound.

The metrics which define the severity of an oxidizer are the mass loss rate, active burning rate and peak convective heat release rate. These metrics can be considered the critical variables that the NFPA 400 define as oxidizer whereas the critical variable of NFPA 400 classification of a material as an unstable reactive is the sensitivity of the material to temperature and pressure rise. The variable associated with classifying ammonium nitrate as an oxidizer by the International Fire Code (and ultimately HMEx as well) are the severity with which the material increases the burning rate of the combustibles which it comes in contact with. Being that HMEx classified AN as an unstable reactive 3D (as well as an oxidizer 1), we can determine that the critical variables associated with the unstable reactive 3D classification are ammonium nitrate’s instantaneous power density and sensitivity to thermal or mechanical shock.

The UN, through the ADR and the Manual of Tests and Criteria, have classified Ammonium Nitrate Based Fertilizers (UN 2067) as a Division 5.1 Oxidizer Packing Group 316. This is a result of Test O.1, Test for Oxidizing Solids. This test compares the burning rate of a mixture of the substance and cellulose to the burning rate of a mixture of potassium bromate and cellulose. The critical variable of this classification is the burning rate of an ammonium nitrate and cellulose mixture. Contamination is also identified to be an important parameter for causing AN explosion by the action of heat alone. Kiiski developed a benchmark bulk density that can be considered relatively safe in terms of withstanding detonation. The study indicates the effect of density is very important. Along with the bulk density, separation distance was discussed and in terms of this report can be considered as another critical variable of AN classification.

There is some ambiguity in these critical variables due to the differences in test methods, test materials, and test configurations that were used. However each article that was summarized in this report provides insight into the behavior of Ammonium Nitrate in different environments. Variables identified and their effect on the classification of Ammonium Nitrate is critical and should be considered.
References


G. Eck, O. M. (n.d.). Detonation characteristics of commercial ammonium nitrate prills. USA: UTeC corporation, LLC.


