

# Explosions of ammonium nitrate fertilizer in storage or transportation are preventable accidents

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## Abstract

Ammonium nitrate (AN) is a detonable substance which has led to numerous disasters throughout the 20<sup>th</sup> century and until the present day, with the latest disaster occurring on 17 April 2013. Needed safety lessons have not been learned, since typically each accident was viewed as a great surprise and investigations focused on finding some unique reason for the accident, rather than examining what is common among the accidents. A review is made of accidents which involved AN for fertilizer purposes, and excluding incidents involving ANFO or additional explosives apart from AN. It is found that, for explosions in storage or transportation, 100% of these disasters had a single causative factor—an uncontrollable fire. Thus, such disasters can be eliminated by eliminating the potential for uncontrolled fire. Two actions are required to achieve this: (1) adoption of fertilizer formulations which reduce the potential for uncontrolled fire and for detonation; and (2) adoption of building safety measures which provide assurance against uncontrolled fires. Technical means are available for achieving both these required measures. These measures have been known for a long time and the only reason that disasters continue to occur is that these safety measures are not implemented. The problem can be solved unilaterally by product manufacturers or by government authorities, but preferably both should take necessary steps.

*Keywords:* ammonium nitrate; building fire safety; detonations; oxidizer fires; product stewardship; transportation accidents.

## 1. Introduction

On 17 April 2013 a massive explosion occurred in West, Texas, a small town in central (not western) Texas<sup>1,2,3</sup>. The West Fertilizer Co. operated a facility for storing, blending, and retailing of fertilizers and other agricultural goods and services. The company functioned as a manufacturer (blending of chemicals is defined as a manufacturing activity in the US), a retailer, and a provider of services. The building dated from 1962 and was of Type V-N, unprotected wood-frame, construction. The town of West possessed a volunteer fire department but had neither a building code nor a fire code<sup>†</sup>. Shortly after closing time on the day of the disaster, a fire origin erupted in a seed storage room adjacent to the ammonium nitrate (AN) storage areas of the facility. The building had no alarm system nor fire sprinkler protection, and the fire department was notified only when a man walking his dog in a nearby park saw smoke rising from the building<sup>4</sup>. The volunteer fire department arrived to find a large working fire within the premises. They were able to apply two hosestreams without much effect, but could not get a better water supply since the closest fire hydrant was some 1600 ft (490 m) away. At 1951 hours, some 21 minutes after the original phone call and 11 minutes after the arrival of the first fire engine, a massive explosion occurred (Figure 1). Fifteen persons were killed, mostly volunteer firefighters, and some 260 persons were injured. The explosion registered a magnitude of 2.1 on the Richter scale<sup>5</sup>. Not only the fertilizer facility, but a number of nearby buildings were demolished, including a nursing home. The facility was storing some estimated 40 – 60 tons of AN inside the building, not all of which detonated. In addition, 100 tons of AN were located in a railcar outside, and this railcar overturned in the explosion but did not explode.

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† In fact, the State of Texas prohibits sparsely populated rural areas from enacting a fire code (Local Government Code Title 7, Chapter 233). However, as shown below, since US fire codes invariably rely on NFPA 400 for regulation of AN, and the latter is inadequate to prevent explosions, if the town would have had a fire code, the outcome would likely have been no different.



(a) Before the explosion



(b) After the explosion

**Figure 1** The site of the West Fertilizer Co. before and after the explosion (Source: ATF)

Investigations concluded that the fire was accidental and did not reveal any improprieties on the part of the staff of the fertilizer company. The fire likely originated due to an electrical fault of an undetermined nature. What is of great concern is that the facility that exploded was constructed and operated similarly to most rural AN fertilizer facilities in the US. The Texas State Fire Marshal identified that there are at least 104 facilities in that State which store 5 tons or more of AN<sup>6</sup>, while in the US as a whole there are over 1300 storage establishments<sup>7,8</sup>.

## 2. History of AN fires and explosions

In the aftermath of the West explosion, an Italian combustion journal published an article<sup>9</sup> titled *Ammonium Nitrate—A Century of Explosions*. This is an accurate assessment, and it is useful to examine some of the details. Factory production of AN began in the late 19<sup>th</sup> century, as did explosions of the substance. Many explosions have occurred in manufacturing facilities. These accidents often entail high temperature processes, high pressures, pumps, steam injection, and other chemical plant operations. A relatively recent example was an AN factory explosion in Port Neal, Iowa in 1994 which killed 4 workers<sup>10</sup>. Manufacturing processes present different hazards than those encountered when AN has left the factory. Since the subject of this paper is solely the hazards in storage and

transportation environments, manufacturing incidents are not further considered here. Nor are occasional accidents due to shipments of hot AN solutions, which sometimes takes place between factories. Attention is focused solely on accidents involving storage or transportation of solid-phase AN. It is this author's thesis that there is no substantive difference between circumstances leading to the potential for detonation of AN stored in an immobile warehouse, or located on a truck, railcar, or ship. The material is not motion sensitive, thus motion cannot contribute to the hazard created. Also excluded from consideration here are accidents which involved ANFO, a mixture of AN with fuel oil, and accidents where additional explosive materials were known or suspected, e.g., the notorious 1921 explosion in Oppau, Germany<sup>15</sup> or the 2001 explosion in Toulouse, France<sup>11</sup>.

**Table 1** Incidents involving AN storage or transport facilities, not including incidents involving ANFO, nor ones with involvement of explosives other than AN

Date	Site	Incident	Fire	Explosion	Dead	Ref.
Apr-1920	Barksdale, WI	Warehouse fire with barrels of AN	✓			12,13
14-Apr-1920	Brooklyn NY	Steamer Hallfried, poss. due to contamination	✓			12,13, 14
4-Apr-1925	Muscle Shoals, AL	Rail cars with barrels of AN, poss. due to wood material of barrels	✓			12,13
3-May-1925	Muscle Shoals, AL	Rail cars with barrels of AN, poss. due to wood material of barrels	✓			12,13
Apr-1940	Gibbstown, NJ	Fire destroyed a large quantity of bagged and drummed AN, no explosion. Fire was at a manufacturing establishment, but in the warehouse, not production.	✓			12
16-Apr-1947	Texas City, TX	S.S. Grandcamp was in port and its cargo of AN ignited. This ignited neighboring buildings and also the ship S.S. High Flyer. Both ships detonated, but some AN warehouses on shore only burned.	✓	✓	552	15
28-Jul-1947	Brest, France	S.S. Ocean Liberty carrying AN detonated after a fire in the cargo hold	✓	✓		12,15
1947	USA	Truck fire due to cellulosic rope contacting AN cargo; cargo was hot	✓			13
14-Oct-1949	Independence, KS	Fire in Air Force warehouse involved AN, but no explosion	✓			12
23-Jan-1953	Red Sea	S.S. Tirrenia. Fire in AN, followed by explosion. Poss. role of paper goods next to AN in hold.	✓	✓		12,16, 17
1957	USA	Truck suffered collision, fire ignited gasoline, ignited AN which exploded	✓	✓	?	16
1958	USA	Truck fire burned AN, no explosion	✓			16
1959	USA	Rail car fire ignited AN, but was extinguished	✓			16
10-May-1960	Boron, CA	Fire in warehouse of AN, but no explosion	✓			12
17-Dec-1960	Traskwood, AR	Rail car derailed, bagged AN ignited due to mixing with other chemicals, detonated	✓	✓		16,18
Feb-1963	Traskwood (Norphlet), AR	Rail car derailed, AN burned, but no explosion	✓			16,18

9-Nov-1966	Mount Vernon, MO	A fire started in an AN production facility, but the detonation was due to fire engulfing a 50 T pile bags of AN in their storage area	✓	✓		12
24-Nov-1966	Peytona, WV	Fire was in an explosives factory, and fire impinged on AN stored in a truck trailer and a rail car, no explosion	✓			12
24-Oct-1967	Potosi, WI	Rail car with bagged AN ignited, no explosion	✓			12,16,19
30-Aug-1972	Taroom, Australia	Truck carrying LD AN ignited, burned, detonated	✓	✓	3	16,20
1972	UK	Truck with bagged AN ignited, poss. due to contamination	✓			16
17-Jan-1973	Pryor Creek, OK	Fire in Cherokee Ammonia manufacturing plant, but stored AN caught fire and fire was not in production machinery. Major detonation due to fire.	✓	✓		21
1976	France	Truck with bagged AN ignited, fire extinguished	✓			16
1977	USA	Rail car derailed, causing ignition of AN	✓			16
1978	Rocky Mountain, NC	Warehouse fire, stored AN burned up completely but no explosion	✓			22
1979	Australia	Bagged AN ignited in truck	✓			16
1981	Australia	Bagged AN ignited in truck	✓			16
1982	Australia	Bagged AN ignited in truck	✓			16
Oct-1982	UK	AN storage ignited and led to major fire; explosions occurred, but deflagration and not detonation.	✓			19
1984	Australia	Fire in engine of truck ignited bagged AN	✓			16
1989	France	Truck carrying AN ignited, extinguished	✓			16
1991	France	Truck carrying AN ignited, extinguished	✓			16
1991	Australia	Fire in truck carrying AN due to collision	✓			16
1991	UK	Small fire in truck carrying AN	✓			16
Apr-1992	UK	Fire in warehouse storing AN, no detonation	✓			23
1993	Australia	Fire in truck carrying bagged AN, cargo burned up	✓			16
Mar-1997	Spain	Fire in drums involving AN; appears minor	✓			23
Jul-1997	Brazil	Fire and collision of trucks carrying AN and gasoline; LD AN ignited and detonated	✓	✓	17	23
4-Jan-1998	Maysville, KY	Fire in Cargill Farm Service Center, involved AN. Probably electrical fire in nature. Propane tanks exploded, but AN did not.	✓			23
28-Jun-2000	Duette, FL	Fire and collision of trucks carrying AN and gasoline	✓			16,23
Feb-2003	USA	Warehouse fire storing AN	✓			23
2003	USA	AN fire in a farm supply store, poss. minor	✓			23

2-Oct-2003	Saint-Romain-en-Jarez, France	AN fire in a small agricultural storage facility leading to a detonation	✓	✓		20
Oct-2003	UK	Fire involving AN in a small farm store	✓			23
18-Feb-2004	Neyshabur, Iran	Major train derailment, caused a fire to ignite; AN burned and exploded	✓	✓	328	16,24
9-Mar-2004	Barracas, Spain	Truck collision, leading to fire and AN detonation	✓	✓	2	16,20
22-Apr-2004	Ryongchon, North Korea	Train carrying AN collided with truck carrying oil; resulted in fire and explosion	✓	✓	161	25
24-May-2004	Mihăilești, Romania	Truck carrying bagged AN overturned, fire resulted, then detonation	✓	✓	18	18,20, 26
Aug-2004	USA	Fire in a dry bulk blending and distribution center that held AN	✓			23
6-Mar-2007	Pernik, Bulgaria	Truck carrying AN caught fire and exploded	✓	✓		27
Jun-2006	France	Fire on a truck hauling bagged AN; extinguished by fire service	✓			23
22-Sep-2006	Suisun City, CA	Fire involved E.B. Stone & Son facility as an exposure from a grass fire	✓			23
30-Jul-2009	Bryan, TX	Fire at El Dorado Chemical Co. started by welder in warehouse, burned down warehouse	✓			18
8-Aug-2009	Mt. Isa, Australia	Truck carrying AN caught fire	✓			27
21-Jan-2012	Mariveles, Philippines	Fire destroyed an AN warehouse at a shipyard	✓			27
17-Apr-2013	West, TX	The subject fire	✓	✓	15	
29-May-2014	Athens, TX	Fire at East Texas Ag Supply warehouse involving AN; no detonation, building burned up	✓			28
5-Sep-2014	Charleville, Australia	A double-trailer truck carrying 52 tonnes of AN overturned, ignited, and exploded	✓	✓		29

The accidents tabulated in Table 1 involve a wide variety of circumstances, locales, and modes of storage or transport. But they share one essential trait in common: **100% of the explosions were the outcome of an uncontrollable fire.** It does not matter if the fire originated in a warehouse, a truck, a railcar, or a ship—no explosions and no loss of life occurred unless there was a fire, and the fire was not controlled.

### 3. Characteristics of AN

A large number of reference works are available which examine the characteristics of AN, including the *Ignition Handbook*<sup>15</sup>, the *Kirk-Othmer Encyclopedia*<sup>30</sup>, and *Ullmann's Encyclopedia*<sup>31</sup>, plus numerous additional references cited in each. Ammonium nitrate [CAS 6484-52-2],  $\text{NH}_4\text{NO}_3$ , is an inorganic compound first discovered in 1659. It can be made in diverse ways, but modern manufacturing generally entails reaction of nitric acid with ammonia,  $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$ , an exothermic reaction which produces  $175 \text{ kJ mol}^{-1}$  of heat. The substance produced is a concentrated aqueous solution, while AN used for agricultural purposes in the Western world requires a solid, granular material. Thus, the hot solution containing 83 – 87% AN is then evaporated to remove water until it becomes around 97% concentrated<sup>32</sup>. At that point, the heated solution must be converted to solid form. In North America, this is done normally by prilling, whereas in other parts of the world granulation may be used<sup>33</sup>. In either case, the product is spherical prills or granules, about 2 mm in diameter.

AN is a complex substance since it shows 6 or more allotropes, i.e., different crystal structures, and the phase transitions between these occur at certain temperatures<sup>34</sup>. Especially problematic is a phase transition at 32°C. The

latter is a temperature which can be transitioned numerous times in the summer, and more problematically, in the spring in southern parts of the US. A phase transition is destructive to the prill and can lead to pulverization. The sensitivity of pure AN to detonation increases after it has gone through a few cycles of the transition at 32°C<sup>35</sup>, presumably due to the formation of fines. Some coatings however can ameliorate this problem. But since AN is a hygroscopic material, causing pulverization also means the material becomes much more prone to uptake moisture. The outcome is termed ‘caking,’ whereby the AN sets up into a solid mass and loses its granular nature. For a fertilizer, this makes the product unusable. Consequently, manufacturers invariably need to apply a coating or an additive to provide phase stabilization and reduce the caking tendency<sup>36</sup>. In the 1940s, a wax coating of around 0.8 – 1.0% was used for this purpose. Wax however is an organic substance, while AN is an oxidizer. The combination of an organic substance (fuel) and an oxidizer leads to oxidative reactions. The danger of this was learned when the ships S.S. GRANDCAMP, S.S. HIGH FLYER, and S.S. OCEAN LIBERTY, which were carrying cargos of wax-coated AN, exploded in 1947 within a short time of each other<sup>15</sup>. Subsequent to this, manufacturers switched to coatings which had an organic content below 0.2%, which is considered to define the regime below which oxidative reactions are not promoted.

AN is often classified into different ‘grades.’ The relevant terminology has changed over the years, so care must be exercised in consulting older references. Currently, three grades are recognized: fertilizer grade, explosive grade (or technical grade) and CP grade (chemically pure). Fertilizer grade refers to dense prills or granules, of roughly 1000 kg m<sup>-3</sup> density. Explosives grade refers to lower density (around 800 kg m<sup>-3</sup> or lower, and typically porous) material. CP designates high purity material, typically specified for producing N<sub>2</sub>O. Historically, ‘fertilizer grade’ connoted AN with 0.8% or more organic coating, while ‘explosive grade’ was not necessarily low-density material<sup>15</sup>.

International shipping safety requirements are delineated in the UN Orange Books<sup>37,38</sup>, and these classifications of hazardous chemicals are the regulatory norm which is used worldwide and is generally adopted into the national regulations of various countries. In the case of AN, the UN treatment is complex. While in principle AN would need to be tested by O.1 test for oxidizing solids, for products of standardized ingredients the actual classification is determined by the SPs (Special Provisions) and not by testing. Detailed rules are explained in a Fertilizers Europe document<sup>39</sup>, but notably fertilizers with an AN content ≥ 90% and an organic content ≤ 0.2% are classified as Class 5.1 (Oxidizing substances) according to SP 306. Meanwhile, a product with 80% AN and 20% calcium carbonate (termed calcium ammonium nitrate, CAN) is Unclassified, that is, is not declared to be hazardous. Conversely AN products with > 0.2% organic content and without significant inerting additives, e.g., ANFO, are classified in Division 1 (Explosives).

## 4. Research on explosive properties of AN

The decomposition and reaction properties of AN, especially its explosive properties, have been appreciated for centuries; for example they were already discussed in an 1800 chemistry textbook<sup>40</sup>. In his classic textbook on explosives (published in 1892 in the English edition) Berthelot<sup>41</sup> described the results of extensive research on the ammonium nitrate, identifying 7 decomposition reactions—some exothermic and some endothermic—and quantifying the heats of reaction for each. He observed that if heated beyond 230°C, an explosion can occur. During later decades, various other authors<sup>42,43,44</sup> studied AN reactions in more detail and conjectured a number of reaction pathways, which are still not fully resolved<sup>45</sup>. When contaminants are involved, reactions become even more complex<sup>36,46</sup>.

It was already well-known in 1958 that, for solid or liquid substances which are detonable due to exothermic decomposition, detonation may be initiated by various means of adding energy to the system, foremost of which being heat, impact, or shock<sup>47</sup>. At that time, Prof. Bowden further noted that<sup>47</sup> “*The growth of the explosion is governed by thermal considerations and, in the early stages, is frequently a precarious process. Very often it is the failure to grow, rather than the failure to initiate, which prevents explosion.*” He then observed that the engineering tests typically used in the explosives testing field “*have little physical significance....Hitting a solid with a hammer or rubbing it with a piece of sandpaper is perhaps an experiment more proper to a carpenter than a physicist.*”

A very large number of studies on AN hazards have been published. Here, some pertinent highlights of this research will be presented in three categories: (1) small-scale heating tests; (2) tube tests and similar; and (3) tests in more realistic geometries. In subsequent sections, research on oxidizing-properties testing of AN and tests to compare safety of AN to alternative nitrogen-based fertilizer products will be presented.

As will be shown, much of the literature focuses on the point that pure AN is difficult to detonate, but that detonation becomes much easier for contaminated material, and there are large classes of compounds<sup>48,49</sup> (metal or metal-salt catalysts; organic fuels) which sensitize AN. In view of the loss record reviewed above, focusing on pure material is a serious misjudgment. No accident is known where pure AN resulted in a fire, and subsequent explosion. In fact, fire is impossible without a fuel, and any fuel is *ipso facto* a contaminant. On the other hand, both standard and research tests exist and will be discussed below where large quantities of cellulosic contaminant are intimately mixed in with AN. Such arrangements also do not correspond to any known accident and does not help understanding scenarios in which accidents develop. (Note that in transportation accidents, the view is sometimes offered that liquid fuels will get intimately mixed, in sizable amounts, with AN. There are no investigation results that would support this view, and it appears much more likely that transportation accidents will involve a pool fire burning in the vicinity of AN, not commingled with it.)

It will also be seen that the literature focuses greatly on the issue of confinement provided to the AN. This is in accord with standard explosives engineering principles, which emphasize the role of rigid containment in achieving detonation<sup>15</sup>. These findings have been misapplied by safety authorities, and this important concept will also be developed below.

#### 4.1 SMALL-SCALE HEATING TESTS

The melting point of pure AN is 169.6°C, but prills start to soften at around 140°C<sup>62</sup>. It is found that decomposition of uncontaminated material starts at around the melting point and becomes vigorous at 220°C<sup>56</sup>. Heating AN can be dangerous in general, but not under all conditions. Nitrous oxide, N<sub>2</sub>O, is generally produced by controlled heating of AN between 200 and 230°C<sup>30</sup>. Guiochon<sup>50</sup> found that when temperature enters the range of 240 – 400°C, reactions become so rapid that he was not able to track them with thermal analysis instruments. The potential for heated AN to explode has been appreciated for a very long time. In 1800 already, Chaptal<sup>40</sup> wrote<sup>‡</sup> “*When this salt is exposed to the fire, it liquefies, emits aqueous vapors, dries, and detonates.*” However, the distinction between deflagration and detonation was only learned at the end of the 19<sup>th</sup> century, and Chaptal presumably only observed a mild deflagration and not a detonation. Saunders<sup>42</sup> heated small amounts of AN in a narrow tube and obtained minor explosions upon reaching 260 – 300°C, which comprised runaway AN decomposition reactions which were explosive, but not detonations. The role of contaminants in this was also early appreciated, e.g., in 1843 Reiset and Millon<sup>51</sup> noted that a mixture of powdered AN and charcoal explodes on being heated to 170°C.

Kaiser<sup>52</sup> placed pure AN into a glass tube and found that, heated to 260 – 269°C, molten AN decomposed violently, ending in an explosion, but again only a deflagration. The UK Working Party<sup>13</sup> conducted similar tests in glass tubes, but with no temperature monitoring; they too were able to achieve explosions. In their tests, they used specimens with a wax and kaolin coating, and also prills without coatings or organics. Despite the extremely small specimen amounts (0.1 g), they also obtained explosions. Braconier and Delsemme<sup>53</sup> heated 10 g samples of pure AN in a pressure vessel and found that pressure and temperature rise were controlled until a temperature of 290°C was reached, at which point a pressure of 160 bar was attained and thereupon a runaway decomposition reaction ensued, resulting in an explosion. In their experiments, the *p-T* relationship was such that 1 bar corresponded to 238°C. Macy et al.<sup>63</sup> heated AN mixed with paper in glass flasks held at 175°C; two of four test runs ended in a gas explosion inside.

Herquet<sup>54</sup> heated pure AN in an open dish up to 410°C without getting an explosion. He also concluded that a gas-phase detonation is not sufficient to detonate sympathetically a vessel of liquid AN. But he also showed that if heated while placed in a tube where pressure can build up, AN can be detonated. Adding as little as 0.1 – 1.0% organic matter reduced the minimum temperature needed to achieve explosion. He also sensibly observed that all risk of explosion will be eliminated if a temperature elevation does not occur. This exactly reflects the essential point made in this paper, that AN safety can only be assured by eliminating the potential for uncontrolled fire.

The US Bureau of Mines (BM)<sup>55</sup> used open-top test tubes heated to only moderate temperatures (117 – 199°C), but two tests led to explosion (not detonation), both of which included a zinc contaminant. Saunders<sup>42</sup> identified that 0.1% chloride contamination has a large effect in destabilizing AN with regards to thermal decomposition. Taken as

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<sup>‡</sup> Misattributed by Munroe in his oft-cited 1922 paper to Turner’s 1835 **Elements of Chemistry**, which does not contain this statement.



a whole, the various chemistry-laboratory heating tests show that explosion of small amounts of AN may often (but not in every case) be achieved, but, unless confined—which gets into the next category of tests—a detonation does not result. It also bears keeping in mind that these types of laboratory tests generally did not entail vessel sizes sufficient to reach the critical detonation diameter.

## 4.2 TUBE TESTS AND OTHER STANDARD EXPLOSIVES TESTS

Since heating AN in small vessels reveals little about its hazards, diverse investigators subjected the material to tests where a larger amount of material is used and confinement is provided, generally in the form of a standard steel pipe. Fedoroff et al.<sup>56</sup> reviewed much of the early literature on engineering tests with AN. One of their main conclusions was that while AN can be detonated in various tests and configurations, it is “*much more difficult to detonate or explode than any of the standard explosives.*” Detonations within AN typically proceed at lower velocities (1500 – 2500 m s<sup>-1</sup>) than in many other explosives, and AN shows an explosive power of roughly 25% to 55% that of TNT.

The first major paper on the topic was published by Sherrick<sup>57</sup> in 1924, giving extensive results for lead-block tests of AN, where he showed that explosive power directly increases with both the degree of confinement (rigidity of tube walls) and amount of booster charge used. For light confinement or small booster charge, no explosive effect (i.e., no lead block compression) was found. This became the—imprudent—guideline for innumerable safety authorities for decades thereafter. In a companion paper, Sherrick<sup>58</sup> also reported his conclusion that “No detonation of ammonium nitrate by application of fire or heat was obtained in any of our tests, and theoretical consideration of the reaction of thermal decomposition indicates that this reaction in itself could never attain explosive violence.” This, of course, was an equally incorrect conclusion, in view of the subsequent disasters that have been documented. In the same year, R.M. Cook<sup>59</sup> ran experiments with AN confined in 1.5-inch pipes. He found no significant damage from AN alone, but AN mixed with 1% petrolatum led to total shattering of the pipe. Much later, M.A. Cook<sup>60</sup> measured the sensitivity (not explosive power) of AN and documented that around 0.75 – 1.5% hydrocarbon loading required the smallest booster charge to detonate.

The UK Working Party<sup>13</sup> reported tests where an iron pipe was filled with pure AN and heated. Without a tight cap, a temperature of 239°C was reached, but not an explosion. With the cap tightly sealed and reaching a temperature of 318°C, the pipe split due to gas pressure, but the material inside remained undetonated. They also filled ammunition shells with coated or uncoated AN prills, and got explosions when heated internally with a Nichrome wire. Various other shell and pipe bomb tests gave diverse results.

The BM<sup>55</sup> conducted tests on small amounts of sample in a tightly sealed pipe, then heated electrically. Both uncontaminated AN and AN mixed with oil exploded up reaching moderate (166 – 170°C) temperatures. They also found that uncontaminated AN confined in a pipe could be detonated by a No. 8 detonator if preheated to 146°C, but not at room temperature (21°C). They conducted<sup>61</sup> other tests using pipes with small vent holes—presumably to represent imperfect confinement—and heated internally with Nichrome wire. Explosions were possible even with CP AN, but only with small vent sizes, while wax-coated AN and wax-coated AN mixed with paper exploded even with larger vent sizes. Also, specimens with organic content needed less heating to explode than did pure AN. They also ran card-gap tests<sup>62</sup> where four different brands of unwaxed AN prills were tested in pipes at various temperatures. No detonations were observed at 120°C or below, but heating the assembly to 140°C sufficed to detonate all brands. Larger pipe diameter or heavier pipe construction reduced these values so that room-temperature detonations were observed for a 6-inch pipe of heavy construction. Workers at Picatinny Arsenal<sup>63</sup> constructed numerous vented pipe tests and heated 10-lb charges of waxed AN material until end caps were blown off, but detonation did not occur. They finally constructed some pipes in a different manner and got partial or complete detonation for 5.7 lb charges of AN mixed in with paper. Further tests<sup>64</sup> using 2000 – 3000 lb charges confined in steel bombs that were sealed detonated due to external electrical heating, while if the bombs were unsealed, no detonation occurred. Medium (1800 – 3200 lb) bomb tests were also run at Aberdeen Proving Ground<sup>65</sup> but in two variants, electrically heated and heated by fire. Both series produced the same outcome: AN enclosed in bombs and heated by electricity or fire detonated only if the bomb was sealed, but burned out without detonation if it was not. Such studies led to the often repeated, grossly misleading and unsafe conclusion that “*Ammonium nitrate will not detonate when exposed to heat or flame in vented containers.*”



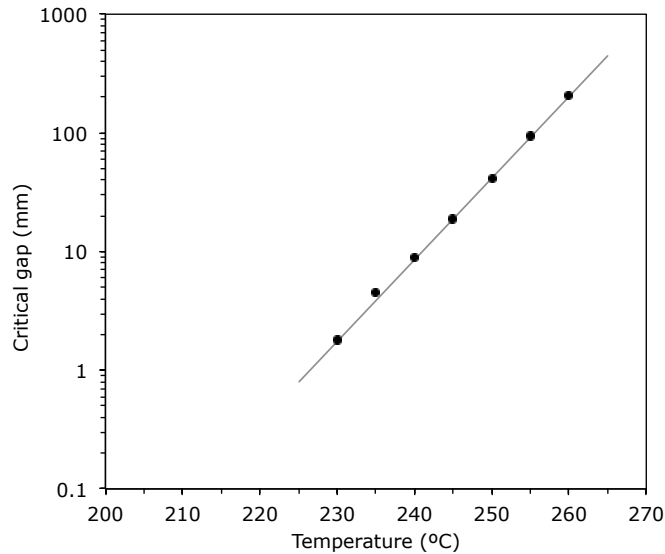
In the EU, some specifications for AN-based fertilizers are established by regulations<sup>66</sup>. This includes a 4-inch tube test generally known as the *EU Resistance to Detonation Test*. For products to be acceptable in the EU scheme, they must pass this test. However, Kersten et al.<sup>67</sup> showed that fertilizer-grade, straight-AN does not detonate in the EU test, making it a regulatory requirement which does nothing to reduce AN hazards or accidents. They also concluded that detonation is not likely to occur, in the absence of “large quantities of booster,” a conclusion at odds with disasters such as Saint-Romain-en-Jarez or West, Texas, neither of which had any booster explosives involved whatsoever. However, they were able to detonate a 28 tonne pile of FGAN without confinement, albeit with a large booster.

### 4.3 TESTS IN MORE REALISTIC GEOMETRIES

Since neither test-tube tests nor steel pipe/tube tests re-create the environment of an accident where a large fire leads to AN detonation, a few researchers have attempted to conduct tests that were larger or more realistic. In 1945, Davis<sup>14</sup> reported several open-burn tests of 10-lb quantities of AN, fed with gasoline, paper or wood. No explosions occurred. Workers at Picatinny Arsenal<sup>63</sup> placed 50 – 100-lb samples in welded steel containers in a bonfire, which ruptured the containments but did not detonate. In the second series<sup>68</sup>, they conducted intermediate-scale tests on bags of wax-coated AN by sealing them in bomb casings, but with small vent openings. In the four tests, some 800 – 1500 kg AN was used, with fire exposure but no primers or boosters. Two of the bombs detonated, while two did not.

Subsequent to the 1947 Texas City disaster, both the US and the UK governments attempted more realistically configured tests. The UK Working Party<sup>13</sup> conducted large-scale tests both in bunkers and onboard ships using CP grade AN, held in paper-lined drums. A large amount of wood fuel was included in the tests, yet they only got fire and no explosion in each case. Similarly, the US Bureau of Standards<sup>69</sup> mocked up a ship’s deck section, filled it with waxed AN and stoked the fire by burning ropes. They achieved fume-off, but no explosion. BM<sup>62</sup> ran tests on AN and ANFO, exposing to fire up to 540 kg piles of material, but obtained only burning and no detonations.

The presence of molten AN due to fire can be the crucial factor leading to detonation accidents<sup>21</sup>. And more specifically, impact of objects falling into molten AN may lead to detonation. In an early study, Kast<sup>70</sup> was able to detonate room-temperature AN by dropping a 10 kg weight from 0.2 m height or more, or a 20 kg weight from a height of 0.12 m or more; although fewer repeat runs gave a denotation than a non-explosion. But the sensitivity of AN to detonation increases with temperature. This was already determined by Munroe<sup>72</sup> in 1922. Beyond its melting point of 169°C, the sensitivity further increases with increasing temperature. King<sup>71</sup> showed that, between 230°C and 260°C, the sensitivity increases by two orders of magnitude, as measured in the card-gap test (Figure 2), and at 260°C becomes comparable to that of nitroglycerin dynamite. But by the time that 245°C is reached, there is already violent bubbling due to boiling, and bubbles are the primary cause of sensitization of liquid explosives. He also showed that the critical diameter for unconfined detonation is in the range of 95 – 120 mm at 220°C, dropping down to less than 46 mm at 260°C.



**Figure 2** Effect of temperature on the sensitivity of molten AN in the card-gap test using PMMA wafers

In view of what Kast and King had determined, then, it is interesting that various researchers<sup>63,72,73</sup> tried dropping weights into molten AN, but did not achieve detonation. But some positive results are more important to consider. Sherrick<sup>58</sup> described tests where AN itself was dropped into a heated iron vessel, and detonations were obtained when the temperature was brought up over 340°C. This was evidently uncatalyzed and uncontaminated material, but procedure details were not given. Hainer<sup>74</sup> heated a Dewar flask with CP grade AN to 250°C, added some K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> catalyst, placed a No. 6 blasting cap above the liquid level, so that shock was transmitted to the liquid only via air, and was not able to detonate the liquid. But when he repeated the experiment but lowered the blasting cap into the liquid AN, this produced so severe a detonation that personnel a half mile away rushed out to investigate. This finding is exceedingly important and illustrates that AN can be detonated under conditions of:

- molten AN material
- presence of a catalyst
- absence of confinement
- absence of a booster, and use of but a very small detonator.

Hainer's study did involve a catalyst which would rarely be found as a contaminant. However, the conservative inference has to be made that burning combustible material in direct contact with the AN may likely play a similar role.

In the aftermath of a Canadian accident where a truck which was hauling ANFO and other blasting agents, crashed, took fire, and then detonated, the Canadian Explosives Research Laboratory (CERL) conducted various tests, of special interest being unconfined burn tests<sup>75</sup>. They ran 29 tests with stacks of bagged ANFO ranging from 25 to 1262 kg, but were able to obtain no detonations, only sustained burning. They also ran a test<sup>76</sup> where a truck loaded with 20 tonnes of ANFO was set afire. Even though temperatures up to 1200°C were reached and a sizable amount of ANFO melted, no detonation occurred. Even when the test was repeated using a mixed load of explosives, including both a TNT-based slurry and a cap-sensitive emulsion, a detonation could not be obtained, yet the testing was done in an effort to re-create an accident where a truck ran off the road, a fire ignited, and 30 minutes later a detonation ensued.

A number of researchers conducted tests ostensibly showing that fire presents no hazard stored AN. Researchers at BM<sup>62</sup> exposed a cubical tray of 0.3 m dimensions filled with AN to diesel fire flames, then reran tests using progressively larger amounts of AN, up to 2.5 tons, and got no explosive or dynamic response, although a significant fraction of the material got consumed. They also burned ANFO and got more dynamic fires, but no explosions. van Hijfte<sup>77</sup> also reported similar experiments where (a) a wood pallet loaded with AN sacks was exposed to a burning straw bale; (b) a 1.5 tonne heap of AN was exposed to a straw bale fire, then augmented by

burning 2 gallons of diesel fuel; and (c) four FIBCs, each holding 500 kg of AN were placed in a 2x2 array and exposed the straw bale burning at the side. All of the tests resulted in quiescent burning only.

Research on AN explosions at Arthur D. Little has been perhaps the most technically promising, from the point of view of understanding some of the science pertinent to actual disasters. In the first project<sup>78</sup> (1952-4), they concluded that the reactions in molten AN are such that an equilibrium temperature of 292°C is reached, and the material will progressively vaporize but the liquid will not rise above this temperature. This however holds only if the material has absolutely no confinement; otherwise, pressure will rise and this will translate into a temperature rise. In the second project<sup>79</sup> (1963), they investigated in more detail the conditions needed for AN that gets molten in a fire to detonate. Here, they concluded that liquid AN can detonate due to external shock, or due to internal pressure buildup. But there is a pool-depth effect, whereby the hydrostatic pressure imposed on bubbles at the bottom of the pool can become appreciable; effectively, the material becomes self-confining, meanwhile the generation of bubbles due to rapid decomposition can generate the initiating shock wave. Based on some simplified modeling, they concluded that, under some circumstances, a pool depth as small as 60 mm could suffice to initiate a detonation from the decomposition/boiling process. These researchers did not conduct experiments to prove their hypotheses, but at least provided a useful starting point for future work. An elaboration of this scheme was later offered by other researchers<sup>80</sup>, but again without actual testing.

It can be concluded from the above research history that no investigators have been successful in simulating the course of AN detonation disasters by means of laboratory testing. On this basis, already many years ago, the US Federal government<sup>81</sup> concluded that *“Many small-scale tests indicate that in the absence of confinement and without added combustible or contaminating material it has not been possible to cause the detonation of ammonium nitrate fertilizer by the application of heat.”* This viewpoint, in fact, has been the “safety” advice for the last century. Yet, disasters keep occurring, and the reason why is clear: Apart from the fact that a number of researchers have documented AN detonability, albeit in tests not much similar to accident scenarios, the position statement is hollow and misleading. As described above,

- (a) No disaster has occurred in the absence of fuel. The fuel may be packing materials, or building materials, or an external pool fire, but fuel is needed for fire to burn and to melt AN. Thus, the behavior of “uncontaminated” AN is irrelevant and misleading with regards to understanding accidents.
- (b) As Sykes et al.<sup>79</sup> learned, “confinement” should not connote a pipe-bomb type of configuration. Instead, a pool of molten AN may provide its own self-confining effect within the liquid. Similarly, in the solid phase, a large pile of AN may provide its own confinement simply due to the dead weight<sup>82</sup>.

Thus, Marlair and Kordek<sup>20</sup> were correct in concluding that *“Indeed, it is hard to believe...that in all cases a big confinement favoring an important pressure build-up had actually contributed in the detonation process observed.”*

## 5. The oxidizing properties of AN

In broad terms, AN disasters have two causative factors due to the chemistry of the substance: (1) its ability to detonate; and (2) its ability to enhance a fire by means of its oxidizing behavior. Thus, the nature of its oxidizing ability must be considered.

AN is not a fuel and cannot burn of itself. But since it is an oxidizing chemical, it can promote combustion reactions of fuels. As an oxidant, it is a weak one and is classified in the lowest class, Class 1, of oxidizers as viewed by NFPA 400<sup>83</sup>. Unlike some stronger oxidizers such as calcium hypochlorite, there are no normally encountered products with which it combines to produce a hypergolic ignition at room temperature. Unless quantities of AN so massive were involved that self-heating would become an issue, for an AN + fuel reaction to occur, application of heat is necessary. The reactions thereby occurring are complicated and not entirely unraveled, but it is likely that evolution of HNO<sub>3</sub> dominates, which is effective in igniting some fuels by contact<sup>15</sup>. Molten AN can ignite carbonaceous fuel by contact<sup>73</sup>.

AN will show accelerated thermal decomposition reactions when combined with a long list of contaminants. Many of these, e.g., chromium compounds, are less likely to be encountered in actual accident scenarios, but chlorides and copper can more readily be expected to be present; zinc can also be important since it is contained in galvanizing coatings for steel. In some cases, there can be a combined effect of organic material and chlorides or copper reacting with AN.

Findlay and Rosebourne<sup>49</sup> published the first study on the oxidizing properties of AN in 1922. They mixed AN with ‘wood meal,’ i.e., fine sawdust, placed it in a test tube and heated it to 100°C. They also repeated the experiment using powdered starch as the cellulosic fuel. In both cases, they got evolution of N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, but no CO or oxides of nitrogen. Kistiakowsky and Guinn<sup>84</sup> conducted oven-heating tests on AN mixed with paper, and found that ignition occurred when a temperature of 132 – 154°C was reached. Macy et al.<sup>63</sup> determined the ignition temperature of AN-saturated paper bags to be 177 – 232°C, but a more intimate mixture of sawdust or paper with AN will ignite at 150°C. All of these results are below the normal ignition temperature of paper<sup>15</sup>, ca. 250°C, confirming the oxidizing properties of AN. The important safety implication is that molten AN at 169.6°C or higher is likely to greatly accelerate spread of fire by direct ignition on contact, as it flows.

Despite the fact that chemists have been studying oxidizing chemical properties for a century or more, no standardized test emerged for assessing the oxidizing potential of chemicals that has engineering meaningfulness. In fact, there even have been very few attempts to develop a standardized test, and no attempt has resulted in a test which would be provide usable engineering data, i.e., data that can be used as input to make some calculation. Instead, all of the research has only produced schemes to compare one substance against another on some arbitrary scale. The earliest studies aimed at producing a standard test were conducted at BM<sup>85</sup>, who proposed a horizontal trough test. The oxidizer is to be mixed with wood sawdust, ignited by a propane flame at one end, and the rate of fire propagation timed. Materials showing a faster rate of progress are deemed to be more hazardous. BM proposed classifying the results into 4 categories already used by NFPA<sup>86</sup>. Researchers at General Electric then conducted two follow-up studies<sup>87,88</sup>, where they endeavored to achieve better reproducibility and also tested additional materials. In the course of this, they confirmed AN to be an oxidizer of Class 1, in terms of the NFPA classification scheme. This test did not come into widespread use and development, instead, shifted to the UN and its Orange Book collection of tests. In this context, Uehara and Nakajima<sup>89</sup> described test development efforts during the early 1980s, while Wildner<sup>90</sup> described further development starting in 1986 which culminated in the publication of the O.1 test in the UN Manual of Tests and Criteria<sup>37</sup> in 1995. The UN test involves mixing the test material with cellulose powder, forming it into a conical heap, and igniting it with a Nichrome wire (Figure 3). Quicker time to burn up is considered more hazardous, and classification is done in comparison with a certain reference material sample. The UN Test O.1 has not changed significantly to this day, although in 2013 UN introduced a second test, O.3<sup>91</sup>, which is similar to O.1 but includes a mass loss rate measurement, as suggested by NFPA<sup>92§</sup>.



**Figure 3** Ammonium nitrate being tested in the UN Test O.1 (photograph by author)

It should be noted that classification of most AN-based fertilizer products is *not* based on conducting the O.1 test. Instead, product classification is accomplished by means of Special Provisions (SPs), which are based on the chemical constituency of the product<sup>93</sup>. Only products which do not fall under the pertinent SPs would be classified by means of testing.

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<sup>§</sup> The NFPA project included use of some standardized engineering tests (heat release rate tests), however, this does not form a part of the UN testing or classification.

## 6. Learning from disasters

Viewed at a level of fine-enough granularity, every disaster is unique. Thus, this point of view is singularly unhelpful towards promoting of safety and preventing of future disasters. **Instead, a prudent risk management philosophy has to entail examining past disasters and identifying what is common among them, not what is unique and different**<sup>94</sup>. For example, after the S.S. HIGH FLYER exploded, the Government panel focused on the fact that there was nearby stowage of sulfur<sup>81</sup> (a unique factor) instead of focusing on the existence of uncontrolled fire (the common factor). As a result, the necessary lesson was not learned. But by now, nearly 70 years later, the record is so lengthy and so diverse, that hopefully the overwhelming importance of the common factor—uncontrolled fire—in AN detonations can be appreciated. This perspective allows one to see that there is nothing substantively different between transportation and storage disasters. In each case, a fuel is present, an ignition occurs, a fire burns fiercely, aided by the oxidizing nature of AN, and effective fire control fails to be achieved. The outcome then, at best, is a physical disaster without dead persons or, at worst, a large life loss disaster. Conversely, not a single AN explosion accident exists in a storage or transportation environment where there was no fire, or where there was a small fire which was successfully controlled.

It is especially troubling that the fertilizer manufacturing industry, while aware of the immense hazards of AN, persistently attempted to minimize the implications of known accidents, instead of learning from them. For example, the representatives of a large AN manufacturer in the UK, who clearly knew the literature very well, wrote<sup>95</sup>: “*the conditions of pressure...and temperature required to explode ammonium nitrate are extreme...such severe conditions are very unlikely to be met.*” And, “*It is generally believed that a fire involving an unconfined mass of ammonium nitrate will not lead to an explosion.*” And, “*...shock initiation of solid material is discounted as a serious risk.*” The attitude of government authorities, at least in the US, has been no better. The safety provisions for dangerous substances in workplace is handled in the US primarily by the Occupational Safety and Health Administration (OSHA), whose regulations, as shown below, have been so ineffectual as to be castigated by other Federal government agencies.

One prior incident is specifically noteworthy. In 2003, a French farm barn containing stored AN suffered an fire which was not successfully controlled. This led to detonation and widespread destructions, but fortunately no fatalities. The West, Texas incident, 10 years later, was very similar to the French accident, but with a disturbing life loss outcome. The details of the French accident were documented both in a technical article<sup>96</sup> and in an ARIA report<sup>97</sup>, yet the lesson went unheeded.

## 7. Preventing uncontrollable fires

There are two main techniques that can be used to prevent uncontrollable AN fires: (1) reduce the fire hazard propensity of AN; and (2) provide constructional fire safety measures for the facility. Both should be implemented for assuring safety in storage environments. But it is generally impossible to implement safety measures with regards to trucks or other transportation environments which would reduce or eliminate potential fuels for fire. Thus, since the second technique is not available for guarding against transportation disasters, it is crucial that the first technique be implemented across-the-board.

### 7.1 REDUCING THE HAZARDS OF AN

Safety improvements in the chemical industry often follow the precepts of Inherently Safer Technology (IST). This is a wide-ranging series of chemical safety tactics, originally taught by Kletz<sup>98,99</sup>. The relevant IST principle here is *substitution—replacing a hazardous material with a safer option*. The IST ‘substitution’ principle is also known as *alternative safer design* in product defect literature. As will be shown below, alternatives for AN which constitute safety improvement in regards to both fire safety and explosibility exist, and some have existed for many decades.

Straight-AN, that is AN where the only added chemicals are a small amount of coating chemicals used to reduce caking tendency, is susceptible to disastrous detonation accidents. Already before 1920, the dangers of this were recognized and the BASF factory at Oppau<sup>\*\*</sup> produced ANS (a double salt of ammonium sulfate and AN) since

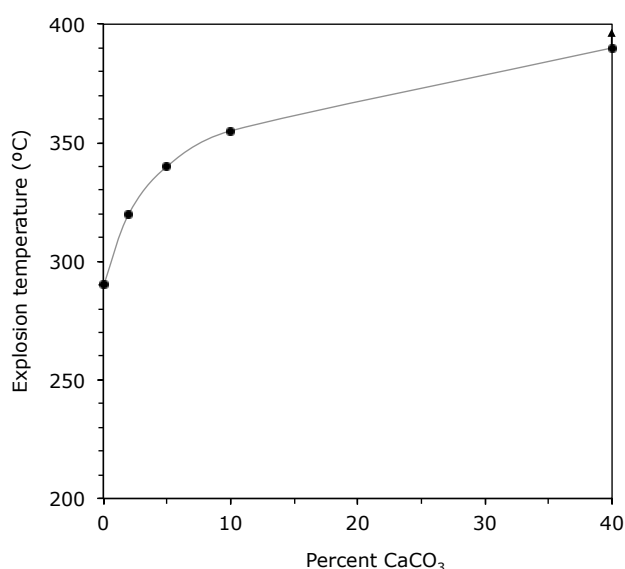
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<sup>\*\*</sup> It might be asked why ANS (also referred to as ASN) would be considered a safer alternative, if this particular product was associated with the largest ever life loss detonation involving an AN-family product. Even though ANS is less sensitive than

straight AN was recognized to be<sup>100</sup> “*too dangerous to handle for fertilizer purposes.*” While this particular product is indeed less susceptible to detonation than straight AN, additional alternatives were subsequently developed, and the patent literature contains a large number of such inventions. Here, three such products are considered: (1) CAN, (2) Ferti-Safe, and (3) Sulf-N 26.

Calcium ammonium nitrate, CAN, has been made since the 1920s<sup>19</sup>. It involves adding powdered calcium carbonate into the AN at the hot liquor stage, in an amount of 20% (currently) to 40% (prior to the 1980s)<sup>101</sup>. CAN has been described as<sup>102</sup> “*a non-detonable alternative to pure ammonium nitrate.*” This overstates its nature, but it is appropriate to view that<sup>30</sup> “*calcium ammonium nitrate essentially removes any explosion hazard.*” Compared to AN, CAN is (a) less likely to lead to uncontrollable fire, since it is a less potent oxidizer; and (b) is both much less sensitive towards detonation, and exhibits greatly lowered explosive power if boosted enough to detonate. CAN, or alternative safety enhanced products, are utilized to the exclusion of straight-AN fertilizer in a number of European countries<sup>103</sup>, which includes Belgium, Denmark, Eire, Finland, Germany, The Netherlands, Northern Ireland, and Switzerland. This is directly due to the safety characteristics of CAN versus AN.

With regards to the effect on fire of CAN, one of the earliest demonstrations of the safety improvement that can be achieved by CAN were the pressure-vessel experiments of Braconier and Delsemme<sup>53</sup>, discussed above. They concluded that the explosion temperature is a useful criterion for examining the negative effects of contaminants and the positive effects of inerting additives. Adding 0.001% of chlorine lowered the explosion temperature of AN from 290°C to 260°C, while 0.1% lowered it to 240°C. Similarly, adding 1% of paraffin wax dropped the temperature to 240°C. But a notably positive effect on AN stability was obtained by adding calcium carbonate (Figure 4). More recently Oxley et al.<sup>104</sup> and Kiiski<sup>105</sup> studied a variety of substances for inerting AN decomposition. Both concluded that, of substances examined, calcium carbonate was the most beneficial.



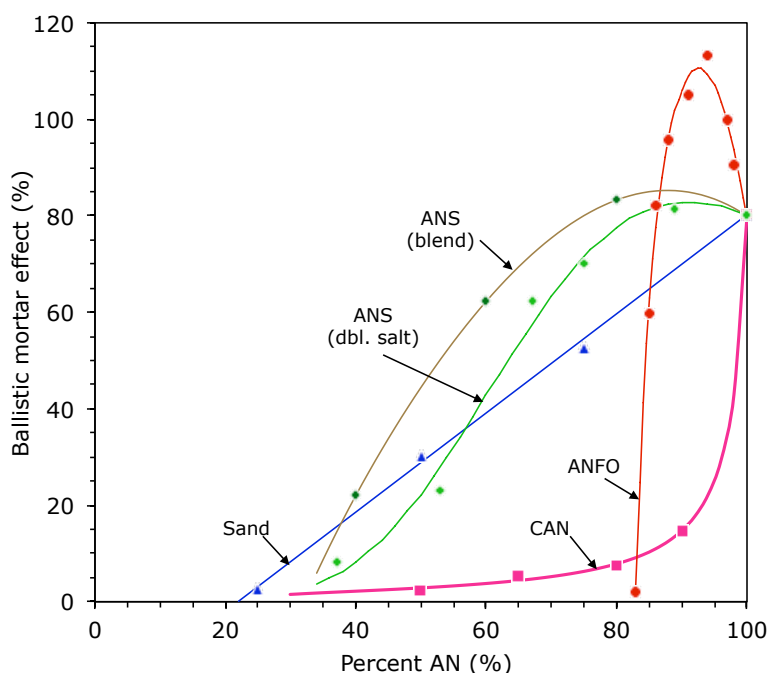
**Figure 4** Effect of adding calcium carbonate to AN on raising its explosion temperature

Hainer<sup>74</sup> conducted fire tests in moderately large scale by burning 136 kg of wax-coated AN prills in a 55-gallon drum, stoked with charcoal and wood and ignited with 10 kg of thermite. He then added 45 kg of clay-coated AN prills and more thermite and got a violent fire, albeit not an explosion. He judged that such a fire would not be extinguishable. However, he then added 68 kg of CAN, and this actually controlled the fire to the extent that even adding more thermite failed to make it severe or difficult to extinguish. This demonstration clearly showed that CAN not only does not promote burning, but acts to suppress burning.

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straight-AN, the disaster at Oppau was provoked by blasting of caked product with dynamite, the most dangerous conceivable action.

With regards to detonation properties of CAN, Shaffer<sup>106</sup> conducted sensitivity tests on AN compounds to determine how much booster is needed for detonating a tube filled with the test material. In these tests, he found that commercial CAN specimens with AN content of 81% showed a detonation sensitivity of 22%, as compared to straight AN. With sufficient boosting, CAN can be detonated, even though much greater boosting would be required. But even under that unlikely scenario, the outcome would be notably less severe. Clancey and Turner<sup>107,108</sup> showed test results for the explosive power of CAN, compared to AN and some other diluents, based on ballistic mortar tests (Figure 5). This shows that by incorporating 20% of calcium carbonate, the explosive power of AN can be reduced by more than 90%. Results consistent with this were also obtained by BM<sup>61</sup>. Even more ambitious were tests conducted by TNO to compare AN and CAN in a very large layout. Bags totaling 28 tonnes were assembled of each material and initiated with a very large ANFO booster<sup>109</sup>. The CAN pile did not detonate, while AN detonated and showed a detonation velocity of 4500 m s<sup>-1</sup>. Perbal<sup>110</sup> showed that CAN samples containing 0.4% organic material are still resistant to detonation.



**Figure 5** The effect in the Mark IIIc RARDE ballistic mortar of AN with various additives (Clancey and Turner), with results being expressed as a percent of the effect for pure picric acid. Pure AN shows 80% the energy value of picric acid. ANS (blend) denotes a mechanical blend of ammonium nitrate and ammonium sulfate, while ANS (dbl. salt) denotes a 1:1 molar ratio double salt.

It should also be observed that the UN Test O.1 is not a good measure of the potential of AN-based fertilizers to act as oxidizers promoting a fire, as documented by Babrauskas<sup>111</sup> for AN, CAN, and two other improved products. The only criteria for the test are based on the assumption that the safer the material, the longer will be the duration of burning. This is one way that fire-retardant formulations work, but it is not the only way. Some formulations work in the opposite way—not only is the peak burning rate diminished, but the combustion terminates quicker<sup>112</sup>. Testing with AN and safer alternatives indicated that while some traits of products can be examined with O.1 testing, numerical evaluation by the O.1 criteria would make no sense, since some improved, safer products would be declared less safe.

The inappropriateness of O.1 testing was earlier demonstrated in graphic detail by Bureau of Explosives<sup>17</sup> tests on AN, CAN, and some other products. They conducted three series of tests. The first test series entailed conical mounds similar Test O.1, but using 4.5-kg instead of 30-g samples. Since sawdust was well-mixed into the fertilizer, little difference was seen between CAN and AN. They then conducted tests with a more realistic disposition of fuel *vis-à-vis* oxidizer. In the second series, they built bonfires and stacked bags of fertilizer on a grate above them, using 14 – 182 kg of specimen. Instead of uniformly commingled sawdust, the combustibles comprised paper bags in which the specimens were poured, plus some additional paper torn up and inserted inside. In some tests, 1 – 2% oil



was applied to the prills. The third series differed mainly in the geometric arrangement used. In both those series, a remarkable difference between AN and CAN performance was found. The results for a typical configuration are shown in Table 2.

**Table 2** Results of oxidizer testing by Bureau of Explosives for from the second series of tests involving 14 kg of fertilizer

Sample	Fertilizer	Combustible	Percent remaining at end of test
AN	14 kg	1/3 bag, 1% oil	0
CAN #1	14 kg	" "	93
CAN #2	14 kg	" "	83

The reason that the Bureau of Explosives saw a highly beneficial effect of CAN in the second and third test series, but not in the first one, is because these series did not involve an intimate commingling of sawdust, but a much more realistic arrangement that is a reasonable representation of the circumstances of an accidental fire. Thus, while Test O.1 may represent a worst-case situation (and the test conditions were apparently selected to optimize test reproducibility), this worst-case is so extreme that it does not allow one to distinguish well-performing AN-based fertilizer products from hazardous ones. This had already been explicitly recognized by Herquet<sup>54</sup>, who concluded that what created the worst-case conditions was not a large quantity of organic material, but a “more intimate mixture.”

In recent years, some additional products have been developed which are also a significant safety improvement over straight-AN. Two notable ones are *Ferti-Safe* and *Sulf-N 26* (now marketed as ASN-26). *Ferti-Safe* was developed by Taulbee<sup>113</sup> as a way of fruitfully using coal-combustion fly ash products for agricultural purposes. This product entails standard AN prills coated with a 20% coating of fly ash product which is mostly calcium sulfate. Extensive detonation testing with the product showed a superior performance to CAN and a greatly superior performance to AN<sup>114,115,116</sup>. *Sulf-N 26* was developed by Honeywell International Inc. as a variant of the ANS double salt, specifically for improved safety performance purposes<sup>117</sup>. While testing details have not yet been published, the product has already entered production. Note that this is not an across-the-board recommendation for ANS. In view of studies<sup>70,107,118</sup> where some grades of ANS detonated readily, it should be concluded that beneficial effects of ANS are realized only for very specific formulations.

Interests opposed to alternative safer design products sometimes claim that any of these alternatives are impractical since they either lower the nitrogen content, or raise the price of the fertilizer, or both. It is generally true that any safety improvements are likely to carry some cost or functionality penalties. However, the widespread adoption of CAN in many European countries demonstrates that the penalties are small enough to make the safety improvements gained very worthwhile.

Military authorities sometimes propose to take actions against improvised explosive devices (IEDs), which are often based on AN. Thus, there have been campaigns<sup>119</sup> to discover modifications to AN which would make it non-explosive and ‘irrestorable.’ The latter concept means that the modified substance could not be re-manufactured to yield an explosive material. Such efforts to create a non-explosive and irrestorable version of AN have all come to naught<sup>120</sup>. But it is exceedingly important to realize that this campaign is solely a *security* campaign and unrelated to *safety* concerns of this paper. To reduce the potential for accidental detonations involving AN, it is not necessary to evolve a substance which is non-explosive and irrestorable. What is needed is a formulation with reduced oxidizing potency, reduced detonation sensitivity, and reduced explosive power. Unlike the objectives of military authorities, these objectives are demonstrable practical and feasible.

## 7.2 MAKING BULDINGS FIRE-SAFE

Safety improvements in the AN-based product may be the only strategy available for improving transport safety. But for storage buildings, the buildings themselves can be constructed so as to preclude the possibility of an uncontrolled fire, and this should be done as an additional layer of protection. A short list of crucial fire safety features would suffice to prevent AN disasters, such as occurred at West. While the Texas facility was only one of more than 1300 such in the US, it is useful to focus on its shortcomings, since many agricultural AN storage facilities are built in a similar manner.

- AN storage bins should be made of noncombustible, non-reactive materials. Wood or galvanized metal should not be used. It has been known since at least 1936<sup>121</sup> that wood in contact with AN can get saturated with the material and then, when ignited, will burn “*with a much stronger flame than non-saturated wood.*” But wood bins would be an unacceptable source of fuel in proximity to stored AN, even if some surface treatment were adopted which reduces direct impregnation, since the fuel value of the wood is not reduced thereby.

In 1947, as a result of the tragedy in Texas City, the US Federal government<sup>81</sup> concluded that “*The most common hazard to ammonium nitrate fertilizer...is fire involving combustible containers or adjacent combustible material that may be present...*” Unfortunately, many decades later, matters had not changed, leading directly to the West tragedy. The AN was stored there in wooden bins, comprising a large fuel load in direct contact with the AN.

- The building construction should be of non-combustible materials except for very small components for trim, wiring, or other purposes where noncombustible alternatives do not exist.

The building wherein AN was stored was of ordinary, wood-framed construction, with much exposed timber not even protected by plaster or gypsum wallboard. Ordinary timber construction can be ignited from very small ignition sources (e.g., electrical faults), while the large amount of timber present serves to create a long-burning fire. It is highly unlikely that the fire and detonation at West would have taken place, had the bins and building materials not been combustible.

- Any AN storage facility should be equipped with smoke or heat alarm system monitored by a central station.

The fire occurred about 2 hours after close of business for the day. The fire department was notified only when a person in a nearby city park observed smoke. By the time the fire department arrived, they faced a fully involved fire. Had there been a fire or smoke alarm system monitored by a central station, notification would have come to the fire department much earlier, and it is likely that the fire would have been suppressed successfully, rather than overwhelming the firefighters.

- Any AN storage facility should be protected by an automatic fire sprinkler system, properly designed for this purpose.

Apart from fire extinguishers, which are of no benefit to an unattended facility (nor if the fire grows beyond a very early stage), there was no fire suppression system. Had there been a properly designed fire sprinkler system, this would have controlled the fire and, upon responding to the fire, the firefighters would have encountered a suppressed, or nearly so, fire.

- Floors in an AN storage facility should be constructed so that there are no elevator pits, drains, grates, or pipes to where molten AN could flow into and accumulate.

At the West Fertilizer facility, the elevator contained a pit about 3 m deep into which molten AN could flow. It is most probable that the actual explosion originated at this pit. With a floor design that does not allow molten material to be trapped, the molten AN would have been less prone to detonation due to absence of a critical depth of liquid material.

- To be effective, all of the above provisions need to be mandatory and not just in the form of advisory suggestions.

As explained below, no mandatory safety requirements were laid upon the owners of the West Fertilizer Co., beyond OSHA regulations, and these did not include any of the above fire safety provisions.

## 8. The role of codes and suppliers

### 8.1 FIRE SAFETY MEASURES FOR STORAGE ENVIRONMENTS

Staff of agricultural fertilizer distribution companies are normally knowledgeable only on matters of agronomy and do not have technical knowledge on the fire or explosion safety of chemicals. Consequently, the only way that agricultural fertilizer distribution facilities can be provided with adequate fire safety is if there are mandatory requirements laid down and enforced by technically competent entities, of which there are two: (1) government

authorities, and (2) AN manufacturers. Disasters such as the one at West, Texas occur when neither takes effective action. In the case of manufacturers, they actually have a dual role—to provide for safety improvements in the product itself, discussed above, and to require safe facilities at their customers. In a number of sectors of the chemical industry, raw chemical suppliers have Product Stewardship procedures in place so that they will not ship product to any facility that they have not inspected and approved. The US suppliers of fertilizers had chosen not to implement such requirements. Also, in West, as in much of other rural parts of Texas, there exists no building code and no fire code. This is true of many other locales in rural US, where codes are either absent or there are no local authorities competent to inspect and control hazardous chemical facilities. But even a competent authority will not be able to achieve adequate safety unless there exists a suitable document for them to enforce. Thus, it is important to examine some of the salient documents concerned with AN safety.

Various codes and guidance documents often provide a plethora of provisions regarding storage of AN, which tends to create the impression that effective fire safety measures have been adopted, even when the provisions adopted are marginal, obscure, or do not address the primary fire safety needs. The requirements laid down by some of the relevant documents are described in the sections below and summarized in Table 3. It is of utmost importance to realize that adherence by the owners of the West Fertilizer Co. to any of the documents discussed would not have averted the disaster. The FM Global data sheet is the only one that contains even a reasonable fraction of the pertinent safety features, but this is a purely advisory document. Only if there were a means of making its provisions mandatory might raising of the fire safety level occur. But this could have been accomplished had the manufacturers of the AN made such compliance a sales condition for supplying AN.

**Table 3** Presence or absence of essential fire safety features for some codes, regulations, and guidance documents (summary evaluation; details are provided in connection with each institution below)

Safety measure	OSHA	NFPA 400	FM Global	TFI	W.A.
Product with combustion and detonation resistant behavior	✗	✗	✗	✗	✗
Non-combustible bins	✗	✗	?	✗	✓
Non-combustible building construction	✗ <sup>(a)</sup>	✗	✓	✗	✓
Monitored alarm system	✗	✗	✗	✓	✗
Automatic fire sprinkler system	✓ <sup>(b)</sup>	✗	✓ <sup>(c)</sup>	✗	✗
Absence of places where molten AN could pool	✓	✓ <sup>(d)</sup>	✓	✗	✓
Mandatory language	✓	✓ <sup>(e)</sup>	✗	✗	✗
<p><sup>(a)</sup> In some cases, fire-resistive walls may be required, but these do not have to be non-combustible; also, nonconforming facilities can be allowed.  <sup>(b)</sup> Only for facilities storing in excess of 2500 tons.  <sup>(c)</sup> Only for portions of the facility containing combustible components.  <sup>(d)</sup> Provision exists, but ineffective, since scope does not include pits.  <sup>(e)</sup> Many of the provisions turn out to be non-mandatory, since they are couched in terms of subjective decisions by the AHJ, and especially allowing the AHJ to permit nonconforming structures to continue being used.</p>					

### 8.1.1 OSHA REGULATIONS

In the US, section 29 CFR 1910.109(i) of OSHA regulations<sup>122</sup> include provisions for the storage of explosives or blasting agents comprising AN. However, these safety features are weak and compliance with them would not have prevented the West disaster. Notably, wood construction is not prohibited, while sprinkler protection is required only for facilities storing over 2500 tons of AN (Table 3). The West facility, at the time of the explosion, held 40 – 60 tons of AN, not counting the 100 tons in the parked railcar which did not get involved. Furthermore, any reasonable reading of the regulation indicates that it applies only to entities manufacturing or storing explosives, but not to distributors of agricultural fertilizer. After the West disaster, OSHA responded with a self-serving letter<sup>123</sup> claiming that such fertilizer storage facilities were subject to the above-cited section. However, the whole section, not just subsection (i), of the regulation is titled *Explosives and blasting agents*, with its scope being specified as: “This section applies to the manufacture, keeping, having, storage, sale, transportation, and use of explosives,

*blasting agents, and pyrotechnics*” while fertilizer-grade AN is not classified as by any governmental entity as being an explosive, blasting agent, or pyrotechnic<sup>8</sup>. Two different, but non-regulatory, Federal agencies<sup>8,124</sup> documented the ineffectiveness of OSHA towards establishing viable fire and explosion safety in agricultural AN storage facilities. It is also of interest that OSHA inspected the West facility in 1985 and cited it only for minor violations unrelated to the AN storage building. Yet, the wooden building, the wood bins, the elevator pit, and other relevant hazards were the same at the time of the inspection as in 2013.

## 8.1.2 NFPA 400 HAZARDOUS MATERIALS CODE

The best-known document in the US concerned with the safety of AN storage is the NFPA Hazardous Materials Code (NFPA 400<sup>83</sup>), which is considered here in its pre-West-disaster (2013) edition. It is published by a private organization, but assumes the force of law in many US jurisdictions since it is directly referred to by most US fire codes. Unfortunately, this is a document which is inordinately opaque and confusing<sup>††</sup>. In addition, it is unreasonably wordy, being some 214 pages long<sup>‡‡</sup>. While technical knowledge necessary to adequately describe safe storage of AN is not trivial, it unreasonable to expect even a chemist or an engineer to read and comprehend a 214-page treatise in order to arrange for safe storage of AN. An even more severe shortcoming of NFPA 400 is that it relies extremely heavily on subjective assessments and approvals or disapprovals from the pertinent Authority Having Jurisdiction (AHJ). This creates a lack of rigor and objectivity. But in a locale which lacks a fire code and an AHJ, it makes the concept of AHJ-dependent requirements illogical. An additional weakness is the ‘grandfathering’ of existing facilities. Sec. 11.5.5 specifies that *“the continued use of an existing storage building or structure not in strict conformity with this code shall be approved by the AHJ in cases where such continued use will not constitute a hazard to life or adjoining property.”* In a locale with has no AHJ, this implies that no restrictions can be made with regards to existing buildings.

The NFPA Code does not require that bins be made of a non-combustible materials, instead of being made from wood. The only bin materials prohibited (Par. 11.3.2.3.3.2) are ones made of galvanized iron, copper, lead, or zinc. Par. 11.3.2.3.3.3. states that “wooden bins protected against impregnation by ammonium nitrate shall be permitted” but does not prohibit wooden bins of any other kind. Furthermore, the concept of “protected against impregnation” is meaningless since there does not exist any test for this, nor are any instructions or specifications given in the NFPA Code for establishing what constitutes protection.

The NFPA Code does not require that any other combustible construction features of the building itself be eliminated. Par. 11.1.5 requires that the building *“be constructed in accordance with the building code,”* but this is meaningless for a locale that has no building code. Furthermore, building code provisions are written to govern the *construction* and not the *operation* of buildings. In other words, apart from some optional additional provisions for existing buildings that localities can include by local ordinance, any building already in existence when a building code is adopted does not fall under the scope of its regulation.

The NFPA Code has no requirement that an alarm system be installed. There is a placeholder in Sec. 11.2.10, but no requirements or text.

The NFPA Code does not require that an automatic fire sprinkler system be installed in the facility. Sec. 11.2.6 specifies that sprinkler requirements are laid down in Sec. 6.2.1.1, but the latter only requires sprinklers for chemicals which fall into Protection Levels 1 through 4, while AN is outside the scope of Protection Levels, per Table 5.2.1.1.3. In fact, the wording of the Code actively discourages installation of sprinkler systems for AN: *“11.2.6.1.2 Sprinkler protection shall be permitted to be required by the AHJ for the storage of less than 2500 tons (2268 metric tons) of ammonium nitrate where the location of the building or the presence of other stored materials can present a special hazard.”*

The provisions in the NFPA Code against pooling of molten AN are poor, at best. Sec. 11.3.3.2 restricts drains, pockets, etc., within “flooring in storage and handling areas.” The straightforward architectural interpretation of

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<sup>††</sup> One example:

**11.2.3.1** Secondary containment shall be provided for ammonium nitrate in accordance with 6.2.1.9.3.

**11.2.3.2** For ammonium nitrate solids, the requirements of 6.2.1.9.3 shall not apply.”

This text reads more like a satire of ineffective technical communications than a cogent regulation.

<sup>‡‡</sup> It must be noted that NFPA 400 became the NFPA standard governing AN only in 2010. Previously, the governing standard was NFPA 490. In sharp contrast to NFPA 400, this was a short, simple, and easily comprehensible document. Unfortunately, it did not provide any better fire safety than does NFPA 400.

these requirements is that they literally only prohibit drains, gutters, trenches and channels coming down below the floor level; an elevator pit such as was present at the West facility might be considered simply a change in floor level, not an appurtenance extending below the floor.

After the West disaster, an NFPA spokesperson<sup>125</sup> admitted that NFPA is still “learning more about ammonium nitrate” and proceeded to revise AN provisions for the 2016 edition. An analysis<sup>126</sup> of this forthcoming edition indicates that it is still unlikely to prevent AN disasters, despite some improvements.

### 8.1.3 FM DATA SHEET

In stark contrast to NFPA 400, the FM Data Sheet 7-89<sup>127</sup> is only 12 pages long, is written in clear, non-convoluted English, and lays out fire safety provisions in readily comprehensible terms. Its main drawbacks are that, being published by an insurance company, it is necessarily only advisory, and that it includes some, but not all of the safety provisions discussed above. It does not establish requirements for products safer than straight AN, nor a monitored alarm system. However, it specifies non-combustible building construction, and clearly prohibits pits where molten AN could pool. An automatic fire sprinkler system is required anywhere that combustible items might be installed. In the case of an agricultural fertilizer facility, it is generally difficult to provide non-combustible elevators and conveyor belts; thus, these would require sprinkler protection. It is not clear if combustible bin materials are prohibited, but even if they are allowed, this would have triggered a sprinkler requirement. If the West facility had been rebuilt in non-combustible construction, had sprinklers provided for combustible components, and had its elevator pit eliminated, it is highly unlikely that a severe fire could have developed that ended as a detonation.

### 8.1.4 TFI GUIDELINES

In response to the West disaster, The Fertilizer Institute (TFI) issued in 2014 “Safety and Security Guidelines” for AN<sup>128</sup>. But this is a shockingly inadequate document. There are basically only three provisions addressed directly at the construction safety of storage buildings:

- (1) Steel or wood bins should be protected by a coating such as sodium silicate, epoxy, or PVC;
- (2) If not continuously occupied, the building should have an automatic detection and alarm system; and
- (3) AN piles should not exceed a height of 40 ft (12.2 m).

Had these guidelines been in effect on 17 April 2013, nothing would have changed. First and foremost, the document is presented in non-mandatory language, e.g., “should,” not “shall.” Thus, any operator of an AN storage facility would be entitled to conclude that compliance is optional and that there is no burden to comply. But even if the wording were changed to mandatory language, the safety level would be grossly inadequate. It may be noted that research has shown AN piles over 1.5 m high are susceptible to detonation<sup>129</sup>, so limiting height to 12.2 m (much taller than at West, Texas) is ineffectual. Since the consequences of an AN explosion can be so dire, it should be clear that a strategy of protection-in-depth is necessary. In other words, not only must all pertinent aspects of fire safety be included, but there must be some redundancy, so that more than one layer of protection would be in place to guard against deaths of exposed population. TFI document, on the other hand, not only lacks any useful redundancy, but fails to require even the most elementary safety precaution, noncombustible construction.

### 8.1.5 WESTERN AUSTRALIA CODE OF PRACTICE

An instructive contrast is the AN safety document issued by the government of Western Australia (W.A.) in 2012<sup>130</sup>. This notably predated the West disaster, yet the treatment of constructional safety issues is dramatically superior to the post-West TFI document. The document is also issued in a non-regulatory context and thus is presented in “should” language. But at least it includes a number of important safety issues:

- (1) The entire building should be built of non-combustible materials;
- (2) A clear explanation is given that drains pipes and tunnels should not exist within which molten AN could accumulate;
- (3) If there is any other facility within the AN storage building, a 5 m clear spacing should be established between the AN storage facility and other uses within the building. Much greater distances are to be provided for storage quantities in excess of 10 tonnes.
- (4) Bins should be made only of non-combustible materials.

In addition, the document makes clear that chlorides are incompatible with AN. This speaks directly to the issue at West where the same conveyor system was used to transport KCl and AN, necessarily leading to contamination of AN with KCl, since no cleaning regimen existed.

## 8.2 MANUFACTURERS' ROLE

In the absence of effective government regulations, manufacturers of the material can take active steps to ensure safety in transport and storage using two tools: (1) a safety data sheet (SDS) for the material which contains necessary prescriptions for safe transport, handling, and storage of the product; and (2) a buyer qualification program, and these tools are best used in concert. In the US, the manufacturers of AN have not taken either task seriously. Even after being revised subsequent to the 2013 disaster, the safety data sheets of the manufacturers remain totally inadequate. They lack prescriptive language, and simply refer the user to NFPA 400 for actual fire and explosion safety recommendations. Furthermore, the intention of a SDS is defeated by such an approach. A useful SDS should be self-contained with regards to safety requirements, and authors should not evade their responsibility by simply suggesting that the user consult another document.

The manufacturers involved, however, could have prevented the West, Texas disaster (and disasters which may occur in the future) by including in the SDS the safety issues identified above, and doing this in a prescriptive and clear language. This would need to be accompanied by an effective program to inspect the buyer's facilities to ensure that they comply with the fire safety requirements laid down in a suitably effective SDS. It is noteworthy that in the case of the West, Texas disaster, employees testified that they would have complied with any constructional safety requirements that they would have been required to observe<sup>131</sup>.

## 9. Conclusions

Explosions of stored ammonium nitrate are rare events. But they are recurrent, catastrophic, and preventable. The reason they have not been prevented is because persons charged with safety responsibilities focused on the differences characterizing each disaster, instead of examining what is common among the disasters. The recent explosion killing 15 persons in West, Texas, is but the latest disaster in a century's worth of AN explosions. By examining this long record, it emerges that the common factor is an uncontrollable fire. This is true irrespective of whether the material is stored in a warehouse, or on a transportation conveyance. In the database compiled, it is found that 100% of AN explosions in storage or transportation environments (excluding manufacturing accidents or accidents involving other explosives) have been caused by uncontrolled fire. Conversely, 30% of uncontrolled fires involving AN have resulted in explosions, and about half of these resulted in deaths.

There are some two centuries' worth of chemistry studies on the characteristics of AN. These are helpful towards understanding AN behavior, but do not enable reconstructions of accidents to be made. Explosives researchers understand how AN can be detonated when a detonator and a booster charge are used. But only some unvalidated theories exist to explain how AN detonates in fires where neither of these is present. A handful of researchers also tried to re-create such fire-induced detonation events, but every one of them was unsuccessful. Yet, the tragic record of recurring explosions due to fires demonstrate that the phenomenon is not only real, but is a major hazard.

To avoid a second "century's worth of ammonium nitrate explosions," the solution is simple and should have been recognized already, even though it has never been acknowledged. Stored AN disasters will not occur if uncontrollable fires do not occur. The technology needing to be implemented for this is twofold: (1) manufacturers must switch from making straight AN to making fire- and detonation-resistant products; and (2) owners of storage facilities need to implement building construction features which preclude the possibility of an uncontrolled fire. The needed technology to achieve both these objectives has existed for many decades and is in no way novel.

There are only two entities that can prevent future disasters—government and manufacturers. In the US, both have been wholly ineffectual. US government regulations can be on a Federal, State, or local level. But building construction regulations are administered only on a local level. AN fertilizer is predominantly stored and used in rural areas, and construction regulation in such areas is generally ineffective or, as in the case of Texas, nonexistent. Regulations to prohibit straight AN in preference to safer fertilizer products could be enacted on a Federal level, but two different non-regulatory Federal agencies, the US Chemical Safety Board and the Government Accountability Office, explicitly documented the ineffectiveness of OSHA, the agency which does have regulatory authority. The latter agency could also abate hazards in most storage occupancies since they constitute workplaces. However, the existing regulations are misguided and ineffective towards achieving needed fire safety.

The AN manufacturers could prevent disasters in the absence of viable governmental regulations. But unlike in some other areas of the chemical industry, the manufacturers in this sector have consistently failed to recognize the

importance of Product Stewardship as a means of avoiding death and injury. This means that product is routinely sold to parties not competent to safely store the material. Finally, codes and standards in this area have also been comprehensively defective. Notably, NFPA 400 has not required safety features which are crucial towards avoiding AN disasters and its recent improvements are insufficient.

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