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THE HAZARDOUS PROPERTIES OF AMMONIUM NITRATE FERTILIZERS AND THE
REGULATIONS TO WHICH THEY ARE SUBJECTED

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SUMMARY

Two EEC Directives which will affect the handling and storage of concentrated ammonium nitrate fertilizers are examined relative to the known properties of ammonium nitrate.

The Ammonium Nitrate Directive (80/876) has little relevance to the conditions in which ammonium nitrate is stored. The Major Accident Hazards Directive (82/501/EEC) will make a significant contribution to safe storage. It does this in terms of insisting on demonstration of safe practice. Safe practice depends on adherence to Codes of Practice drawn up by manufacturers. Adherence to these codes is the main factor in safe storage and handling of ammonium nitrate fertilizers.

An oxidising capacity test under consideration by a United Nations Group may ask questions about the oxidising status of some fertilizers not currently classified in U.N. Division 5.1.

1. INTRODUCTION

That ammonium nitrate can be manufactured, stored and handled safely in very large tonnages is illustrated by the good record of the Fertilizer Industry, over the last two decades. Ammonium nitrate for fertilizer use is usually manufactured in the form of hard, dense prills or granules, in contrast to that for use as a component of blasting agents which is usually in the form of porous prills. Despite the accident at Taroom in Australia in August 1972, in which an explosion occurred in a lorry load of porous prills, history indicates that the porous prills can be handled safely, again in large tonnages.

Ammonium nitrate has been involved in several devastating incidents, four of which are summarised in Table 1. Although these occurred a relatively long time ago, they still colour the thinking of people, both within the Industry and in regulatory authorities, who are responsible for setting standards for the safe handling and storage of ammonium nitrate.

TABLE 1

Examples of Explosions Involving Ammonium Nitrate

Date	Place	Amount Involved (Approximate)	Comment
1921	Oppau, Germany	4,500 te *	Explosives used to break up caked heap. Over 600 fatalities.
1942	Tessenderloo, Belgium	150 - 200 te	Explosives used to break up caked heap. Over 100 fatalities.
1947	Texas City, U.S.A.	3,000 te	Explosions in two ships following fire. Over 500 fatalities.
1947	Brest, France	3,000 te	Explosion in a ship following fire. About 20 fatalities.

* Material was a double salt of 2 moles ammonium nitrate and 1 mole ammonium sulphate.

Because of these and other incidents ammonium nitrate is placed, without question, on any list of dangerous substances drawn up by authorities responsible for legislation or codes of practice. The Industry has altered the physical state of the product, making it more dense, and has taken a positive stance against the use of explosives to break up caked heaps. Also to avoid classification as an explosive the organic matter is lower than that in the material involved at Texas City and Brest. These things reduce the risk of, and power of, a potential explosion, but the basic chemical that exploded at Texas City is the one used in fertilizers today; the hazard potential remains. Nevertheless the risk of incidents with ammonium nitrate tends to be exaggerated in some areas as suggested in a paper "Ammonium Nitrate Fertilizer - Exploding the Myth" presented to an A I Chem E Meeting by L Greiner.⁽¹⁾

Knowledge of the conditions in which ammonium nitrate will decompose or detonate has increased since the incidents noted above. Pertinent questions to ask therefore are (1) whether the legislation to which ammonium nitrate is subjected is relevant to the known hazardous properties and (2) whether the self-imposed Industry codes complement or obviate the need for, some of the regulations? This paper attempts to discuss these questions. The regulations considered are mainly those currently in force or impending in the EEC, although due to their importance in transport matters the current UN Rapporteurs deliberations on oxidising capacity are included. Regulations within the EEC are considered by means of the appropriate Directive. These Directives are in general not regulations as such but directives to member countries to amend or approximate their own National Regulations in particular areas.

2. DIRECTIVES, REGULATIONS AND CODES CONSIDERED

Principal Directives considered are:-

(1) Directive 80/876/EEC on the Marketing of Straight Ammonium Nitrate Fertilizers of High Nitrogen Content.

This is often called the 'AN Directive'. It sets out criteria for straight ammonium nitrate as a fertilizer to distinguish such material from ammonium nitrate intended for non-fertilizer purposes.

(2) Directive 82/501/EEC on the Major Accident Hazards of Certain Industrial Activities.

This is often called the 'Seveso' Directive. Its objective is to ensure a system of control over industrial activities that present a significant risk of a "Major Accident", by a system of notification and survey of installations.

(3) Directive 67/548/EEC on the Classification, Packaging and Labelling of Dangerous Substances and the

Proposed Directive on the Classification, Packaging and Labelling of Dangerous Preparations.

These directives set out the criteria for classification of dangerous substances/preparations and specify the hazard warning information that shall be given on the packages.

(4) UN Recommendations on the Transport of Dangerous Goods (2).

These recommendations and the classification system contained therein are used as the basis of several international transport codes, for example the IMO IMDG Code (3) which deals with the transport of packaged goods by sea. Ammonium nitrate fertilizers, considered in this paper, are included in the UN Classification system in Class 5, Division 5.1 - Oxidising Substances. Currently the UN Group of Rapporteurs is considering the adoption of an "oxidising capacity test" as a criterion for new substances in Division 5.1. Such tests are also used in the Substances and Preparations Directives mentioned above.

3. HAZARDOUS PROPERTIES OF AMMONIUM NITRATE FERTILIZERS

The hazardous properties of ammonium nitrate and fertilizers based on it have been the subject of considerable investigative work. This is well documented, hence only an outline summary of major points is included here.

3.1 Detonation

The major hazard from ammonium nitrate arises from its ability to detonate. Conditions under which it can be made to detonate have been the subject of many studies, most recently by Bauer (4) and his group in Canada. Bauer concluded that ammonium nitrate was relatively insensitive and the large shock necessary to induce detonation in solid material is unlikely to be met in normal storage conditions. However Bauer and earlier workers (5,6) showed that the sensitivity was increased by a reduction of the density of the material, and by a reduction in particle size. The sensitivity is also increased by mixing the nitrate with combustible material. Hence the use of oil-treated porous material as a commercial blasting agent (ANFO). Bauer showed that molten ammonium nitrate, particularly when its density was lowered by the presence of gas bubbles (e.g. produced by thermal decomposition), was more sensitive than the solid.

3.2 Thermal Decomposition

Again there is extensive literature on this topic; a review of this was included in the reports prepared by Bauer and his group (7). Ammonium nitrate melts at about 169°C; it decomposes at a significant rate at 200°C and an easily measurable rate at 220-230°C. In these regions the exothermic decomposition to give nitrous oxide and water is in competition with the endothermic dissociation to ammonia and nitric acid vapour. At higher temperatures the course and rate of reaction changes; other nitrogen oxides and nitrogen become major products. Saunders (8), an early worker in the field, referred to these higher temperature reactions as "the explosive decomposition of ammonium nitrate".

The decomposition of ammonium nitrate is catalysed by acid, chloride and certain metal ions e.g. Cr, Co, Cu. The catalysis by chloride is of importance to the fertilizer industry as potassium chloride is the major potash carrier in compound fertilizers.

The hazard from the decomposition is the evolution of toxic fumes and in confined conditions the theoretical possibility that the rate of decomposition will increase and a transition to detonation will occur.

3.3 Oxidising Properties

Ammonium nitrate is not in itself combustible. However in a fire it will enhance the combustion of other materials. This can be demonstrated by igniting mixtures of ammonium nitrate and sawdust or wood shavings.

3.4 Crystal Phase Transitions

Ammonium nitrate undergoes three crystal phase transitions as its temperature is raised from ambient to its melting point. The temperatures at which these transitions occur and the volume changes involved ⁽⁹⁾ are illustrated in Table 2.

TABLE 2

Crystalline Phase Transitions in Ammonium Nitrate⁽⁹⁾

Phase	Transition Temperature (°C)	Heat Absorbed Cal/g	Volume Change (%)
IV	32.3	4.7	3.6 Expansion
III	84.2	4.0	1.3 Shrinkage
II	125.2	12.6	2.1 Expansion
I	169.6		
Molten			

These solid phase transitions are not in themselves "hazard" properties; however one of them, the Phase IV to Phase III transition, which occurs at about 32°C, features in the AN Directive (80/876/EEC). Continued temperature cycling of the particle through the IV to III transition causes the particle to swell, hence become less dense, and eventually degenerate into powdered form. It is this reduction in density that is considered important in Directive 80/876/EEC in terms of enhanced sensitivity to detonation ⁽¹⁰⁾. The mechanism of the transition is complex; for current purposes it will suffice to be aware that the temperature of the transition is dependent on the moisture content of the particle and the presence of other materials, for example, magnesium. In very dry ammonium nitrate Phase III does not appear and a transition directly IV to II occurs at about 55°C ⁽¹¹⁾. The temperature of 32°C can readily be exceeded in surface layers of granules in plastic sacks stored in direct sunlight.

4. HAZARD SCENARIO

The Fertilizer Industry adopts the pragmatic approach of carrying out production, handling and storage operations in such a way that the risk of initiation of the hazard properties is reduced to a negligible level. The record of the Industry illustrates the success of this approach. However accidents do occur and the types of event that could lead to an incident are illustrated in Fig 1. This is a generalised fault tree covering both manufacturing and storage operations; hence the term 'explosion' is used to cover both detonation and pressure burst resulting from thermal decomposition in closed pipelines/vessels. A fault tree of this sort would require to be developed extensively to be of use in risk assessment. It is however adequate for the present purpose. For example, for the storage of solid ammonium nitrate a detonation (explosion) can only occur if the ammonium nitrate is in a form in which detonation is possible and there is an initiating event. Minimising the likelihood of these events is the aim of the storage codes produced by the Industry and regulations introduced by National Authorities.

The work on detonation of ammonium nitrate prills already mentioned illustrates that the cold solid material is insensitive. Large boosters and/or severe confinement are necessary to induce detonation. The work of Bauer⁽⁴⁾ suggests that all ammonium nitrate can be brought to detonation providing there is sufficient present and the detonative shock used is big enough. Short of detonation of relatively large amounts of conventional explosives adjacent to the storage heaps, which comes into the realms of sabotage, the severe shock necessary is not a credible event in normal storage conditions. This applies to the dense prills used in fertilizer operations and the more porous prills normally used as a component of an ANFO explosive.

The increase in sensitivity of the ammonium nitrate with temperature (12) and the enhanced sensitivity of molten material⁽⁴⁾ means that involvement of ammonium nitrate in a fire is a possible scenario for the accidental detonation of stored ammonium nitrate. Bauer⁽¹³⁾ in his review of past incidents with ammonium nitrate concluded that involvement in fire was the event most likely to result in a major incident. Fire prevention is therefore the main concern of storage codes.

Whether sufficient quantity of solid ammonium nitrate could be heated to induce a vigorous decomposition (or deflagration) in a storage heap, or induce a significant risk from possible missile impact in the relatively unconfined situation of normal storage, is a matter of conjecture. An indication of one type of behaviour of ammonium nitrate in a major fire, in which considerable quantities of combustible material were involved, is given by the fire at Cory Brothers Warehouse, Ipswich in 1982 (14).

The store contained over 10,000 te of fertilizer of which some 3,600 te was high nitrogen content (above 28%N) material. Of the latter only about 1,400 te were damaged by the fire or water used to combat it, illustrating that even in a major fire the majority of the ammonium nitrate in the warehouse did not become involved.

The detonation of a pool of molten ammonium nitrate, by the impact of falling masonry or roof beams is a possible scenario; this was given weight by the work of Bauer et al⁽⁴⁾ who demonstrated the sensitivity of molten ammonium nitrate. To produce a major accident from this scenario would require the detonation induced by the missile to propagate through the melt and initiate the residual solid.

The possibility that deflagration, once induced in decomposing ammonium nitrate, could transfer into a detonation has been investigated by van Dolah⁽¹²⁾. He was able to demonstrate such a transition only if the ammonium nitrate was fuelled. The possibility that a deflagration could be induced in a solid heap by the detonation of a molten pool cannot be ruled out.

5. REGULATIONS, DIRECTIVES AND STORAGE CODES

It is of interest to attempt to relate the hazardous properties and hazard scenarios outlined above to various regulations and codes applicable to ammonium nitrate fertilizers. As already commented storage codes drawn up by the Industry, either by international organisations such as IFA/APEA or individual companies, attempt to minimise risk by preventing the onset of the decomposition reactions or hazardous situations. The EEC Ammonium Nitrate Directive on the other hand attempts to distinguish between 'fertilizer ammonium nitrate' and, by implication, more hazardous ammonium nitrate by regulating physical and chemical parameters of the material itself.

5.1 The United Nations Classification

The ammonium nitrate contents and permitted combustible matter content of fertilizers in U.N. Class 5, Division 5.1, are illustrated in Figure 2. The Division is labelled "Oxidising Substances" which are defined as "Substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material". In the IMDG code the possibility of an explosion with 5.1 fertilizers in the event of a major fire aboard ship is mentioned.

Not all the fertilizers illustrated in Figure 2. are covered by the legislation considered. The AN Directive (80/876/EEC) covers only straight ammonium nitrate fertilizers containing 80% or more ammonium nitrate. Although the original Seveso Directive (82/502/EEC) refers only to "ammonium nitrate", a proposed amending Directive (85/C305/07) defines ammonium nitrate fertilizers more precisely. However, as it uses the specification of straight ammonium nitrate fertilizers given in the AN Directive, it limits its scope to those fertilizers containing more than 80% ammonium nitrate. It does, however, cover some fertilizers defined by UN No. 2070 (compound fertilizers) in addition to those in UN 2067 (part) and 2068 straight ammonium nitrates, covered by the AN Directive. Fertilizers defined by UN 2069, the ammonium sulphate nitrate type, are not covered by these Directives. This is not a serious omission at present as there are no fertilizers defined by UN 2069 on the market in the EEC. The Substances Directive and the proposed Preparations Directive do not specifically mention Division 5.1 fertilizers. The UK legislation implementing the Substances Directive, however, uses the precise definitions in UN Division 5.1.

5.2 The Oxidising Capacity Test

Ammonium nitrate fertilizers classed as 'oxidising substances' in the UN system are those defined under the appropriate entries in Division 5.1. These definitions were based on experience and knowledge of the properties of the substances. Currently the relevant UN Group of Rapporteurs is attempting to specify an oxidising capacity test as a criterion for Division 5.1. It is understood that no extensive reclassification of substances is intended or envisaged and that the test is intended for new substances. It will not be easy to maintain this position indefinitely. Once adopted the test will, eventually, be applied to materials currently transported.

Two broad versions of the oxidising capacity test are relevant. In one the solid mixture of oxidising substance and fuel is formed into a train of triangular cross section and the horizontal burning rate measured over a specified distance. In the other the mixture is formed into a cone; the time taken for the whole cone to be consumed is measured. The tests have relevance to potential practical conditions and attempt to measure the property "contribute to the combustion of other material" specified in the definition of the class.

A substantial amount of work on oxidising tests was carried out by an IFA/APEA group⁽¹⁵⁾. In this unpublished work, attempts were made to obtain consistent burning rates in various co-operating laboratories. Chemical and physical differences in the fuels and physical differences in the oxidisers were contributing factors in the failure to achieve this objective.

An EEC group⁽¹⁶⁾ compared two variants of the train test, one using sawdust as fuel (UK Laboratory of the Government Chemist) the other cellulose as fuel (FRG, BAM). Inter-laboratory comparisons were made on the basis of placing the oxidisers in a 'ranking order' of burning rates rather than consistent burning times. Although results did not give a clear cut preference between the two variants, the EEC authorities, selected the BAM procedure as the criterion for the oxidising classification; materials giving higher burning rates than barium nitrate are classed as oxidisers⁽¹⁷⁾.

The UN Group have not completed their work in this field, but are giving serious consideration to a cone test. Cone tests are relatively simple to carry out and give reasonably reproducible results.

Typical results, obtained at Levington, with a cone test are shown in Table 3. These serve to illustrate a problem that faces the Fertilizer Industry in the adoption by the UN of such a test as criterion for Divisions 5.1. For inclusion the material should give a more rapid burning time than that of a selected reference. Currently the ammonium nitrate fertilizer is included in Division 5.1 and calcium ammonium nitrate fertilizer (below 28%N) used in the tests is excluded, by definition.

All potential reference materials given in Table 3 classify both fertilizers as oxidising substances or neither of them. The Industry would obviously prefer that any test adopted would leave currently marketed fertilizers precisely where they are at present with regard to inclusion or exclusion from Division 5.1. However, it is unrealistic to expect results of a single test to draw lines for Division 5.1 precisely where they are at the moment. To specify that this is the result that must be obtained from the test is to say that a test is not needed, for fertilizers at any rate.

TABLE 3

CONE OXIDATION TEST

OXIDIZER	BURNING TIME (SECONDS)	VARIANCE (%)
Ammonium Nitrate A.R.	53	10
Ammonium Nitrate Fertilizer	65	10
Calcium Ammonium Nitrate Fertilizer	80	10
Lead Nitrate	90	15
Potassium Dichromate	360	10
Sodium Peroxide	10	-
Chromium Trioxide	10	-
Potassium Nitrate	13	-
Sodium Nitrate	15	10
Ammonium Persulphate	50	15
Barium Nitrate	150	20
Sodium Percarbonate	240	15
Potassium Persulphate	420	10

SAWDUST AS FUEL

ALL MIXES 1:1 OXIDIZER:FUEL

CONE 100g TOTAL WEIGHT

It is not conceivable that the UN Group will agree to the exclusion of straight ammonium nitrate fertilizers, UN Nos. 2067 and 2068, from the list of dangerous substances. Hence it must be expected that a test will be adopted, with a suitable reference material, to include ammonium nitrate in Division 5.1. The Industry may be faced therefore with the inclusion in Division 5.1 of some calcium ammonium nitrate fertilizers that are not currently regarded as oxidising substances. Discussions on technical aspects of this situation are required. It could be agreed the lower limit of 80% ammonium nitrate currently in the UN list should be lowered, or the test does not measure the right parameter with regard to the hazard. The safety record of such material certainly indicates that transport conditions need be no more severe than used at present.

5.3 Ammonium Nitrate Directive 80/876/EEC

5.3.1 General

This Directive attempts to specify physical and chemical parameters of straight ammonium nitrate fertilizers distinguishing the fertilizer material from ammonium nitrate used as a component of an explosive. In the introduction the Directive comments that "...ammonium nitrate fertilizers of high nitrogen content should conform to certain characteristics to ensure that they are harmless,....". The Directive therefore attempts to specify material that is safe, or rather safer, than material used as a component of an explosive, in normal storage and marketing conditions. Characteristics defined in Annex I are given in Table 4.

Table 4

Characteristics and Limits for Ammonium Nitrate

Directive 80/876/EEC (Annex I)

Characteristic	Limit
Porosity (oil retention)	4% by weight maximum
Combustible Matter	
>90% Ammonium Nitrate	0.2% by weight maximum
80 to 90%	0.4% by weight maximum
pH (10g fertilizer in 100ml water)	4.5 minimum
Particle size	<5% through 1mm mesh <3% through 0.5mm mesh
Chlorine	0.02% by weight maximum
Copper	10ppm maximum

In addition Annex II specifies a detonation test that should be used if member states believe that further testing is necessary.

For the oil retention test (Annex I) and the optional detonation test (Annex II) the material must be thermally cycled between 25 and 50°C; two cycles are required before the oil retention test and five cycles before the detonation test.

The Ammonium Nitrate Directive (Article 3) stipulates that material must only be supplied to the final user in packaged form.

The relevance of these points is considered.

5.3.2 Detonation Test (Annex II)

The detonation test as a measure of the hazard presented in storage operations has been criticised by Bauer et al⁽¹⁸⁾. Their view is that the test was unnecessarily severe for the intended purpose; it represented an overkill situation. Bauer made his criticism on details published in an early version of the Directive⁽¹⁹⁾. At that time the booster suggested was 500g dynamite containing 22 to 28% explosive oil. In latest draft descriptions of the test the booster was changed to 500g PETN containing 83 to 86% explosive. This certainly meets one of Bauers criticisms, that dynamite was an unreliable booster, however if anything it has increased the severity of the test. Multipoint ignition of the booster is also a permitted option in the latest draft. These refinements are presumably designed to increase the consistency of results obtained; an acceptable objective for the designers of the test. Whether Bauers criticisms are, wholly or partially, accepted, any increase in the severity of the test must be questionable in terms of relevance to conditions likely to be encountered in storage operations.

The test is not relevant to the behaviour of ammonium nitrate in a fire; the situation in which a hazardous situation can be envisaged. The conceivable, though still not demonstrated, scenario for the detonation of a storage heap in a fire is via the detonation of a pool of molten ammonium nitrate. Whether a pool of sufficient dimensions to propagate a detonation, supposing this could be initiated by a falling object, depends on the geometry of the store. Whether the detonating pool could initiate detonation of residual solid is unknown. It must be conceded, however, that the latter would be a more likely event in the case of porous prills than in the case of dense prills. Any additional hazard or risk that this represents could, however, be covered by a less severe detonation test.

5.3.3 Thermal Cycling (Annex I and II)

The mechanism of the transitions in ammonium nitrate are complex and the kinetics of the process are influenced by many factors. However, all that is relevant in the present context is whether the process is or can be a factor in the safe storage and handling of ammonium nitrate.

Before the oil retention and detonation tests associated with the Directive the fertilizer is cycled between 25 and 50°C.

In the thermal cycling procedure the material must not be in layers so thick that cycling of material in the centre is not possible in a reasonable time; thicknesses of about 45mm are suitable. This fact alone must throw doubt on the validity of the process as an enhancement of hazard. Filled fertilizer sacks (50Kg) are usually of the order of 120mm thickness. In the conditions favourable for cycling therefore one would only expect the surface layer, say the top 25mm or so, to be affected. This is illustrated in work carried out by RARDE at Woolwich⁽²⁰⁾, in which the temperature of material at the centre of a 50Kg sack of fertilizer, and that 10mm below the surface of the sack, was followed as the whole sack was cycled between 10 and 50°C, using 12 hour periods at each temperature.

Results, reproduced with permission of the Ministry of Defence, are shown in Fig 3. These illustrate that the material 10 mm into the sack would cycle through the 32°C transition, whereas the material in the centre was only subjected to a temperature fluctuation of + 1°C.

In an experiment at Levington during the summer of 1975 a stack of 15 sacks (5 sacks high and 3 sacks wide) was exposed to direct sunlight; for a period June 1st to October 2nd. Thermocouples situated at various points in the stack, were held at a depth of 15mm below the surface of the fertilizer. The fertilizer used in this test was not stabilised with magnesium.

Thermocouple readings indicated that material at a depth of 15mm into the side of the stack exposed to direct sunlight underwent a maximum of 37 cycles during the experiment. Damage to surface layers, illustrated in Figure 4, was restricted to a depth of 20mm. Protection afforded by the sack on top of the one illustrated, can be seen in the figure. In terms of an enhanced hazard, it is difficult to visualise a situation in which detonation could be induced in this surface layer. In a fire situation, the one most likely to result in a hazard, the surface layers exposed to the heat of the fire would melt. In this situation cycling damage would be irrelevant. Although cycling damage was restricted to material in the surface layers exposed to direct sunlight, it would have rendered the material unsaleable.

Cycling damage is therefore a quality factor; it is not a hazard factor in normal storage situations. Inclusion of a thermal cycling procedure in the Directive is an unnecessary restraint regarding safe storage and handling. One possible defence of the thermal cycling test is that it simulates the worst possible case. Data presented here illustrates that this defence is weak as complete breakdown in a good summer in the UK is extremely unlikely.

The above remarks made in the context of bags apply with equal validity to bulk, either loose bulk heaps, which are usually under cover, or storage silos, which can be in the open. In silos, as with bags, it is only the material in contact with the walls that is at risk. The amount at risk is small and is unlikely to create a quality problem.

In bulk storage and bulk transport, the problem of moisture pick up and the effect of this on cycling damage must be considered. Ammonium nitrate is hygroscopic and the rate of the IV III phase transition is affected by moisture. These facts are presumably a basis for the comment in the draft of a Commission Directive⁽²¹⁾ detailing test procedures for the Ammonium Nitrate Directive, implying that the thermal cycling procedure simulates conditions within the application of the Ammonium Nitrate Directive, but that they may not necessarily simulate all conditions relevant to bulk transport by water.

Moisture pick up will be confined to the surface layers of ammonium nitrate. This pick up could conceivably increase the rate of thermal cycling damage in the surface layer. This will not in itself present an enhanced hazard. As with damage in dry material it is difficult to envisage a situation in which a detonation could be induced.

Inclusion of the comment concerning transport by water (21) is therefore unnecessary.

5.3.4 Porosity (oil retention; Annex I)

Porosity of the particles affects the sensitivity of the ammonium nitrate to detonation. In a Directive aimed at distinguishing between material intended for fertilizer use and that intended for use in explosives, a limitation on porosity (set at a maximum of 4.0% oil retention) would seem reasonable, although the association with a prior thermal cycling procedure is unnecessary (Section 5.3.3). Fertilizers are usually made in the form of hard, dense particles and the limitation would not cause problems. If, however, the limitation implies that the less dense prills present a significantly greater hazard in normal storage conditions, it is questionable. Porous prills are made and stored safely in large quantities. The stability of such material and the fact that it can be handled and stored in conditions less stringent than those applicable to explosives is a factor in its large scale use. The limit of 4% is unnecessary in terms of a hazard in storage but acceptable as a means of distinguishing fertilizer products from others.

Although porosity is known to affect the detonability of ammonium nitrate particles it is of interest to note that Hahnefeld et al⁽²¹⁾ did not find a consistent relationship between sensitivity and oil retention. This perhaps suggests that oil retention is not a true measure of the porosity of the particles. The oil retention test itself has also been the subject of much refinement in attempts to improve reproducibility. An interesting exercise in terms of designing a test but of questionable value since the property has little significance in terms of hazard in storage.

Bauer⁽¹⁷⁾ was severe in his criticism of the thermal cycling and oil retention capability aspects of the Directive. He was perhaps too severe as he seemed to imply that the Directive sought to limit porosity from the point of view of restricting oil retention capability. An alternative view is that the Directive uses oil retention as a measure of porosity; regarding the increase in porosity itself as the enhanced hazard.

5.3.5 Combustible Matter (Annex 1)

The combustible matter limits are the same as those used in the United Nations Classification. The limits can be justified in terms of the known enhancement of sensitivity to detonation by small amounts of hydrocarbon fuel^(2.2). The deflagration to detonation transition obtained in van Dolah's tests⁽¹²⁾ with fuelled ammonium nitrate supports the need for a restriction on combustible matter content.

This is a relevant parameter in safe storage.

5.3.6 pH (Annex I)

The pH limit is one used by producers in their manufacturing operations, usually to minimise the risk of decomposition in areas where the ammonium nitrate exists in the molten form. In terms of safety in storage a pH above 4.5 would inhibit a self-heating tendency in the event of accidental contamination with organic matter. Although a pH above 4.5 would hinder the onset of thermal decomposition the effect this would have in a fire is marginal; acidity would develop as the nitrate is heated. The limit in the product is reasonable and gives an indication of correct manufacture.

5.3.7 Particle Size (Annex 1)

The size limits are less severe than many manufacturers use in their own operations. Although the proposed size limitation is no problem the Industry should be prepared to challenge it as it could inhibit future developments.

5.3.8 Chlorine Content (Annex I)

It has been known for many years that chloride has a marked effect on the thermal decomposition of ammonium nitrate⁽²³⁾. Whether the low level specified in the Directive, maximum 0.02% by weight, is justifiable in terms of a hazard in handling and storage operations is arguable. Data given in Figure 5 show the effect of chloride levels of 0, 100, 200 (the EEC limit), 500, 1000 and 1500 (the limit used by the US Industry) ppm. At all these low chloride levels the enhanced decomposition that set in soon died away and the behaviour of the system reverted to that of pure ammonium nitrate. This loss of small levels of chloride and decomposition rates reverting to that of the pure nitrate was reported by Saunders in 1922⁽⁸⁾. In a fire situation the chloride, at these low levels, would be rapidly lost from any molten material formed. The hazard presented by all these systems would be the same. The low level set by the EEC is reasonable in terms of manufacturing operations in which the nitrate goes through a molten stage. This is a usual stage in the majority of methods of production of hard dense particles. However ammonium nitrate can also be produced by a rotary granulation procedure in which it may be more difficult to meet the EEC specification. There is no justification in terms of enhanced hazard to legislate against such products.

Some limitations on chloride can be justified in terms of hazard in the molten form (lowering of density by gaseous decomposition products⁽⁴⁾), when chloride levels are such that complete loss is not possible; the US level would not be excessive. It is worth noting, however, that early versions of the ADR (road) and RID (rail) transport codes listed potassium chloride as an acceptable diluent in ammonium nitrate.

5.3.9 Copper (Annex I)

Copper is the only metal for which a specific limit is set. The need for a limitation of the copper content is generally accepted in view of its known effect on the decomposition and sensitivity to detonation of ammonium nitrate, confirmed in the recent work by Bauer⁽⁴⁾. Other metal ions are known to effect the decomposition but their effect on the detonation is not in the same order as copper. These metal ions are catered for in general terms by the provision in the Directive that additives should not increase the sensitivity to heat.

5.3.10 Packages or Bulk (Article 3)

There is controversy within the Industry on the question of the safety of storage and handling of ammonium nitrate in bulk compared to bags. The proponents of storage in bags claim that the best way of preventing contamination is to bag the material. Contamination is important in terms of increasing sensitivity to detonative shock and, as van Dolah⁽¹²⁾ showed, in terms of permitting a transition from deflagration to detonation in a fire situation.

All possible steps should be taken to avoid contamination of bulk heaps. However accidental uniform contamination of bulk storage heaps is not easily achieved. Contamination represented by the packaging materials and pallets in bagged material is more homogeneously distributed through the stack than could be achieved by accidental contamination of bulk. Cook⁽²²⁾ showed that maximum sensitivity to detonation in ammonium nitrate - hydrocarbon mixtures occurred at lower levels than required for maximum power. RARDE work⁽²⁴⁾ showed that high hydrocarbon levels (say 20%) had a marked depressant effect on the power of the explosion. Accidental contamination of the surface of a bulk heap would produce a range of nitrate-fuel mixtures. Only a small fraction would be in the range for maximum sensitivity. In a fire situation the surface contamination would be relatively readily consumed.

Van Dolah et al⁽¹²⁾ conclude from their work on the behaviour of ammonium nitrate in fire that bulk storage is preferable to bags from the safety point of view. Van Dolah also comments that the channels in palletised stacks permit fire to penetrate into the interior of the stack. Bulk heaps are impervious to such penetration.

Storage in bulk can, therefore, be as safe if not safer, than storage in bags. Storage in bulk on the farm (the final user) can be a safe operation provided the supplier assures himself that the storage area is suitable for the purpose. Also that the farmer is aware of the need to avoid contamination at all times. Farmers can, however, once the supplier has left the site, destroy the suitability of the storage area. However, similar comment can be made on bagged storage on the farm. Bags can readily be moved and stacked against hay or straw. The plastic storage silo is an attractive answer to bulk on the farm. The material is in bulk but is contained. Contained, not confined, as the silo will melt and release its contents into the open if involved in fire.

Ammonium nitrate can be stored safely in bulk and in bags and options should be kept open to suit particular situations. Further discussion on this topic will undoubtedly occur but will only be of value if this is free from commercial implications.

5.3.11 Comment on Directive

The Ammonium Nitrate Directive liberalises marketing of straight ammonium nitrate fertilizers within the EEC and sets a quality standard. The considerations in Sections 5.3.2 to 5.3.10 support the view that the Directive does not in general relate the known hazardous properties of ammonium nitrate to normal storage and handling operations. It is unnecessarily severe on the solid material and has little relevance to the behaviour of ammonium nitrate in a fire; the situation in which a major incident is more likely to arise. Prevention of fire has more influence on safe storage and handling of the fertilizer than many of the parameters in the Directive. This Directive does, however, set a specification for ammonium nitrate fertilizer which with some modification, deletion of thermal cycling, liberalising chloride levels, modification of the detonation test, could be an acceptable quality standard. Maintenance of high quality through good storage conditions, would be a significant factor in safety.

5.4 Directive on The Major Accident Hazards of Certain Industrial Activities, 82/501/EEC. The Seveso Directive.

Comment on the Ammonium Nitrate Directive indicates the Author's view that the conditions in which ammonium nitrate fertilizers are stored is more important, from the safety view point, than the specification of the material itself. Safe storage is of concern to the Manufacturer and Legislator alike; the manufacturer has the additional incentive of commercial interest. The Seveso Directive is based on the concept that manufacturers should know the hazards and risks of their operations, including storage and handling, and should be in a position to demonstrate this knowledge to appropriate authorities.

Basically the Directive, as far as storage is concerned, stipulates that people who store dangerous materials above certain specified tonnages must be in a position to demonstrate, on request, that they are aware of potential hazards and the steps they have taken to minimise the risk that the hazards will be realised. At specified higher tonnages a written report must be supplied to the appropriate authorities. This report, known as 'The Safety Case', must contain details of the operations on site, potential hazards, situations in which the hazards could be realised, the risk of these occurring, means of minimising hazards, site emergency plans and details of the geographical location. In addition to this "Safety Case" information must be given to people at risk in the vicinity of the site. Information must be provided to enable an off-site emergency plan to be drawn up by the appropriate authority. There is also a requirement to report major accidents.

The original Directive listed ammonium nitrate among the dangerous substances to which the above requirements applied. Threshold tonnages of 500 te for demonstration of safe practice and 5000 te for preparation of the "Safety Case" were stipulated. The ammonium nitrate entries were subject to a footnote which indicated that the requirements only applied when the material was in a state in which it was capable of creating major accident hazard.

The footnote was taken to mean that ammonium nitrate that conformed to the Ammonium Nitrate Directive 80/876/EEC would be exempt. However, the EEC Commission have published (COM(85)572) a proposal to amend the original Directive. These proposals comment that in the light of current knowledge ammonium nitrate is always in a state which gives it properties capable of creating a major accident hazard. The proposals define two forms of ammonium nitrate viz:-

- a) Ammonium nitrate
- b) Ammonium nitrate in the form of fertilizers.

Ammonium nitrate in the form of fertilizers covers material that conforms to the parameters in the Ammonium Nitrate Directive, 80/876, and to compound fertilizers where the nitrogen content, derived from ammonium nitrate is greater than 28% by weight.

Non fertilizer ammonium nitrate and solutions containing more than 90% ammonium nitrate by weight are covered by the "ammonium nitrate" entry. Threshold tonnages for the preparation of the Safety Case are given as:-

Ammonium nitrate	2,500 te
Ammonium nitrate in the form of fertilizers	5,000 te

It should be mentioned that these figures are the subject of further discussion within the EEC. The above figure for the "non-fertilizer" ammonium nitrate represents a lowering of the threshold for this type of material compared to the figure in the original Directive. No justification for this change has been advanced. It must be accepted however that fixing tonnage levels is an arbitrary process as it is not possible to present a firm technical case justifying one level against another.

The Directive requires manufacturers, store managers etc to demonstrate their safety procedures. On receipt of this information the authorities can surely comment on their suitability or efficacy. Authorities could use this procedure to enforce safeguards they deem necessary in particular circumstances and avoid the need to have different tonnage levels implying that there is a major difference in the hazard presented by the two types of ammonium nitrate. Providing good storage conditions exist there is room for argument on this.

Manufacturers have as much, probably more, knowledge of the conditions in which their products become hazardous than legislators. Self-regulation by means of the storage codes etc. is therefore a logical option.

On this premise the Directive on the major accident hazards of certain industrial activities (the Seveso Directive) will make an important contribution to safety.

Fertilizers will be stored, in situations not entirely under the manufacturers control, in quantities below the level at which it is necessary to be able to demonstrate safe operation. Manufacturers must take all possible steps to ensure that their products are stored safely in these situations. If this is not done and an incident results, it can be expected that the EEC Authorities will seek to lower the threshold tonnages. Manufacturers must exercise self-discipline in selection of such stores. Commercial pressure such as "we only need to store for two weeks so this wooden shack will do" must be resisted.

5.5 Directive on the Classification, Packaging and Labelling of Dangerous Substances 67/548/EEC, and Proposed Directive on the Classification, Packaging and Labelling of Dangerous Preparations

These Directives aim to ensure that substances and preparations are classified, according to particular hazards and risks, and are packaged and labelled accordingly.

Ammonium nitrate fertilizers, as defined in UN Division 5.1 would be expected to be regarded as "oxidising". However, the test adopted by the EEC is based on the BAM test in which these materials give negative results. It would be inappropriate for Industry to accept a "non-oxidising" category for these products for the purposes of this Directive. Advice given to customers by means of leaflets informs them that they are "oxidising" and should not be stored near combustible materials. Labelling for international transport also makes the "oxidising" status clear; as noted earlier Industry wants the Division 5.1 status of these fertilizers in the UN system retained (Section 5.2).

Fertilizers other than 5.1 materials may be covered by the Preparations Directive under "harmful" and/or "irritant" categories. These may require test work. Fertilizers have been marketed for a considerable time and the problems they present in handling operations should be known. It may be possible for Industry, acting together, to agree with the EEC Authorities the hazard category for various types of fertilizers and the requisite labels. This could avoid the need for a considerable amount of test work.

5.6 Codes of Practice

Manufacturers will have their own Codes of Practice governing the safe handling of ammonium nitrate at all stages of their operations. Compliance with these codes is ensured by dissemination of information, training and vigilance.

Codes produced by individual companies will obviously take note of any legal rules and guidance notes applicable to the particular country. They will in many cases be based on general codes produced by Industry Associations. The revised version of the Storage Code issued by the IFA/APEA Working Party on Safety in Fertilizers, which should become available during 1987, will be an example of a general code which can be adapted to suit the needs of particular situations.

Storage codes are usually based on the concepts that

- 1) solid ammonium nitrate is a relatively stable material.
- 2) ammonium nitrate itself is not combustible, but if involved in fire it will enhance the severity of the fire.
- 3) ammonium nitrate affected by fire, or other sources of heat, will decompose with the evolution of toxic fume.
- 4) in severe fires, particularly if the material becomes contaminated and confined, there is a small risk of an explosion.

Sufficient comment has been made in this paper and in quoted references to support these concepts. Codes based on them therefore have prevention of fire and contamination, and the avoidance of confinement as their principal aims. Fire precautions involve minimising possible ignition sources and as far as possible the exclusion of combustible matter. In general therefore, codes aim to prevent conditions in which decomposition of the nitrate can occur.

If the storage codes are strictly followed the form of the solid ammonium nitrate is irrelevant. The dense prills/granules used by the Fertilizer Industry, and the porous prills destined for use in ANFO explosives can both be stored safely.

As well as recommendations on the prevention of fire the codes often contain recommendations on maintenance of the quality of the product. These recommendations complement safety regulations and ensure absence of contamination and free flowing products.

6. CONCLUSIONS

Good Codes of Practice, strictly observed are the best way to ensure safety in manufacture, handling and storage of ammonium nitrate. Legislation in terms of regulating the chemical and physical make up of the ammonium nitrate particles cannot replace the need for such codes.

The Fertilizer Industry uses a large quantity of ammonium nitrate and has considerable knowledge of the properties of the material. In terms of practical conditions in storage etc their knowledge must exceed that of legislators. The Industry should therefore be in a position to influence new legislation at the discussion stage, and update old legislation if thought appropriate. Industry will only gain and maintain a credible voice in discussion with authority if they make genuine efforts to reach a uniform position. To do this commercial considerations must be excluded from technical discussions relating to legislation concerned with safety aspects. Legislators have nothing to gain by introducing unnecessarily severe legislation. Consistent and uniform advice from the Industry is one way of avoiding this.

7. ACKNOWLEDGEMENTS

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The author thanks the Directors of Norsk Hydro Fertilizers Limited for permission to present this paper. It is emphasised that the views expressed are those of the author and do not necessarily reflect the views of the Company.

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Figure 1.

Explosion - Ammonium Nitrate in Fertilizer Operations

General Fault Tree

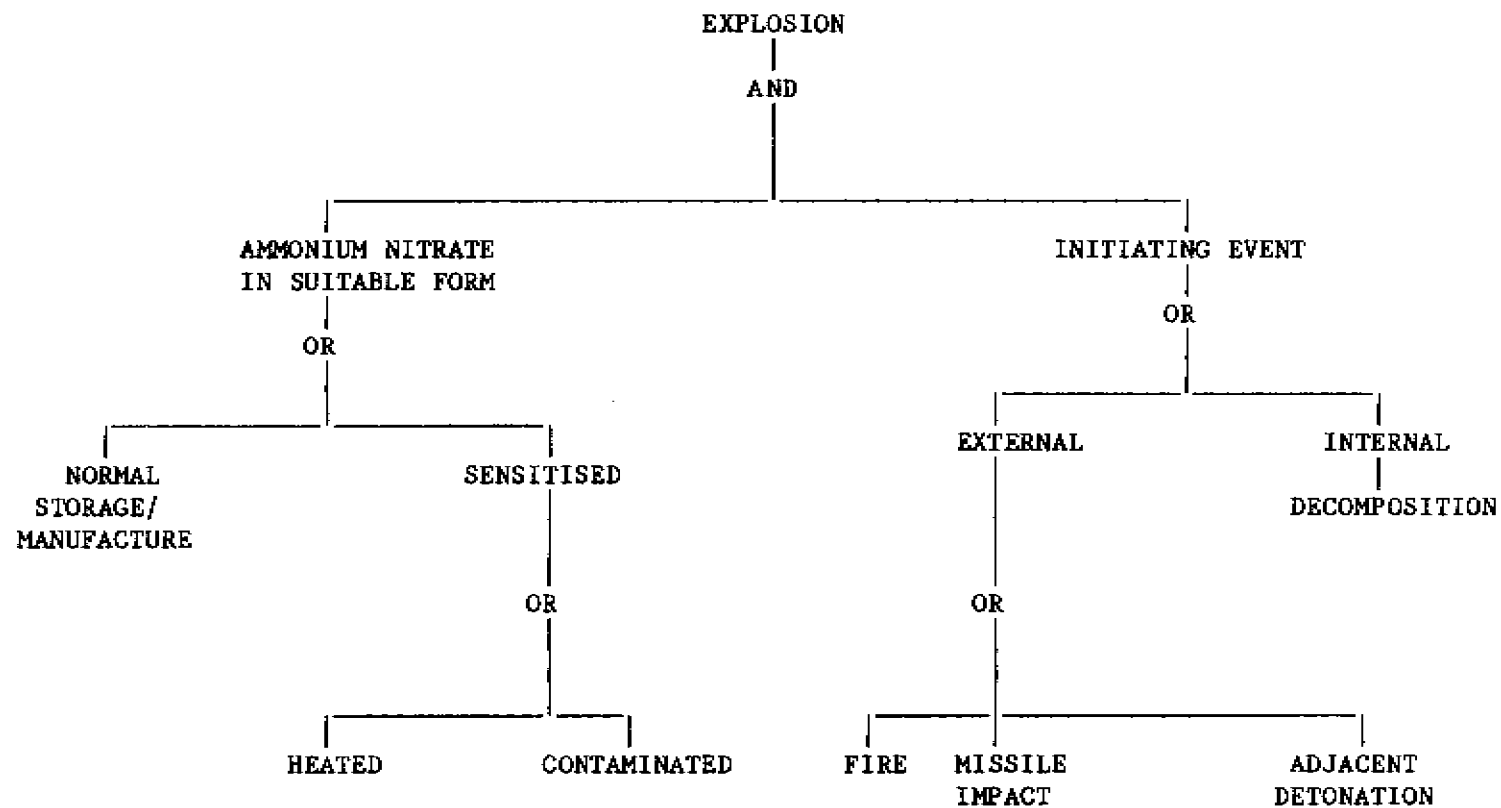
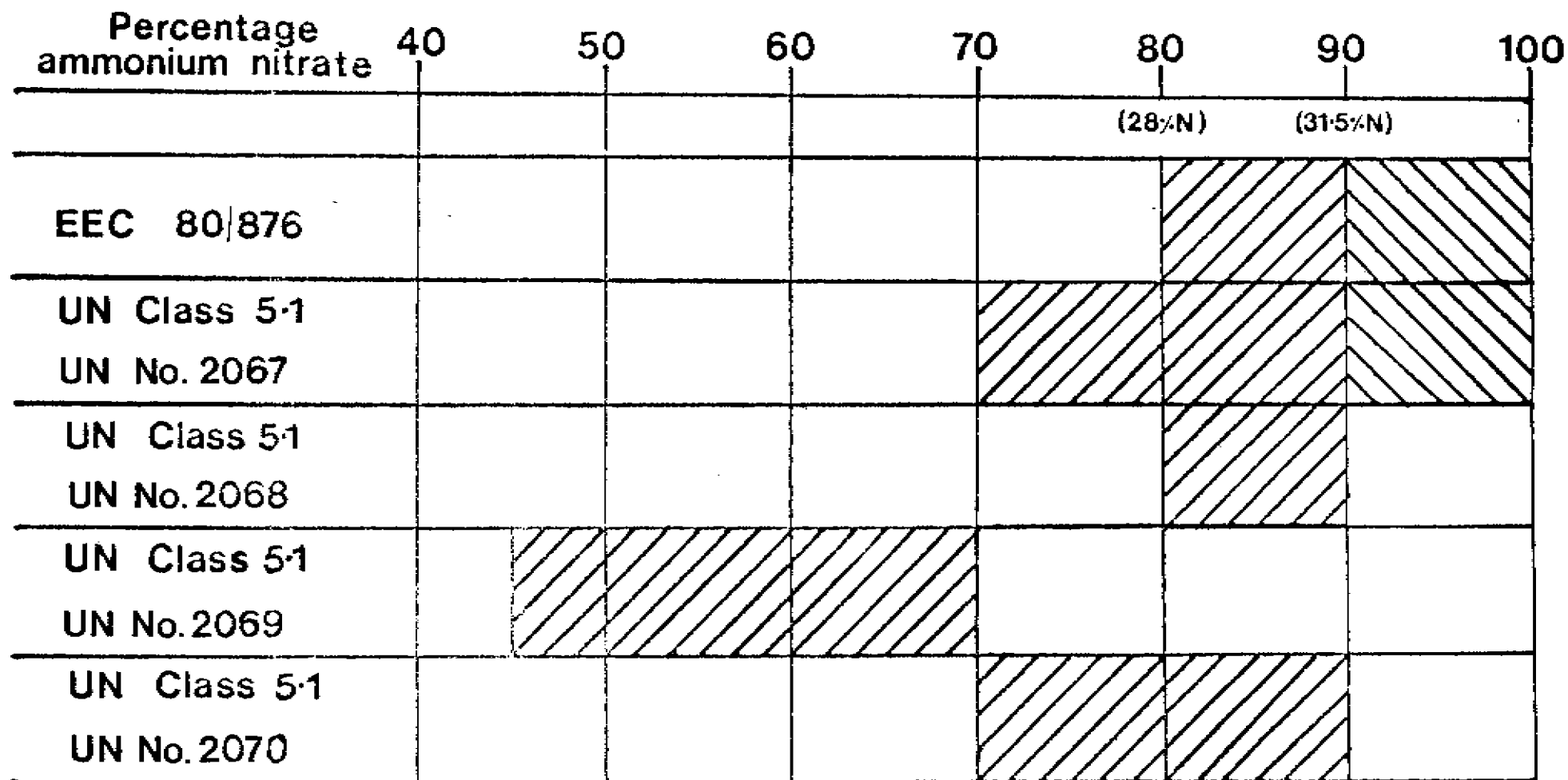


Figure 2.

Ammonium Nitrate Fertilizers



Not more than 0.2% combustible material 


Not more than 0.4% combustible material 

Figure 3.

Temperature Cycling of a 50Kg Sack of Ammonium Nitrate Fertilizer

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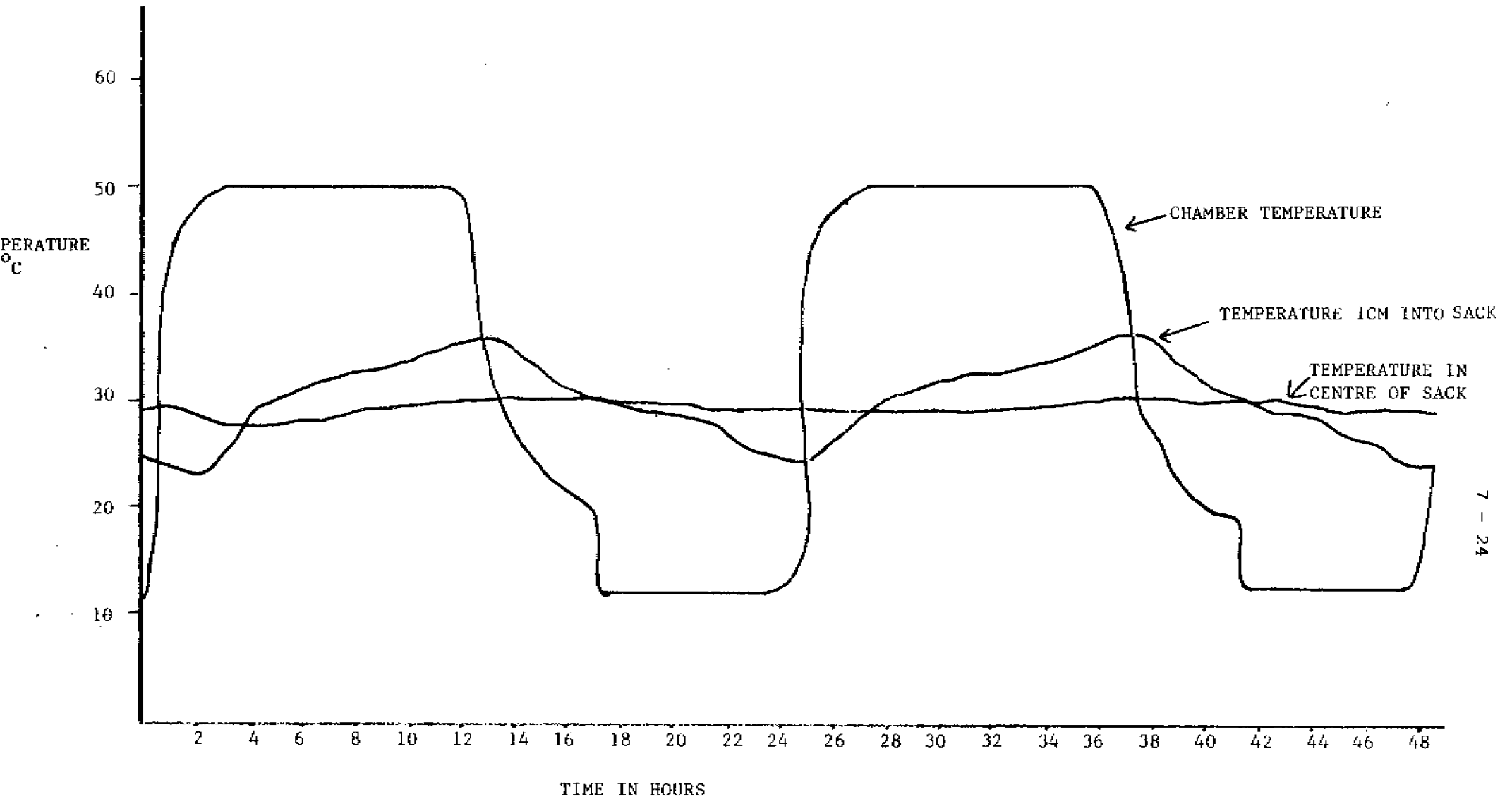


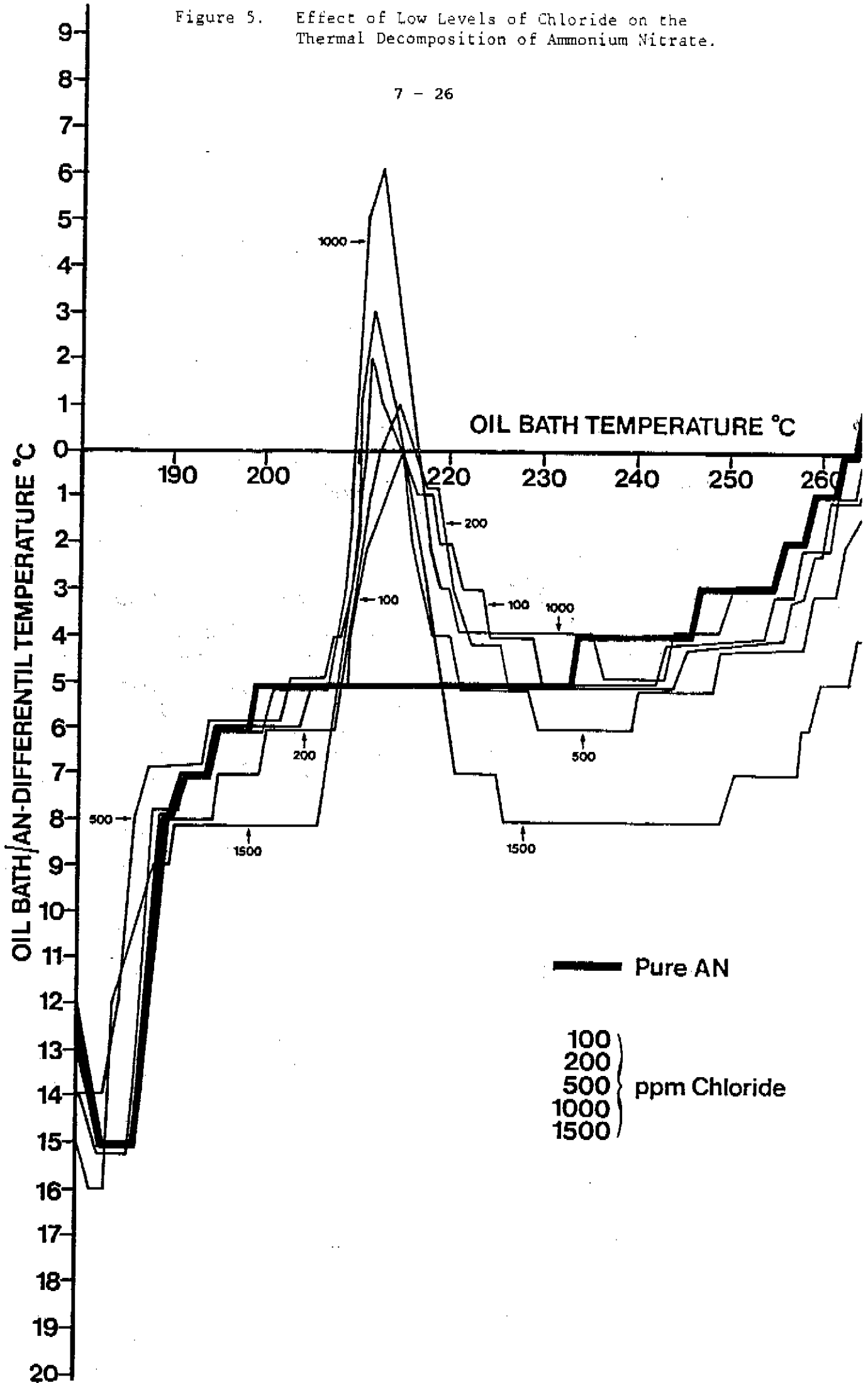
Figure 4.

Thermal Cycling Damage to Ammonium Nitrate.



Figure 5. Effect of Low Levels of Chloride on the Thermal Decomposition of Ammonium Nitrate.

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TA/86/7 The hazardous properties of ammonium nitrate fertilizers and the regulations to which they are subjected by K.S. Barclay, Norsk Hydro Fertilizers Limited, United Kingdom

DISCUSSION : (Rapporteurs Messrs A. Constantinidis, SICNG, Greece & V. Bizzotto, NSM, Netherlands)

Q - Mr J.B. PEUDPIECE, AZF, France

Do you think that the distinction between ammonium nitrate containing more or less than 80% NH_4NO_3 , indicated in EEC regulations, corresponds to a barrier separating products with different risk factors, mainly between 26-27% N and 33,5% N?

A - As noted in the paper the specifications in EEC regulations do not always correspond to the specifications in the UN system of classification. It would be unrealistic, however, to suggest that any limit in these systems represented a sharp break between hazardous and non-hazardous products; a gradation of properties across the boundary would be expected. With regard to "oxidising capacity" behaviour it is noted in the paper that the tests used do not distinguish between the 26/27% N and the 33.5% N products. A distinction between these two may be possible in some cases by means of a detonation test. In practice however, the difference in risk in normal storage and handling is small.

Q - Mr S. ORMBERG, Norsk Hydro, Norway

I understand that the political objective for EEC activity is to ease the trade across borders. However, since harmonization to UN system was given no priority, I would like to ask for the authors views on:

1. will the EEC-developed tests and criteria give restriction to trade in or out of EEC - as trade and distribution means transport.

2. If so, is the author observing other local initiatives to deliberately restrict trade by establishing new rules designated SAFETY?

A - One objective of EEC activity is to eliminate barriers to trade between member states. Material meeting specified criteria can therefore be traded freely within the EEC. Material coming into the EEC from outside can also be traded freely within the EEC provided it meets the same criteria. It is agreed that transport is included in trade. However, the AN Directive mentioned in the paper stipulates that International rules for the carriage of dangerous goods still applies to the transport of the fertilizers. This could be used to impose more stringent tests than given in the Directive and constitutes a loophole.

With regard to local initiatives on "safety" grounds one member state placed a restriction on the import of ammonium nitrate in bulk by sea. As storage and sale in bulk were permitted within that country it is difficult to see a strictly safety reason behind the restriction on the import in bulk.

Q - Mr G. SAID, SAEPA, Tunisia

It was indicated on a paper, published by IFA in 1983, that the storage with exposure to the sun of fertilizers containing high quantity of ammonium nitrate can induce swelling and disintegration of particles. According to your paper, it seems that you support a thesis excluding any disintegration of particles. Can you explain your opinion?

Is the transport of bulk ammonium nitrate by ship permitted?

Does a law governing this means of transportation exist?

What is the maximum height allowed for stacks of bagged ammonium nitrate?

If this limit exists, how can the charge of ammonium nitrate inside the ship to a height of 12 metres be tolerated?

A - Thermal cycling can and does induce swelling and disintegration of ammonium nitrate particles. In practice exposure to the sun will only induce this behaviour in the surface layers of the storage heap, whether this is bagged or bulk. The majority of the material in the heap will remain unaffected; hence the contention that the problem is a quality one rather than a hazard.

Yes, ship transport of bulk ammonium nitrate is permitted and is an acceptable practice. It is necessary to conform to transport codes governing such transport. The International Maritime Code governing bulk transport requires that the ammonium nitrate should give a negative result in a detonation test similar to that described in the EEC AN Directive, or a test deemed equivalent for the purpose by the appropriate National Authority. It would also be necessary to conform to local regulations in the ports or harbours involved in the operation.

In the UK advice used to be given that stacks of bagged ammonium nitrate should be restricted to a height of 7 metres. This to minimise the risk of propagation of a detonation in the stack. The current advice, however, is to restrict the size of the stack to 300 t at sites other than those under the control of the manufacturer.

There is no restriction on the size of stacks at manufacturers' premises.

In a ship or on land avoidance of involvement of the material in a fire is important. The height of the stack can then be governed by the space and handling equipment available.