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AMMONIUM NITRATE: DEVELOPMENTS IN REGULATORY CONTROLS AND INDUSTRY RESPONSE *

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SUMMARY

This paper gives an historical perspective of the developments in applications of ammonium nitrate (AN) and various statutory and voluntary measures taken over the years. Various products based on AN, which serve the main industries viz., agriculture and explosives are briefly described. Impact of major accidents involving AN is discussed. Risk reduction measures taken by the regulatory authorities in the form of legislation and by the industry in form of various activities are covered. The main instruments of legislation affecting AN have been summarised. Activities undertaken by the fertilizer industry through its trade associations such as EFMA, IFA and TFI to minimise the risk of AN accidents have been described.

1 INTRODUCTION

Ammonium nitrate (AN) is well known to those working in the fertiliser and explosives industries, as it has been used over more than a hundred years with considerable success and benefit to mankind. Although a simple substance as regards the chemical formula, NH_4NO_3, it possesses complex physical and chemical properties, which make it very interesting. Over the years much work has been done to determine and understand these properties and its potential hazards. The findings have helped in the preparation of guidance and the development of various regulations. It is fair to say that no major conference on fertilisers would be complete without a paper concerning ammonium nitrate.

At the IFA conference in Chennai in 2002 I presented an ammonium nitrate paper (Ref 1) focussing on some of the significant accidents and what was learnt from them. In this paper I would like to describe the major developments in the regulatory regime and industry codes or guidance pertaining mainly to the fertiliser industry and with focus on

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the European scene, following certain major accidents and the generation of new technical knowledge over the last 3-4 decades.

2. INDUSTRIES BASED ON AMMONIUM NITRATE

The three main industries based on ammonium nitrate are fertiliser, explosives and production of other chemicals, for example, nitrous gas. Although ammonium nitrate has been known to chemists for more than three hundred years it was only around the 1900-1920 period that large-scale production at low cost became possible thanks to the commercial development of processes for ammonia synthesis based on atmospheric air and for nitric acid by air oxidation. In the fertiliser industry, products based on AN such as calcium ammonium nitrate (CAN, mixtures of AN and limestone) and ammonium sulphate(AS) and ammonium nitrate (ASN) were developed and became very popular. Compound fertilisers based on AN also started to appear. It was not until the 1960's that the production of high density thermally stabilised prilled AN started to a significant extent. Over the last forty years or so fertilisers based on AN have seen phenomenal growth in the US, Canada, Europe and former Soviet Union.

The main types of AN based fertilisers include:

-AN prills as a straight nitrogen fertiliser with typically ~34% N
-CAN, mixtures of AN and limestone with around 80% AN (28%N)
-ASN, mixtures of AN with ammonium sulphate
-Compound i.e. NPK fertilisers
-UAN solution, solution of AN and urea containing typically 30% N

In the explosives industry ammonium nitrate has always been regarded and used as an oxidising substance, as by itself it is too insensitive to detonation to be classified as an explosive. It was mixed with combustible substances and other materials, which make the products more sensitive and thus suitable as commercial explosives. The development of the prilling process for low density porous AN prills brought about a major change in the explosives industry's operations. Porous explosive grade AN prills could be safely transported to mines and quarries and there mixed with fuel oil (the mixture being called ANFO) just prior to the blasting operations. This has avoided the more hazardous practice of transportation and storage of actual explosives and possibly has saved many lives in addition to reducing the costs.

3. IMPACT OF MAJOR ACCIDENTS

The first major accident involving AN was the Oppau tragedy in 1921 (Ref 2), which occurred when explosive was used to break-up a badly caked heap of ASN fertiliser. This led to the strict guidance, which prohibited the use of explosives in AN fertiliser.

The second major tragedy was the accident at Texas City (1947), in which cargoes of wax-coated AN aboard two ships were involved in major explosions. This led to much investigation into the fire and explosion hazards associated with AN and the development

of guidance and regulations for sea transport. The upper limit of 0.2% for combustible matter (expressed as carbon) in the fertiliser AN came to be accepted as an international specification for AN to be classified as an oxidising substance as opposed to an explosive.

The 1960's brought substantial growth in the production of compound fertilisers based on AN by granulation and prilling processes. These fertilisers, particularly those capable of the self-sustaining decomposition (Ref 3), are more potentially hazardous in terms of release of toxic fumes than straight AN fertilisers. Consequently, incidents for fire and decomposition resulting in the release of toxic fumes deserved and received appropriate attention. Appropriate guidance for safe handling, storage and transportation was developed by the industry.

The tragic events of September 2001 viz., the terrorist attacks on the World Trade Centre in New York on the eleventh and the explosion at the AZF factory in Toulouse, France on the 21st have raised a number of concerns in the AN fertiliser industry. Whist AN was not a factor in the September 11 attack; the event has drawn attention to the wider problem of such activities and raised awareness towards possible abuse of various chemicals and other agents. The concerns facing the industry include, for example, the use of AN fertilisers (and other chemicals) for terrorists purposes, lack of clearly identified cause of the Toulouse explosion and the need for robust management systems for handling AN reject materials. (It is important to note the fact that the heap which exploded in Toulouse contained reject materials from operations relating to two different products: the fertilizer AN and the more sensitive porous ANFO grade AN prills.) Both the regulatory authorities and the industry have addressed these issues as described later in this paper.

4. CONTROL MEASURES

Fertiliser manufacturers as well the regulatory bodies (international, regional and national) have recognised the valuable contribution AN makes to agriculture and explosives industry. At the same time they recognise that AN presents potential hazards which need to be controlled in practical and effective ways.

The authorities have seen the need to put in place various regulations (see section 5 below). The fertiliser industry has been very aware that fertilisers, produced in quantities of million of tonnes per year, need safe production processes, storage and distribution chains. In order to achieve this it has, through its trade associations, produced many useful guidance notes and other helpful literature, some of which are described in section 6.

5. REGULATIONS

They relate to various aspects such as the products, production, storage and transportation.

5.1 Product

For fertilisers much of the legislation has focussed on the nutrient content, their permitted sources and quality related criteria. In the European Union, the first main piece of legislation came in as the Fertiliser Directive (76/116/EEC) in 1970's to remove barriers to trade within the Community on the more widely traded fertilizer products. Some member countries were concerned about the potential explosion hazard of AN and wanted to have safety-related criteria specified for the AN, which could be traded as a fertiliser. Directive EEC/80/876 (Ref 4) was adopted in 1980 which specified a number of physical and chemical criteria e.g. maximum content of combustible ingredients (0.2% by weight), maximum chlorine content (0.02% by weight), a measure of porosity by an oil retention test (4% by weight maximum), detonability as measured by a Resistance to Detonation test. The objective is to distinguish the fertiliser grade AN from more sensitive products of AN such as the porous prills and crystalline. Testing work was performed by the industry and authorities to check the correlation between the detonability and the porosity. The detonation test involves subjecting the sample, after 5 cycles of thermal cycling, in a 114 mm external diameter 1000 mm long steel tube to shock initiation with 500 g of a high explosive and the propagation of the detonation is assessed by the extent of compression in 6 lead cylinders.

Following a major review of all the EEC Directives related to fertilisers, a new EU Regulation, (Ref 5) has been adopted, which consolidates and replaces the previous fertiliser directives. Within this i.e. the new Regulation, the detonation test is now applied to compound fertilisers as well as straight AN when they contain more than 28%N (80% AN).

5.2 Production and storage

The main EU legislation is the 'Seveso II' Directive. In the amended 'Seveso' Directive of 1982 AN was covered by 2 entries: one for the AN based fertilisers with 28%N derived from AN and second for the remaining forms, such as porous and crystalline.

Following the Toulouse disaster, the EU Commission held a workshop on AN safety involving experts from the member states and the industry. Based on the discussion at the workshop and subsequent exchange of views the 'Seveso' Directive was revised to increase the scope of AN based fertilizers (Ref 6). The number of entries was increased from 2 to 4, the new entries covering the NPK fertilisers of the self-sustaining type and reject AN materials.

In the UK new regulations specific to AN (Ref 7) were enacted, which came into force on 1 May 2003. Their objective is to reduce the risk of explosion with straight nitrogen AN fertiliser by permitting only those products which have a high resistance to detonation. The products require testing regularly for the detonation resistance. It is the most far-reaching and demanding legislation specific to AN concerning production, sale, import, storage and supply. It applies to all AN based solid products with >80%AN, when the inventory exceeds 500 kg. It requires manufacturers in the EU to carry out the EU Detonation Resistance Test (DRT) for product from every batch of maximum 90 days production run. Material coming from outside the EU must be accompanied by a DRT certificate relating to that consignment and that must be provided to the UK authorities 5 days prior to the arrival into Great Britain. Those storing are required to keep certified copies of the original DRT certificate and pass on further certified copies when selling to other merchants. Farmers are exempt from these requirements. Those dealing in non-fertiliser AN materials e.g. porous grade for ANFO, are required to have exemption certificates issued by the Health & safety Executive on application.

5.3 Transportation

International transport regulations are formulated by the United Nations and the main recommendations are given in the 'Orange Book' (Ref 8), from which regional regulations for the different modes e.g. road, rail and sea, are produced. After a long period of little change relating to AN fertilisers in these regulations, there have been three notable changes in the last few years.

(i) There were several entries for AN fertilisers with the same shipping name and also some entries were no longer applicable to the modern day products. Based on proposals made jointly by USA, Canada and the European Fertilizer Manufacturers Association (EFMA) the UN Committee of Experts on the Transport of Dangerous Goods rationalised and simplified the existing entries.

The main changes were: -Deleted 0223, 2068-2070 and 2072.-Rationalized and combined 2067,2068, 2069 and 2070 into a new 2067.
-New Special Provisions: 306 and 307.
-Changed Shipping Name: Ammonium Nitrate Based FertilizerThe new entries covering the AN based products (not classified as explosives), which were published in the thirteenth edition of the Orange Book are as follows:

UN Number	Class	Shipping Name
1942	Oxidizing, 5.1	Ammonium Nitrate
2067	Oxidizing, 5.1	Ammonium Nitrate Based Fertilizer
2071	Miscellaneous, 9	Ammonium Nitrate Based Fertilizer

The details of the compositions have been transferred to a new special provision, number 307, which states:

This entry may only be used for uniform mixtures containing AN as the main ingredient within the following composition limits:

a) Not less than 90% AN with not more than 0.2% total combustible/organic material calculated as carbon and with added matter, if any, which is inorganic and inert towards AN; or

b) Less than 90% but more than 70% AN with other inorganic materials or more than 80% but less than 90% AN mixed with calcium carbonate and/or dolomite and not more than 0.4% total combustible/organic material calculated as carbon; or

c) Nitrogen type AN based fertilizers containing mixtures of AN and AS with more than 45% but less than 70% AN and not more than 0.4% total combustible/organic material calculated as carbon such that the sum of the percentage compositions of AN and AS exceeds 70%.

It is worth noting that for mixtures of AN and AS Special Provision 307 c) applies; it is not correct to use Special Provision 307 a) even when AN >70%.

(ii) In the aftermath of the 11 September events several countries have felt the need to improve security provisions in the transport regulations. Following intense discussions at the UN Committee of Experts on the Transport of the Dangerous Goods a new chapter concerning security has been included in the 13th edition of the Orange Book. For dangerous goods listed in the Orange Book new general requirements have been specified. In addition, for certain dangerous goods, listed as 'High consequence dangerous goods' further measures such as the provision of security plans have been specified. This list includes AN based fertilisers belonging to class 5.1, when transported in bulk. Clearly, these new requirements will have to be put in place by the industry and the national regulatory authorities in due course. EFMA is considering preparation of guidance for EU operators to assist them with compliance.

(iii) The Bulk Cargo Code (Ref 9) issued by the International Maritime Organisation (IMO) specifies a resistance to detonation test, D.5, for AN based fertilisers of Class 5.1, when carried in bulk. This test was not clearly defined. In year 2000 EFMA took initiative and made successful proposals to IMO for greater clarity and a fuller specification of the test. This is now virtually identical to the EU detonation test (see 5.1).

6. ACTIONS BY INDUSTRY

In Western Europe and USA the main trade associations representing fertiliser manufacturers are the European Fertilizer Manufacturers Association (Brussels) and The Fertiliser Institute (Washington, USA). Globally the industry is represented by the International Fertilizer Industry Association, IFA (Paris). Over the years they have produced and published a number of guidance booklets. EFMA has been particularly active in this regard and their publications include:

-Recommendations for Safe Storage and Handling of Wet Process Phosphoric Acid, IFA/EFMA, 1990

-Handbook for the Safe Storage of Ammonium Nitrate Based Fertilizers, 1992 by IFA/EFMA, shortly to be revised

-Selected Tests Concerning the safety Aspects of Fertilizers, 1992, IFA/EFMA

-Guidance for the Compilation of safety Data Sheets for Fertilizer Materials, 1996, EFMA

-Guidelines for Transporting Nitric Acid in tankers 1998, EFMA

-Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry: 8 booklets, EFMA 2000.

-Guidance for Safe Handling and Utilization of Non-Conforming Fertilizers and related Materials for Fertilizer Producers, 2003 EFMA

TFI and EFMA have jointly completed a programme of testing under the voluntary initiative of the International Council of Chemical Associations (ICCA). Twenty-three fertiliser substances have been surveyed and/or tested for risk assessment concerning their use. Further work is in progress to take it to the next stage of assessment.

These associations also compile performance data relating to safety with the purpose of achieving continuous improvement.

A major initiative on Product Stewardship was recently undertaken by EFMA, which commits its members to a number of safety, health and environment related improvement plans and actions. It requires them to implement a programme for achieving compliance with what is legally required as well as to EFMA core values and guidance documents. In addition the companies have to do a self-assessment based on a questionnaire that has been developed together with an independent third party. To assist the companies in implementing the programme checklists were developed for the areas of main concern i.e. transport, storage and contractor management.

These actions clearly demonstrate industry's high level of commitment and a very responsible attitude towards safety and environment.

7. OVERVIEW AND CONCLUDING REMARKS

Ammonium nitrate is very efficient fertiliser, supplying its nutrients in both viz. ammoniacal and nitrate forms. These are the only from in which a plant can take up nitrogen. AN is particularly suited to Europe and other parts of the world with temperate climate, where other fertilisers such as urea do not perform as well (Ref 10). With AN, high uptake by plants means very low loss of ammonia to the environment. Thus its contribution to the agriculture is considerable.

However, it is known to present certain potential hazards. In order to minimise these, the industry and regulatory authorities have taken a number of effective measures. In the last 50 years hundreds of millions of tonnes of AN fertiliser have been safely produced with a very low number of serious accidents. Unfortunately AN and other materials have been used also for illegal purposes with tragic consequences. Were AN to be removed from the market place, such activities would not stop as suitable alternatives will be sought and used in abusive manners. However, such activities and major damaging incidents, although rare, have prompted some to raise the question about the future of AN. In my opinion AN justifies its future in the market place, as it is too valuable and is not readily replaceable.

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