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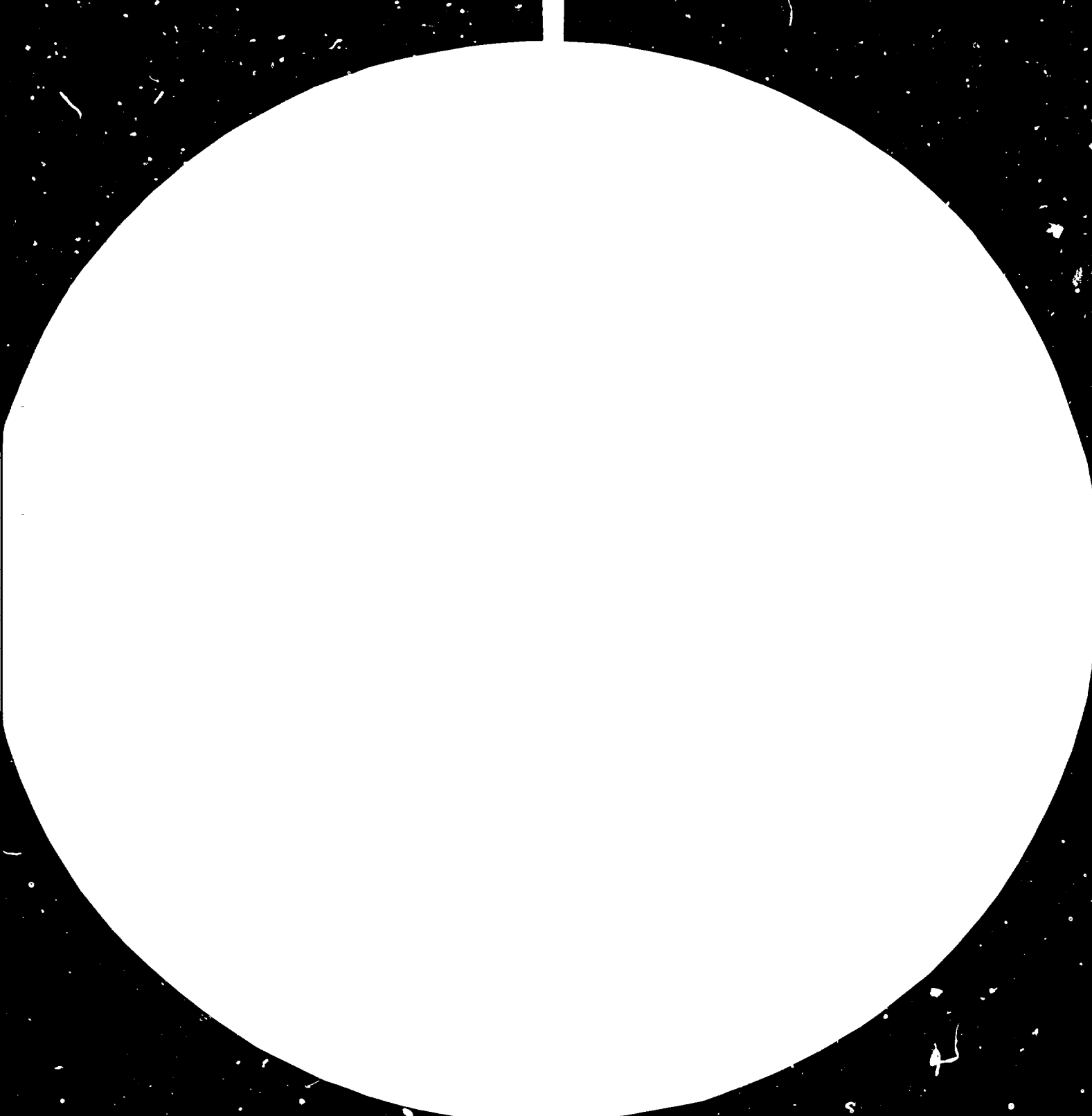
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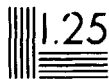
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SAFETY ASPECTS OF PRODUCTION, STORAGE AND TRANSPORT OF
FERTILIZERS CONTAINING AMMONIUM NITRATE *

by

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901017

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1. Introduction

The safety aspects of production, storage and transport is a very extensive subject, so a choice has to be made over the contents of this paper.

After a brief summary of the hazards inherent to fertilisers containing ammoniumnitrate this paper will highlight the special features of the transport and storage regulations. In this connection special attention will be paid to new developments. Further much attention is being paid to selfheating risks in production and storage.

2. Hazardous properties of ammoniumnitrate containing fertilisers

Fertilisers containing ammoniumnitrate posses a very complicated hazardous character.

In order to clarify the meaning of the terminology used in this paper, a short description will be given of the most important hazardous properties of these fertilisers.

- Detonation

First it should be explained that only fertilisers with an ammoniumnitrate content of more than 70 - 80% can have this property; see also chapter 3.

Detonation is a heterogeneous explosion where the energy transport is mainly accomplished by a shock wave. The shock wave propagates with supersonic velocity through the mass of product. Detonation speeds can vary from about 2000 to 8000 m/sec. in different substances. For ammoniumnitrate and mixtures thereof the shock-wave velocities vary between + 1800 - 2800 m/sec.

The pressure in the shock-wave can reach values of about 100.000 bar so that the gases expand extremely fast after the detonation wave has passed. It is obvious that detonation waves are very powerful and destructive. Detonations are extremely dangerous and many of the explosion disasters with fertilisers are the result of detonations (Oppau, Brest, Texas City).

On the other hand, the sensitivity to detonation of ammoniumnitrate and in properties comparable mixtures is very low. As a result for initiation a strong booster charge is needed.

- Self_sustaining_decomposition (cigar burning)

The phenomenon self-sustaining decomposition of compound fertilisers is actually a very slow form of what in explosion technology is called a deflagration. Self-sustaining decomposition is characterized by the propagation of a reaction zone with a velocity between 2 and 150 cm/hr.

The transfer of energy to the successive layers takes place by heat conduction, convection and radiation. The self sustaining decomposition can be started by heat sources. In general surface temperatures > 110°C can be dangerous within a relative short period.

Depending on the composition of the fertiliser, reaction zone temperatures have been measured between 300 and 550°C. The hazard of a self-sustaining decomposition is the simultaneous development of large amounts of gases containing N₂, NO, NO₂, HCl, NH₄Cl and a high percentage of water vapour (+ 65%). The amount of gas developed can vary between 20 and 45% by weight of the fertiliser. It should be emphasized that the self-sustaining decomposition needs no oxygen from the air for its reaction mechanism.

- Self heating

By self-heating is understood the phenomenon whereby the temperature rises spontaneously throughout the entire mass. Self-heating occurs when the heat production throughout the whole mass of product exceeds the heat loss through conduction. Such self-heating may reach temperatures where hazardous decomposition reactions of AN become dominant. Depending on the composition of the fertiliser it can lead to either a slow decomposition or a very violent one (if the fertiliser possesses also the property of self-sustaining decomposition). Fundamental to this type of self-heating is the self-insulating effects of the granular mass. Consequently this mechanism will hold only if the mass retains its granular structure. Should melting occur then a different situation appears due to heat loss by convection.

It has to be emphasized that self-heating is not an inherent property of fertilisers containing ammoniumnitrate and will only occur under certain conditions as will be explained later in chapter 4.

- Fume off

Fume off is a type of self-heating generally used to denote a homogeneous decomposition of molten product. In such cases where no self-insulation is present and heat loss takes place by convection, the entire mass must be at a uniform high temperature in order to establish such a homogeneous decomposition; i.e. generally at temperatures > 180°C.

Depending on the composition of the fertiliser the character of the decomposition can vary between violent and very violent and can under atmospheric conditions reach temperatures between 200 to 300°C. It is obvious that fume off can take place almost exclusively in the production process.

- Oxidizing capacity

Oxidizing capacity is the potential of a product to support combustion. Although ammoniumnitrate has oxidizing properties it is generally considered as a very weak oxidizing substance. In fertilisers it has been shown that this property becomes measurable above 70% AN, whereas mixtures able to perform self-sustaining decomposition have no oxidizing properties. From this it may be concluded that oxidizing capacity is of minor importance. Especially if it is realised that this oxidizing capacity is overruled by the far more important property of detonability which may be covered by the same range of AN-contents.

3. Transport and safety regulations

A number of accidents in the sixties started extensive research into the hazards of transporting and storing fertilisers containing ammoniumnitrate. The results of these investigations were the basis of a new hazard classification for the fertilisers in the IMCO-Dangerous Goods Code for Seagoing Vessels and the legal storage regulations in the Netherlands; both adopted in 1968. Afterwards this classification system got international recognition and became adopted in many countries particularly in Europe.

A brief summary of this hazard classification will be given.

The following groups are recognised:

- Type_A (class 5.1 of IMCO-code)

Ammoniumnitrate fertilisers of this group may present a risk of explosion (detonation) when involved in a major fire or being subjected to a detonation shock wave.

The following compositions are considered to be of type A:

| <u>mixture</u> | <u>AN-limits</u> | <u>added combustible matter (organic matter calculated as carbon)</u> |
|---|------------------|---|
| AN/inert | ≥ 90% | < 0,2% |
| AN/inert | ≥ 70% and ≤ 90% | < 0,4% |
| AN/CaCO ₃ AN/CaCO ₃ .MgCO ₃ | ≥ 80% and ≤ 90% | < 0,4% |
| NP/NK/NPK | ≥ 70% and ≤ 90% | < 0,4% |
| AN/(NH ₄) ₂ SO ₄ | ≥ 45% and ≤ 70% | < 0,4% |

- Type_B (IMCO class 9)

Ammoniumnitrate fertilisers of this group are free of the risk of explosion but may be subject to self-sustaining decomposition when heated.

Classification of this group of fertilisers is bound to testing. The assessment is ascertained by means of the so called "trough test" as described and dictated in the IMCO Dangerous Goods Code.

Note: Fertilisers containing chloride and with AN-contents between 15 and 60% are regarded to be suspected of self-sustaining decomposition.

The classification of Type A and B is used as well in transport as storage and is also included in the United Nations list of hazardous substances; UN no. 2067, 2068, 2069, 2070 and 2071. The following classifications are only being used for storage purposes.

- Type_C

Ammoniumnitrate - and nitrate - containing fertilisers free of the risk of explosion and self-sustaining decomposition i.e. not of type A and B.

This group of fertilisers is of low risk. For instance many can decompose during external heating (in a fire) and then develop

poisonous gases and fumes. Others, such as calcium, potassium and sodium nitrates, can support a fire by supplying oxygen. Nitrate impregnated wood e.g. floors, walls etc. can be very combustible.

- Type_D

Fertiliser solutions or suspensions containing not more than 45% AN and which can present an explosion risk when dry.

Note: This class of products is only regulated accordingly in West-Germany.

New technical developments in the production of fertilizer grade AN (type A) have resulted in a more safe product; i.e. products stabilized against detonation. This stabilisation is of physical nature and will only work as long as the granules retain their structure. When desintegrated or molten, the product has lost this stabilisation. The aim of stabilisation is the prevention of a mass detonation and consequently a disaster. What this aim means is that a small explosion in contact or in the vicinity of a large pile will not set off a detonation in the pile. Within the EEC these views have led to the opinion that such stabilized products can be allowed to be stored under less stringent rules. This has resulted in an EEC-directive adopted last July. This directive contain requirements in order to safeguard a minimum quality. The requirements are given in the annexes of the directive and are detailed here:

Annex_1 - (Requirements to be observed by the manufacturer)

Characteristics of and limits for straight ammonium nitrate fertilisers of high nitrogen content

1. Porosity (oil retention)

The oil retention of the fertiliser, which must first have undergone two thermal cycles of a temperature ranging from 25°C to 50°C, must not exceed 4% by weight.

2. Combustible material

The percentage by weight of combustible material measured as carbon must not exceed 0,2% for fertilisers having a nitrogen content of at least 31,5% N by weight and must not exceed 0,4% for fertilisers having a nitrogen content of at least 28% but less than 31,5% by weight.

3. pH

A solution containing a soluble portion of 10 g of the fertilizer in 100 ml of water must have a pH of at least 4,5.

4. Size analysis

Not more than 5% by weight of the fertiliser must pass through a 1 mm mesh sieve and not more than 3% by weight must pass through a 0,5 mm mesh sieve.

5. Chlorine

The maximum chlorine content is 0,02% by weight.

6. Heavy metals

Heavy metals should not be added deliberately, and any traces which are incidental to the production process should not exceed the limit fixed by the Committee of EEC.

Annex 2 - (Control test method of the authorities)

Description of the test of resistance to detonation referred to in Article 7

The test must be carried out on a representative sample of fertiliser. Before being tested for both resistance to detonation and oil retention, the whole mass of the sample is to be thermally cycled not more than five times.

The fertiliser must be subjected to the test of resistance to detonation in a horizontal steel tube under the following conditions:

Seamless steel tube:

Tube length 1,000 mm

Nominal external diameter 114 mm

Nominal wall thickness 5 mm

Booster the type and mass of the booster chosen should be such as to maximize the detonation pressure applied to the sample in order to determine its susceptibility to the transmission of detonation

Test temperature 15° to 25°C

Witness lead cylinders 50 mm diameter

for detecting detonation 100 mm high

placed at 150 mm intervals and supporting the tube horizontally. The test is to be carried out twice. The test is deemed conclusive if in both tests one or more of the supporting lead cylinders is crushed by less than 5%.

This directive will be incorporated in the Dutch Storage regulations as "Type A 2" products; "Type A 1" is then applicable to products only satisfying the old definition.

For the purpose of drafting internal safety procedures a review is given of some safety regulations or recommendations, which should be regarded as being up to date and which also follows the previously described classification.

In this connection important are:

Sea transport

- IMCO - Dangerous Goods Code (IMDG-Code).

This code regulates only the transport in packaged form.

- IMCO - Code of Safe practice for Bulk Cargoes.
This code deals only with bulk shipments.

Both codes are obtainable from the secretariat of the Inter-Governmental Maritime Consultative Organization, 101 - 104 Piccadilly London W1V 0AE, England.

Storage

- The storage of ammonium nitrate fertilisers and fertilisers containing ammonium nitrate (English and France).
Brochure issued by ISMA/APEA (at the moment under revision).

Obtainable in due course (+ 9 months) from the secretariats of both organisations.

ISMA ltd.
28 Rue Marbeuf
75008 Paris
France

APEA
Bleicherweg 33
CH 8002 Zurich
Switzerland

- Report on the safe transport and storage of nitrate containing fertilisers. (English). Report of the committee "Prevention of disasters caused by dangerous substances" (Dutch legal regulations).

Obtainable from: Ministerie van Sociale Zaken
Directoraat Generaal van de Arbeid
Balen van Andelplein 2
2270 HV Voorburg
Netherlands

- Storage of ammonium nitrate and fertilisers containing ammonium nitrate (German). West-German legal regulations.
Arbeitsstoffverordnung Anhangs II nr. 11
Ammoniumnitrat
Bundesgesetzblatt Teil 1, nr. 107 (17-9-'75).

from: Bundesgesetzblatt
Postfach 624
53 Bonn 1
West-Germany

ISMA/APEA is just printing a new leaflet giving "Recommendations for the Safe Handling of Fertilisers containing Nitrogen".

The aim of this leaflet is to inform the dealers and consumers in developing countries about the safe handling of fertilisers containing nitrogen (including ammonium nitrate). ISMA/APEA have pleasure to present this leaflet at the UNIDO seminar in New Delhi; about 60 copies will be made available at the seminar.

Obviously all these codes contain directives for:

- Measures intended to prevent the starting of a fire, self-sustaining decomposition or detonation.
- Measures intended for fighting a fire or self-sustaining decomposition once it has started.
- Measures intended to limit the consequences of a fire, self-sustaining decomposition or detonation.

Detailed treatment of these recommended safety codes is too extensive for this paper, the most relevant parts will be dealt with at the seminar.

4. Self heating of complex fertilisers

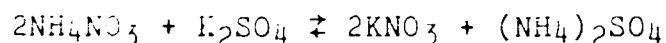
An explanation of the phenomenon of self heating has already been given in chapter 2. Serious self heating that leads to an accident is not an inherent property of this group of products. Studies of accidents have shown that in each of the events the fertiliser were produced in a faulty way. When not correctly produced, fertilisers with an ammonium nitrate content as low as 5% can give rise to serious self heating i.e. they can warm up the entire pile in a store to temperatures higher than 100°C. As a result of this ammonium nitrate content not only type C products, but also type B products may be involved.

It is obvious that self heating of type B products may result in an serious accident. In such cases temperatures between 300 and 600°C can be reached.

Experience with compound fertiliser production has shown that continuous rise in temperature may occur during the first days of storage. This rise in temperature is very common and will generally not exceed 3 - 10°C above the initial storage temperature and may be regarded as non hazardous.

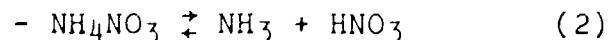
This heating effect can be explained by:

- The completion of reciprocal conversions, e.g.



- Heat of crystallisation, due to the inclusion of small amounts of under cooled salt solution.
- The formation of double salts of ammonium nitrate with other salts, e.g. $\text{NH}_4\text{NO}_3 \cdot \text{KNO}_3$, $\text{NH}_4\text{NO}_3 \cdot 2(\text{NH}_4)_2\text{SO}_4$, etc.

In itself these heat effects are not sufficient to reach a temperature of about 70°C, the temperature range where the decomposition of ammonium nitrate becomes measurable. Above this temperature ammonium nitrate decomposes mainly according to the following reactions:



Above 200°C other decomposition reactions will occur simultaneously and will become dominant at higher temperatures.

The necessary H⁺-ions to catalyse the decomposition reactions are being produced by the loss of ammonia, due to its higher vapour pressure than that of the nitric acid; see reaction (2).

Summarising it may be concluded that hazardous self heating can only occur when some other exothermal reaction serves as the initiating reaction to pass the 70 - 80°C.

Since the mechanism of self heating is different for temperatures below and above 70°C, it is obvious that the treatment of the subject will be accordingly divided into two parts.

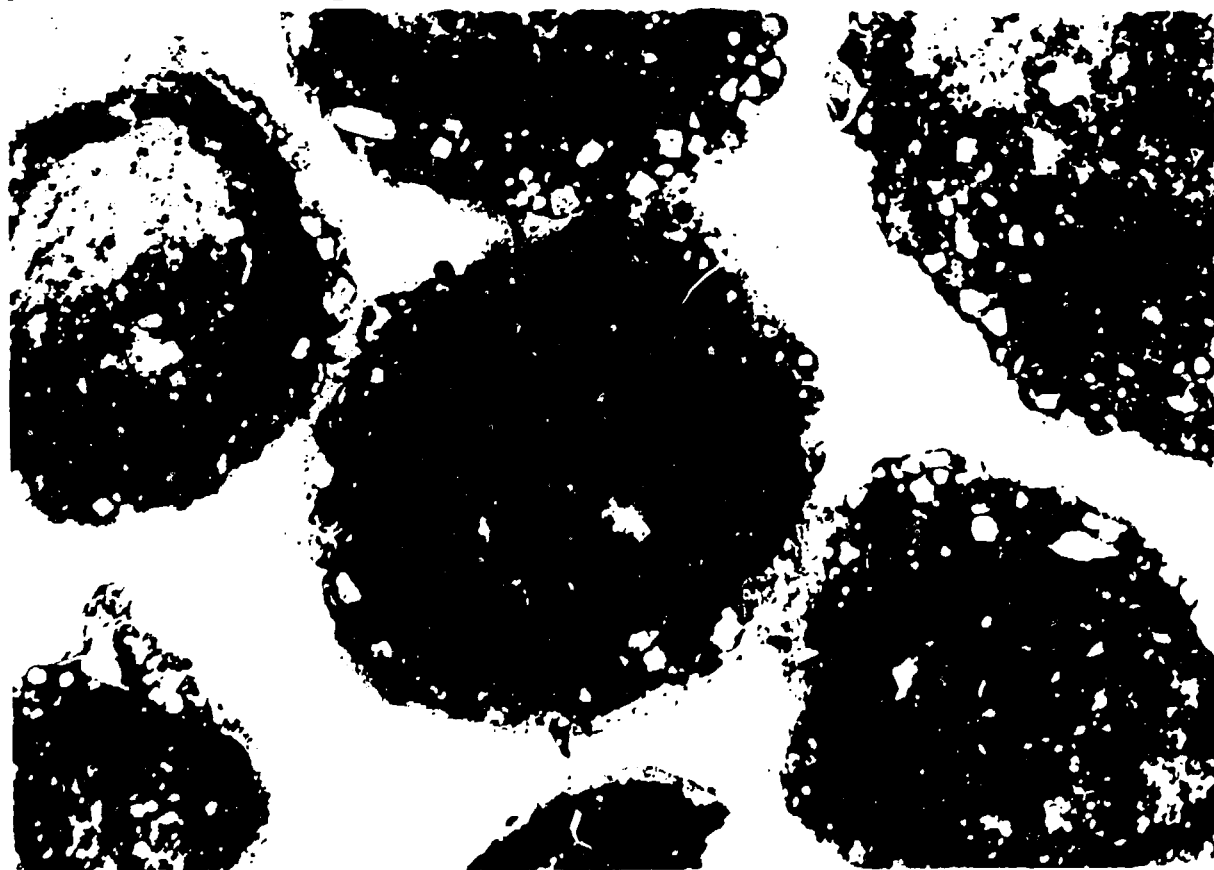
Self heating below 70°C:

As already stated this part of self heating is crucial for the safe storage and transport of these fertilisers. It has to be emphasized that according to the IMCO Dangerous Goods Code the transport of self heating fertilisers is not allowed.

As already mentioned the rise in temperature of about 3 - 10°C during the first days of storage, are considered to be normal and not sufficient to start a runaway reaction. As a consequence self heating from about 40°C can only develop in cases of faulty production. From accidents in the past the following causes are known:

1. Delayed neutralization effects during storage (e.g. due to slow reaction alkalis such as Limestone. The same may happen when the granules do not possess a homogeneous structure, so that an overall neutralization is not accomplished during production.
2. Organic material originating from the phosphates or the coating of the granules become oxidized when the pH is below about 4,5; the pH of ammonium nitrate itself.
3. Contamination. Depending on the quantity, dispersion and nature of the contaminants, this may result in general self heating or the formation of so called "hot spots". Known examples of such events are contamination by sulphur-powder and metal powders viz. Fe en Zn.

It is obvious that combinations of these points may occur in practise. What is meant under point 1 may be illustrated by the photomicrograph below showing a crosssectional preparation of compound fertiliser granules (6+24+18).



The granule has a heterogeneous build up and consists of a triple super phosphate nucleus with an annulus made up of ammonium nitrate, di-ammonium phosphate and muriate of potash. In storage this product showed self heating to a temperature as high as about 150°C, due to its heterogeneous structure with free phosphoric acid and a high content of organic matter inside the triple super phosphate nucleus. The dark rim around the triple-super phosphate nucleus represents the layer where these self heating reactions took place. In this connection it should be mentioned that single super phosphate is produced sometimes by using spent acids, which may give rise to an excessive high content of organic matter. In connection with point 3 it should be remarked that also foreign trace elements such as copper, chromium, cobalt and nickel have a lowering effect on the decomposition temperature.

Self heating of ammonium nitrate containing compound fertilisers under storage conditions can be prevented if the following points are observed during production:

- Control of organic substances in raw materials and coating. If necessary followed by measurement of the effect of these organics on the tendency to self-heating.
- pH of the fertiliser preferably not lower than 4,5. Be sure that neutralization is complete before fertiliser is sent to storage.
- Raw materials should preferably be finely divided before use.
- Cooling of final product to at least below 50°C and preferably below 40°C before it is sent to storage.
- If foreign trace elements have to be added, investigations should be made to estimate the effect on the self heating characteristics of the original fertiliser.

If difficulties are encountered during production, temperature of the product must be followed during storage. This can be done by the aid of thermocouples. Moreover direct measurement of the temperature in the heap is the best test method for self heating. It should be emphasized that the heap must be dismantled immediately if the temperature in the centre passes 70°C.

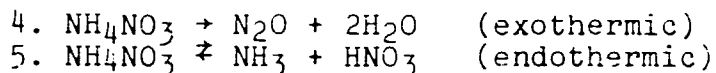
Self heating above 70°C

This part of the self heating trajectory is important for situations in the production process where temperatures much higher than 70°C can occur.

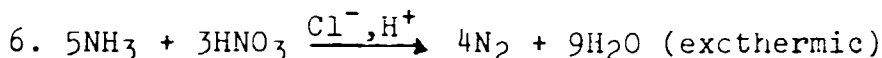
As already explained ammonium nitrate decomposes only under the condition that the pH < 4,5. The lowering of the pH takes place during the so called induction period where the following reactions may occur.

1. $(\text{NH}_4)_2\text{HPO}_4 \rightarrow \text{NH}_4\text{H}_2\text{PO}_4 + \text{NH}_3$
2. $\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow \text{H}_3\text{PO}_4 + \text{NH}_3$
3. $\text{NH}_4\text{NO}_3 \rightarrow \text{HNO}_3 + \text{NH}_3$

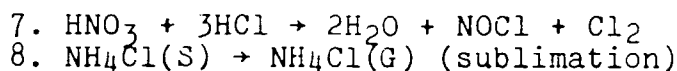
After this induction period and between 70 - 180°C ammonium nitrate decomposes mainly as follows:



Above 180°C the decomposition mechanism becomes much more complicated e.g. in the presence of Cl⁻ ions, Cu, Cr or Co the reactions of the self sustaining decomposition become dominant, following the overall reaction



In this connection the following secondary reaction occurs,



To which extent the above mentioned reaction will take part in the self heating reaction mechanism, depends on the composition of the fertiliser itself. Self heating problems may be solved theoretically by the Frank and Kamenetzki mathematical model. According to this model the risk of self heating is expressed as the critical radius above which self heating occurs. For a spherical mass this relation is expressed as follows:

$$R_c = \left(\frac{3,32 \lambda T^2}{nQB} \right)^{\frac{1}{2}}$$

where: R_c = critical radius
 λ = coefficient of thermal conductivity
 R = gas constant
 n = number of mols/cm³
 Q = heat of reaction
 K = rate of reaction
 B = activation energy for reaction
 T = initial uniform temperature (Kelvin)

However the self heating mechanism in these fertilisers, outlined in the above given reactions, is far too complicated to allow such a theoretical treatment.

The solution to this problem was found by estimating this critical radius empirically with an isothermal method of TNO-Netherlands. The Frank - Kamenetzki equation for standardized conditions can be simplified to

$$R_c = C_1 + \frac{C_2}{T}$$

It is obvious that if the empirically estimated figures follow the theory, a linear function will be obtained when R_c is plotted against $1/T$.

For a number of compound fertilisers the critical dimension for cube shaped masses were estimated and plotted accordingly.

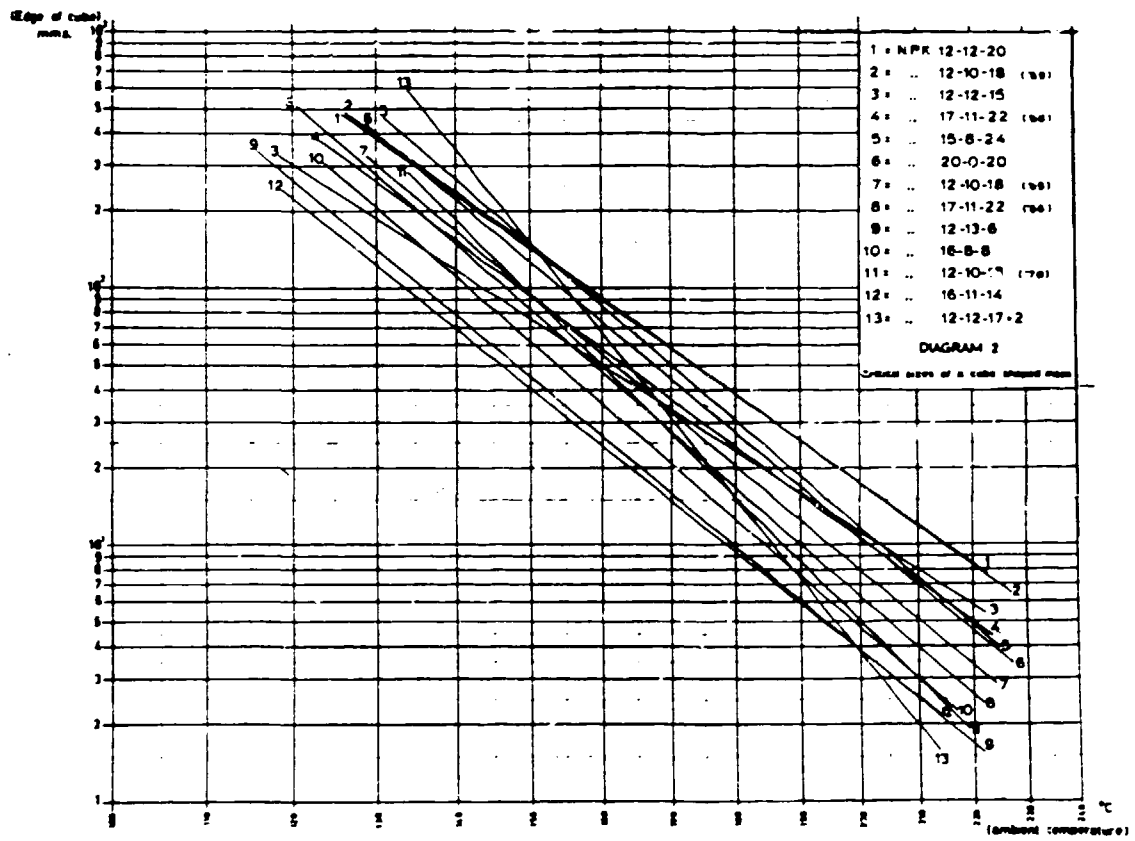


Fig. 2 - R_c -plot of various compound fertilisers.

The chemical analyses of these compound fertilisers are shown in the following table.

Table 1

Chemical analysis of the compound fertilisers under investigation

| product | total N | NH ₃ -N | water soluble P ₂ O ₅ | citrate soluble P ₂ O ₅ | acid soluble P ₂ O ₅ | K ₂ O | Cl ⁻ | SO ₄ ²⁻ (total) | CaO (total) | H ₂ O (KF) | pH | horizontal decomposition velocity (trough-test 15x15x50 cms) cms/hr |
|--------------------------|---------|--------------------|---|---|--|------------------|-----------------|---------------------------------------|-------------|-----------------------|------|---|
| 12-12-20 | 11.9 | 6.5 | 4.0 | 11.7 | 11.7 | 20.7 | 1.3 | 22.9 | 7.8 | 0.97 | 5.90 | 6 |
| 12-10-18 | 13.1 | 8.0 | 7.3 | 10.6 | 11.0 | 18.0 | 10.6 | 12.5 | 7.0 | 0.55 | 6.00 | 11.3 |
| 12-12-15 | 12.9 | 7.1 | 9.7 | 10.8 | 11.2 | 15.8 | 3.4 | 18.3 | 6.5 | 0.79 | 5.80 | 5 |
| 17-11-22 | 17.5 | 10.6 | 10.9 | 11.4 | 11.6 | 22.1 | 17.7 | 0.7 | 6.1 | 0.3 | 7.09 | 10 |
| 15- 8-24 | 15.2 | 9.0 | 6.9 | 7.2 | 7.6 | 25.2 | 14.1 | 8.9 | 2.0 | 0.49 | 7.70 | 10 |
| 20- 0-20 | 19.6 | 11.0 | - | - | - | 20.4 | 16.0 | 9.2 | - | - | 6.9 | 18.2 |
| 12-10-18 | 12.4 | 7.7 | 9.0 | 9.8 | 10.2 | 18.2 | 13.2 | 14.4 | 5.8 | 1.9 | 4.95 | 15 |
| 17-11-22 | 16.7 | 10.2 | 10.5 | 10.5 | 11.2 | 22.0 | 17.3 | - | - | 0.18 | 7.1 | 10.6 |
| 12-13- 6 | 12.6 | 7.2 | 10.1 | 13.0 | 13.3 | 5.6 | 6.1 | 17.8 | 13.9 | 0.6 | 5.07 | 11.3 (trough test 10x10x50 cms) |
| 16- 8- 8 ¹⁾ | 12.6 | 7.6 | 8.0 | 8.9 | 9.1 | 9.8 | 11.1 | 12.1 | 6.5 | 1.1 | 5.85 | 10.3 |
| 12-10-18 | 12.1 | 7.1 | 8.2 | 9.8 | 10.2 | 18.1 | 14.5 | 14.5 | 7.5 | 0.49 | 5.0 | 20.6 |
| 16-11-14 | 15.4 | 7.9 | 4.2 | 10.7 | 10.7 | 15.3 | 11.8 | 5.3 | 6.9 | 1.1 | 5.6 | 32 (trough test 5x5x50 cms) |
| 12-12-17-2 ²⁾ | 12.1 | 6.5 | 5.0 | 11.9 | 12.2 | 17.9 | 8.0 | 9.4 | 9.4 | 0.31 | 5.77 | 40 (trough test 10x10x50 cms) |

1) MgO = 4.5%
 Cu = 0.35%
 Co = 0.04%

2) MgO = 1.7 %
 B = 0.1 %
 Mn = 0.1 %
 Cu = 0.04 %
 Zn = 0.02 %
 Co = 0.0005%

According to this plot, self heating will only take place when a cube shaped storage represents a situation above the given lines. Below the lines all situations are subcritical and will only show further cooling due to dissipation of heat. Extrapolating the line of the most hazardous product (nr. 12) to a temperature of 70°C, then it is found that this may represents a self heating hazard when the edge of the cube shaped storage is over 7 m. From these figures it may be concluded that self heating from temperatures of below 70°C cannot be caused by the common decomposition reactions of ammonium nitrate.

The addition of foreign trace elements such as Cu, Co, Cr, etc. generally result in a lowering of the critical lines and usually also in a change of the slope of the lines; see in this connection fig. 3.

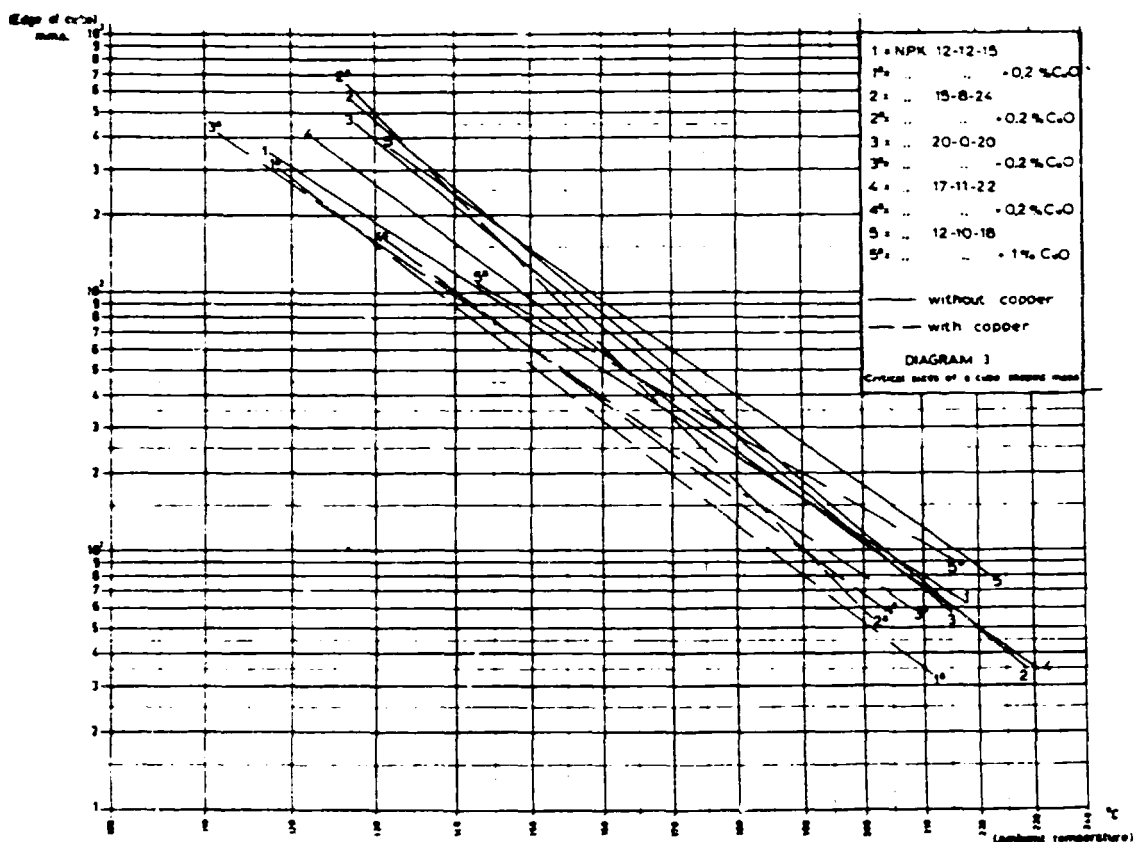


Fig. 3 - effect of Cu on the critical dimensions.

It should be emphasized that addition of Cu or other foreign trace elements not only affects the critical dimensions but also considerably accelerates the decomposition velocity of the self sustaining decomposition.

As already explained in the beginning of this paragraph this part of self-heating is particularly important for situations in the production process. The next chapter will deal with the application of diagram 2 to rotary dryer operation.

5. Safety in rotary dryer operation

To obtain a product of high quality generally the water content is an important factor. In the production process two points control this water content viz. the ammonium nitrate concentrator and the rotary dryer or the spherodizer. Generally the ammonium nitrate concentration plant is rightly considered as hazardous when incorrectly operated.

Changing of the process conditions such as temperature and pressure, will only be done after full consideration and additional safety requirements. On the contrary the attitude with respect to safety of the rotary dryer or the soherodizer is not of the same level, especially if the product is regarded as non-hazardous. This type of equipment is operated with inlet flue gas temperatures ranging from 100 - 400°C.

A high temperature of the inlet flue gases will not necessarily result in an accident, but in case of mal functioning of the equipment this heat input may start off a spontaneous heating of the entire mass in the dryer. Many people are not aware that most of the dryers are being operated in the temperature range of the induction period of spontaneous heating of the fertiliser. Under such conditions spontaneous heating may even occur with products with rather low ammonium nitrate contents. The hazard of such an accident is brought about by development of tons of decomposition fumes, containing NO, NO₂, HCl and Cl₂, within seconds. Two serious fatal accidents of this kind have happened in the past.

The main part of this chapter will be devoted to the safe temperature conditions in relation to spontaneous heating and the measures to be taken to prevent such accident in rotary dryer operation.

It should be mentioned that also in the past small decompositions have occurred in rotary dryers. Generally this is caused by the hot inlet flue gases blowing against fertiliser caked to the lifters or in case of oil-firing sparks may occur and also start local decomposition. However both cases can be prevented by a proper design of the equipment and is outside the scope of this chapter.

With the aid of the evidence given in the former paragraph, diagram 2 and table 3, a short review will be given about the lines which have been followed and have led to the proposed safety condition for rotary dryer operation.

For the study, use has been made of the critical radius lines, representing the most hazardous and practically non-hazardous products e.d. R_c-lines 1, 12 and 13 of diagram 2.

Extrapolations of the critical radius lines has been carried out by the aid of the equation

$$R_c = K_1 + \frac{K_2}{T}$$

The risk analysis will be made by means of a number of fictitious operation disturbances, which are considered to be reasonable.

- A failure of the electrical supply which results in a stand still of the drum. The inlet flue gases are switched automatically to the open air. In case of a rotary dryer of a diameter of 3 m, a layer product of 65 cm height is regarded as normal. To use the critical radius diagram it may be assumed that the layer is comparable to a cube with edges of 60 cm. Extrapolation of line 1 and 12 to a cube size of 60 cm result in the following figures.

(line 1) $R_c = 600 \text{ mm}$ $T_a = 122^\circ\text{C}$

(line 12) $R_c = 600 \text{ mm}$ $T_a = 105^\circ\text{C}$.

From these figures it may be concluded that it is sensible to maintain the product temperature not higher than about 105°C . Otherwise there is a risk of self heating of the entire content of the drum under the assumed conditions.

- This new case is nearly identical to the former one. In contrast to that case, it is now assumed that the inlet flue gases will still be fed to the dryer during this stand-still. Next to the self heating effect as described in the previous case, the flue gases are now heating the surface of the fertiliser bed. This process result in a temperature gradient which starts an accelerated self heating effect in the surface layer. The influence of higher temperatures is illustrated by the following figures read off in diagram 2.

| | <u>160°C</u> | <u>200°C</u> |
|-------------------------|--------------|--------------|
| R_c (product line 1) | 9 cm | 1,7 cm |
| R_c (product line 12) | 2,4 cm | 0,4 cm |

These figures confirm that this risk is realistic, especially in the case of 200°C where the critical radius (cube edge) approaches even the size of a granule. Under such conditions the induction period is very short and becomes a matter of minutes. The mathematical relationship between the induction period (time) and T is of the same form as R_c and T i.e.

$$t_{\text{ind}} = K_1 + \frac{K_2}{T}$$

where t_{ind} = the induction time

T = initial uniform temperature

K_1 and K_2 = constants

To get an impression of the order of magnitude of the induction period, some experimental data obtained from the underlying investigation are given below:

| | 2 cm edge | | 8 cm edge | |
|---------|-----------|----------|-----------|------------|
| | 160°C | 200°C | 160°C | 200°C |
| line 1 | ND | ND | ND | 3 hrs. |
| line 12 | ND | + 9 min. | 10 hrs. | + 18 mins. |

Where: ND = no decomposition; the mass is sub-critical.

It have to be emphasized that at the higher temperature, the bigger size cubes will show discrepancies. This is explained by the fact that the surface layer turned out to be super critical before the whole cube reaches this state.

As a consequence burning of the outer layer will occur. Returning to the postulated conditions of the dryer, it is obvious that in case of a flue gas temperature of 200°C this will lead in a rather short period to surface burning. decomposition is not so hazardous as decomposition of the entire mass as described in the first case, but due to its high product temperature the decomposition velocity is much higher than measured in the trough-test. However it may still be a serious accident.

For a safe dryer operation, flue gas temperatures not higher than about 160°C seem to be preferable.

- Another risk arises if the temperature control of the inlet flue gases will not work, perhaps due to a defect in which the hot flue gases ($t > 200^{\circ}\text{C}$) are not switched to open air. This may especially be dangerous when starting up the plant and the product is recirculated over the dryer. Obviously this gives a steady increase of the product temperature and results in a decomposition of the entire mass of the rotary dryer in a few seconds. This happened in the two accidents mentioned in the start of this chapter. Since in this case the product is continuously moving in the rotary dryer the mass of product is not able to build up the self insulating effect. This means that heating will be continued till the critical diameter is equal to the granular size. Extrapolation of diagram 2 to granular size results in the following figures.

| | | <u>line 13</u> | <u>line 1</u> |
|----------------------|---------------------|----------------|---------------|
| $R_c = 2 \text{ mm}$ | $t_{\text{crit}} =$ | 210°C | 263°C |
| $R_c = 3 \text{ mm}$ | $t_{\text{crit}} =$ | 204°C | 255°C |

From these figures it may be concluded that an important part of the NPK-fertilisers will be super critical in granular state at temperatures between 205 and 265°C. Moreover at these temperatures induction periods are very short; generally a matter of minutes.

- Summarising the recommendations for safe rotary dryer operation:
The given analysis leads to the following recommendations:

- . product temperature not higher than 105°C;
- . the inlet flue gas temperature not higher than 160°C.

To safeguard these conditions the following provisions have to be observed:

- . temperature control + alarm on the inlet flue gases;
- . temperature indicator + alarm on the outlet flue gases;
- . when the dryer comes to a stand still the flue gases must be switched to open air or the burners must be stopped automatically.

Note: If the period of stand still is more than half an hour, the temperature of the product in the dryer has to be measured continuously. When a steady increase in temperature occurs, the works fire brigade should be warned and, if necessary, can fight this with water.

. co-current operation is to be preferred.

It is realized that some existing dryers cannot meet these requirements because of the original design. This will not necessarily lead to an accident if additional precautions have been taken. The foregoing analysis made clear how close the operating conditions can be to a hazardous situation. In general it is suggested to consider the hazard profile of the product in relation to the inlet flue gas temperature; very hazardous products should be deleted from the production programme. Since the induction periods are very short at these high temperatures, the dryer or spherodizer should be equipped with fixed water-jets. Easily accesable emergency exits for the operators should be provided. All personnel in the building should have escape respirators.

6. General comment

When a new product is being considered for marketing, it is necessary beforehand to evaluate the hazard profile of the product in order to satisfy the legally required hazard classification. Moreover on basis of this hazard evaluation safety procedures have to be established so that a safe production, storage, transport and handling procedure can be guaranteed.

With this objective ISMA/APEA has issued the booklet "Selected methods of test for the thermal stability of compound fertilisers containing ammonium nitrate".

7. Literature

1. Frank - Kamenetzki. Diffusion and heat exchange in Chemical kinetics (Princeton University Press) 1955.
2. Hainer, Fifth Symposium on Combustion 224 - 30 Pittsburg 1954.
3. Perbal, G.
The thermal stability of fertilisers containing ammonium nitrate. Paper read before the Fertiliser Society of London on 25th November 1971.
4. Perbal, G.
Safety of products and raw materials. Paper read before the Fertiliser Society of London on 22nd November 1973.
5. Perbal, G.
Safety in rotary dryer operation. Paper read before the ISMA Technical Conference, 16th September 1976. The Haque, Netherlands.
6. Selected methods of test for the thermal stability of Compound fertilisers containing ammonium nitrate. Booklet issued by ISMA /APEA.

