# Safe storage of Ammonium Nitrate (AN) based fertilizers

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**Summary**

The paper is intended for the use of manufacturers and suppliers. It sets out recommendations for the handling and storage of straight ammonium nitrate fertilizers and compound fertilizers containing ammonium nitrate hereinafter called Ammonium Nitrate based Fertilizers. The recommendations are based on the specific properties of the fertilizers. The paper provides advice on conditions in which ammonium nitrate based fertilizers can be handled and stored safely in both bulk and packaged form. It does not recommend one form of storage in preference to the other. The issuing fertilizer organisations believe that if users of this paper carefully follow these recommendations the potential hazards of these fertilizers during storage and handling are minimised.

Appropriate precautions should be taken to protect the product from moisture pick up, for example by air conditioning or covering with plastic. Wood or other readily combustible materials should not be used in the construction of new bays or bins. Where existing wood structures are used the exposed parts should be protected, for example by covering them permanently with tough resilient plastic sheeting. Silos must be provided with a venting device in order to prevent a vacuum being created during tapping operations. Silos should be constructed of plastic or steel such that moisture absorption and product contamination are avoided during storage.

# SAFE STORAGE OF AMMONIUM NITRATE (AN) BASED FERTILIZERS

## Introduction

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## HYGROSCOPICITY

If fertilizers are more or less hygroscopic which means that they start absorbing moisture at a specific humidity or at a certain water vapour pressure? Some very hygroscopic fertilizers attract moisture much more readily and at lower humidity than others. Water absorption takes place if the water vapour pressure of the air exceeds the water vapour pressure of the fertilizer.

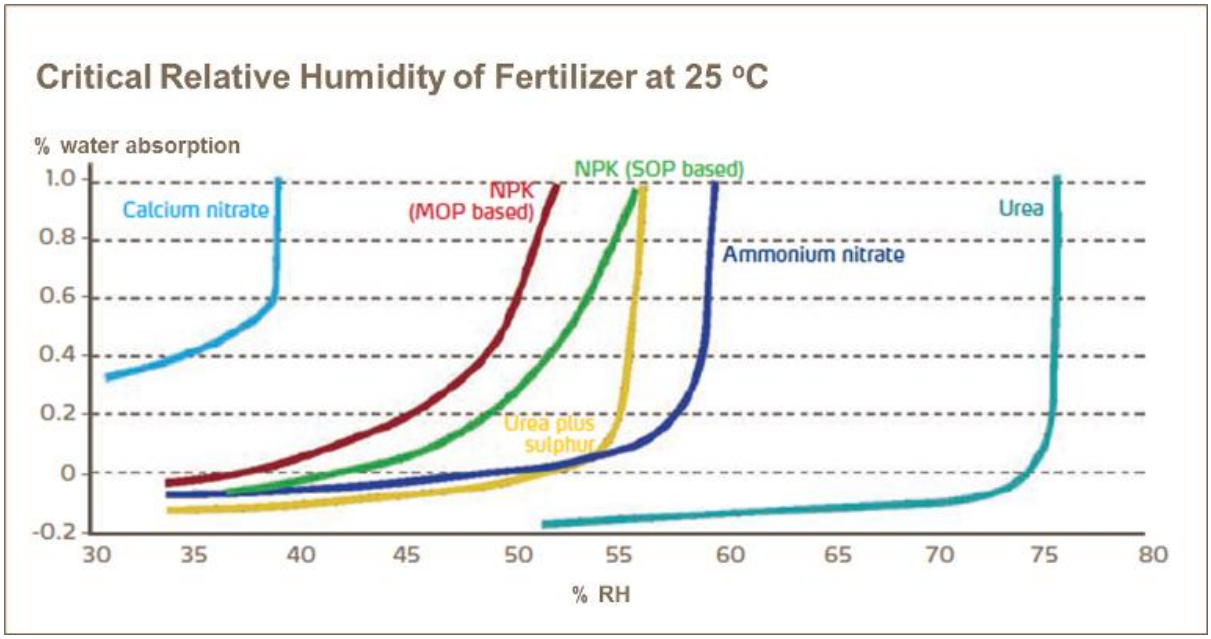
Air contains moisture as water vapour and therefore exerts a water vapour pressure (p H2O) that is determined by humidity and temperature. Hot air can contain more water than cold air. The water content is expressed by the relative humidity (RH).

Specifically, the moisture absorption is an important characteristic of fertilizers. Everything must be taken in dissolved form by plant roots. Fertilizers materials that cannot absorb moisture or that have limited atmospheric or soil moisture to absorb will not be taken in by plant roots and in fact cause damage just by being located in undissolved form near plant underground body parts.

All whey powders are more or less hygroscopic, and it is therefore important to determine free water content at the same time as the hygroscopicity.

| **Hygroscopicity** | |
|---|---|
| Non hygroscopic: | ;<10% |
| Slightly hygroscopic: | 10.1-15% |
| Hygroscopic: | 15.1-20% |
| Very hygroscopic: | 20.1-25% |
| Extremely hygroscopic: | >25% |

When the air is saturated with water vapour the relative humidity is 100 % and 50 % RH if half saturated. Water vapour will move from both high to low water vapour pressure. At 30˚C the air can contain 30.4 g of water pr m3 (100 % RH). The water vapour pressure of the air varies with humidity and temperature of the air.

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Absorption of moisture during storage and handling will reduce the physical quality. By knowing the air temperature and humidity and the surface temperature of the fertilizer, it can be determined if water absorption will take place or not.

Typically, a water absorption curve ascends slowly at low humidity (as illustrated), but at a certain humidity or humidity range it starts to increase steeply. This humidity is called the critical humidity of the fertilizer. The critical humidity goes down when the temperature increases.

Significant water uptake has undesirable consequences for fertilizer products:

- Particles gradually become soft and sticky
- Particles increase in volume
- Particles start to crack
- Bleaching, change of colour
- Reduced particle strength
- Caking tendency increases
- Formation of dust and fines increases

- Warehouse floors become damp and slippery
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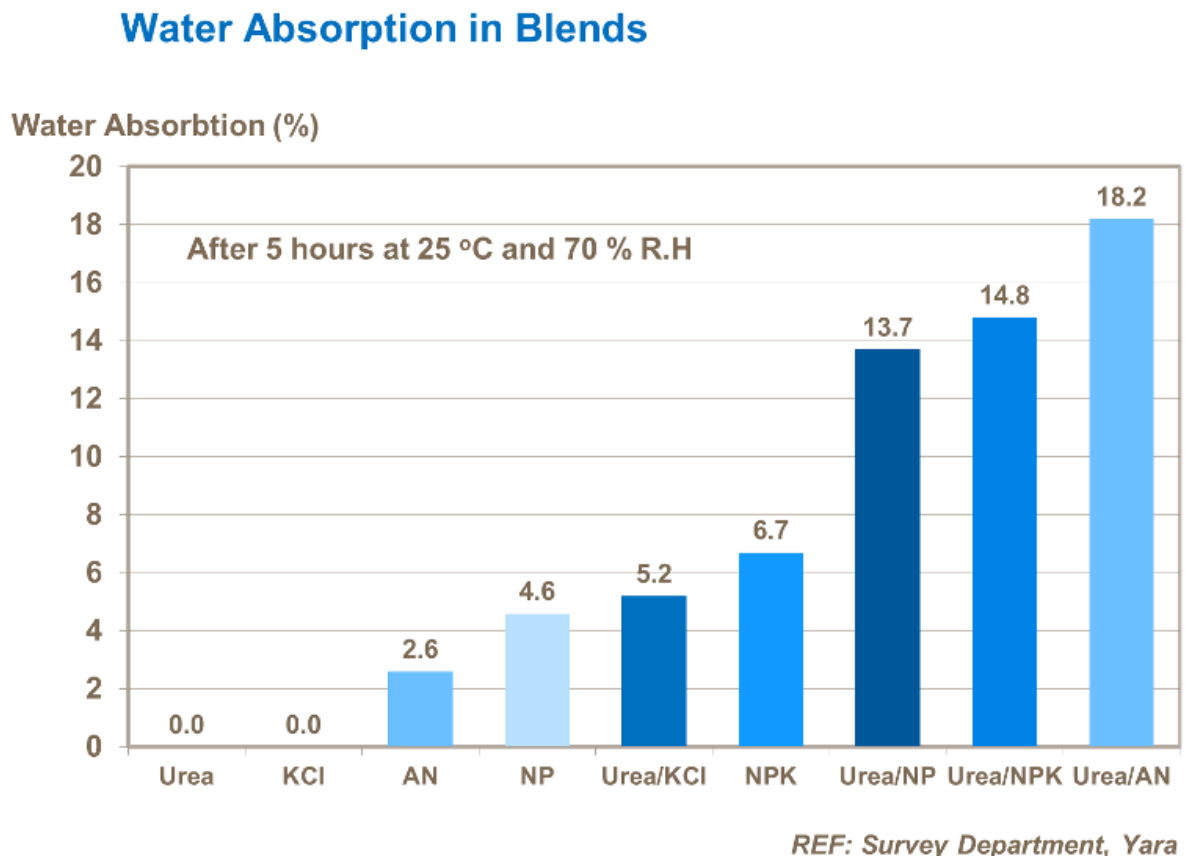
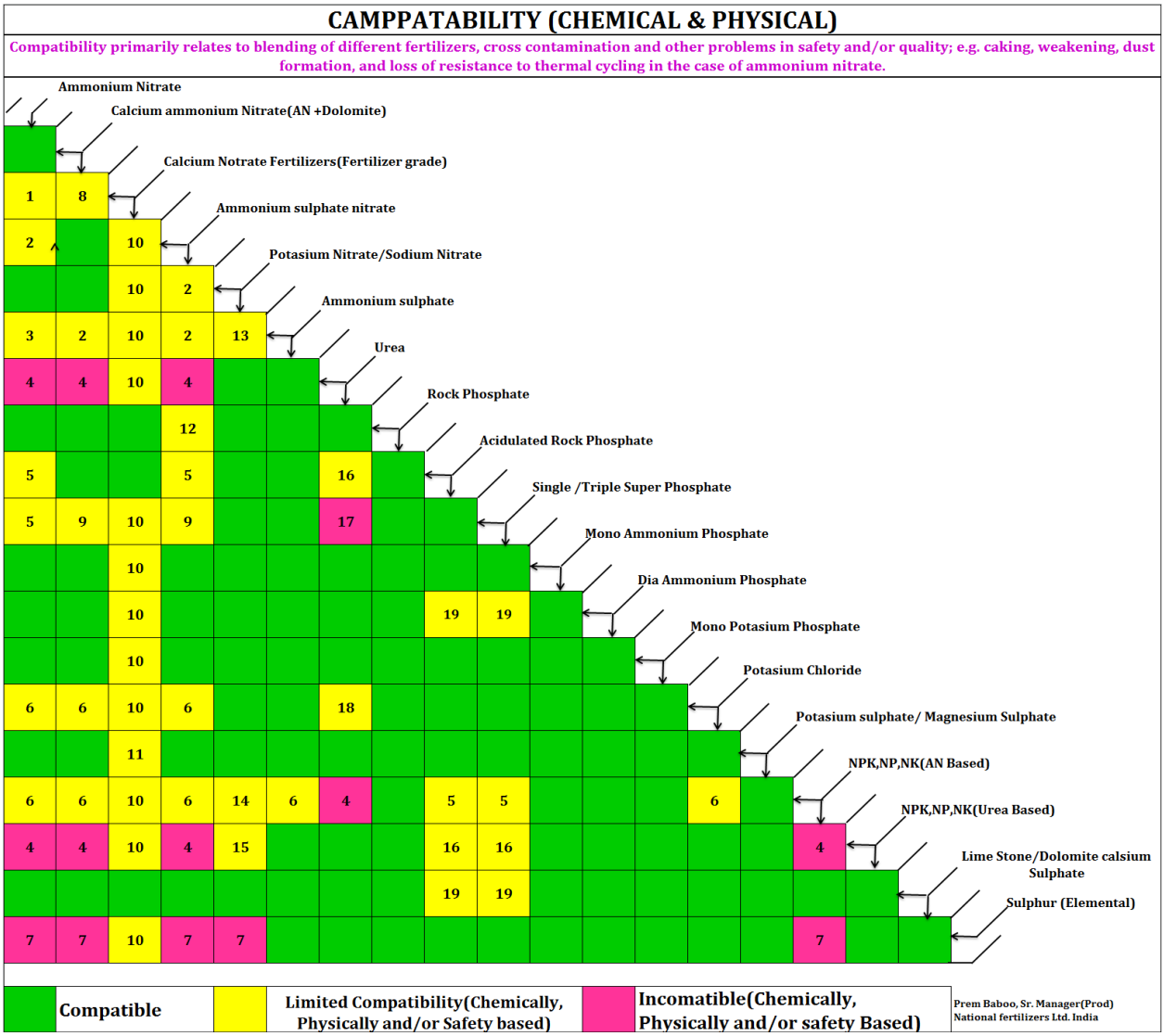



A blend of two components can be more hygroscopic than the components on their own, as seen in the graph.

**Compatibility (chemical and physical)**

Compatibility primarily relates to blending of different fertilizers, cross contamination and other problems in safety and/or quality; e.g. caking, weakening, dust formation, and loss of resistance to thermal cycling in the case of ammonium nitrate.




Guidance for the compatibility of fertilizer blending materials

1. Due to the hygroscopic behaviour of both products, the type of stabilisation of the ammonium nitrate grade could influence the storage properties.
2. Consider the safety implications regarding the deniability of the blend (AN/AS mixtures) and legislative implications.
3. Consider the safety implications regarding the deniability of the blend (AN/AS mixtures), the impact of free acid and organic impurities, if present, and legislative implications.
4. Mixture will quickly become wet and absorb moisture resulting in the formation of liquid or slurry. There could also be safety implications.
5. If free acid is present it could cause a very slow decomposition of AN, affecting, for example, the packaging.
6. Consider the possibility of self-sustaining decomposition and the overall level of oil coating.
7. Sulphur is combustible and can react with nitrates e.g. AN, $KNO_3$ and $NaNO_3$.

8. Due to the hygroscopic behaviour of both products the type of stabilisation of the ammonium nitrate based fertiliser could influence the storage properties.
9. Consider the moisture content of the SSP/TSP.
10. Consider the relative humidity during blending.
11. Risk of formation of gypsum.
12. No experience but this can be expected to be compatible. Confirm by test and/or analysis.
13. Consider impurities in AS and the drop in the critical relative humidity of the blend.
14. Consider the likely impact of additional nitrate.
15. Consider the possibility of ammonium phosphate/potassium nitrate reaction with urea and the relative humidity during blending, to avoid caking.
16. If free acid is present, there is a possibility of hydrolysis of urea giving ammonia and carbon dioxide.
17. Formation of very sticky urea phosphate.
18. Potential caking problem due to moisture.
19. If free acid is present, consider the risk of a reaction e.g. neutralisation with ammonia and acid attack with carbonates.

**The following are the factors contributing to fertilizer caking problem:**

1. **Hygroscopicity**

One of the primary causes of caking in fertilizers is their Hygroscopicity. It is well known that all commercial salts exhibit a higher level Hygroscopicity at critical humidity than pure salts due to minor impurities contained. One also has to consider the environmental relative humidity at various points of distribution, right up to the end-user storage. The hygroscopic nature of the fertilizer increases their tendency to bind together and cake on storage.

2. **Moisture Contents**

Fertilizer granules always carry a certain amount of moisture due to limitations in achieving complete drying of a fertilizer product. The varying humidity conditions during the storage of a fertilizer product and constant repeated phenomenon of migration of saturated solution to the neck of the adjacent fertilizer granule and its recrystallization resulting in the formation of strong bonding is continuously observed.

3. **Granular Size.**

The granular Size, Shape, Strength, Uniformity and Porosity of the fertilizer are other factors that determine the extent of severity in the caking of fertilizers. Large sized uniform granules exhibit low bond strength power unit mass on storage and hence caking observed in such condition is generally low. Small sized uniform spherical granules show medium bond strength per unit mass on storage. Caking tendency is more than that observed with large sized uniform spherical granules. Granules in wide

size rage exhibit severe caking tendency due to very much increased number of contact points. Bond strength per unit mass of the fertilizer is very high in this case. The problem is further compounded if increased porosity and low granular strength are also present. Increased percentage of fines in the fertilizer product increase the total surface area under contact leading to compaction of the fertilizers kept under storage.

4. **Pressure**

If the granules are packed in bags and stacked over one another, or alternatively large quantities of fertilizer (more than 10,000 metric tons) are stored in an open silo, the pressure on the bags/ fertilizer granules at the bottom layers of the pile force the granules in closer contact of a wide size rage. Due to this compaction can be quite severe and in extreme cases where the granule strengths are low, the granules can be crushed. The solubility of the fertilizer increased with the increase in pressure; copious quantities of solution may be formed under high local pressure at the points of contact. The solution will then tend to flow into voids where pressure is lower and recrystallize, forming hard cakes.

5. **Ambient temperature**

The major effects of variation in ambient temperature are nitrogen loss of the fertilizer at higher temperatures and humidity variations leading to caking and saturated solutions thus formed, losing Nitrogen even at lower temperatures.

6. **Storing Conditions**

The method of storage also plays an equally important role in the nature of caking. Occasionally, the storage yards and the silos are dehumidified. The humidity in the silo is maintained below the critical humidity of the fertilizer to ensure lesser degree of caking of fertilizers on long storage. Depending on the nature and porosity of the fertilizer HDPE, HDPE lines with Polythene, Polythene lines jute bags or jute bags are selected for bagging the fertilizer. If the bag is more permeable to moisture attack from outside, more is the tendency of fertilizers to cake. Finally the length of storage also determines the extent of caking. Greater the period of storage, more intensive is the caking.

Manufacturers have the responsibility of ensuring that all personnel under their control, Engaged in handling and storage of ammonium nitrate based fertilizers have adequate Knowledge of the potential hazards, means of prevention of the hazards and action to be Taken in the event of an emergency. Manufacturers should take steps to ensure that this Information is passed down the distribution chain to the final user so that all engaged in handling fertilizers are aware of the safe practices to be followed. Fertilizers are normally manufactured as high quality materials in the form of prills or granules. It is in the interest of all concerned with the handling and storage of fertilizers to ensure that the quality is maintained right up to the point of usage: namely no moisture pick up or

**caking, free from contamination and of minimal dust content. The general principles for the preservation of quality are:**

1. Prevention of moisture pick up and caking. This may require covering

   Bulk material with plastic sheets during storage or transportation and the essential principles which govern the preservation of quality and safe storage of ammonium nitrate based fertilizers are:

2. Avoidance of moisture uptake.
3. Prevention of contamination with foreign matter, whatever its composition, but particularly combustible matter, farm chemicals such as weed killers, organic materials, oils and greases, acids and Observance of good housekeeping principles.
4. Avoidance of involvement of fertilizers in a fire.
5. Storage away from sources of heat.
6. Observance of fire precautions.
7. Avoidance of serious confinement.
8. Storage away from explosives.

**PROPERTIES AND POTENTIAL HAZARDS OF AMMONIUM NITRATE BASED**

**FERTILIZERS**

**General**

All ammonium nitrate based fertilizers are, under normal conditions stable materials which in themselves present no risk. Most fertilizer grades of ammonium nitrate are manufactured in such a way that the resistance of the product to detonation is high. They are not combustible. However, they can decompose under fire conditions and may enhance the severity of the fire and give off toxic fumes and gases. With fertilizers containing a high concentration of ammonium nitrate, melting may also occur. Under extreme fire conditions, particularly if the fertilizer is contaminated with combustible material and confined in an enclosed space, there is the possibility of an explosion. The risk is minimised if the recommendations in this Handbook are followed. Ammonia gas can be liberated from ammonium nitrate based fertilizers (as from all ammonium salts) when they come into contact with alkaline materials such as lime. Ammonia is a toxic gas: it is colourless but its presence can be detected because of its characteristic strong smell. Mixtures of ammonium nitrate dust and air do not present an explosion hazard

**Properties of Type A Fertilizers**

Types A1, A2 and A3 Fertilizers

Fertilizers containing ammonium nitrate are generally manufactured in a prilled or granular form which enhances their quality and safety. In some formulations inclusion of materials such as dolomite or calcium carbonate suppresses acidity. In many cases additives are incorporated to prevent the disintegration of the product that could otherwise occur when the temperature is cycled through 32°C. This disintegration is caused by the significant increase in volume of the particles associated with the crystal structure change that occurs at about 32°C in products without such additives, These manufacturing procedures result in a limitation in the ammonium nitrate content. giving a practical maximum of 34,5% nitrogen in the product. (Pure ammonium nitrate contains 35% nitrogen.) Highly concentrated ammonium nitrate fertilizers are specifically made in the form of high density prills or granules of low porosity and high purity to minimise any detonation risk. These materials are very resistant to detonation. These concentrated ammonium nitrate fertilizers are oxidising agents and in fire conditions can assist the combustion of other materials. They may melt at temperatures somewhat lower than the melting point of pure ammonium nitrate (1690 C). When heated sufficiently, for example in fire conditions, they can decompose giving off gases containing toxic oxides of nitrogen. In unfavourable storage and handling conditions these fertilizers may absorb water from the atmosphere. In addition, when stored in direct sunlight, or in conditions such as in transport where fluctuations between high and low temperatures can occur the surface layers of the product may swell and disintegrate particularly if water has been absorbed, The effect is usually restricted to the surface layers of the product whether the material is in bags or in bulk, This results in material of unacceptable quality. In some cases with packaged material it can also result in damage to the bags.

**Properties of Type B Fertilizers**

**General**

In these fertilizers the ammonium nitrate content is lower than in Type A4 (That is, they contain less than 70% ammonium nitrate), Type B covers only those fertilizers in which thermal decomposition continues even when the external initiating heat source is removed. This distinguishes them from fertilizers covered under Type C. They may also suffer product disintegration when cycled through a temperature of 32°0 C. An understanding of the particular properties of Type B fertilizers, namely thermal decomposition, self-sustaining decomposition and self-heating is essential when considering safe storage and handling practices and these properties are discussed in more detail Potential Hazards of Type A and Type B Fertilizers Potential Hazards of Type A and Type B Fertilizers

**General**

These types of fertilizers are potentially more hazardous than Type C in nature. A brief description of their likely behaviour in hazardous conditions is given here to illustrate the reasons for fire Hazard Fertilizers are not combustible hence the risk of fire is

dependent on other combustible materials which may be present, such as parts of equipment. Fuels/fluids used in the handling equipment and combustible materials stored or used in the construction of the store or bays. Experience has shown that if fires occur in fertilizer stores they are usually initiated in combustible materials present outside the fertilizer stacks or heaps. The size and intensity of fire is significantly dependent on the nature and quantity of these combustible materials, when bagged material is involved in a fire the packaging material may melt and break, releasing the product. Polythene and similar packaging materials do not generally propagate burning through the stack. Hot or molten fertilizer can, however, oxidise the packaging material, but the amount of the packaging material is too small to make a significant effect on the fire. The hot spilled fertilizer may cause burning and continued smouldering of wooden pallets, if present, generally in the area of contact. In addition. Pallets can allow heat and flame to penetrate into the interior of the stack, In the case of bulk material there are no packaging materials and wooden pallets involved; hence fire cannot penetrate into the heap. Involvement of the fertilizer depends. As with bagged material, on the severity of the fire and on other materials present. Thermal and Self-Sustaining Decompositions Both Types A and B will decompose, if involved in fire; fumes containing toxic components will be evolved. Type B will undergo self-sustaining decomposition when exposed to an external heat source. Sources can be relatively minor such as buried

Inspection lamps or hot metal from welding operations. The properties of Type B fertilizers, namely thermal decomposition, self-sustaining decomposition and self-heating are as follows:

**Thermal and Self-Sustaining Decompositions.**

When these fertilizers are acidic (that is with a pH of a 10% solution/suspension of fertilizer in water lower than pH 4.2) and/or contain materials which have a catalytic effect, such as chlorides and/or copper, thermal Decomposition can take a different course to that of the straight ammonium nitrate fertilizers considered above. Decomposition can start when the fertilizers are in the solid state; toxic oxides of nitrogen together with hydrochloric acid vapour and chlorine gas can be evolved, Chloride contents as low as 0.5% (expressed as chlorine) in a mixture containing ammonium nitrate can be sufficient to have a significant effect on the decomposition. In many cases the decomposition, initiated by an external heat source, will stop when the heat source is removed (Type C). With some fertilizers (Type B) however, the decomposition will continue and spread deep into the mass of material even when the heat source is removed. This is the phenomenon of self-sustaining decomposition sometimes referred to as cigar burning where the decomposition propagates through the mass of the material. The characteristics of the self-sustaining decomposition phenomenon, (speed of propagation, temperature in the decomposition zone, amount of gas produced), depend on the composition of the fertilizer and on the extent of melting at the decomposition temperature. The presence of trace elements such as copper compounds and impurities such as chromium compounds exert an influence. The

volume of the gases, which include steam, nitrogen oxides and chlorides, can reach 400 times the volume of the mixture; the temperature in the decomposition zone is usually in the range 300- 500°C Self-heating during storage. The presence of combustible materials in ammonium nitrate fertilizers can, when the mixture is acidic, induce a spontaneous heating reaction, this results from the slow oxidation of the combustible materials. In the majority of cases this heating is of very modest proportions. In an extreme case. However, particularly if the initial temperature of the fertilizer is high, the heating can lead to the thermal decomposition of the fertilizer with the evolution of gases which contain toxic compounds. Reactions between components of the fertilizer during storage can also be a cause of self-heating. The extent of such heating is low, seldom exceeding 100 C, and normally presents no hazard,

**Ammonium Nitrate and explosives**

Aside from that, ammonium nitrate is also the main component of an explosive called ANFO which stands for Ammonium Nitrate Fuel Oil. It is an explosive mixture which is used widely in mining. ANFO is composed of 94 percent ammonium nitrate and 6 percent fuel oil. The ammonium nitrate will serve as the oxidizing agent for the fuel. Another interesting fact about this compound is that it is actually hygroscopic. A hygroscopic substance is something that can easily collect water molecules from the environment where it is placed. Because of this reason, ammonium nitrates should not be stored in humid areas since water can easily affect the compound's explosive function. Ammonium nitrates are now regulated by the government since it is already used to create fertilizer bombs. These are improvised explosive devices that other people use in terrorism. Ammonium nitrate can be very helpful in agriculture but correct storage and handling should always be observed.

Absorption of moisture during storage and handling will reduce the physical quality. By knowing the air temperature and humidity and the surface temperature of the fertilizer, it can be determined if water absorption will take place or not. Typically, a water absorption curve ascends slowly at low humidity (as illustrated), but at a certain humidity or humidity range it starts to increase steeply. This humidity is called the critical humidity of the fertilizer. The critical humidity goes down when the temperature increases.

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8. Warehouse floors become damp and slippery
9. Stabilised straight ammonium nitrate loses thermo stability
10. Quality of spreading can be affected
11. Clogging of equipment
12. Increased off-spec
13. Air humidity
14. Temperature and ambient pressure
15. Moisture content of product
16. Particle strength and shape
17. Chemical composition
18. Storage time

## Caking is affected by several factors:

19. Air humidity
20. Temperature and ambient pressure
21. Moisture content of product
22. Particle strength and shape
23. Chemical composition
24. Storage time

Caking tendency remains low if these parameters are controlled. In addition, application of an appropriate anti caking agent is often needed. There are small caking tendencies in calcium nitrate, but very important phenomenon in NPKs, AN and Urea. Coating of fertilizers reduces the products water absorption rate.

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It has now been found that the hygroscopicity of ammonium nitrate can be considerably reduced by incorporating onto the surface thereof a minor amount of ammonium carbonate. This surface treatment may be readily effected by any one or more of several techniques. One of the easiest Ways to coat ammonium nitrate is to simply mechanically intermix finely pulverized ammonium carbonate with the ammonium nitrate. For example, 0.5 gram of ammonium carbonate pulverized with a mortar and pestle was shaken in a glass bottle with 50 grams of ammonium nitrate prills (average prill diameter of about inch). When exposed for 22 hours to an atmosphere at 25 C. having a relative humid it of 62%, this coated ammonium nitrate absorbed only about 0.58 gram of water, whereas an identical ammonium nitrate sample without the ammonium carbonate coating absorbed about 0.98 gram under the same conditions.

Examples of such compounds are potassium nitrate, sodium nitrate, calcium oxide, magnesium oxide, calcium nitrate, magnesium lead nitrate, magnesium silicate, silica, Titania, Zinc oxide, zinc sulphate, ferrous sulphate, aluminium silicate, and the like. Many of these compounds will actually tend to increase the hygroscopicity over that of ammonium nitrate alone. Treatment of such ammonium nitrate-containing mixtures with ammonium carbonate according to the present invention will very effectively decrease the hygroscopicity of the mixtures. For example, an ammonium nitrate composition containing about 2 weight percent of magnesium nitrate gained about 1.5 percent in weight (by absorption of moisture) when exposed for about 10 hours to an atmosphere at 25 C. and 62 percent relative humidity, whereas an identical composition coated with 1 percent by weight of pulverized carbonate gained only about 0.5 weight percent under the same conditions. Consequently, a preferred embodiment of this invention constitutes ammonium nitrate compositions containing a minor proportion, preferably between about 0.5 and about 20 percent, and more preferably between about 1.0 and about 10 percent by weight, of an inorganic compound as noted above, and coated with ammonium carbonate. Most calcium ammonium nitrate is used as a chemical fertilizer. Fertilizer grade CAN contains roughly 8% calcium and 21-27% nitrogen. CAN is preferred for use on acid soils, as it acidifies soil less than many common nitrogen fertilizers. It is also used in place of ammonium nitrate where ammonium nitrate is banned. Calcium ammonium nitrate is used in some instant cold packs as an alternative to ammonium nitrate.

## Conclusion

Appropriate precautions should be taken to protect the product from moisture pick up, for example by air conditioning or covering with plastic. Wood or other readily combustible materials should not be used in the construction of new bays or bins. Where existing wood structures are used the exposed parts should be protected, for example by covering them permanently with tough resilient plastic sheeting. Silos must be provided with a venting device in order to prevent a vacuum being created during tapping operations. Silos should be constructed of plastic or steel such that moisture Absorption and product contamination are avoided during storage.

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