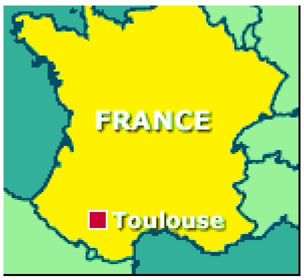
Storage or Mixing of Incompatible Chemicals

The U.S. Chemical Safety and Hazard Investigation Board estimates that about 36% of hazmat incidents in U.S. industry are caused by chemical incompatibility, due to improper storage and/or mixing of different chemicals. We don't have a percentage internationally, but we will look at an incident which occurred in France and see what the PEAC tool can tell us.

<u>Ammonium Nitrate Fertilizer Explosion in France</u>



On 21 September 2001, at 10:18 AM, a massive explosion occurred at the Azote de France (AZF) agricultural chemical factory near Toulouse, France. At least 31 people died and 650 people were hospitalized. The total number of people injured was said to be 2442, mostly from lacerations from flying glass and other fragments. The explosion occurred in a warehouse where between 200 and 300 tonnes of granular ammonium nitrate fertilizer was stored flat, separated by partitions. The force of the explosion resulted in a crater more than 10 meters deep and 50 meters in diameter. Windows were blown out in the center of Toulouse 3 km away, and window breakage occurred up to 5 km away. An electrical goods store 300 meters from the AZF plant collapsed. More than 500 homes became uninhabitable. Several thousand buildings were severely damaged. The Institute for Geophysics at Strasbourg registered the blast at 3.4 on the Richter scale.

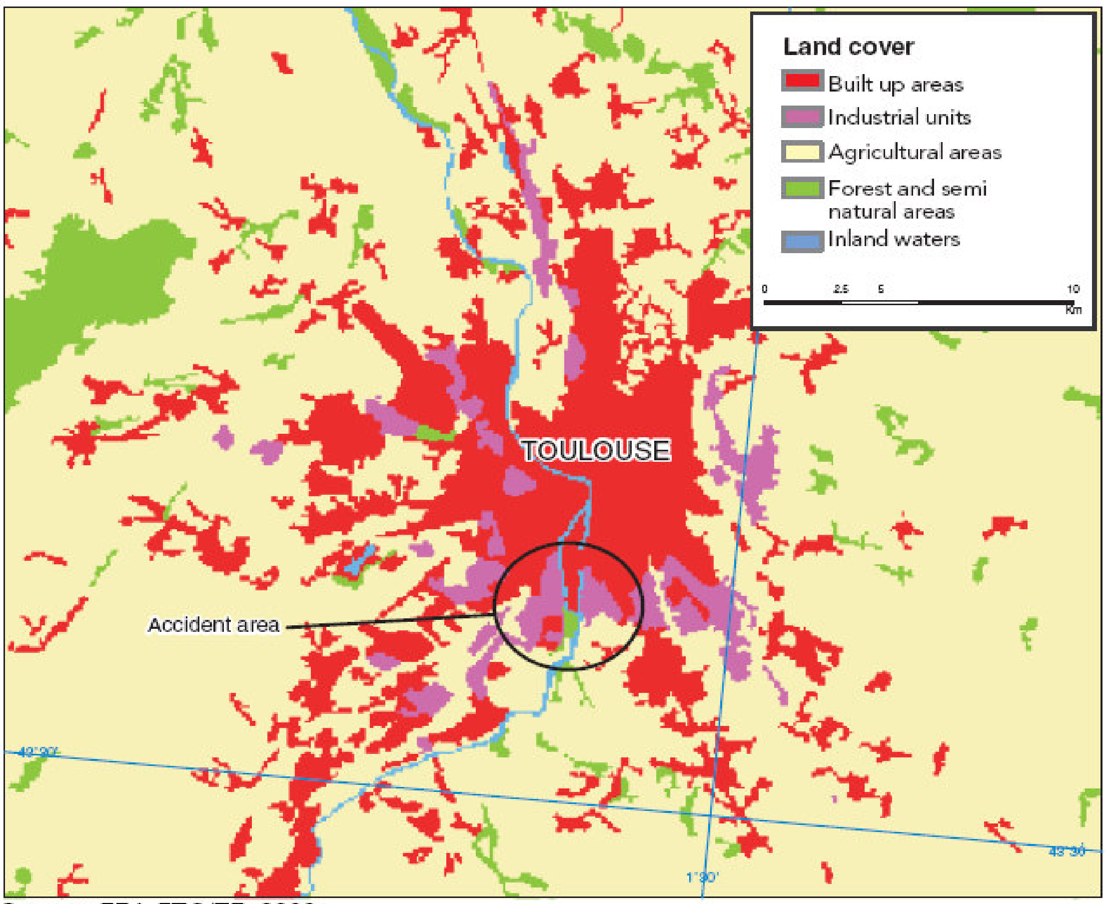
The AZF plant was originally opened in 1924 in what then was countryside, but urban sprawl allowed homes and businesses to be built right up to plant boundaries. The population of Toulouse is close to 600,000 today. The AZF facility was completely destroyed and not rebuilt.

Initially, the possibility of terrorism was suspected as the event occurred shortly after 9-11, and one of the plant workers killed by the explosion was known to the police for possible Islamic fundamentalist sympathies. Police found the worker's apartment completely stripped when they searched it several days later, and the worker before the explosion had interrupted a French peaceful gathering of respect (displaying the American flag) in honor of the 9-11 victims. There was a fair amount of confusion and inconsistent stories during the early stages of the investigation as to the role of possible terrorism and other causes. The cause of the explosion was eventually concluded to be accidental.

Employee interviews led investigators to conclude that the cause of the explosion was a chlorine-based pool maintenance chemical and off-spec ammonium nitrate fertilizer stored in the same hanger. The two chemicals mixed, and the reaction caused the explosion. Specifically, a mislabeled 500 kg bin of sodium dichloroisocyanate (the chlorine-based pool maintenance chemical) was mistakenly thought to be ammonium nitrate and placed in the same warehouse where the fertilizer was stored. Add to this summer heat and humid conditions. Exactly what happened next is not clear, but the most reasonable explanation is that the two chemicals reacted to form the highly unstable nitrogen trichloride. The nitrogen trichloride became the detonating agent for the ammonium nitrate.

Dry, uncontaminated ammonium nitrate is stable by itself and is safe to handle. A detonator is required.

Location of the Toulouse accident

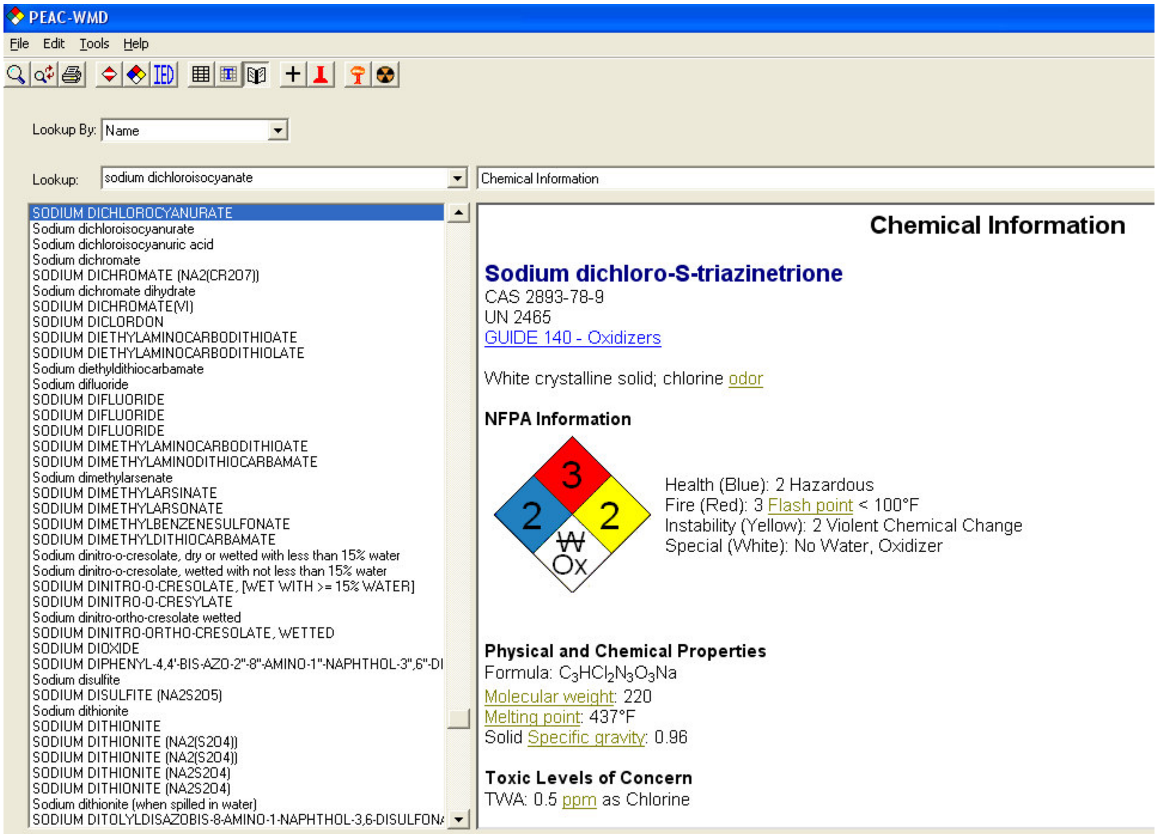


Source: EEA-ETC/TE. 2003.

Source of Figure: European Environmental Agency, Report No. 10, Copenhagen, 2003
Approximate blast location: 43.572°N latitude, 1.434° E longitude from Earth Tools

<u>What Can the PEAC Tool Tell Us?</u>

We can look up information about the individual chemicals, ammonium nitrate fertilizer and sodium dichloroisocyanate. When sodium dichloroisocyanate is pulled up, the PEAC tool routes the information to "sodium dichloro-S-triazinetrione". Sodium dichloro-S-triazinetrione and Sodium dichloroisocyanate are two different names for the same chemical. Many chemicals are known by different names but are the same thing. The PEAC tool attempts to list the different synonyms and spellings of this and other chemicals in the drop-down list.



We read that the chemical is subject to violent chemical change, and should not be stored with water. In fact, if the chemical is wetted or stored in a very moist environment it gives off heat and some chlorine gas. The heat is enough that it could ignite nearby combustibles.   However, the chemical by itself is not explosive.

Under ammonium nitrate, we read in the PEAC tool that heat or shock may cause the material to detonate.   Like sodium dichloroisocyanate, ammonium nitrate is also an oxidizer.   However, there are many different grades and variations of ammonium nitrate. This may be confusing to the PEAC tool user who wishes to select a particular ammonium nitrate entry from a drop down list. The different grades have different explosive characteristics. The screen for ammonium nitrate fertilizer (low carbon content) in the PEAC tool is shown below.   Ammonium nitrate fertilizer is stable by itself but under conditions of heat and shock it can detonate.

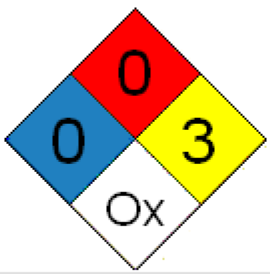
Chemical Information

Ammonium nitrate fertilizers (containing <=0.2% carbon)

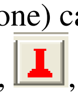
CAS 6484-52-2
UN 2067
GUIDE 140 - Oxidizers

Grayish white solid pills

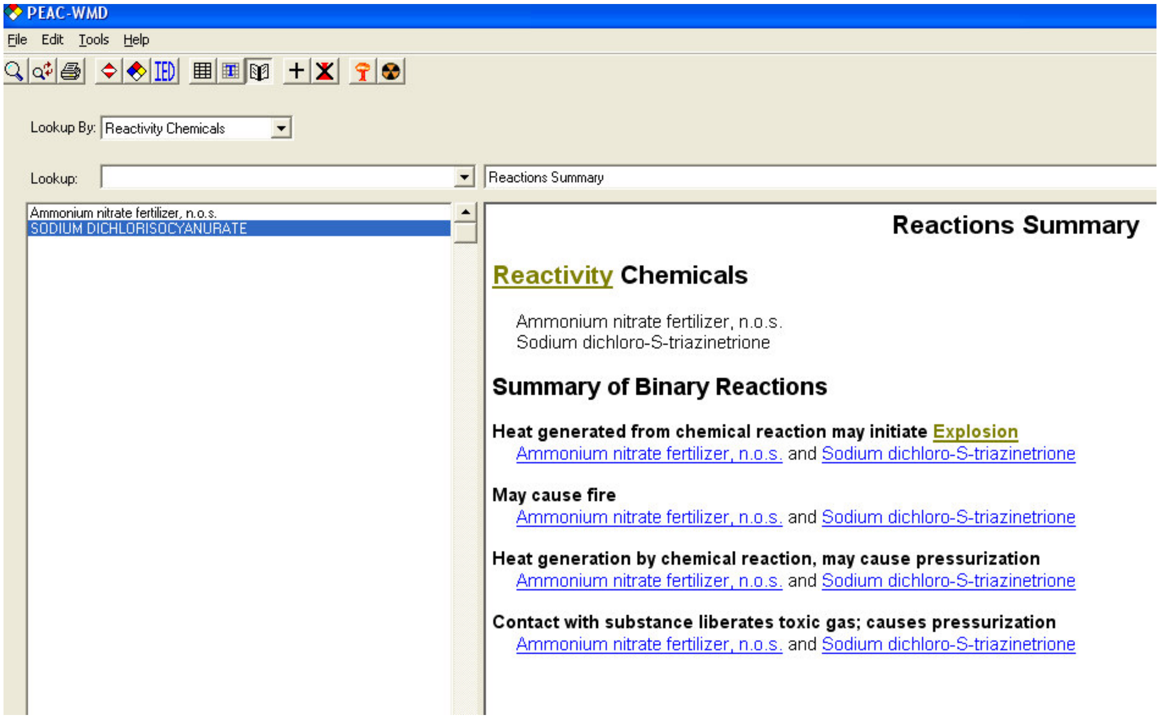
NFPA Information



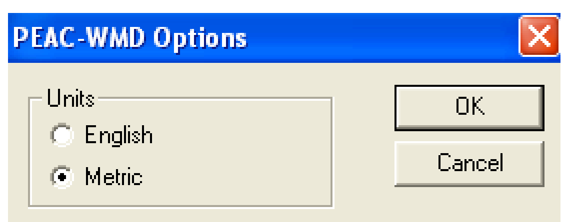
Health (Blue): 0 Normal Material
Fire (Red): 0 Will not burn
Instability (Yellow): 3 Shock/Heat may Detonate
Special (White): Oxidizer

Information about what happens if ammonium nitrate fertilizer is mixed with sodium dichloroisocyanate (= sodium dichloro-S-triazinetrione) can be obtained using the PEAC tool. The first step is to click on the reactivity icon, , which appears in the tool bar shown below.

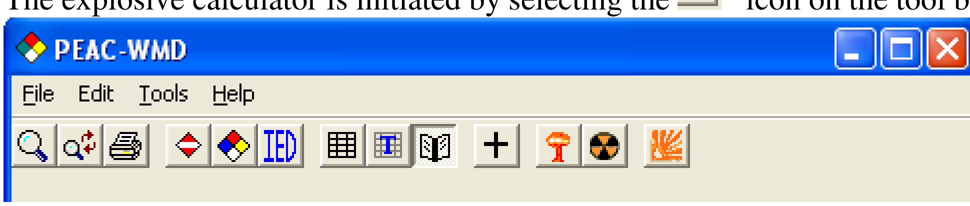
The next step is to make a list of chemicals that are to be mixed together, in this case, ammonium nitrate fertilizer and sodium dichloroisocyanate. The list appears on the left part of the screen. The user under “Lookup By” selects “Reactivity Chemicals”. A display, as shown below, appears. The heat generated by the chemical reaction may initiate an explosion, which is what happened.



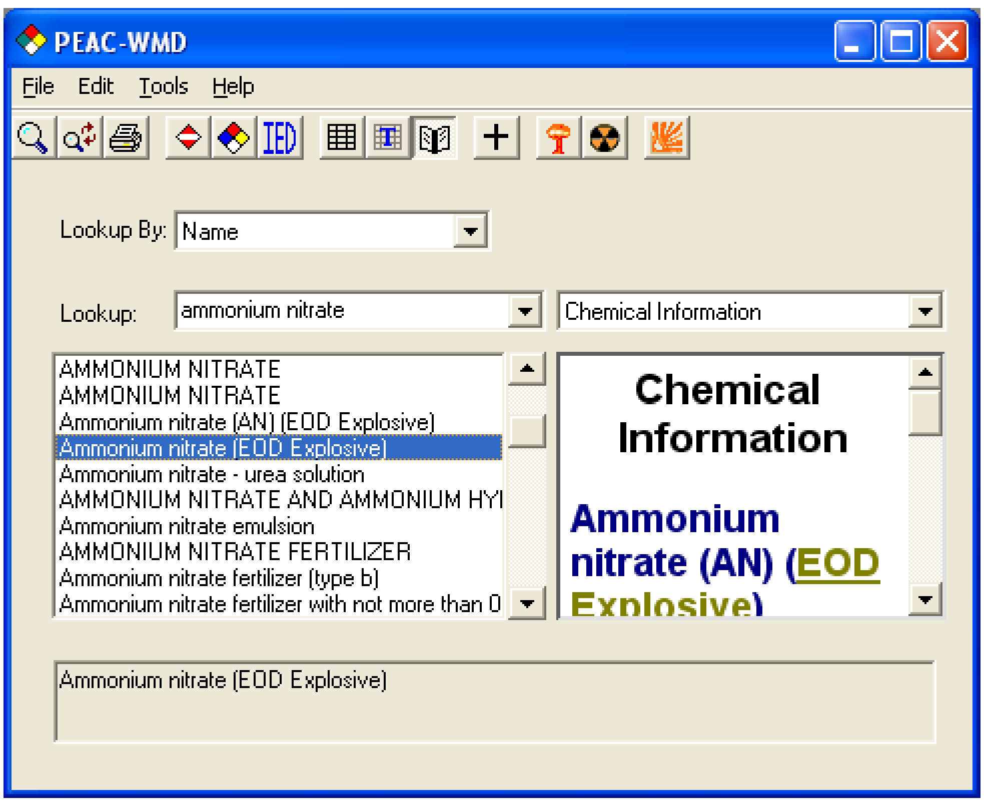
Could the chemicals stored at Azote de France (AZF) result in that much explosive damage? There was between 200 and 300 tonnes (metric tons) of ammonium nitrate (another report said 300 tonnes) and 500 kg of sodium dichloroisocyanate stored in the building. There was more ammonium nitrate elsewhere at the AZF factory, and there were probably secondary explosions. The sodium dichloroisocyanate was the source of the detonator. It was the ammonium nitrate that exploded. We will therefore look at the explosive potential of 200 to 300 tonnes of ammonium nitrate. One tonne equals 1000 kilograms. We will work in metric units. To use metric units, the PEAC user selects “Options” under the “edit” toolbar, and then selects “metric” when the PEAC-WMD Options screen appears



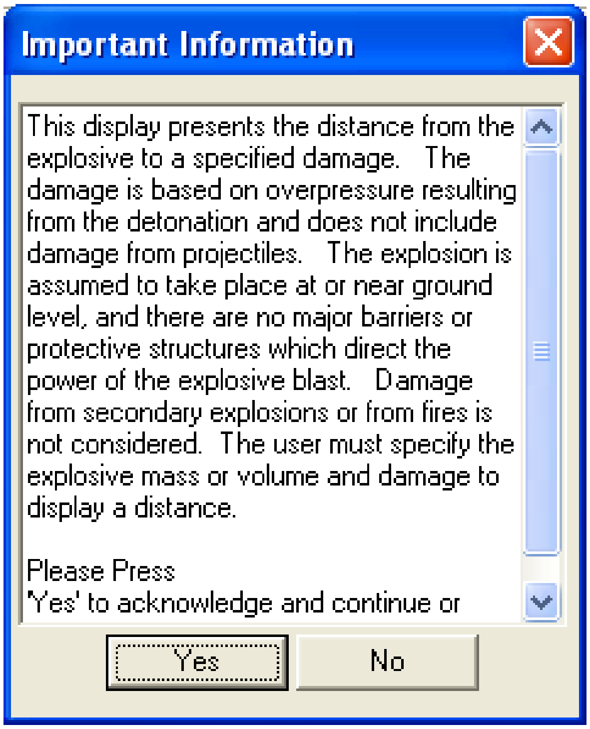
The explosive calculator is initiated by selecting the  icon on the tool bar

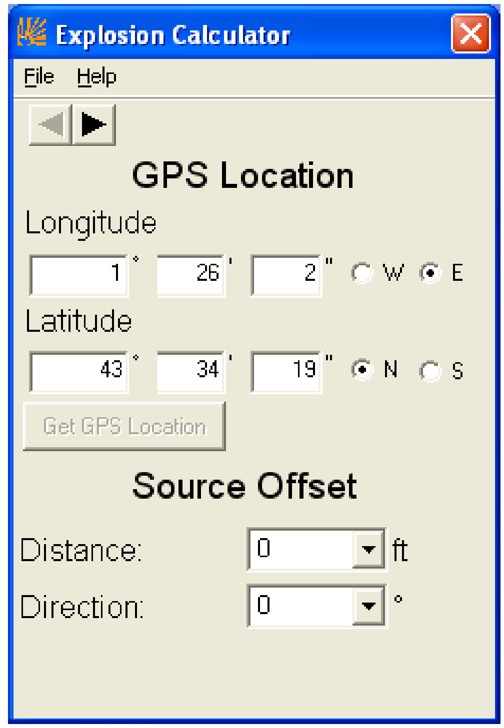


But there is a problem. The explosive calculator icon does not appear on the PEAC toolbar if ammonium nitrate fertilizer is selected. The reason is that the explosive power of ammonium nitrate (in terms of TNT equivalents) depends upon the form or type of ammonium nitrate, specifically, how much the material is compressed. All we know that it is off-spec ammonium nitrate fertilizer, it is in granular form, and was stored flat separated by partitions. This is not enough information to specify an explosive power of ammonium nitrate in terms of TNT equivalents. The PEAC tool lists many varieties of ammonium nitrate, most of which will not pull down the  icon because the description is too vague. What we will do instead is use the military (U.S. Navy) calculator for explosive ordinance disposal (EOD). We will select "Ammonium nitrate (EOD Explosive)" . This will link up to a military specification of ammonium nitrate which has a defined TNT equivalent. Ammonium nitrate fertilizer will probably have a lower TNT mass equivalent because the bulk material will likely be less dense.

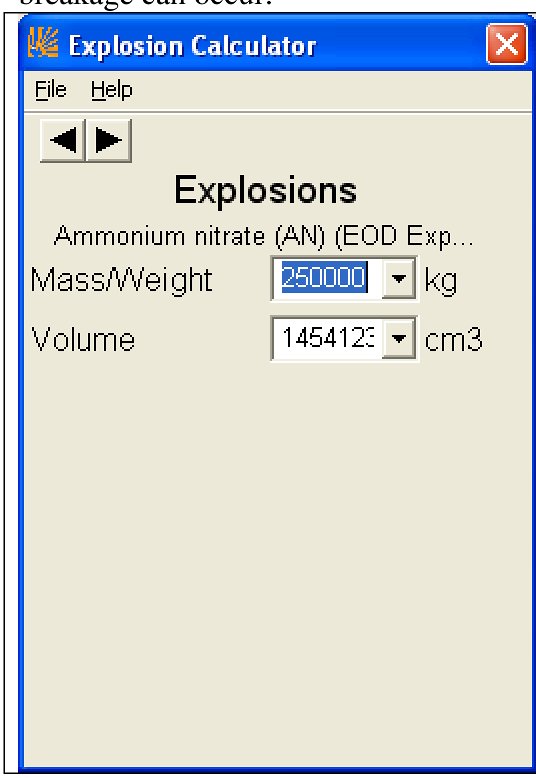


A qualification statement then appears (below, left). The PEAC tool then asks the user to specify a GPS Location. It is not necessary to specify a location to do an explosive blast calculation unless we wish to overlay the results on a map, but we will do it anyway. If 43.572 (see figure for Location of the Toulouse accident" is entered, the calculator automatically displays as degrees, minutes, and seconds. If the GPS measurements are not done remotely, there is no Source Offset.

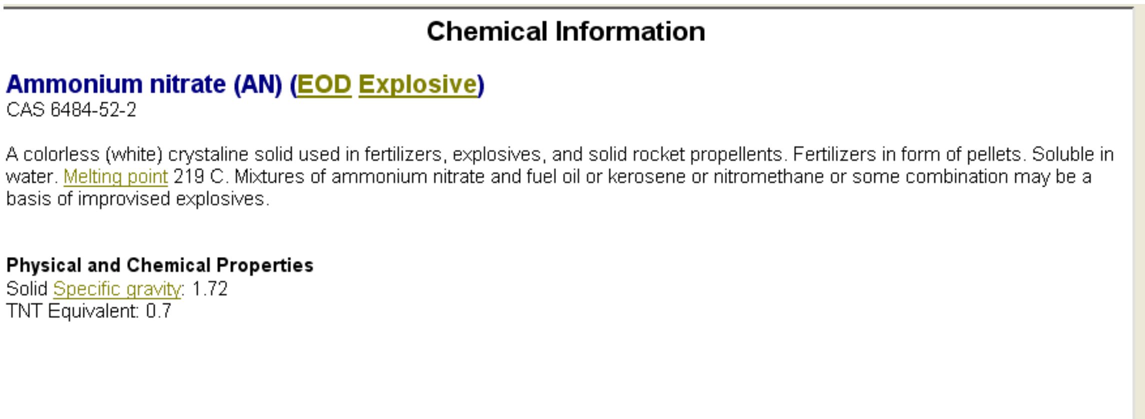




The weight (mass) of ammonium nitrate is entered. We will use 250 tonnes (= 250000 kg). An overpressure of 0.7 kPa is about the minimum pressure that window glass breakage can occur.



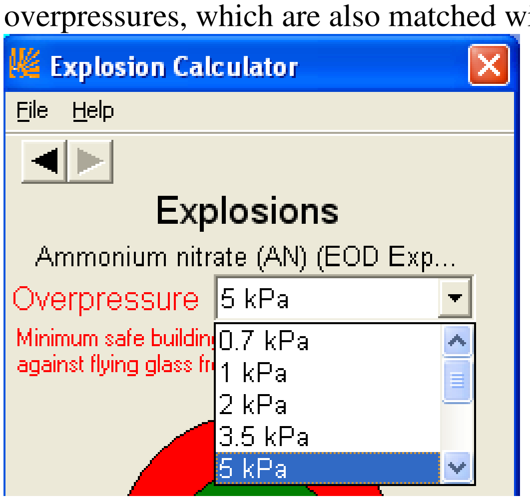
The distance corresponding to an overpressure of 0.7 kPa is 5415 meters. This is very roughly consistent with the observation that glass breakage was observed up to a distance of 5 km. The EOD military calculation may have over predicted the distance, but we don't know the characteristics of the off-spec ammonium nitrate fertilizer stored in the warehouse, and we are using a military calculator that has a set TNT mass equivalence. The TNT equivalence used in the calculation can be examined by pulling up the chemical information screen.



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/cm^3).

The U.S. military defines hazardous fragments as a fragment thrown from the blast center having an impact energy of 79 joules (58 ft-lb) or greater. The range is based on one hazardous fragment per 55.7 square meters (600 square feet). Hazardous fragments do not include glass injury from shattered windows which are broken due to blast effects at some distance from the blast center. The distance for hazardous fragments is 794 meters (almost 0.8 km).

The PEAC user can use the drop-down box to calculate distances corresponding to other overpressures, which are also matched with damage assessments.



A table can then be constructed.

Overpressure, kPa	**Damage**	**Distance (meters) for 250 tonnes ammonium nitrate**
0.7	Possible breakage of windows under stress; very loud noise	5415
1	Minimum safe evacuation distance, possible breakage of windows	4243
2	Some minor damage to frame house, typically 10% window breakage	2590
3.5	Significant window breakage, other minor damage to frame house	1707
5	Minimum safe building distance for protection against flying glass	1298
7	Partial demolition of houses; skin laceration from flying glass	992
20	Partial collapse of walls and roofs of houses; Eardrum rupture; significant human lethality from flying glass and missiles	455
70	Probable total building destruction; many deaths; lungs hemorrhage	213

The numbers roughly approximate what actually happened.