Ammonium Nitrate – Fertiliser, Oxidiser and Tertiary Explosive. 
A Review of Ammonium Nitrate Safety Issues 
based on Incidents, Research and Experience in the Safety Field

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UKELG, Loughborough – 10th September 2008
- Governmental Regulations – Storage and Transport
- Safe Process Operation
- Threat from “Improvised” explosives
- Recent incidents
- Debate around testing of AN
- Novel products
- Increased use of AN based explosives (Chinese economy)
Ammonitrat-Explosion in Oppau 1921
561 Todesopfer, mehr als 7000 Obdachlose in der Nachbarschaft

Explosion of fertilizer transporting truck on Monday morning

An ammonium nitrate transporting truck exploded on Monday morning in Romania, Buzau county. The ammonium nitrate is used in the agriculture as fertilizer. 15 persons died, 11 injured. Among the dead there are 7 firemen, 2 journalists and 8 passengers of the cars parking nearby. 1 soldier and 3 inhabitants are missing. The number of the dead is not definite. Due to the explosion the roof of 17 houses damaged, the windows broke. At the site of the detonation an approximately 10 meters deep crater opened. The explosion damaged the pavement of the road on a 40 meter long section.

FgyelelNet portal 24th May 2004/

Mexican Blast: A truck carrying fertilizer has exploded in Mexico, killing dozens and wounding more than one hundred, including rescue workers.
Ammonium Nitrate

Hygroscopic solid and oxidant, Melting Point 169 deg C

“stable” *unless contaminants present*

– eg organic species, metallic & other fuels, halides, pH

Known and characterised tertiary explosive
Reversible endothermic dissociation

\[ \text{NH}_4\text{NO}_3(s) = \text{NH}_3(g) + \text{HNO}_3(g) \] - \( \Delta H = 186 \text{ kJ/mole AN} \)

followed by a number of irreversible exothermic reactions at higher temperature e.g.

\[ \text{NH}_4\text{NO}_3(s) = \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g) \] - \( \Delta H = -37 \text{ kJ/mole AN} \)

\[ 2\text{NH}_4\text{NO}_3(s) = 2\text{N}_2(g) + 4\text{H}_2\text{O}(g) + \text{O}_2(g) \] - \( \Delta H = -118 \text{ kJ/mole AN} \)
**Storage**

**October, 1918 Morgan, New Jersey**
One of the shells released from a shell loading plant explosion caused a large explosion in AN store, but the majority of the ammonium nitrate did not detonate.

**1963 Holland – No Injury**
4000 tonnes of NPK in storage involved in self-sustained decomposition.

**1966 USA – No injury**
A fire involving AN fertiliser and other combustibles lead to an explosion

**1973 USA – No injury**
A fire in an AN wooden store resulted in the explosion of a few tonnes of AN. 14,000 tonnes were unaffected.

**1975 Germany – No injury**
Self sustained decomposition in NPK fertiliser initiated by welding resulted in evacuation of 1000 residents.

**1978 USA – No injury**
500 tonnes of AN involved in a warehouse fire – no explosion

**1982 UK – No injury**
Major fire with wooden furniture stored near AN fertiliser. Resulted in a deflagration and toxic fume release. Local evacuation undertaken.
1987 France — No injury
Self sustained decomposition in 1450 tonnes NPK fertiliser.
Mass evacuation due to toxic fume release but bulk AN not affected

1978 Yugoslavia – No injury
Self sustained decomposition in 17,000 tonnes of bulk NPK fertiliser.
Mass evacuation necessary.

1998 Kentucky, USA
A warehouse containing 4000 tonnes of AN in basement was allowed to burn out.
Two explosions reported from propane cylinders stored there. Mass evacuation took place.

September 21st, 2001 AZF Fertilizer Toulouse France 31 fatalities, 350 injuries
The explosion had occurred in a warehouse in which granular ammonium nitrate was stored flat, separated by partitions. The amount is said to be between 200 to 300 tonnes of ammonium nitrate, which is used to make fertilisers. A spokesman for the Interior Ministry in Paris ruled out a criminal attack, saying the explosion had been caused by an accident following an "incident in the handling of products". The exact cause remains unknown in public domain – contamination ?.
Disaggregation

July, 1921 Kriewald Germany (Poland) - 19 fatalities
Workers tried to dislodge 30 tonnes of ammonium nitrate which had aggregated in two wagons when blasting explosives were used the wagons exploded.

September 1921 Oppau, Germany – 450 fatalities
The fertilizer was a 50:50 mixture of ammonium nitrate & ammonium sulphate & the factory had used dynamite to disaggregate over 20,000 times without incident. It is thought that poor mixing had led to certain parts of the mass to contain more ammonium nitrate than others. Only 450 tonnes exploded, out of 4500 tonnes of fertilizer stored in the warehouse.

April 1942, Tessenderlo, Belgium - several hundred fatalities
An attempt to disaggregate a pile of 150 tonnes of ammonium nitrate with industrial explosives ended tragically.
**Transport**

April 1947, **Texas City, United States** - several hundred fatalities
A cargo ship was being loaded when a fire was detected in the hold: 2600 tonnes of AN in sacks were already aboard. The captain responded by closing the hold and pumping in pressurised steam. An hour later, the ship exploded and set fire to another vessel, 250 metres away and contained 1050 tonnes of sulphur and 960 tons of AN: this exploded the next day.

July 1947, **Brest, France** – 29 fatalities
A cargo ship was loaded with 3300 tonnes of AN & various inflammable products when it caught fire. The vessel was towed out of the harbour and exploded.

1954, **Red Sea** – No Injury
A fire in a ships hold containing AN, paper & organics/ copper resulted in an explosion. The ship was abandoned.

1960, 1963 **Traskwood, USA** – No Injury
Wagons were derailed with AN, nitric acid & hydrocarbons involved in a fire & explosion.
Transport contd

1965 Atlantic – 3 drowned
4000 tonnes of NPK in bulk storage in self-sustained decomposition.

1967 USA – No injury
A fire involving 50 tonnes of AN in paper bags in wagons with wooden interior was allowed to burn out.

1972 France – 2 fatalities
Decomposition of lagging contaminated with AN & organics lead to an explosion and release of hot AN solution.

1972 Australia – 3 fatalities
A fire in a semi-trailer with low density AN & oil lead to an explosion.

1997 Brazil - several fatalities
AN truck fire compounded by fire in petrol tanker trying to pass.
A detonation was thought to have been initiated by an exploding propane bottle.
Fatalities were largely in a parked coach near to the fire.

2000 Florida, USA – one fatality
Collision between an AN truck and gasoline tanker resulted in a fire.
(Fatality due to collision).
1994 Terra, Port Neal, US – AN neutraliser
In a 1994 accident, AN solution (about 70 tonnes of AN) exploded during a manufacturing process, causing a number of deaths and injuries. During a procedure to shut down the process, compressed air was applied to the nitric acid line into the neutralizer, followed by pressurized steam at 200 psig and temperatures up to 220 deg C. After the steam had passed through the nitric acid line for several hours, the ammonium nitrate exploded in the neutralizer. The solution was highly acidic and was contaminated by chlorides.
Dust Explosions in Air

AN is basically an oxidant. It has no measurable dust explosion characteristics e.g. minimum ignition energy, minimum ignition temperature, KST etc.
Deflagration and Minimum Burning Pressures

Deflagration – steady state burn of condensed phase media
– pressure dependent with defined cut-off pressure (MBP)

A number of studies have been carried out on AN and various additives & stable deflagration of pure solid AN has not been observed < 0.1 GPa

The presence of a halide salt or fuel can reduce this threshold pressure by a factor of 100 e.g. to 10 bara. Molten AN exhibits a lower MBP also
Minimum Burning Pressure Facility - CERL

- 10 cm long straight NiCr wire imbedded in explosive
- 25 mm diameter PVC cell
- Cylindrical geometry
- Cell suspended in 4-L high-pressure vessel
Thermal Explosion/ Reaction runaway

Near simultaneous exothermic reaction - small thermal gradients.

For pure AN, with endothermic & exothermic reaction pathways, onset temperatures for thermal explosion are high, ie ~ MPt.

This onset temperature can, however, be dramatically reduced by the presence of a fuel or catalyst for thermal decomposition.
Detonation, Shock to Detonation- AN as a tertiary explosive

Diameter > critical diameter (density, particle characteristics, confinement)

Shock Stimulus > shock pressure & critical area normally requiring donor charge
TNT Equivalence of pure Ammonium Nitrate solid

- assuming 100 % efficiency
- chemical equilibrium
- adiabaticity
- ideal detonation (Chapman Jouguet)
Approach taken

• commercially available ideal detonation computer program

• best fluid EoS

• with/ without water condensation

• range of AN initial densities

Conservative estimate
Solves water condensation issue
Finite rate phenomena not incorporated here
Ideal Detonation Model

In an idealized model of detonation, explosive performance is dependant on

- equilibrium thermodynamics of detonation products (fluid and solid phases)
- initial density of the explosives
- heat of formation of the explosive

![Simple ZND Model of Detonation](image)

- Detonation Products
- Reaction Zone
- Unreacted Explosive
- Shock Wave
- $P$
- $T$
- Simple ZND Model of Detonation
ZND Detonation and Rarefaction

\[ p \text{ or } r \]

\[ p \text{ or } r \]

Taylor wave

CJ spike

von Neumann spike

Sonic Plane

D

Reaction zone

x

q

l
Ideal Detonation Computer Programs

• EoS (fluid/solid) - inter/intra molecular contributions

• Chemical Equilibrium Algorithm

• Calculation Options

• Databases
  - ingredient explosives
  - product thermodynamics

• Windows/ GUI etc
Ideal Detonation Codes EoS

Fundamental – **WCA** or similar – CHEQ, IDeX, Cheetah, TDS

Based on statistical mechanics – hard sphere perturbation theory

Parameters from other sources
Well behaved higher derivatives
Good match ALL experimental data

More sophisticated calculation
Some remaining uncertainties
Livermore’s largest two-stage gas gun is 20 meters long. Its projectile flies down the barrel at speeds up to 8 kilometers per second to produce a shock wave millions of times the pressure of air at the surface of Earth. Technicians Leon Raper (left) and Keith Stickle are setting up the gas gun for an experiment.
Water Hugoniot: shock pressure

Pressure, GPa

Reduced Volume, $V/V_{cj}$

Pressure, GPa

Temperature, K

Water Hugoniot: shock temperature

Exptl
WCA EoS
JCZ3 EoS
BKW EoS

Exptl
WCA EoS
JCZ3 EoS
BKW EoS
<table>
<thead>
<tr>
<th>Detonation parameters</th>
<th>CJ</th>
<th>CJ</th>
<th>CJ</th>
<th>CJ</th>
<th>CJ</th>
<th>CJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detonation mode</td>
<td>CJ</td>
<td>CJ</td>
<td>CJ</td>
<td>CJ</td>
<td>CJ</td>
<td>CJ</td>
</tr>
<tr>
<td>Detonation velocity, km/s</td>
<td>8.33395</td>
<td>8.17468</td>
<td>8.06125</td>
<td>7.96207</td>
<td>7.71477</td>
<td>7.56861</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>4421.53</td>
<td>4455.03</td>
<td>4476.71</td>
<td>4511.35</td>
<td>4537.05</td>
<td>4555.65</td>
</tr>
<tr>
<td>Density, kg/cub.m</td>
<td>2309.58</td>
<td>2268.66</td>
<td>2237.85</td>
<td>2186.5</td>
<td>2133.5</td>
<td>2080.03</td>
</tr>
<tr>
<td>Mol.weight, kg/kmole</td>
<td>29.2136</td>
<td>29.2455</td>
<td>29.2702</td>
<td>29.3136</td>
<td>29.3696</td>
<td>29.4121</td>
</tr>
<tr>
<td>Ra/Ra0</td>
<td>1.3049</td>
<td>1.31136</td>
<td>1.31635</td>
<td>1.32845</td>
<td>1.33344</td>
<td>1.34196</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component mole fractions in system, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous phase</td>
</tr>
<tr>
<td>C1s/diamond</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component mole fractions of phase &quot;Gaseous phase&quot; in phase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
</tr>
<tr>
<td>H2O</td>
</tr>
<tr>
<td>NH3</td>
</tr>
<tr>
<td>H2</td>
</tr>
<tr>
<td>NO</td>
</tr>
<tr>
<td>CH4</td>
</tr>
</tbody>
</table>

**Calculation statistics**

- Iterations done: 19
- Precision reached: 8.33e-07
- Precision reached (iv): 1.64e-07
Adiabatic Gamma plots

Reduced Volume, $V/V_{cj}$

Adiabatic Gamma

WCA EoS
JCZ3 EoS
JWL EoS
BKW EoS

Adiabatic Gamma plots
The consensus of opinion on ammonium nitrate hazards is that, in the event of a large fire at an fertiliser store, a pool of liquid ammonium nitrate will be formed at the side of the stack that is nearest to the fire. If this pool is struck by a high speed missile (e.g. something falling or part of a drum that has exploded) then a local explosion will occur sending a shock wave into the main fertiliser stack that has not melted. If this stack contains just less than 300 tonnes it will not support a detonation but will deflagrate and, in doing so, will release an amount of energy equivalent to 41 tonnes of TNT. This figure is calculated on the basis of a TNT equivalence of AN of 55% and an efficiency of 25%. The $6.5 \times 10^3$ Pa (1 psi) overpressure hazard range from such an explosion is 500m.

### Table 4: TNT Equivalence for some explosive substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>TNT Equivalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chlorate</td>
<td>0.04</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>0.14</td>
</tr>
<tr>
<td>High strength hydrogen peroxide</td>
<td></td>
</tr>
<tr>
<td>Dibenzoyl peroxide</td>
<td>0.09</td>
</tr>
<tr>
<td>t-butyl-peroxyacetate</td>
<td>0.17</td>
</tr>
<tr>
<td>t-butyl-peroxypropionate</td>
<td>0.14</td>
</tr>
<tr>
<td>t-butyl-peroxy maleate</td>
<td>0.14</td>
</tr>
<tr>
<td>Methyl-ethyl-ketone 50%</td>
<td>0.26</td>
</tr>
<tr>
<td>Peroxyacetic acid (40%)</td>
<td>0.05</td>
</tr>
<tr>
<td>Tertiary butyl peroxidebenzoate</td>
<td>0.4</td>
</tr>
<tr>
<td>Dibenzoyl-peroxy benzoate</td>
<td>0.25</td>
</tr>
<tr>
<td>Di-tet-butyl peroxide</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The TNT equivalent used in the calculation is 0.7, and the ammonium nitrate is assumed to be compressed to a specific gravity of 1.72 (1.72 grams/cm³).

\[
\text{AN TNT Equivalency} = \frac{\text{Thermodynamic TNT equivalence}}{\text{Efficiency Factor}}
\]

Table 1: TNT equivalence and AN

<table>
<thead>
<tr>
<th>TNT equivalent (tons)</th>
<th>Efficiency coefficient</th>
<th>Tons of off spec AN involved as reactant</th>
<th>Estimated mass stored</th>
<th>Proportion of mass of AN involved in the reaction / storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 - 40</td>
<td>0.3 (AN in accordance to NFU 42.001) to 1 (AN mixed with 6% fuel)</td>
<td>20 - 120</td>
<td>390 - 450</td>
<td>5 to 31%</td>
</tr>
<tr>
<td>Explosive</td>
<td>TNT</td>
<td>AN H₂O gas only</td>
<td>AN</td>
<td>AN H₂O gas only</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>----------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Density kg/m³</td>
<td>1640</td>
<td>800</td>
<td>800</td>
<td>760</td>
</tr>
<tr>
<td>CJ Internal Energy MJ/kg</td>
<td>1.7579</td>
<td>-4.15</td>
<td>-4.15</td>
<td>-4.17</td>
</tr>
<tr>
<td>Internal Energy – 1 atm MJ/kg</td>
<td>-4.890</td>
<td>-6.31</td>
<td>-6.49</td>
<td>-6.30</td>
</tr>
<tr>
<td>Particle Velocity km/s</td>
<td>2.017</td>
<td>0.914</td>
<td>0.914</td>
<td>0.892</td>
</tr>
<tr>
<td>Energy Release MJ/kg</td>
<td>4.6139</td>
<td>1.742</td>
<td>1.9223</td>
<td>1.732</td>
</tr>
<tr>
<td>TNT Equivalence</td>
<td>38</td>
<td><strong>42</strong></td>
<td>38</td>
<td>41</td>
</tr>
</tbody>
</table>
AN TNT Equivalence – Disparity in Estimates

- some results are based on explosion and not detonation state data
- assumptions regarding the composition of detonation products
- different (less accurate) equations of state
- different ammonium nitrate densities
- inclusion of heat loss and/or kinetic energy
- combining efficiency and TNT equivalence in one datum
AN Bases of Safety

- AVOID – contamination, shock and sources of heat >170 deg C
- MITIGATE – compartmentalise hazards to avoid single event barriers between inventories, shock absorbers, deflectors
- PROCEDURAL – site security, surveillance
- ELIMINATE – inventories less than critical mass

TNT Equivalence/ separation distances – uncertainties ambiguities overly conservative not economic

More holistic safety approach desirable.
Pure ammonium nitrate

(i) it cannot form an explosible dust in air

(ii) it does not deflagrate until comparatively high pressures eg (\( \sim 0.1 \) GPa) are reached

(iii) it is thermally stable, even in an adiabatic environment until temperatures \( \gg \) ambient conditions eg \( \sim \) MPt

(iv) Detonation (pure solid AN) requires large shock stimulus and large diameter/ confinement

**Concern is contamination, accidental or deliberate.**
Don Quixote