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SAFETY REQUIREMENTS IN FERTILIZER PLANTS

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Summary

Those factors and problems important for the safety of fertilizer plants are presented with special reference to the Odda process and the production of straight nitrogen and NPK fertilizers. The subject is treated on the basis of BASF's standard scheme for the review of safety considerations.

The potential hazards arising from the properties of the substances handled that are important from the point of view of safety are pointed out, and information is given about measures taken by BASF within the framework of plant safety schemes to avoid, detect, and deal with hazardous situations. Finally, matters relating to the safety of the final products are discussed.

SAFETY REQUIREMENTS IN FERTILIZER PLANTS

B. Purucker, BASF, Germany

1. Introduction

BASF's safety scheme covers:

- personal safety,
- plant safety, and
- product safety.

The many organizational and psychological questions and measures involved in personal safety would be beyond the scope of this paper, and will not be discussed here.

BASF brings in plant safety at the very outset of planning new chemical plants, making use of a method of stepwise review of safety considerations (Table 1).

This method ensures that matters relating to plant safety are dealt with comprehensively and in detail. The same method is also applied to existing plants.

Here we shall be concerned with some factors and problems that are of special importance for the safety of fertilizer plants, particularly plants used in the Odda process and for the production of straight nitrogen and NPK fertilizers.

Questions of product safety arise in connection with the storage of large quantities of fertilizers in particular, but some relate to transport or to handling by the user. Such questions are also considered here.

2. Ammonium nitrate

The substance that concerns us most is ammonium nitrate, NH_4NO_3. If it receives a certain amount of energy - which must be applied in making solid fertilizers - it can decompose in a number of different ways (see Fig. 1), all of which involve an increase in volume and most of which release heat (dissociation is the only endothermic reaction). The higher nitrogen oxides formed, NO_x, where x is 1 or 2, are acutely or subacutely toxic.

The greatest potential danger lies in the ability of ammonium nitrate to detonate when subjected to mechanical shock. This is the property that has led to a number of serious accidents.

The exothermic decomposition reactions can be considerably accelerated by suitable catalysts. Knowledge of these is of special importance for the industrial synthesis and concentration of ammonium nitrate solutions and for the production of solid ammonium nitrate.

2.1. Ammonium nitrate solution

The 65% ammonium nitrate solution provided by the BASF-Odda process must be concentrated to about 94% for use in the production of straight nitrogen or NPK fertilizers. This can be done economically in, for example, triplex evaporators, partly under reduced pressure. Before the solution enters the first evaporator its pH is automatically adjusted with ammonia to values between 4.5 and 5.0. At the final stage it is heated to a temperature of 170 °C by steam at a pressure of 8 bar.

In the synthesis of ammonium nitrate a number of industrial processes are carried out, at various temperatures and pressures, that make use of the heat of neutralization for concentrating the solution or for producing steam (or both). The simultaneous flow of the required amounts of the reactants must be assured and in addition the reactor temperature and pressure have to be kept within safe limits. The reactor conditions have a considerable effect on ammonia losses, and hence on potential environmental pollution. For instance, when neutralization is carried out under pressure, at higher melt temperatures, safety requires that the pH be kept at about 5, which is the value corresponding to complete neutralization of the ammonia. Whereas the pH of the condensed vapors is a quantity to be controlled because of its importance as an indication of reactor operation that is optimum with respect to nitrogen yield, it is the pH of the reactor output that has to be controlled for safe operation.

The properties of ammonium nitrate and its solutions that are relevant to safety are known in detail[1]). The dependence of crystallization on temperature, pressure, and concentration is also well understood. The substances that catalyze decomposition of ammonium nitrate, even when they are in low concentrations, include free acids, chloride ions, heavy metals - especially copper -, and organic carbon compounds. Their presence often cannot be completely avoided in industrial processes, but we keep a careful check on their sources and concentrations (see Table 2).

Apart from checking process parameters and starting materials we pay particular attention to the following points:

- Only saturated steam is used, to avoid overheating. Adjustment of the required temperature and pressure is carried out in steam coolers or water-injection equipment.
- Piping and vessels are heated by pipes carrying saturated steam at a pressure of 4 bar or 1.5 bar, to avoid crystallization and prevent overheating.
- Vapor condensers are operated with water pressures greater than the pressure on the vapor side, to avoid accidental contamination of the cooling water.
- No copper or copper alloys (brass or bronze, for instance) are used for any part of the plant with which the product comes into contact, to avoid the introduction of traces of copper. This applies to fittings and instruments in particular.

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[1])see K.D.Shah and A.G.Roberts in Fertilizer Science and Technology Series, Vol.4 -11 (171-196).

- Levels in reactors and storage vessels are measured preferentially by radiometric methods, because classical methods are subject to interference by incrustations or by foaming.

We also take special care that pumps are safe, especially from the possibility of dry-running at shaft seals and blockage on the pressure side. Particular precautions are as follows:

- Barrier-water systems with monitoring of losses and electrical conductivity are employed.
- The radial centrifugal pumps are fitted with double-acting slip-ring seals; unlike pumps with stuffing boxes they minimize the amount of barrier water getting into the product. Other kinds of shaft seal could be employed.
- The flow of barrier-water is monitored at each pump: if the rate of flow drops below a minimum for a certain time the pump is switched off (FS^-).
- Minimum flow pipe is provided after each pump (with FS^-) with return to the suction side.
- To guard against the effects of blockages the running of each pump motor is monitored (XA^-) and on the pressure side there is a shut down actuated either by excessive temperature (TS^+) or inadequate flow (FS^-).
- When any pump stops running various other safety switches are actuated, depending on the system of interlocks employed for the process.

Regarding constructional details we take care that there are no dead spaces, so that there is no danger of explosion of accumulated ammonium nitrate through overheating; here we are thinking in particular of overheating during repair work. In this connection it must be kept in mind that ammonium nitrate can creep into cavities through the finest gaps or cracks and accumulate there. The following are particular points to be observed:

- If at all possible cavities and hidden cavities are eliminated from all parts of the apparatus.
- Leaks may not be repaired by means of patches: the damaged area must be cut out and replaced by a flush-fitting piece of material.
- If the use of a hollow part is unavoidable, as in the case of hollow shafts, the cavity must be provided with two plugged holes on diametrically opposite sides, so that it can be flushed; it is an advantage to be able to look inside the whole of the cavity.

2.2. Calcium ammonium nitrate (CAN)

In the case of products containing a high proportion of solid ammonium nitrate, CAN for instance, the safety aspect of another property of ammonium nitrate has to be considered. This property is its polymorphism: as a function of temperature ammonium nitrate undergoes several changes in crystal structure. These phase changes are accompanied by distinct changes in volume.

Because of the dilution, fertilizers that contain both ammonium nitrate and high proportions of different nutrient salt or other additives are not capable of detonation. This is of course true only if there is no possibility of formation of a fraction extremely rich in ammonium nitrate by demixing. The condition that the mixture must be homogeneous and stable is fulfilled ideally by granulated fertilizers made from concentrated slurries or from melts of the constituents. However, thermal decomposition and changes in the crystal form of the ammonium nitrate can still occur, to a greater or lesser extend.

The first stage of the CAN process is concentration of 94% ammonium nitrate solution from the Odda process. This solution is pumped through a steam-heated line - 1.4 km long at BASF's Ludwigshafen works - to the steam-heated storage vessel at the beginning of the CAN plant, where the pH is readjusted to the required value ($4 < pH < 5$) with ammonia. A centrifugal pump delivers solution from stock via a preheater to the head of a descending-film vacuum evaporator, which is operated with high surface loading.

As a matter of principle BASF uses only saturated steam (steam into which sufficient water has been injected) for the further concentration of ammonium nitrate solution. In addition the following safety precautions are taken:

- The storage vessel for 94% ammonium nitrate solution is provided with an emergency water feed, which is turned on automatically if decomposition should start to take place.
- The ammonium nitrate solution that has been concentrated to a 98% melt passes freely in controlled quantities via a barometric trap - to maintain the reduced pressure in the evaporator - to the vessel where it is mixed with calcium carbonate; intermediate storage of the 98% ammonium nitrate melt is thus avoided.
- The barometric trap is eqipped with means for ammoniation.
- An overflow pipe connected to the storage vessel provides for immediate dilution of any excess of 98% ammonium nitrate.

In the mixing vessel the ammonium nitrate, calcium carbonate, and additives for stabilization are blended to form a homogeneous slurry. Important know-how relating to the quality and safety of the product is embodied in the following points about making CAN slurry:

- The use of calcium carbonate obtained from CNTH in the BASF-Odda process, which is already moist with ammonium nitrate solution and whose particle size is constant, leads to the formation of CAN of uniformly high quality. We have optimized the conditions under which the calcium carbonate is precipitated so that the particle size is small enough to meet the requirements of product safety but large enough to satisfy the need for good filterability and granule formation.

- The reaction by which calcium carbonate is formed from calcium nitrate is reversible:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightleftharpoons 2\ NH_4NO_3 + CaCO_3$$

  Since the extend of the reverse reaction - which depends on temperature and pH value - has a considerable effect on the hygroscopicity of CAN, we have carefully designed the mixing vessel so as to minimize residence time.

- The quality of the product can be adjusted within wide limits by the use of internal inorganic stabilizers. The additives are uniformly distributed, and thus develop their maximum effect. Those additives that inhibit the phase transitions of ammonium nitrate kinetically are of particular importance.

The CAN slurry is pumped to the granulation drum by centrifugal pumps, which have the same safety devices as those used in synthesis of ammonium nitrate.

The temperature of the CAN slurry is controlled at a level that ensures good flow and optimum granulation. As a consequence the heat content of the slurry is sufficient to allow all the following processing stages up to the final product to be carried out without additional heating. This has the following advantages:

- By autothermic granulation and drying open flames are completely avoided, even when starting up.
- The risk of contamination of the product by organic carbon from fuel (gas or oil) is thus completely excluded.
- Formation of nitrogen oxides and consequent contamination of the off-gases is avoided likewise.

BASF's coating process is chosen so that it can be carried out on the product stream after screening. In this way we ensure that no organic carbon from the coating material can get into the granulator, and hence into the granules, by beeing carried with recycled fines and oversize.

As in the case of solid - granulated or prilled - ammonium nitrate one can establish parallels between the product quality and product safety of CAN. Hygroscopicity leads to caking, disintegration of granules, and increased dusting. Insufficient resistance to cyclic temperature changes means that there is a change in volume every time the transition point at 32°C is passed through, which can easily happen during the normal daily cycle, with a resultant increase in porosity.

Both increased fines and porosity reduce product safety, although in the case of CAN detonation resistance is only slightly decreased. To measure this we use the steel pipe test developed by the Federal German Bundesamt für Materialprüfung. A modified form of this test has recently been included in an EEC Directive[2]).

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[2])Official Journal of the European Communities, **30**, No. L 38, 1 - 23 (1987).

2.3. Solid ammonium nitrate

Several industrial processes for the production of solid ammonium nitrate as fertilizer (33.5% N) are known.

The value of the pH of the ammonium nitrate solution must be checked both before and after addition of internal stabilizers, since some additives decrease the pH appreciably. Sufficient ammonia must be added to restore the value to about 7.

Attention must be paid to the general principle that the introduction of impurities that act catalytically, such as organic carbon from lubricants, is to be avoided. We exclude the possibility of contamination or intermixing with fertilizers containing chloride by strict separation and proper aligning of process streams (raw materials, production, conveying systems, and storage).

BASF's granulation process is such that only saturated steam at a pressure of 8 bar is used for drying.

The finished product is subjected to a special check. Its porosity is an indication of its safety. Porosity is determined by means of the international oil-retention test[2]). The test is carried out on samples that have been taken through the temperature cycle 25 °C → 50 °C → 25 °C twice; that is to say, samples that have gone through the transition point at 32 °C four times.

The bulk density of the product is another quality criterion that forms part of our regular inspection. It should be noted that the bulk density of the product cannot be used as a measure of its porosity.

An important safety point that we observe throughout the process is the avoidance of fast rotation drives, as in chain mills or elevators, for instance, to minimize energy input.

The storage and transport of ammonium nitrate are covered by a large variety of national and international safety regulations.

3. NPK fertilizers

To deal with the safety aspects of NPK production it is first necessary to consider the substances involved.

Although the ability of ammonium nitrate to detonate is completely lost in mixtures with high proportions of other nutrient salts, they remain capable of thermal decomposition.

NPK products are complex mixtures in which a variety of reactions can take place in addition to those which ammonium nitrate can undergo alone. Some of these are shown in Fig. 2. Ammonium nitrate remains the main source of energy, but the heats of reaction can vary within very wide limits, depending on the natures and amounts of the other compounds involved and hence on the reactions that take place. Dissociation (release of ammonia) and elimination of crystal-water are endothermic reactions, which can therefore absorb heat.

Whether thermal decomposition of an NPK fertilizer continues independently and progressively once it has started - so-called cigar-burning - , or whether the reaction comes to a stop depends on the overall heat balance. This can be calculated only theoretically on the basis of models, since not all the reactions involved and appropriate enthalpy changes are known quantitatively.

The trough test[3]) is used internationally to provide an empirical measure of the self-sustaining thermal decomposition of NPK fertilizers Even though its results are also influenced by kinetic effects (catalytic acceleration of the reactions) and melting (which leads to the breaking off the cigar-burning because of loss of contact in the mass of fertilizer) it allows a realistic estimate of the potential hazard.

Cigar-burning can result in the formation within a short time of large quantities of gases, some of which are highly irritant and acutely toxic.

3.1. Production of NPK slurry

From the point of view of processing the production of NPK fertilizers falls into two parts: first making the slurry and then granulation, drying, and conditioning.

The NP solution formed in the BASF-Odda process is mixed with 94% ammonium nitrate solution and additives, then in several stages it is treated with ammonia and concentrated at atmospheric pressure. In the potash mixing unit potassium salts are added, and to obtain a homogeneous mixture the slurry is circulated by an armored radial centrifugal pump. NPK slurry is drawn off for granulation from the circulating stream.

By using drum granulation, which is energetically favorable, the residual water content of the hot NPK slurry (130 - 150 °C) can be 8 - 4 %.

Apart from the possibility of smoldering decomposition, blockage of the circulating pipe due to solidified slurry or hot running of the pumps are sources of potential hazard, either of which could lead to a pump explosion. We therefore take the following precautions:

- The NPK slurry pumps are equipped with three devices that monitor circulation: two independent flow switches on the pressure side (FS^-) and a minimum-current switch (ES^-) for the motor. If any of the three switches is actuated the motor is turned off, after a short delay to allow recognition of false signals.
- Like many of our pumps delivering material containing ammonium nitrate the NPK slurry pumps are fitted with hydraulically loaded double-acting slip-ring seals. The flow of the barrier-water supplied to the pumps is monitored, and if the flow falls below the set minimum after a time delay the pump is shut down.
- The feed for the barrier-water circuit is provided by a tank whose level is controlled. The level control indicates losses. The electrical conductivity of the return water is monitored to detect leaking seals. The barrier-water pressure is maintained such that it is higher than the pressure on the product side; a stand-by pump is switched on should the pressure fall. The barrier-water is cooled by means of a heat exchanger.

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[3]) D.C.Huygen, G.Perbal, ISMA Technical Conference Edinburgh, 14th to 16th September 1965

3.2. Granulation and drying of NPK

The three process units granulation/drying/recycle screening, conditioning/cooling/final screening, and the conveyor system for taking the product to the store are provided with the usual interlocks, and if production is interrupted the process units are switched to recycling.

Hot air is needed for drying NPK (unlike CAN), and this is formed by burning natural gas or oil. The automatic burner controls and the flame monitoring, supplied completely by the manufacturer, guard against hazards arising from the burner unit itself; they must comply with specific national safety regulations. In addition, we regard it necessary to have a safety scheme for the drying process that minimizes the potential danger of thermal decomposition of the hot granules.

Although we make products that the trough test shows to be incapable of self-sustaining decompostion at ambient temperature, we have to take in account the occurrence of cigar-burning during drying. This may be restricted to a pocket of overheated material, but rapid fume-off of the entire content of a drum is known to occur from the literature.

To prevent gaseous decomposition products from entering the building the installed exhaust systems of the drying units must be highly effective and relieable.

To prevent fume-off it is necessary to avoid a general overheating of the whole content of the drying drum. To this end we take a number of precautions:

- The essential part of our instrumentation scheme for avoiding such overheating of the product is the interlocking of the burner with the process. It entails a number of automatic shut downs following rapid closure of the gas or oil supply.
- Apart from rotation of the drum and adequate exhaust removal it is necessary to ensure a controlled stream of hot air with a uniform temperature profile. When granulation is started or there is a breakdown in the supply of slurry the temperature of the drying air is automatically restricted to about 200 °C.
- The temperature of the incoming hot air is controlled during production. If there is a rise in the temperatures of the drying air, the drying drum off-gas, or the product leaving the drying drum the burner is shut down rapidly.
- During running it is possible to switch from fresh air to granulating unit off-gas as a source for the secondary air used for adjusting the temperature of the drying air (recycling granulation off-gas saves fuel). If there is any interruption of the supply of secondary air the burner is shut down immediately.
- We have designed the construction so that no radiant heat from the burner chamber can enter the drying drum.
- For safety reasons the stream of hot air flows in the same direction as the product, although thermodynamically this mode of operation is not optimum.

Apart from these precautions that overcome the risk of fume-off a number of measures are taken that make even small, locally restricted self-sustaining thermal decompostions relatively exceptional. These are primarily technical matters relating to the geometry of the hot-air inlet into the rotary drying drum and the design of the product feed and features within the drum. Their aim is to avoid incrustations in the region of the incoming hot air.

As the occurrence of a minor decomposition in the drying drum and elsewhere - in the region of elevators, conveyors, dust cyclones, and dust conveyors - can, however, not be excluded completely, it is necessary to make arrangements for their early recognition and elimination.

- For early recognition we have fitted all pipes conveying exhaust gases with detectors for nitrogen dioxide.
- If the nitrogen dioxide detectors respond at a low level the drums are kept rotating (to provide cooling by mixing with intact product) and the decomposition is tried to be localized.
- At higher levels, depending on the degree of decomposition we start operations, ranging from applying water to isolated pockets of decomposition locally to flooding the drum by means of fixed emergency water supplies.

As well as taking steps to avoid, detect, and combat cigar-burning we pay attention to the hazards caused in the area of NPK production by hot work such as welding, cutting, and drilling. Here there can be blocked-off deposits of ammonium nitrate. Hidden voids (for instance doubled sheet) are avoided within drums, and the same safety precautions for hollow shafts of equipment for moving material (screw dust conveyors, for example) are followed as in plants handling ammonium nitrate.

4. Product safety

Besides questions concerning product quality we have to consider those safety matters that address the potential hazard arising from the great mass of the stored material. Even if our products are not prone to self-sustaining thermal decomposition, they are subject to national safety regulations because they contain ammonium nitrate, a substance that promotes combustion. From such regulations one can derive technical and organizational requirements for the running of a fertilizer store. Over and above these BASF has a more stringent policy:

- Products are deposited into the store at temperatures higher that ambient temperature. Moreover large heaps of product cool only slowly. So the stocks have raised heat contents compared to samples tested in the trough test. Therefore it is essential to rigorously exclude from stores sources of heat that could lead to thermal decomposition.
- Some mixtures formed from products that by themselves are not capable of self-sustaining thermal decomposition do show cigar-burning. Table 3 lists examples of these, but it must be pointed out that these results apply only to the products we have tested, that is to say, to specific combinations of substances; it is not applicable to NPK formulas in general. To prevent the accidental formation of such a mixture we follow up appropriate storage plans.

Organizational precautions adopted for the safety of stores holding products capable of cigar-burning were not abandoned when we converted our complete range to compounds which do not undergo this type of decomposition; on the contrary, they were supplemented and extended. Current organizational measures are shown in Table 4.

Technical measures begin with bringing the products into the store:

- We take care that the temperature of the product going to the store does not exceed 60 °C. If higher temperatures are measured the conveyor belts into the store are stopped.
- Hot pieces of metal or pieces of metal that could become hot during conveying are automatically removed by metal separators.
- A rotating screen in each product stream into the store provides for removal of clumps of smoldering material.

Some or all of the following graded measures are adopted for early recognition of the decomposition of fertilizers, depending on local circumstances and the size of the depot:

- Regular patrolling should provide for early warning of fires in the building, decomposition, and hot running of parts of the conveyor systems. Guard-control systems ensure that the patrols are carried out. The frequency of the patrols depends on what other forms of monitoring are available.
- Automatic alarms for detecting decomposition (ionization smoke detectors or nitrogen dioxide detectors).
- Video supervision of the store and critical points in the conveyor system (transfer points).

Technical and organizational measures must of course also be taken to deal with possible fires and decomposition.

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Although we have taken all the above mentioned precautions, in our opinion, the best method to minimize the potential hazards in the production, handling, and storage of fertilizers is to manufacture safe products.

Table 1 Review of safety considerations

Step	Aim	Content
1	Hazard potential of process, sources of hazard in the plant	Description of process: -block diagram -flow diagrams Substances: -quantities, distribution -safety properties Environmental pollution: -off-gases, noise, residues, waste water Regulations Basic safety scheme: -plant scheme -pressure release & emptying devices -special requirements -instrumentation scheme for shut-offs Site considerations
2	Details of basic safety scheme	Site plans, construction drawings Layout plan for equipment Escape routes Ventilation & air conditioning of rooms, positions of air intakes Storage of dangerous substances Safety valves etc. Causes of critical conditions Construction measures Fire protection Protection against explosions Special requirements Instrumentation scheme: -protective & monitoring devices -switching systems; cutout systems -cutout signals -redundance & diversity -safety positions of fittings -protection of instrumentation Measures in case of breakdown of services Emission
3	Departures from normal working; effects	Verification of consistency of safety provisions Self-checking of parts of plant

Figure 1

Basic decomposition reactions of ammonium nitrate

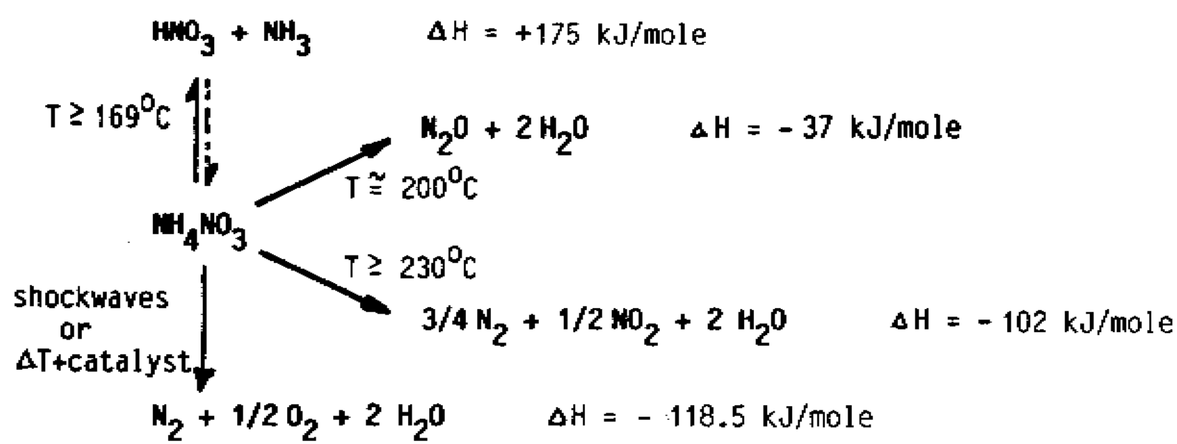

Table 2 Substances that catalyze the decomposition of ammonium nitrate and their control in BASF plants

Hazardous impurity	Possible sources	Operating conditions		How to avoid
		AN synthesis	AN concentration	
Free acid	Process conditions, thermal dissociation	Reactor pH 2.5-4 below 170 °C, 4.5-5.5 above 170 °C	pH 4.5-5.0 before concentration	Monitor pH, add NH_3, avoid overheating, in synthesis base control on amount of NH_3
Cl^-	Raw materials, cooling water	< 10 ppm in HNO_3, zero in NH_3	< 20 ppm	Select raw materials, monitor Cl^- during manufacture of HNO_3
Cu	Raw materials, corrosion of fittings & apparatus	< 1 ppm	< 5 ppm	Use no Cu or alloys (brass, bronze, etc.) for apparatus, fittings, or instruments
Organic C	Raw, auxiliary, and plant materials	< 50 ppm	< 50 ppm	Keep tank area clean, do not return unchecked leakage

Figure 2

Decomposition reactions of NPK fertilizers (examples)

Reactants	Conditions	Products	
NH_4NO_3	$\xrightarrow{T>130°C}$	$NH_3 + HNO_3$	endothermic
$(NH_4)_2HPO_4$	$\xrightarrow{T>100°C}$	$NH_4H_2PO_4 + NH_3$	endothermic
$5\ NH_4NO_3$	$\xrightarrow{Cl^-}$	$4\ N_2 + 9\ H_2O + 2\ HNO_3$	exothermic
NH_4NO_3	$\xrightarrow{T>170°C}$	$N_2O + 2\ H_2O$	exothermic
$4\ NH_4NO_3$	$\longrightarrow$	$3\ N_2 + N_2O_4 + 8\ H_2O$	exothermic
$3\ NH_4NO_3 + 2\ NH_4Cl$	$\longrightarrow$	$4\ N_2 + 9\ H_2O + 2\ HCl$	exothermic
$NH_4NO_3 + KCl$	$\longrightarrow$	$KNO_3 + NH_4Cl$	exothermic
$5\ NH_4NO_3 + 2\ KCl$	$\longrightarrow$	$4\ N_2 + 9\ H_2O + 2\ HCl + 2\ KNO_3$	exothermic
$2\ NH_4NO_3 + C$	$\longrightarrow$	$2\ N_2 + CO_2 + 4\ H_2O$	exothermic

Table 3 Trough tests on 1:1 mixtures of different NPK formulas

12+12+17 S+2	12+12+17 SCl+2	13+13+21 B	13+13+21	15+5+16 S+4	15+9+15 +4	16+16+16	20+20+0	22+22+0	24+8+8	
–	X	X	X	X	X	X	–	–	X	12+12+17 S+2
	–	X	X	X	X	–	X	–	–	12+12+17 SCl+2
		–	–	X	X	–	–	–	–	13+13+21 B
			–	X	X	–	–	–	–	13+13+21
				–	X	–	–	–	–	15+5+16 S+4
					–	–	–	–	–	15+9+15 +4
						–	–	–	–	16+16+16
							–	–	X	20+20+0
								–	–	22+22+0
									–	24+8+8

– no cigar-burning

X cigar-burning occured

Table 4 Organizational measures for stores

1. No admittance for unauthorized persons.
2. No smoking.
3. Regular functional tests of all conveying equipment, electrical installations, and lightning conductors.
4. Cleaning of the store before bringing in stock.
5. No flammable materials (e.g. oil, engine fuels, cleaning rags).
6. No acids or alkali.
7. Removal of caked fertilizer from conveying equipment and parts of the electrical installation.
8. At least 0.5 m clearance between fertilizer and sources of heat.
9. Suspended lamps to be in globes; no covering with fertilizer.
10. Work involving the use of flames or the evolution of heat allowed only when special safety precautions are observed.
11. Comprehensive written operating instructions.

TA/88/15 Safety requirements in fertilizer plants, by Dr. B. PURUCKER, BASF, Western Germany.

DISCUSSION (Rapporteur Mr. P. STOKKA, Norsk Hydro, Norway).

Q - Mr. H. HERO, Kemira Oy, Finland

You consider that NPKs are free of explosive danger. But still they are possible to use as explosives with oil. Is it essential to take into account this hazard ?

A - I think we do not have NPK formulas which, in the limits of maximum 0.4% organic mater, are able to detonate.

Q - Mr. H. HERO, Kemira Oy, Finland

What I mean is exactly that. If there are some impurities in oil, and if there is a danger in some places that it is possible that the oil mixes with, for example, 20:10:10, it can explode then. Have you taken into account that kind of hazard ?

A - We exclude oil impurities in combination with our products, and until now, I do not know of any case that 20:10:10, with the composition of our product, is going to detonate.

Q - Mr. H. HERO, Kemira Oy, Finland

Have you taken any precautions in case of stoppages of spraying nozzles inside of the drum, especially spherodizers ?

A - In the case of drum granulation, we have no special arrangements.

A - Dr. J. ENGERMANN, BASF, Western Germany.

In the case of the spherodizer, we have two things. We have measured the quantity of fluid going to the nozzles. If they are going down, we can clean with vapor very quickly. And the second thing is, when it is not possible, we must drill out the nozzles. The people who are working with this have special clothes to avoid that melt hits the body.

Q - Mr. H. HERO, Kemira Oy, Finland.

Is it the reason you have changed the product from triple 15 to triple 16, that triple 15 made by Odda process is in so called B class ?

A - No, it is not the case. We can also make triple 15 as type "C" fertilizer (free of self-sustaining decomposition).

Q - Mr. H. HERO, Kemira Oy, Finland.

But have you any safety reasons to that change ?

A - No, we have no safety reasons for that change.

Q - Mr. B.K. JAIN, FAI, India

1/ The quantity of the product can be adjusted by the use of internal inorganic stabilizers. Would you please elaborate on what is this internal stabilizer.

.../.../...

2/ The determination of porosity has been mentioned as the indication of the safety. In India, we make 25% N ammonium nitrate. Would you recommend that determination of porosity for that product ?

A - 1/ It is an inorganic salt which does react with the product and stabilizes the product against volume changes by means of temperature changes.

2/ You can measure porosity in your CAN as indication for the safety. But I think in the case of CAN, slight increases in porosity do not change your product to an unsafe product, but you must do the trials.

Q - Mr. A. HAMDI, ICM/SAEPA, Tunisia.

1/ Can you, without any risk, proceed to grinding blocks, approximately 100 to 200 mm, of 33.5% ammonium nitrate ? If so, with which type of grinder ?

2/ Can you recycle low quantities of ammonium nitrate fines in the DAP manufacturing loop ?

A - Dr. ENGELMANN, BASF, Western Germany

1/ I think it is no problem. We use normal centrifugal crushers for this type.

2/ We have no DAP manufacturing loop and I cannot answer your question.

Q - You state that detonation can come from shocks. Is this statement not in contradiction with content of preceding paper ?

A - Dr. R. NITZSCHMANN, BASF, Western Germany.

I think there is a difference between pure ammonium nitrate, and ammonium nitrate from the Odda process having impurities coming from the phosphates, for example Cl-, organic C. So we have higher safety requirements on this ammonium nitrate within our process. And I think the speech given before is only correct for ammonium nitrate which comes from a synthesis of ammonia and nitric acid.

A - Dr. B. PURUCKER, BASF, Western Germany.

Yes, I think I have discussed some differences between types of ammonium nitrate containing material in my paper. The behaviours of pure ammonium nitrate and CAN and NPK are quite different.

Q - Mr. A. BARBERA, Agrimont, Italy

If I have understood you correctly, you do not use oils in the coating drum. How fo you assure the quality of products especially for dustiness ?

A - We use our own method and we have as coating material something like waxtype. We have no oils. Because I think the sensibilisation of ammonium nitrate containing product to go to cigar burning is depending on the incorporation of any organic materials which you bring on the outside of your product. We have done trials with antidusting oils and we could show that, depending on the chemical composition of the NPK product, you can bring safe products with antidusting oil to cigar burning.

.../.../...

Q Mr. G. KONGSHAUG, Norsk Hydro, Norway.

1/ About safety, I feel you are talking very much black and white. In the beginning of your paper, you say that the greatest potential danger lies in the ability of ammonium nitrte to detonate when subjected to mechanical shock. This is the property that has led to a number of serious accidents. Can you tell us more about these accidents ?

2/ You are taking about self-sustaining decomposition and burning due to local overheating in the drying unit. The burner test is a classification test, and I think that we shall stay with that, and not talk about the cigar burning test. Because when you have local overheating, all NPK will decompose. At the end of your paper you say that the best method to minimize the potential hazard is to produce safe products. Can you mention any product which is not safe ?

A - Let me begin with your last question. I think products we produced were capable of cigar burning and capable of cigar burning at a high speed. In my opinion, these are not sufficiently safe products, in respect to storage of fertilizers and accidents which may occur by the burning of stores for instance. If I have understood your question right, overheating in drying drums and smouldering - let me say smouldering - decomposition of products is not excluded when we go to products that in the trough test do not show cigar burning. But I think the potential of decomposition is lowered significantly also in this case. We have set up some other safety rules to lower the danger of decomposition in the drying drum as I have shown this in my paper: some construction details which I have not mentioned in detail, that overcome the risk of overheating in the product inlet of the drying drum.

The potential danger of ammonium nitrate. I wanted to give you an overview of the safety aspects of ammonium nitrate containing fertilizers. I have taken some points out of the literature, and this is a point you can read in the literature according to ammonium nitrate. I do not know in the special case the influence of very little trace amounts, as for instance organic carbon, in so-called pure ammonium nitrate, for the detonation ability and therefore I cannot tell you more.

Q - Mr. J.M. BIRKEBAEK, Superfos Fertilizers, Denmark.

I would like to know how you avoid the potential risk of decomposition of dust in the ductings when you recirculate air from the dryer back to the front end, I suppose you mix that with hot air coming from the burner.

A - The recycled dust amount is very low because it is equal to the amount of dust going out of the plant, and this dust is decomposing in the burner. And you get slightly higher amounts of NOx for instance in your off-gas as without recycling gas, but it is not very significant.