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**TO ALL MEMBERS OF THE TECHNICAL SUB-COMMITTEE AND COMMITTEE**

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**ARCHIVES**



# FERTILISER AMMONIUM NITRATE: USE MISUSE AND REGULATIONS<sup>1</sup>

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## I) INTRODUCTION

Fertiliser ammonium nitrate is a denomination covering a vast range of products in which the chemical "ammonium nitrate" is the predominant component. These products will be considered from two different viewpoints:

- agronomic, as a nutrient,
- chemical, as a combined oxidiser/reducer with oxidising properties, stress being laid on the chemical aspect related to safety.

## II) NUTRIENT

Ammonium nitrate is an "old" chemical and ever, since Justus van Liebig recognised the importance of nitrogen as one of the main plant nutrients, industry has striven to manufacture its agronomically useful components in increasing quantities. Did the market for ammonium nitrate based products develop in the wake of the industrial achievement or the other way round, this is the classical hen-and-egg debate. I will not elaborate further on the nutrient aspect, suffice it to say that half of the nitrogen present being under the nitrate form, is directly available to the plant, the other being very easily transformed. All that should be remembered is that fertiliser ammonium nitrate is one of the most important nutrient-bearing products produced and traded in the world.

As such, ammonium nitrate is what we call a "straight" product, sold either with a nitrogen level above 28% N, mostly as 33.5% N, or with a nitrogen content below 28% N, which version is better known as Calcium-Ammonium Nitrate or CAN. However, it may be also a major constituent of NP, NK, or NPK fertilisers, depending on agronomic/market requirements. Such "mixtures" may or may not present "chemical" problems due to constituents other than ammonium nitrate since they may introduce some undesirable properties of their own or due to impurities. It is therefore not surprising that, for different purposes related to safety, products have been classified in one way or another in various regulations.

## III ) REDUCER/OXIDISER

### A) Reactions

Ammonium nitrate can be considered as a compound made up of a reducing part, ammonium, and an oxidising part, nitrate. Even though the whole product is stable under normal conditions, nobody will dispute the fact that these two antagonistic parts will tend to react under particular favourable circumstances, the first of which would be a temperature increase above the melting point (ca. 170°C). Decomposition reactions have been largely investigated in the past and can be summarised as in table hereafter partly due to Berthelot. Later investigations have shown other possible reactions.

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<sup>1</sup> Presented at the IFA Technical Committee meeting in Prague, Czech Republic on 3 October 1995

TABLE

Number	Reaction	$\Delta H^a$ kcal/mol	Heat release <sup>b</sup> kcal/mol
1	$\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3$	+ 44.6	- 41.7
2	$\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$	- 8.8	13.2
3	$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}$	- 28.2	30.5
4	$2\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{NO} + 4\text{H}_2\text{O}$	- 6.6	9.0
5	$3\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{N}_2\text{O}_3 + 6\text{H}_2\text{O}$		20.8
6	$4\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 8\text{H}_2\text{O}$	- 22.2	29.9
7	$5\text{NH}_4\text{NO}_3 \rightarrow 4\text{N}_2 + 2\text{HNO}_3 + 9\text{H}_2\text{O}$	- 29.4	35.1

<sup>a</sup> Approximate values at constant pressure and 25°C calculated from heat formation data, all products gaseous

<sup>b</sup> Heat release at constant volume, 27°C, all products gaseous.

Reaction 1 is reversible and dissociation is endothermic. All the others are exothermic and irreversible. The principal reactions are 2 and 3. However, in any decomposition, it is believed that, depending on the conditions, all reactions may take place to various degrees with reaction 2 predominant at 250°C while reactions 3-6 occur above 300°C where reaction 3 is believed to be the dominating one. Reaction 1 nevertheless is quite significant above 250°C and since it occurs at the same time as reaction 2, a self limiting, steady-state temperature situation develops provided gases are allowed to escape freely. Should however reaction products be confined, increase in pressure would suppress reaction 1 leading to a runaway situation.

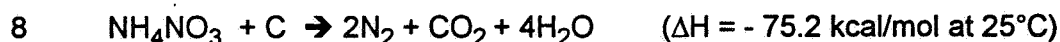
All the above is only valid for pure ammonium nitrate. It is also well known that certain substances have a catalytic effect on the decomposition of ammonium nitrate, the better known being acids, chlorides, chromates, copper and, to a more controversial extent, water. There are also other compounds that have been shown to influence decomposition i.e. bromides and iodides have the same effect as chlorides, while compounds of zinc, manganese, nickel and cobalt have also been shown to accelerate the decomposition rates.

Two special cases have to be mentioned separately:

a) Chloride as an impurity (< 0.5%) can have a very marked effect of increasing rates by 30 to 1000 times. However, the presence of acid seems essential and there is a variable induction period during which practically nothing happens once the usual decomposition temperature has been reached.

- chloride as a constituent of binary or ternary fertilisers, brought in generally by potassium chloride, is the necessary component of the reaction known as "cigar burn" where toxic gases such as chlorine, hydrogen chloride, and nitrogen oxides are given off in a steady state, self-sustained, heat-initiated set of complex reactions which are different from the ones mentioned above even though some may be also present.

b) Organic and carbonaceous materials, either as impurities or as on-purpose constituents of certain mixtures, enhance considerably the decomposition reactions in which the materials are oxidised, as shown by the following reaction:



From the above reactions and remarks it is clear ammonium nitrate is a redox system which is not completely equilibrated. Even though pure ammonium nitrate decomposition reactions do occur under specific conditions, these do not lead to explosive situations. More risky cases occur when certain compounds are present which catalytically accelerate the reactions or under confinement.

The result of these reactions is an oxidative mixture which can further react when supplementary reducing agents are present or intentionally added. This would be the case of organic compounds or mixtures of ammonium nitrate with fuel oil (ANFO), the latter being well known as blasting agents. So, whenever ammonium nitrate or an ammonium nitrate containing product is well mixed with a reducing agent, the risk of runaway decomposition increases, with the possible or sought-for result being an explosion.

## B) Runaway situations

Having shown that there is a possibility of runaway reactions occurring, different situations have to be considered; accidental or voluntary, the latter being split in two again with respect to good and bad use.

### 1) Accidental

#### a) causes:

It is not the purpose of this paper to go once again through all the details of all well documented accidents which have occurred in the past. Suffice it to say that whatever the accident of some consequence, the reasons have always been reduced to the simple conjunction of at least two of the following three specific conditions:

- confinement
- contamination
- temperature rise.

However, the most disastrous have always included the "contamination" element, well above 0.4% level, and this has prompted industry and regulators to spell out some tough rules regarding product definition and specifications. Storage and transport regulations were also laid down with the same objective: avoid the possibility of a product entering dangerous conditions.

#### b) remedies

##### α) Product definitions

Since the early nineteen twenties, product definitions have spawned in different sectors regarding ammonium nitrate production, transport or storage, so as to limit accidents by specifying what type of product could be made, sold, stored and transported. This has given rise to a maze of definitions and/or specifications, not always in accordance. As far as fertiliser ammonium nitrate is concerned, the most comprehensive product definition is in the EEC directive 80/876 of 15.07.1980 and modified since then, which benefits from all the past experience in the field. Briefly summed up, fertiliser ammonium nitrate is entitled to bear the "EEC Fertiliser" label with the denomination "Ammonium Nitrate" and can be put on the market as fertiliser provided:

- nitrogen content derived from ammonium nitrate is more than 28%,
- may contain inorganic additives such as ground natural calcium carbonate or dolomite, calcium sulphate, magnesium sulphate, kieserite,
- added inorganic or inert substances other than those mentioned above shall not increase temperature sensitivity or detonation susceptibility,
- it is put on the market packaged,
- porosity (oil retention) after two specified thermal cycles does not exceed 4% w/w,
- combustible material measured as Carbon does not exceed 0.2% for products having 31.5% N or 0.4% C for products having 28 to less than 31.5% N,
- a 10% water solution has a pH > 4.5,
- the granulometric fraction passing through 1 mm sieve does neither exceed 5% nor the fraction through 0.5 mm exceed 3%,

- the maximum chloride content, expressed as chlorine, is 0.02%,
- there is no deliberate addition of metal or metallic traces originating in the process with the upper limit set for copper at 10 ppm,
- satisfies the detonation test where a Member State has made it mandatory.

## β) Other

Regulations, mainly transport regulations, give also definitions, but none are as exhaustive as the one above. As can be seen from the appendix, the simplified product definitions are relevant only to the field considered and the soundest advice that can be given for any product to be transported, a consultation of a specialist is necessary even though some harmonisation has occurred. This is because several countries have introduced specific, usually more restrictive, rules.

Storage has also its regulations which vary from country to country. One example of a harmonisation attempt can be given in the case of storage in the EEC with the "Seveso" directive. This one sets limits on the amount of product that can be stored under different general requirements with the specific provision that the stored product conforms to the "fertiliser" directive, otherwise the amount of stored product is reduced. It is not possible to go into details of the different national requirements derived from this directive by Member States. Let me just say that, for instance in Germany, the requirements are such that the economics render the sale more than "difficult" when compared to France, Italy, Spain or the U.K.

Last but not least, the fertiliser producers have elaborated guides for safe handling and storage. These are freely available so it would be very difficult to understand how something could go wrong if no human failure is involved.

## 2) Voluntary

When a runaway situation is the desired effect, several conditions have to be fulfilled to obtain the "best" result:

- A reducing agent has to be added to "consume" the existing excess of oxidiser. This is usually accomplished by soaking or intimately mixing ammonium nitrate with an organic compound such as fuel oil. The amount to be added has to be carefully calculated since an excess or default will lead to non-stoichiometric reactions and efficiency will decrease.
- A simple temperature increase is not sufficient to achieve good decomposition front speeds, so the reaction should be initiated by a detonator (a blasting cap) and an explosive booster should be added if large fronts or insufficient confinement are considered.

### a) "GOOD" type voluntary use.

There is no point in going into detail of possible mixtures with fuel oil to make ANFO type or other explosives based on ammonium nitrate. The only point that should be stressed here is that ammonium nitrate is manufactured specifically for such use, the main characteristic being its high porosity which in most cases is well beyond 8%, thus differentiating this specific product from the "European Fertiliser" type which cannot exceed 4%. This latter requirement has been intentionally specified so that accidental contamination can not give rise to a homogeneous stoichiometric explosive mixture which is usually at the level of 6% of fuel oil.

### b) Voluntary MISUSE

From time to time there seems to be no limit to human ingenuity, mostly when trouble making is considered. As cases to point I would like to mention three wilful wrongdoings to illustrate this in the case of fertiliser misuse.

- The **Oklahoma City** explosion was a straightforward ANFO, seemingly with no "frills" attached. The only difficulty for the murderers, besides planting the finished bomb, must have been getting the detonating device but even then, with all the dynamite and other, "disappearing" world-wide from quarrying or mining operations, without the police being always able to track down the thieves and recover the loot, this should have not been so difficult.
- The **World Trade Centre** attack was something completely different since the bomb has been reported to have been made from urea and nitric acid. Skilful chemistry is necessary for such a preparation and this can not be done at the snap of ones' fingers. The operator should have knowledge better than just that coming from textbooks, if he doesn't want to be blown up by his own undertakings. However, once again, the starting materials are quite innocent by themselves and there is absolutely no problem in buying urea, only nitric acid having the correct concentration would be more difficult to get.
- People behind the explosions in the **London City** some years ago have used Calcium Ammonium Nitrate as the base of their explosives. As reducing agents they have added icing sugar and metallic powder. The result was as devastating as the above two, even if the toll of human lives was much lower due to explosion timing and place. They have proven that even a product loaded with more than 20% inert calcium carbonate may be easily transformed into an explosive. The "success" was mainly due to the fact that CAN has been finely ground and, after grinding, intimately mixed with the reducing agents. The reason for the choice of these ingredients is simple, they are very easy to buy, even in large quantities, without raising any suspicion.

From just these three recent examples, it is clear that a troublemaker will have no problem in obtaining the base ingredients to manufacture an explosive product. Even though much has been written and said about "inerting" or making "safer" the eventual starting products through regulations, this is illusory since a material such as CAN or even urea can be used.

More to the point; in the wake of the "Oklahoma" blast, testing has demonstrated that there are no known additives which could eliminate the reactive potential of ammonium nitrate fertiliser in a mixture designed to explode.

A trouble-maker's only real problem would be clearly to detonate the finished "mixture".

#### IV) CONCLUSION

For misuse of fertiliser, particularly fertiliser ammonium nitrate, several conditions have to be fulfilled and we have to think how such conditions can be controlled through regulations.

- **The will to destroy or kill:** this is on individual level and not controllable, only education may be of help.
- **The access to know-how:** only partly controllable since publications abound even though the manual for the perfect terrorist is not freely available. Excessive publicity in the news media could be avoided together with precise compositions of the product.
- **The access to base products:** for organics or other reducing agents, this would be wishful thinking, there are too many possible variations. The same holds for oxidisers.
- **Detonators, boosters and timing devices.** The step of transforming an explosive into a bomb is the incorporation of a detonator coupled to a timing device. Manufacture, sale, transport, possession and use of detonators is already regulated and controlled. The question is: how efficient are the existing rules and their implementation? On country basis, a review can be carried out to assess the existing rules and the degree of enforcement and consider changes where necessary.

European ammonium nitrate fertilisers are stable products. Regulatory measures with respect to product definitions have been enacted to ensure that such products stay so and, at the same time, that the risk of accidental runaway situations occurring is minimised.

To reinforce existing regulations with the view of:

- Limiting access to the product is totally useless (see WTC blast).
- Changing European product specification is equally useless (see London blasts).

The only sensible way to act is to control access to detonators and boosters. This has already been done but it is possible that existing rules or their enforcement are inadequate.

As a complement to the above, too much precise publicity in media could be avoided and, for the sake of safety with respect to accidents, cues by some countries could be taken from the existing European regulations.

FERTILISER AMMONIUM NITRATE AND OTHER NITRATES

21/8/95

UN	Product RID-ADR	Codes CEE	%											Comments	
			4	5	5.0	6	0	7	0	8	0	9	0		10
CI 1 n°0222	CI. 1		15	7.5	17.5	2	1	24	.5	28	31	.5	35	0%	%Ammonium Nitrate % Nitrogen
CI 1 n°0223	CI. 1														Fertiliser AN
CI.5.1 n°1942	CI.5.1														Technical AN (no charge)
CI.5.1 n°2067	CI.5.1/A1														AN + chem. inert mat.
CI.5.1 n°2068	CI.5.1/A2														AN + Ca or Mg carbonates
CI.5.1 n°2069	CI.5.1/A3														AN + ammoniulphate
CI.5.1 n°2070	CI.5.1/A4														NP NK NPK ferts NA based
CI.5.1 n°2072	CI.5.1														AN not specified elsewhere
CI.5.1 n°2426	CI.5.1														AN hot solutions <93%, pH, Cl
CI.9 n°2071	CI.9/B														NPK NA cont cigar burners
		80/876													AN Fert EEC dir 80/876/CEE

maximum



0.4% carbon



0.2% carbon