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**FERTILIZER AMMONIUM NITRATES:
PRESENT CONCERNS REGARDING REGULATIONS
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RESUME

A la suite de l'utilisation volontairement dommageable d'ammonitrate engrais dans des attentats à la bombe dans le passé, il a été suggéré par certains de prendre des mesures réglementaires supplémentaires concernant les ammonitrates comme moyen de réduction, à défaut d'élimination, d'un mal possible.

Une tentative est faite pour considérer quelques-unes des réglementations existantes à travers le prisme de l'expérience et des connaissances acquises en rappelant les propriétés importantes du nitrate d'ammonium et de leur influence sur le comportement du produit dans différentes conditions, suivie d'une discussion de la pertinence de l'actuelle réglementation européenne en vigueur concernant la sécurité du produit. On aborde aussi le sujet de l'action volontairement mal intentionnée face à la réglementation vu à la lumière d'un renforcement des mesures existantes et on tire des conclusions. En bref, ce ne sera d'aucun secours de réglementer davantage l'engrais, plutôt éduquer et mieux faire respecter les règles existantes sur les déclencheurs, les détonateurs et les explosifs.



1. INTRODUCTION

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. Whether the market for nitrogen based products developed in the wake of the industrial achievement or the other way round, is a classical hen-and-egg debate. The point to note however, was the Haber-Bosch synthesis of ammonia leading to cheaper nitrate derivatives such as ammonium nitrate.

Ammonium nitrate has several uses among which one can single out the fertilizer field where the product delivers nitrogen, directly or indirectly suitable for plant nutrition and the mining industry, where the combination of the oxidiser and reducer moieties is used to produce cheap and efficient explosives.

As with any coin there are two sides (at least) and, invariably, value and regulations. Ammonium nitrate is no exception. Take the plant nutrition aspect; the « dark » side of the coin could be over-use leading to nitrate excess prompting regulatory intervention to limit abuse. Take the inherent « oxidizer-reducer » instability and, when explosives are concerned, since human behavior tends sometimes to favour the bad side of things as in the case of the Oklahoma City or the London bombings, regulators spring to action ...

2. NUTRIENT

Fertilizer ammonium nitrate is a denomination covering a vast range of products in which the chemical « ammonium nitrate » is the predominant component. It is one of the most important nutrient-bearing products produced and traded in the world.

It is also 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, ammonium nitrate may be also a major constituent of NP, NK, or NPK fertilizers, 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.

However, one of the concerns today is the fact that the nitrate content of surface and ground water has been increasing in certain areas and, till to the end of the eighties, the blame has been put squarely on mineral fertilizers and their possible over-use. It has been quite a difficult and protracted task to prove that the nitrate increase was due mainly to organic nitrogen bearing products and manure recycling from intensive animal husbandry, of no avail. The European « nitrate » directive went into effect to limit the amount of nitrogen that can be spread per hectare, introduce the notion of sensitive areas and that of « Good

Agricultural Practice ». The idea of sensitive areas and good agricultural practice seems to have been suggested by agronomists and not by the regulators who appeared at the time quite determined to have a simple sweeping regulation based on one limit.

The point here is not whether the limit of 50 mg nitrate per liter of water chosen by the European Community, relying on provisional recommendations of the World Health Organisation was the right one, it is the fact that regulators tend to over-reach. Indeed, some countries have considered designating their entire agricultural acreage as sensitive area with respect to nitrate without any specific reason. Others have put in the same regulation other restrictions, one of them being a limit to the amount of phosphates that can be spread and which have nothing to do with the nitrate « problem ».

The phosphate « problem » is troubling. It is repeatedly said that phosphates contribute to eutrophication through field run-off. Nobody seems however to mind which kind of phosphates (water soluble or insoluble) since the analysis appears to be done on samples as taken, without filtration, for total P_2O_5 , after acidic digestion. I have always wondered how insoluble phosphates can contribute to eutrophication unless mobilized by some rather acidic natural process. This reminds one of the phosphate builder scare in laundry washing powders which led to the phase-out and replacement of polyphosphates. The Rhône Poulenc company battled heavily against that measure arguing that the silicate or zeolite remedy was worse than the illness. They lost. Today however, ten years later, water treatment companies are clearly showing that phosphates should be put back into washing powder boxes.

3. 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 following table taken from a publication by C. Keleti (Fertilizer science and technology series vol n°4, p. 185).

TABLE

Number	Reaction	ΔH^a kcal/mol	Heat release ^b kcal/mol
1	$NH_4NO_3 \Rightarrow NH_3 + HNO_3$	+ 44.6	- 41.7
2	$NH_4NO_3 \Leftrightarrow N_2O + 2H_2O$	- 8.8	+ 13.2
3	$2NH_4NO_3 \Leftrightarrow 2N_2 + O_2 + 4H_2O$	- 28.2	+ 30.5
4	$2NH_4NO_3 \Leftrightarrow N_2 + 2NO + 4H_2O$	- 6.6	+ 9.0
5	$3NH_4NO_3 \Leftrightarrow 2N_2 + N_2O_3 + 6H_2O$		+ 20.8
6	$4NH_4NO_3 \Leftrightarrow 3N_2 + 8H_2O$	- 22.2	+ 29.9
7	$5NH_4NO_3 \Leftrightarrow 4N_2 + 2HNO_3 + 9H_2O$	- 29.4	+ 35.1

^a Approximate values at constant pressure and 25°C calculated from heat formation data, all products gaseous

^b Heat release at constant volume, 27°C, all products gaseous.

The above table is based on work published by Berthelot between 1869 and 1877 whose original calculations for solid and molten ammonium nitrate and gaseous reaction products show approximately the same results as above:

Reaction	1	2	3	4	5	6	7
Solid AN kcal/mol	-41.3	+10.2	+30.7	+ 9.2	+29.5	+23.3	+33.4
Liquid AN kcal/mol approx.	-37.0	+14.0	+35.0	+13.0	+33.5	+27.0	+37.5

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.

Two other reactions should be considered:

- a. for decomposition reactions not exceeding 250°C, H.L. Saunders estimates that besides reactions 1 and 2 the following comes to play



- b. and in the case of reactions taking place near 300°C



with a heat release of 132.6 kcal equivalent to 16.57 kcal/mol of AN

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 increasing decomposition rates by 30 to 1000 times. However, presence of acid seems essential and there is variable induction period during which practically nothing happens once the usual decomposition temperature has been reached.
 - chloride as a constituent of binary or ternary fertilizers, 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 of them 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

a. 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 fertilizer 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, fertilizer ammonium nitrate is entitled to bear the « EEC Fertilizer » label with the denomination « Ammonium Nitrate » and can be put on the market as fertilizer 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.

b. Other

Regulations, mainly transport regulations, give also definitions, but none are as exhaustive as the one above. As can be seen, 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, is that a consultation of a specialist is necessary. 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 European Union 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 « fertilizer » 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 fertilizer 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 Fertilizer » type which cannot exceed 4%. This latter requirement has been intentionally specified for two main reasons:

- accidental contamination would not give rise to a homogeneous stoichiometric explosive mixture which is usually at the level of 6% of fuel oil,
- porosity tends to sensitize products just the same way as hollow glass spheres act for certain explosives.

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 fertilizer misuse.

- The **Oklahoma City** explosion was apparently a straightforward ANFO, seemingly with no « frills » attached even if the FBI has not officially acknowledged the composition. 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. There have also been reports that some ammonium nitrate had been added. A skilful chemist 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 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 fertilizer in a mixture designed to explode.

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

4. CONCLUSION

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

- **The will to destroy or kill:** this is on individual level and not controllable, only education may be of some 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, together with precise compositions of the product, could be avoided.
- **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 fertilizers 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.

Only deep involvement of the industry in the regulatory process, hard experimental work to obtain meaningful facts and some « forward » thinking can bring some common sense to regulatory processes. Industry has to strive hard to avoid being overwhelmed by unnecessary or useless regulatory burdens.