

ISMA* Technical Conference

Edinburgh, United Kingdom

14-16 September 1965

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE DECOMPOSITION OF COMPOUND FERTILISERS

By Ir.D.G. Huygen and G. Perbal,
(N.V. Verenigde Kunstmestfabrieken
Mekog-Albatros, Netherlands).

Introduction

High nitrogen compound fertilisers are produced in large quantities all over the world. In storage, shipment and handling accidents have occasionally been recorded. The origin of these accidents is the possibility of a self-sustaining decomposition arising, which is inherent in some types of these fertilisers.

Examples of recent accidents caused by this phenomenon are the decomposition of 8000 tons of 12+12+17+2 in Germany (1961), 4000 tons of 12+12+12 in Holland (1963) and the loss of the vessel "Sophocles" which contained 5700 tons of 14+14+14 (1965). This self-sustaining exothermal decomposition, generally started by external heating, e.g. small fires, burning handlights, etc., is a rather slow process. The reaction front propagates with a velocity of, say, 10 - 100 cms per hour through the fertiliser material. Depending on the chemical composition of the fertiliser, about 45% of the weight is found in the decomposition gas, containing N_2 , N_2O , water vapour, nitrous fumes, NH_4Cl , Cl_2 and HCl .

The temperature in the reaction front in large quantities of fertiliser will reach a level of about $500^{\circ}C$.

A fundamental difference between a normal fire and this exothermal decomposition is that the latter does not require oxygen either for ignition or for sustaining the reaction. In case of an accident, the fertiliser will be destroyed and the storage building, together with its equipment, will be damaged.

However, the main hazard is in the development of large amounts of toxic fumes, which are dangerous to the staff and the civilian population.

The only practical way to extinguish a decomposition is a strong water jet which pierces into the reaction zone.

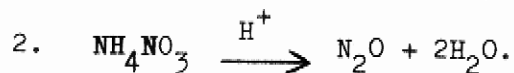
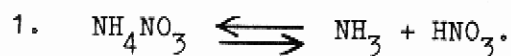
The problem of establishing efficient measures to prevent and combat accidents has been given much attention by authorities and manufacturers in recent years. We shall not deal with it at length.

The importance for the fertiliser manufacturer of reducing the hazards to an acceptable level or, preferably, of eliminating them altogether will undoubtedly be realised.

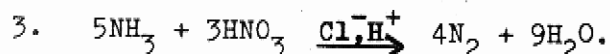
The present paper will deal mainly with the chemical factors governing the decomposition and will show ways of reducing the risks involved. A brief treatment of the physical and chemical reaction mechanism is given in the paper, as well as a description of the test methods which have been developed. Series of tests have been carried out to investigate the influence of fertiliser composition on the rate of decomposition. In the course of the paper reference is made to the relations between critical temperatures and the quantity of the fertiliser.

Reaction mechanism

In principle, a self-sustaining decomposition is possible if NO_3^- , NH_4^+ and Cl^- -ions (1) are present, whatever the counterpart ion may be. If in a compound fertiliser (without "trace elements"!) one of these ions is not present, no self-sustaining decomposition occurs. Known decomposition reactions of ammonium nitrate are:

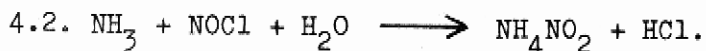


In the presence of Cl^- -ions (lit.:1-2) the following overall reaction takes place:



This is the main reaction of the self-sustaining decomposition. However, the catalytic effect of the Cl^- -ion may be replaced by certain trace elements, e.g. cobalt, chromium (lit.5-6).

Since the reaction zone contains free acid, the following secondary reactions will occur:



Sometimes another reaction is cited in the literature (3-4):



Probably this reaction is the sum of reactions 3 and 4.4.

Depending on the chemical composition, sublimation of NH_4Cl formed by reciprocal conversion may occur during the self-sustaining decomposition.

As an example, the gas analysis of the fumes developed by the self-sustaining decomposition of a 17-11-22 compound fertiliser is in accordance with this reaction scheme.

Table 1

Analysis of 17-11-22 and of the residue after self-sustaining decomposition.

	before decomposition	after decomposition
nitrogen (total)	17.15 %	0.21 %
nitrogen (ammoniacal)	10.60 %	0.21 %
water soluble P_2O_5	11.42 %	18.8 %
acid soluble P_2O_5	11.4 %	22.0 %
K_2O	22.9 %	43.6 %
Cl^-	18.11 %	25.84 %
H_2O	0.43 %	-
pH	6.80	3.10

Composition of fumes developed (decomposition temperature 320°C):

N_2O	=	7.21 % (mol)
N_2	=	20.48 % "
H_2O	=	64.96 % "
NH_4Cl	=	5.98 % "
HCl	=	1.01 % "
Cl_2	=	0.36 % "

The results of table 1 indicate that reaction 3 is an essential part of the decomposition reaction.

It is obvious that the composition of the fumes depends on the ratio of the chemical constituents, and on the reaction temperature. For instance, as the molecular ratio of the NH_3/NO_3 approaches 1 (instead of the value 1.6 in table 1) reaction 3 will produce more free HNO_3 . Due to the heat of decomposition this nitric acid will be fumed off. This

results in a higher content of nitrous fumes, HCl and chlorine, coupled with a decrease in NH_4Cl content of the fumes developed.

Because the toxicity of the gases represents the main hazard for the health of people affected, it may seem advisable to manufacture products with a NH_3/NO_2 mol. ratio of at least 1.5. This ratio has been established by testing a great number of samples and by the systematic study of the three component systems given in this paper.

The stoichiometric ratio of reaction 3 is 1.67, and the discrepancy between this value and the value of 1.5 mentioned above can be explained by the other decomposition reactions which consume NH_3 and NO_2 in the ratio of 1.

On the other hand, a high NH_3/NO_2 ratio - as will be pointed out below - may lead to a high rate of decomposition. It should still be considered undesirable that decomposition is started at all.

In connection with the reaction scheme, it is important to know what happens in the heating period before the actual start of the self-sustaining decomposition.

For this purpose samples of 17-11-22 were held at different temperatures. During the exposure, probes were taken at regular intervals and analysed for their constituents.

It was found that in the temperature range of $140^\circ\text{C} - 180^\circ\text{C}$ the results were of a similar nature. The only difference was that the time scale is contracted as the exposure temperature becomes higher. For this reason, only the test results at 160°C are given here.

In figure 1, the figures corrected for weight loss are plotted against time.

The first change which occurs, is the loss of NH_3 due to the reaction



Coupled with this loss is the decrease in pH. At about pH 4.5 all di-ammonium phosphate has changed into mono-ammonium phosphate, and at the same time the pH of NH_4NO_2 itself is reached, so that the system becomes acid. From this moment the decomposition of NH_4NO_2 is responsible for further NH_3 -losses, at first following reaction 1, but, with the decreasing pH, gradually changing to a complex of reactions 1, 2 and 3.

At about pH 3, reaction 3 turns out to be the main reaction, and self-sustaining decomposition is started.

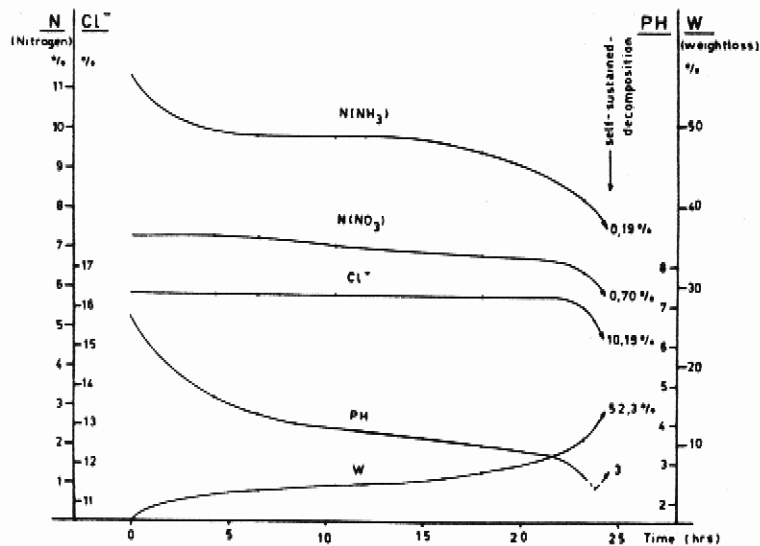


Fig. 1. Changes in composition during the induction period before ignition of the self-sustaining decomposition. Temperature = 160°C .

It is obvious that the pH is an important factor during the induction period. Therefore a high product pH (> 4.5) will contribute to safe storage.

Depending on the physical behaviour of a particular product at decomposition temperature, two types of exothermal self-sustaining decomposition are possible:

- a). The product melts at or below decomposition temperature. In this case the decomposition generally starts at about 230°C and there is a violent reaction throughout the liquid. In practice this "liquid fume-off" is not a serious hazard. Ignition cannot be started locally, because the hot molten product is cooled by the melting of fresh material and the decomposition temperature will not be reached. Only in the case of a large fire, in which the entire mass is molten, may liquid fume-off occur.
- b). If the product does not melt, the decomposition is limited to a zone, which propagates slowly through the mass. It is clear that to start the zonal decomposition only a limited amount of heat is required, in contrast to the liquid fume-off. This type of decomposition is the hazard normally met in practice. A number of decomposition accidents were caused by rather modest heat sources, such as electric torches, steam piping and small

fires. The zonal decomposition has been and still is the main subject of our product safety research.

From temperature measurements and the analyses given in table 1. it can be calculated that the decomposition gases contain about 85% of the heat generated. This high figure suggests that the hot gases play an important role in the propagation velocity of the reaction front.

Careful observation of the reaction zone has shown that the velocity by which the reaction front propagates through the mass depends largely on the amount of liquid phase in the reaction zone. The presence of much liquid phase obstructs permeation of the front by the hot gases to the fresh material. The hot gases then largely escape through vents which form in the decomposed mass.

Only part of the heat is transferred to the undecomposed material, which results in a low propagation velocity.

A low content of liquid phase in the reaction zone enhances the transport of the hot gases through the reaction zone. This improves the heat transfer and thus increases the decomposition velocity. Typical examples of the two modes of zonal decomposition are given in figures 2 and 3, showing dismantled decomposition residues of a 2 tons' test. In figure 3 the gas ventholes in the residue are clearly shown.

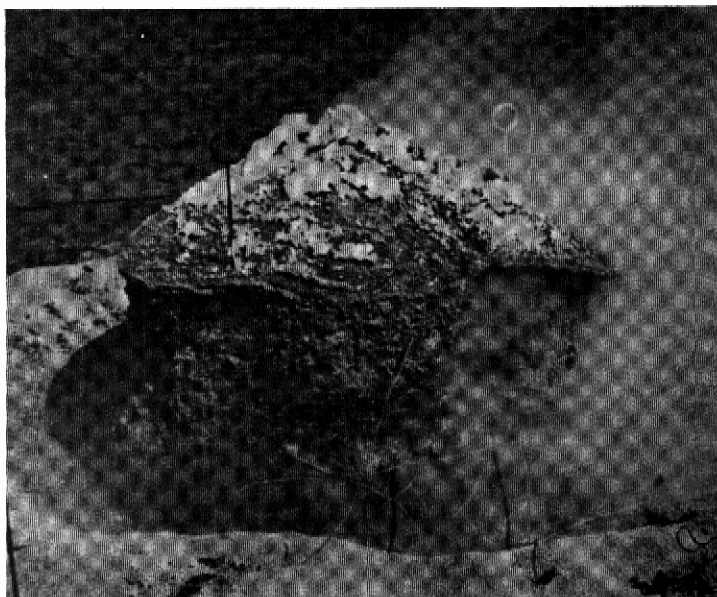


Fig. 2. 17+11+22 rather low content of liquid phase in the reaction zone.

Medium decomposition velocity 12 cms/hr.

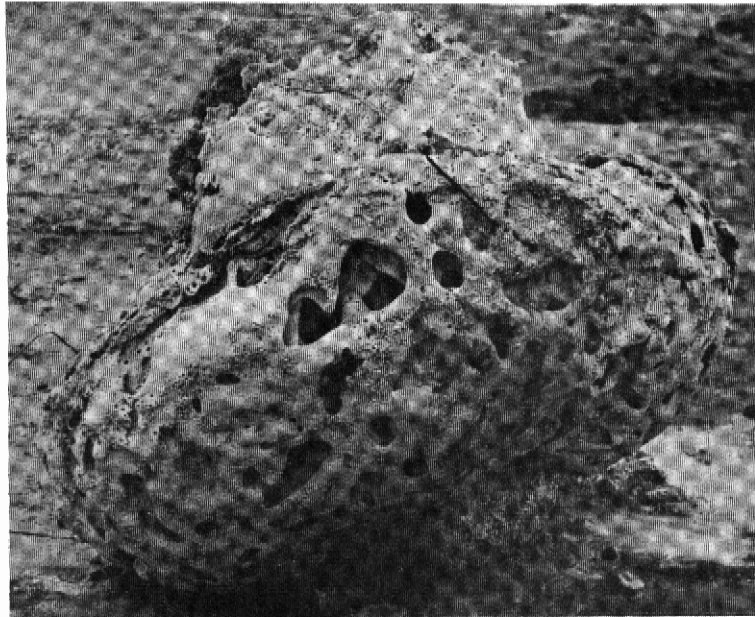


Fig. 3. 21+14+14 high content of liquid phase in the reaction zone.

Low decomposition velocity 3 cms/hr.

It is well known that the toxicity of the developed gases is the main hazard of the decomposition and that the rate of evolution is a determining factor for the extent of the accident.

As the rate of gas evolution is a function of the velocity of the spreading of the decomposition, we have developed a number of tests to measure the decomposition velocity.

Test procedures

In a large bulk quantity the movements of the decomposition front away from the centre are determined by the horizontal and vertical propagation velocities of the reaction. With the aid of the following test methods these velocities can be estimated.

1. The horizontal rate of decomposition

The horizontal rate is tested in a trough, dimensions 10x10x50 cms, made of wire gauze (2.5 mms aperture, 1.5 mm wire, stainless steel type 302). The trough filled with product is heated by two laboratory burners at one end. To restrict the heat supply to the heating end, a shield is placed perpendicular to the trough at 5 cms from this end.

The heating must be done uniformly to obtain a regular

reaction front. Heating should be prolonged for about 30 minutes, depending on the nature of the product. About 20 minutes after completion of the heating period, the progress made by the reaction front is measured with a rule. Measurement is repeated at regular time intervals.

The rate is calculated when the displacement of the reaction front becomes constant with time and is expressed in cms/hr.

Note: wire gauze is used to stimulate the diffusion of the reaction gases.

For a more exact measurement of the horizontal decomposition velocity the following modified test may be used:

In a capillary glass tube (ϕ 2 mms) situated along the axis of the trough a thermocouple is placed. This thermocouple can be moved by a pulley attached to the balancing motor of the Brown recorder (see fig.4). The recorder is fixed at a temperature of 200°C and the slide contact of the printing mechanism is disconnected from the slide wire. Now the recorder will move the thermocouple to that point in the reaction front, where the temperature is 200°C . In this way the recorder will follow the propagation of the reaction front and print displacement against time. The tangent of the recorded line is the decomposition velocity. To suppress jaggging in the recording, the voltage amplifier is made less sensitive.

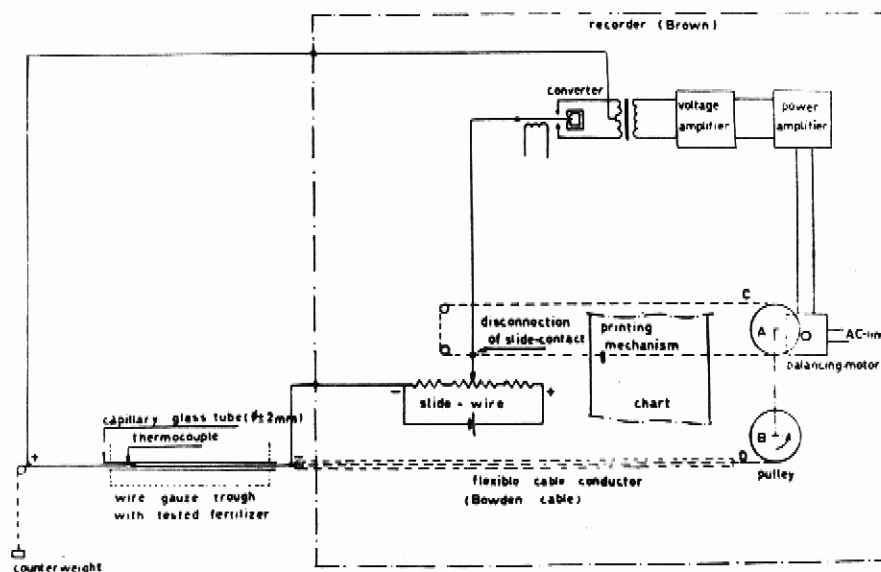


Fig. 4. Automatic device for measuring the horizontal decomposition velocity.

If the product melts to some extent, or if the decomposition

dies out during the laboratory test described above, a large scale test is necessary to find out whether zonal decomposition may occur. This test is carried out with 500 kgs of product in a plate steel circular vessel (diameter 120 cms, height 70 cms). The decomposition is started in the centre of the bulk by means of two lamps, each 200 Watt (65 V). The velocity of the self-sustaining decomposition is measured by thermocouples placed at known distances from the lamps.

The curvature of the reaction front around the lamps has some effect on the decomposition velocity, but this becomes negligible at about 30 cms distance from the lamps.

The horizontal velocity is found by the time necessary for the decomposition to travel from couple to couple. In addition an estimate of the vertical velocity is possible.

Note: The "trough" test is to be seen as a standard test. A discrepancy is found between the results of the "trough test" and the "0.5 ton's test".

	trough test (10x10x50 cms)	horizontal velocity as measured by the 0.5 ton's test
21+14+14	- cms/hr	3 cms/hr
17+11+22	12 "	12 "
16+8+12	20 "	62 "
12+12+17+2	29 "	162 "

These discrepancies appear in case of products which retain their granular structure after decomposition (see the description of the physical mechanism earlier in the text). With this type of product the gases developed in the "0.5 ton's test" are able to pass from the reaction front into the fresh product to a greater extent than in the case of the "trough test". The difference observed may be explained by the lack of large ventholes in this type of residue, and by the ventilation on all sides in the trough test.

2. The vertical rate of decomposition

The velocity is tested in a steel pipe, diameter about 25 cms, length 100 cms, which is closed at one end. The pipe is placed with the closed end below. A layer of product, 13 cms thick, is placed at the bottom of the tube. In this layer decomposition is started by heating the bottom with a laboratory burner. When the reaction front has been established, the tube is entirely filled up with fresh product.

The time needed by the reaction "front" to pierce through the 87 cms of fresh product is measured. This velocity is expressed in cms/hr.

Note: This test is not a laboratory test. Figures obtained show that the vertical velocity is 10 to 20 times the horizontal velocity as measured in the trough test. The vertical test gives some indication of the movement of the front, but the practical importance is less than would seem at first sight. If a decomposition is discovered in storage, this means that the vertical movement is already complete. The height of storage is the limit.

"Liquid fume-off"

This phenomenon was given only a qualitative test. About 50 grams of the product are heated slowly in a beaker. During heating the product is stirred with a thermometer. Heating is prolonged until liquid fume-off starts generally at about 230°C. From the time it lasts a qualitative conclusion may be drawn. The shorter it is, the more violent.

The influence of fertiliser composition on the rate of decomposition

To investigate the influence of certain compounds on the decomposition velocity, the "trough test" is used as a standard test. Although we realize that the velocities measured in this way are no absolute values, we must accept these, because it is impossible to apply the "0.5 ton's test" in this systematic study.

The salt pair NH_4NO_3 -KCl is the simplest combination which fulfills the conditions of self-sustaining decomposition. This combination also is very important in compound fertiliser manufacture. As is well-known, NH_4NO_3 -KCl constitutes a reciprocal salt pair, as shown below:



The investigations started by testing a number of NH_4NO_3 -KCl-mixtures in different proportions. These mixtures were granulated in an Eirich mixer. The granulated material was dried and screened to size between 1.5 - 4 mms. The measurements of zonal decomposition velocities are indicated in fig.5 on the connecting lines NH_4NO_3 -KCl. (Connecting lines are on a molar basis.)

It may be assumed that conversion is practically complete, so that NH_4NO_3 and KCl cannot both be present in the product. It is remarkable that the self-sustaining decomposition soon dies beyond the point of stoichiometric composition when moving towards KCl. This would seem to suggest that the salt pair

$\text{KNO}_3\text{-NH}_4\text{Cl}$ - in spite of the absence of a liquid phase - is not liable to self-sustaining decomposition, because the system would be unable to provide acid conditions. In this connection it should be remembered that NH_4Cl as such may pass into the vapour phase, thus preventing reaction 3.

For this reason the investigations were extended to mixtures of $\text{KNO}_3\text{-NH}_4\text{Cl}$ and $\text{KNO}_3\text{-NH}_4\text{Cl-KCl}$. Because these mixtures are not easy to granulate, they were tested as powder in a plate steel trough, dimensions 10x10x50 cms.

Contrary to the supposition, a number of mixtures appeared to be liable to self-sustaining decomposition (see fig.5).

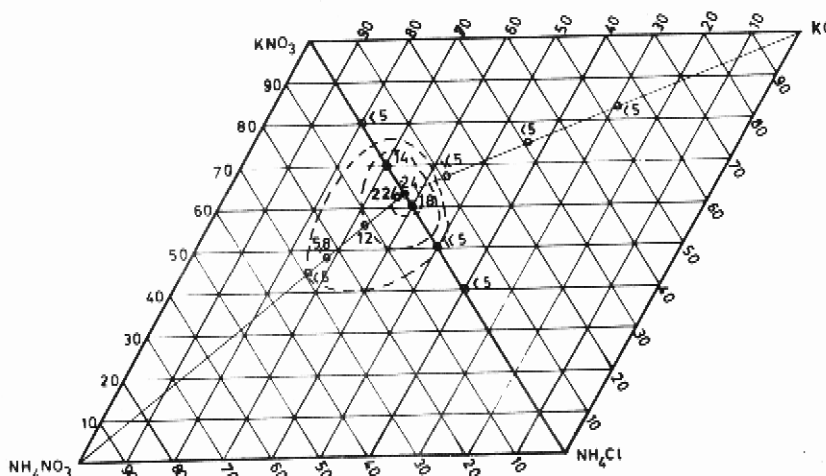


Fig. 5. Zonal decomposition of the reciprocal salt pair $\text{NH}_4\text{NO}_3\text{-KCl}$.

Dotted lines are iso-velocity lines.

The maximum velocity, measured along the connecting line $\text{NH}_4\text{NO}_3\text{-KCl}$, coincides with the maximum on the $\text{KNO}_3\text{-NH}_4\text{Cl}$ axis. This maximum is exactly located at the stoichiometric point.

pH measurements in the heated $\text{KNO}_3\text{-NH}_4\text{Cl-KCl}$ mixtures have indicated that a certain amount of excess KCl is essential to suppress self-sustaining decomposition. The lack of a complete knowledge of the phase diagram including the mixed crystals of $\text{NH}_4\text{Cl-KCl}$ prevents detailed explanation.

The study will now be extended to three component systems. As before, the products were granulated in an Eirich mixer,

dried and screened. The regions of liquid fume-off and zonal decomposition were determined in each of the systems.

Figures 6, 7 and 8 show the influence of ammonium salts such as $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ and $(\text{NH}_4)_2\text{SO}_4$ on the decomposition velocity of the salt pair NH_4NO_3 - KCl .

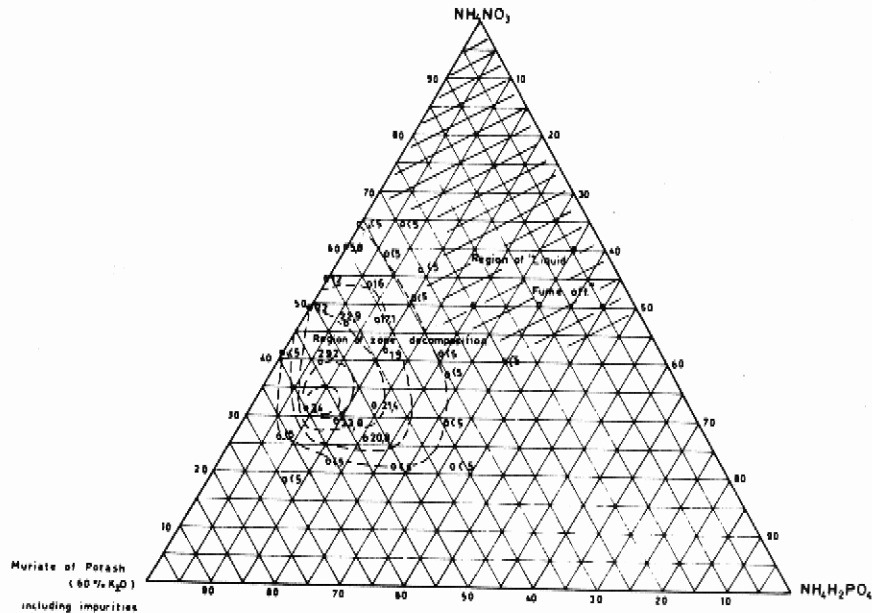


Fig. 6. The system NH_4NO_3 - $\text{NH}_4\text{H}_2\text{PO}_4$ - KCl

--- iso-velocity lines of zonal decomposition.

As may be expected from reaction 3, the maximum decomposition velocity is situated within the diagram. Above this maximum the zonal decomposition velocity decreases with increasing NH_4NO_3 content, and ultimately the system moves into the region of liquid fume-off. The shape of the "transition boundary" to liquid fume-off depends on the amount of liquid phase produced by the three components before decomposition.

The difference between figs. 6 and 7 is essentially caused by the fact that $\text{NH}_4\text{H}_2\text{PO}_4$ increases the amount of liquid phase more than does $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. It is obvious that in some cases $(\text{NH}_4)_2\text{SO}_4$ increases the hazard of decomposition considerably. This is caused by the formation of double salts with NH_4NO_3 and by a high NH_4^+ content at practically the same pH as NH_4NO_3 . The maximum velocity in diagram 8 is the highest ever measured in our laboratory.

Compared with mixtures which contain only KNO_3 , NH_4Cl and KCl , an additional component produces the free acid necessary for self-sustaining decomposition. In the cases described the new

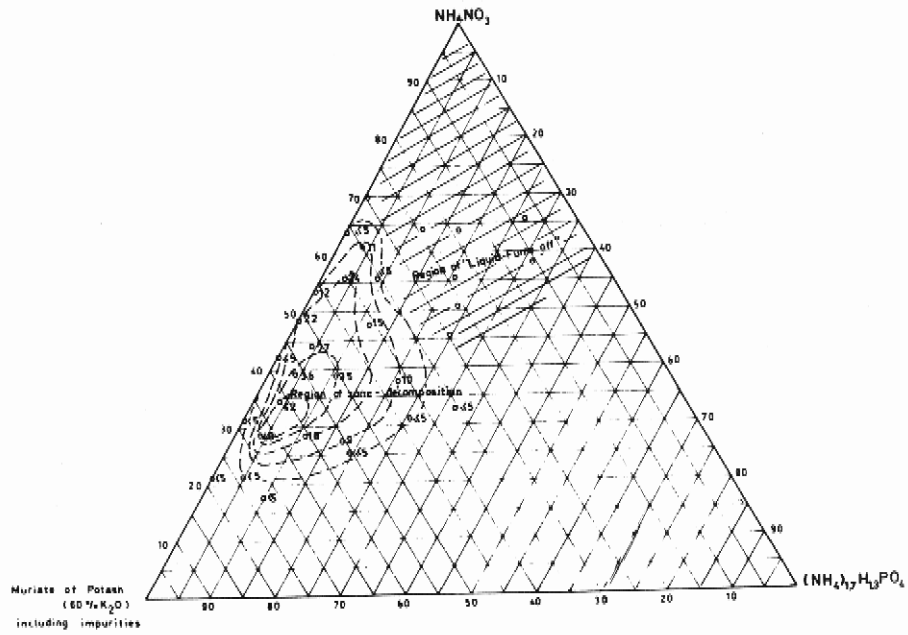


Fig. 7. The system $\text{NH}_4\text{NO}_3 - (\text{NH}_4)_{1.7}\text{H}_{1.3}\text{PO}_4 - \text{KCl}$
 --- iso-velocity lines of zonal decomposition.

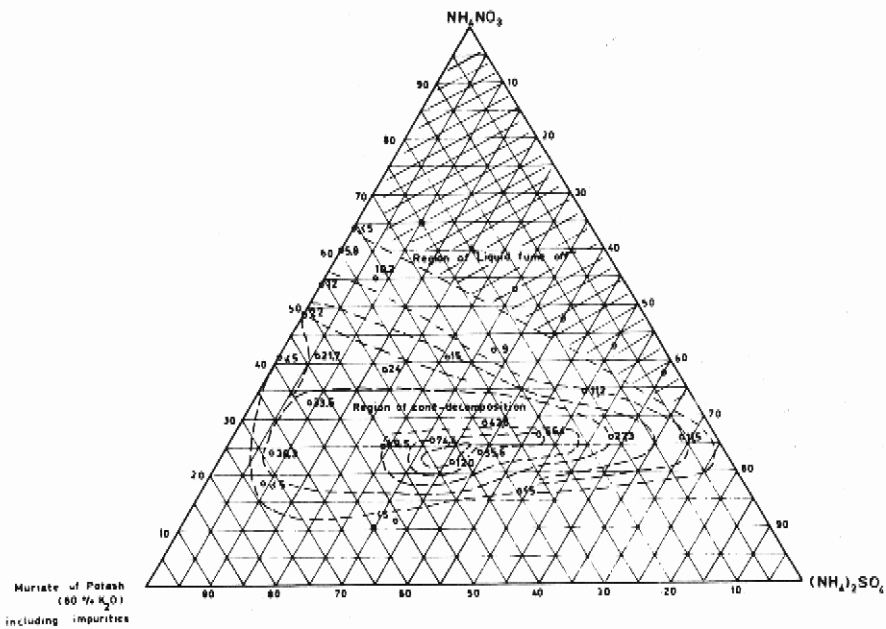


Fig. 8. The system $\text{NH}_4\text{NO}_3 - (\text{NH}_4)_2\text{SO}_4 - \text{KCl}$
 --- iso-velocity lines of zonal decomposition.

component was either NH_4HPO_4 , $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ or $(\text{NH}_4)_2\text{SO}_4$. These salts release NH_3 below the decomposition temperature.

Summarising, the effects which help to limit the region of zonal decomposition in the diagrams are:

1. In the case of a high NH_4NO_3 content, by liquid fume-off.
2. In the case of a high NH_4 -phosphate content, by endothermic reactions such as poly-phosphate formation.
3. The lower part of the region is limited by low nitrate content.
4. The lower part of the NH_4NO_3 -KCl axis, by lack of free acid.

Also important are the systems with Ca-phosphates as a third component. We investigated the influence of CaHPO_4 , single and triple superphosphate (see figures 9, 10 and 11).

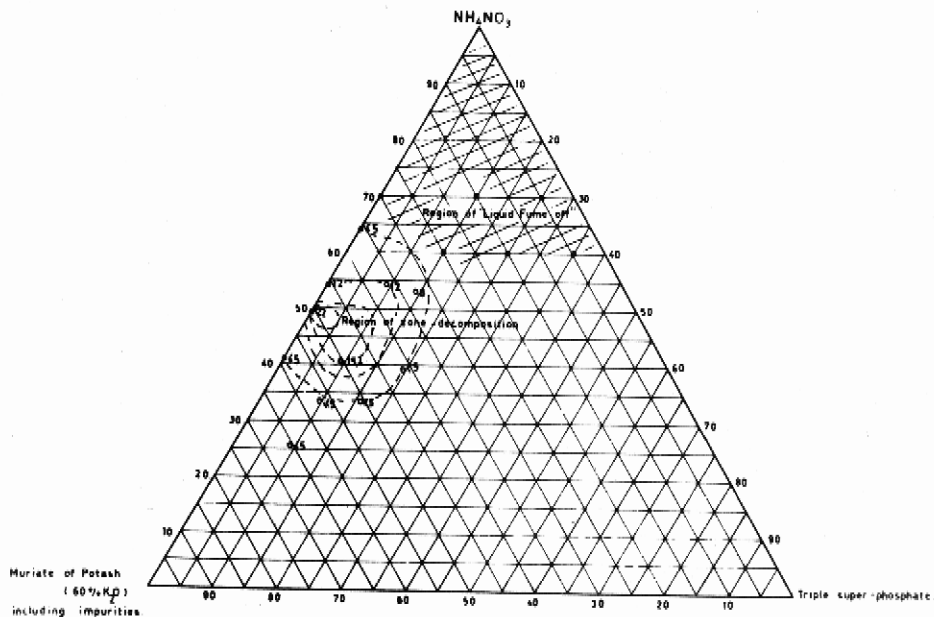


Fig. 9. The system NH_4NO_3 -triple superphosphate-KCl.

--- iso-velocity lines of zonal decomposition.

Because these Ca-phosphates do not take part in the decomposition reaction itself, the maximum velocity is not within the diagram but on the NH_4NO_3 -KCl axis.

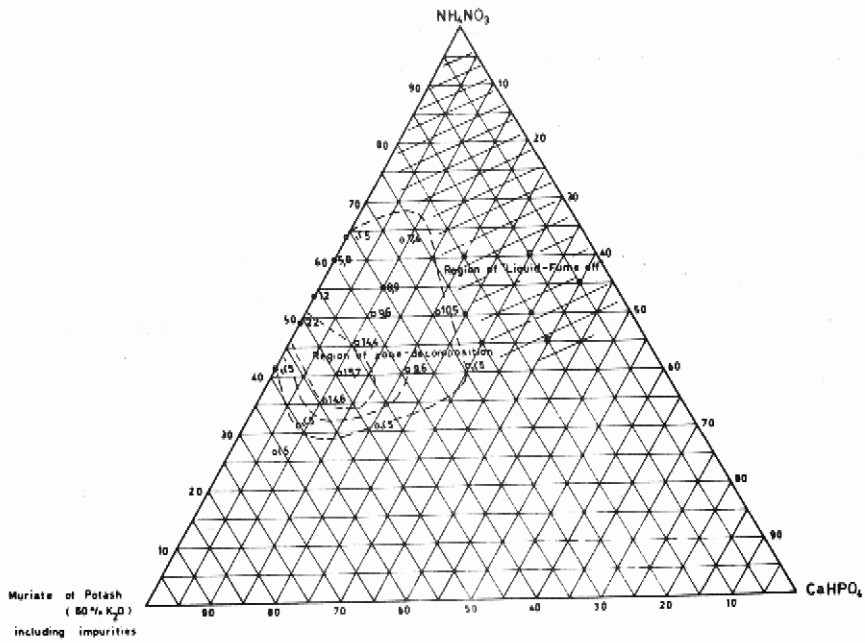


Fig.10. The system NH_4NO_3 -single superphosphate-KCl
 --- iso-velocity lines of zonal decomposition.

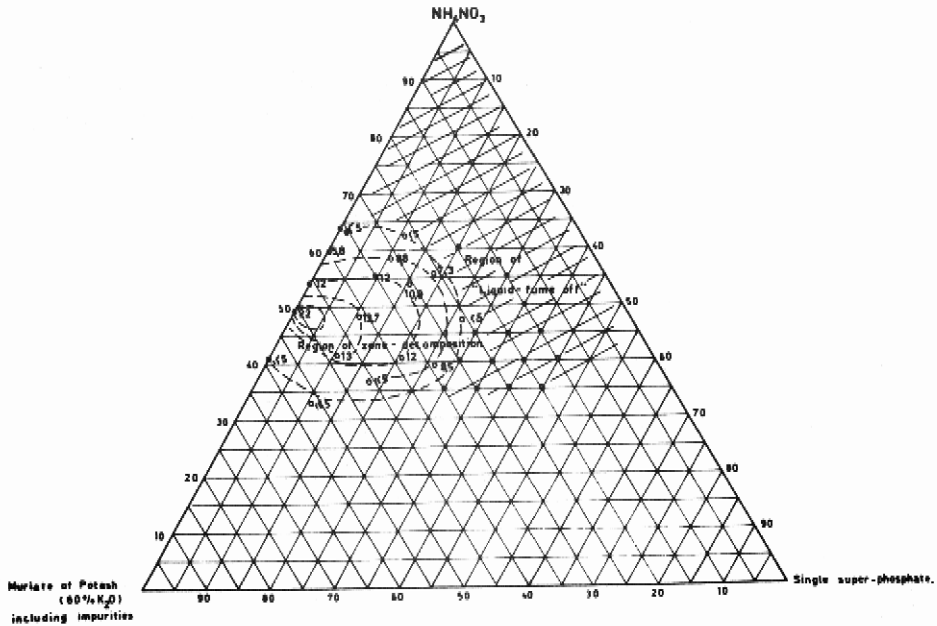


Fig.11. The system NH_4NO_3 - CaHPO_4 - KCl.
 --- iso-velocity lines of zonal decomposition.

From figures 6 - 7, it seems that the phosphate-ion has an inhibiting effect on the decomposition velocity. The same impression is obtained from figures 9 and 10. Of course, the inhibiting effect of single superphosphate would be proportional to its $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ content and therefore smaller than that of triple superphosphate.

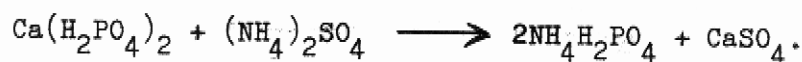
The gypsum content in single superphosphate has no chemical effect, for it consists mainly of $\text{CaSO}_4 \cdot \text{OH}_2\text{O}$ and must be seen as inert. Inerts have only a physical effect, as they reduce the relative amount of liquid phase in the reaction zone. Just the same occurs in the case of CaHPO_4 , which has a relatively large region of zonal decomposition.

From the above discussion of heat transfer in the reaction zone of self-sustaining decomposition it is clear that no simple correlation exists between the composition of a fertiliser and the decomposition velocity. A systematic study of salt systems is the only way to a complete understanding.

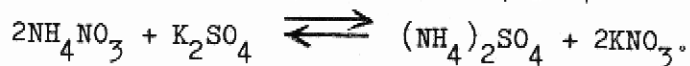
In connection with these diagrams another important observation has been made. It has been demonstrated that a blend of two or more granulated compositions, e.g. one below and one above the region of zonal decomposition, may decompose as if it were evenly granulated. From this it may be concluded that reciprocal changes and other reactions are complete before decomposition takes place.

Application of the diagrams to compound fertilisers containing a higher number of constituents is not possible without the knowledge of the real chemical composition at equilibrium.

For example, granulation of triple superphosphate with $(\text{NH}_4)_2\text{SO}_4$ gives:



Other important reactions are:



Another important factor is the water content. Generally the decomposition decreases with increasing water content.

Finally we want to draw attention again to the fact that the regions of decomposition have been determined with the aid of the "trough test", so that they might have been somewhat larger if the "0.5 ton's test" had been used.

The relation between the ignition temperature and the fertiliser mass.

The ignition temperature of the self-sustaining decomposition can be understood as a borderline case of spontaneous self-heating. Spontaneous self-heating is the phenomenon which occurs if the heat generated by an exothermic reaction in the material exceeds the transfer of heat to the surroundings.

The mathematical treatment of self-heating was developed by Frank-Kamenetskii (8), and was applied by Hainer (7) to the problem of spontaneous self-heating of NH_4NO_3 .

The complexity of the reactions and the changes in heat conductivity in the temperature range concerned prevent a mathematical approach. The practical side of the problem has been solved by using a method of Dr. J.F. van Elteren of the T.N.O.-Institute at Delft (9), which was originally developed for testing the self-heating of materials such as "soft board".

The theories mentioned above show that the logarithm of the critical radius, above which self-heating occurs, is a linear function of the reciprocal value of the initial uniform temperature ($^{\circ}\text{K}$). With the aid of the T.N.O.-method this linear function may be empirically determined.

The experimental method consists of keeping the compound fertiliser in wire gauze cubes of different sizes at a constant temperature. In the test series, cubes are used with edges of 2, 4, 8, 15 and 16 cms. By varying the exposure temperature one finds which cube size decomposes and which does not. The linear function is established by determining the time of exposure, the chemical analysis and the temperature of the exposed product, and the time it lasts before a supercritical mass starts to decompose. The only disadvantage of this method is that it is time consuming. In this way the critical size of cube shaped masses of 12+13+6 were estimated (see fig.12). The edge of the cube was taken as the critical radius.

Table 2 Chemical analyses of 12+13+6

Nitrogen (total)	= 12.7%	K_2O	= 6.6 %
Nitrogen (ammoniacal)	= 7.2%	Cl^-	= 6.1 %
water soluble P_2O_5	= 10.1%	SO_4^{--} (total)	= 17.8 %
citrate soluble P_2O_5	= 13.0%	CaO (total)	= 13.9 %
acid soluble P_2O_5	= 13.3%	H_2O (K. Fischer method)	= 0.57%
		pH	= 5.07

The chemical analysis of 12+13+6 is given in table 2. From the results plotted in fig.12 it may be concluded that the

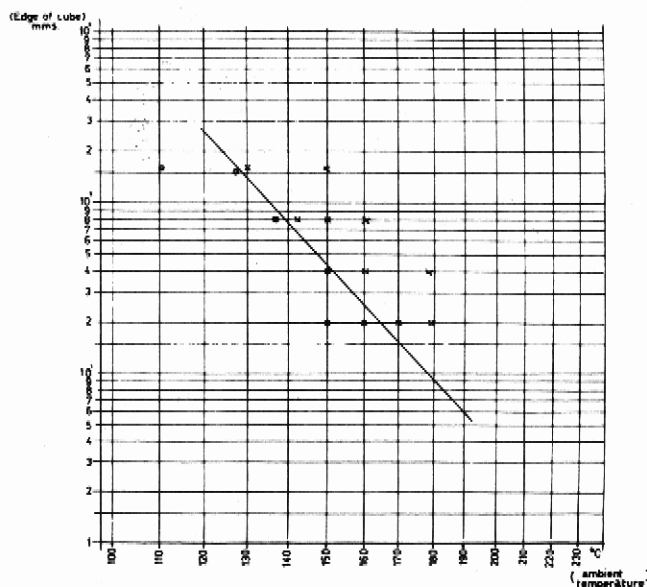


Fig.12. The critical size of a cube shaped mass of 12+13+6

o = sizes found to be subcritical
 x = sizes found to be supercritical.

ignition of the self-sustaining decomposition fits the underlying theory. However, extrapolation to larger sizes, e.g. to edges of 10 ms, is not permitted. It is unknown to what extent certain reactions limit the decomposition reactions at lower temperatures. For example, if the compound fertiliser contains $(\text{NH}_4)_2\text{HPO}_4$, the pH of the product will not decline below about 90°C because the NH_3 vapour pressure of $(\text{NH}_4)_2\text{HPO}_4$ at this temperature is nil.³ This means that spontaneous ignition will not occur, notwithstanding the fact that the product would be supercritical according to the extrapolated diagram.

It has been found that other compound fertilisers with practically the same decomposition velocity - as measured by the "trough test" - show a different slope in diagram 12.

Ignition temperatures of products showing liquid fume-off and other measurements indicate that these functions converge to a temperature of about 230°C .

Summary

This paper deals with the main factors governing the self-sustaining decomposition of compound fertilisers. It has been shown that the decomposition mechanism is a complicated one. A

systematic study of the influence of certain constituents upon the decomposition velocity has revealed the existence of regions of more or less safe compositions.

Decomposition velocity and spontaneous ignition are not directly interrelated.

The study has shown several ways of reducing the hazards in storage and transport.

Literature cited

1. Borland C.C. and Schall E.D. Journal of the A.O.A.C.
Vol.42 No.3, 579-86 (1959).
2. Saunders H.L. J.Chem.Soc.London 121
, 698 ft (1922).
3. Waters, E.C., Smith J.A.,
Novotny, J. Agr. and Food Chem.
Vol.8 no.6 475-81 (1960).
4. Lakota, V. Chem.Prumsyl 13 3-6 (1963).
5. Guiochon, G. Ann.Chim. (Paris) 295-349
(1960).
6. Rosser, W.A., Inami, S.H.
Wise, H. Trans Faraday Soc.
1618-25 (1964).
7. Hainer, R.M. Fifth symposium on combustion
224-30 (Pittsburg 1954).
8. Frank - Kamenetskii Diffusion and heat exchange
in chemical kinetics
(Princeton University Press
1955).
9. Instituut T.N.O. voor Bouwmaterialen en Bouwconstructies,
"Centrum voor brandveiligheid", Delft, Holland.

DISCUSSION

Mr. D. G. HUYGEN (Mekog-Albatros, Holland): The decomposition of compound fertilisers containing ammonium nitrate has received considerable attention in recent years as a result of a number of accidents, some of which we refer to in the introduction to our paper. Accidents of this nature have been rare in relation to the enormous tonnages of compounds being produced, stored and handled throughout the world. However, when a large quantity of such a compound starts to burn, it is quite a serious matter, mainly because of the evolution of toxic fumes. It is therefore very important to reduce the risk of the occurrence of accidents of this type. Our paper is meant as a contribution to this end.

In a number of countries, manufacturing companies and government officials are taking or considering steps to reduce hazards in storing and shipping compound fertilisers. The establishment of certain preventive measures by the specialists, the provision of adequate information in itself, is essential in reducing the risk of this type of occurrence to acceptable levels.

We have described in the paper the reaction mechanism as we believe it to be. Essential to this is the formation of ammonia and nitric acid from ammonium nitrate, catalysed by acidic conditions and, in most cases, by chlorine ions or by other catalysts. More ammonia is consumed in the reaction than corresponds to a 1 : 1 molar ratio (see p. 2, reaction 3). In Table 1, page 3, we give an example of a compound fertiliser capable of self-sustaining decomposition, and we quote the analysis of the material before and after the reaction, as well as the composition of the fumes evolved.

We then discuss the inter-relationship between the fertiliser composition and the fumes evolved. It appears that within the range of compounds containing ammonium nitrate which are susceptible to decomposition, some advice may be given for reducing the toxicity of the gases. But we should prefer to say that the occurrence of decomposition should be eliminated altogether, even if less toxic gases are involved. Any cloud of gas emitted by these products would still be very unpleasant.

As you will have seen, we studied the change in the composition of the fertiliser within the temperature range of 140 - 180°C and as a function of exposure time. Compounds capable of zonal decomposition show considerable exhalation of the reaction at the high temperature, i.e. 180°. Products which retain their granular structure after decomposition show the phenomenon in its most perfect form. They allow the gases to escape through the unreacted material, so allowing the decomposition to proceed at a higher rate to adjacent material.

Apart from zonal decomposition, other hazardous phenomena deserve attention, e.g. liquid fume-off and detonation. The possibility of detonation naturally applies only to mixtures which are close to the ammonium nitrate point in the diagrams in the paper. In actual

practice, there is little chance of this occurring in compound fertiliser manufacture; but nevertheless careful checks should always be made to ensure that this most violent reaction is avoided.

In the paper, we have described in detail our test methods for determining the horizontal and vertical rates of propagation of zonal decomposition, as well as a test to establish the possibility of liquid fume-off. The most important part of the paper is concerned to establish the relationship between fertiliser composition and the horizontal propagation rate as determined by the standard test. To this end, many samples, each consisting of three raw materials, were tested; and we believe that, in presenting these results, valuable information is given over a broad practical field. Nevertheless, it should be borne in mind that products composed of four or more raw materials may show a different behaviour to what might be expected from these triangular diagrams.

Finally, I should like to mention the study we made with a few compounds regarding the relationship between temperature and the critical quantity of fertiliser which is capable of sustaining the reaction to a burning condition. In Fig. 12, page 18, conditions are such that exothermal decomposition will be completed after infinite time. The region to the right of the straight line is super-critical, i.e. spontaneous ignition will occur. Needless to say, spontaneous ignition in a large storage is very dangerous, because of the violent development of toxic fumes within a short time. The establishment of maximum temperature limits is useful in suppressing this type of hazard.

In conclusion, I should like to mention an article by Messrs. Parker and Watchorn which was published in the Journal of Science, Food and Agriculture on 16th June, 1965. This appeared shortly after our paper was written, and we are pleased to say that in many respects we find a remarkable correspondence between our work and theirs. In those cases which are strictly comparable, I think we obtain roughly the same figures, but there is one exception. In the system ammonium nitrate - potassium chloride - ammonium phosphate, Parker and Watchorn state that there is a limited burning range, constituting an inherent safety feature of this ammonium phosphate-based class of fertiliser. They state that even in the centre of the burning range, the maximum reaction velocity is only 15 cm/hour. We agree with the statement concerning relative safety only in so far as the worst points in the diagram are avoided. This is also true for the other systems. As you will have seen from our paper, we found higher decomposition rates than Parker and Watchorn in the ammonium nitrate-potassium chloride - ammonium phosphate system - as high as about 50 cm/hour.

Dr. H. NEES (Chemische Fabrik Kalk, Germany) : The thermal, self-sustaining decomposition of compound fertilisers containing ammonium nitrate has been experimentally investigated by complex fertiliser producers in Germany since the early 1950's. They have examined the causes of decomposition and its propagation in relation to the

reaction mechanism, as well as the possibilities for preventing and controlling it.

As is confirmed by the authors of this paper, the self-sustaining decomposition of compound fertilisers consists in the decomposition of ammonium nitrate which is catalysed by chloride ions and, in the course of the reaction, to an increasing extent by HCl ions. As most of us here will be aware, several large decompositions have occurred since 1961. Following these accidents, which surprisingly demonstrated that no explosion occurred with such large decompositions of 8,000 tons or more, several investigations were carried out- in Germany and then in the Netherlands and the U.K.; and the results of the research in the Netherlands and the U.K. were published. This led to a published discussion of the subject on a broad basis, and here lies the particular significance of our discussion to-day.

I should like to mention the particular features of the work carried out by Messrs. Huygen and Perbal. In examining the reaction mechanism, the authors have found that a high NH_3/NO_3 molar ratio may lead to a high velocity of decomposition. They have confirmed the important effect of chloride and hydrogen ions on the start and subsequent progress of decomposition, as well as the importance of a liquid phase in the prevention of self-sustaining decomposition. They state that the reaction gases contain about 85% of the reaction heat evolved. They have determined the horizontal and vertical rates of decomposition with ingenious apparatus, and the data quoted indicates propagation velocities within the decomposition zone of 5 - 30 m/hour in the direction in which the decomposition gases escape. In short, the progress of decomposition in the direction of the escaping gases is roughly ten times more rapid than in the opposite direction.

The authors have also tested the influence of fertiliser formulation on the rate of decomposition. They have determined the zones of self-sustaining decomposition for a variety of formulations. The accelerating effect of ammonium sulphate was particularly striking. The authors state that there is no simple correlation between the composition of a fertiliser and its rate of decomposition. Furthermore, they say that a mixture of two or more granular constituents, each of which lies outside the decomposition zone, may decompose as if it were evenly granulated.

The liability of a compound fertiliser containing several constituents to self-sustaining decomposition can be estimated only with a knowledge of the actual chemical composition at equilibrium. The tendency of a complex fertiliser to decompose decreases with increasing water content of the product. The authors finally point out that the test results obtained depend on the testing methods applied and must therefore not be generalised. This should apply especially to the last section of the paper, in which work on the relationship between ignition temperature and the fertiliser mass is discussed. The relationship given for the critical mass of a fertiliser and the ignition of its self-sustaining decomposition as a function of the ambient temperature must not be extrapolated to large fertiliser masses of temperatures below 130-140°C. For, provided no external heat is admitted, the self-

sustaining decomposition of a commercial fertiliser can only take place after the supply of internal heat by exothermal reaction within the fertiliser. According to our present knowledge, such reactions are not to be expected below 130-140°C.

Mr. HUYGEN: I should be greatly interested in hearing the results of the research carried out in Germany, particularly with regard to ways of preventing and controlling decomposition. We have also studied these aspects, which could, of course, form the subject of a separate paper. But in general I think that if proper information is given on the materials to be handled and shipped and if normal fire prevention measures are taken, the chance of decomposition occurring is very small.

With regard to your remark that high temperatures correspond to high rates of decomposition, I would say that we have not confirmed this in our work. Furthermore, I think your statement that spontaneous decomposition is not likely to occur below 130°C is merely based on experience. We do not have any experience of spontaneous fires which have started below this temperature, but I think our measurements in the laboratory have also indicated that great care should still be taken at considerably below this temperature.

Dr. NEES: Provided that the fertiliser is fully ammoniated and has a pH of roughly 6 - and I am speaking of commercial fertilisers - a spontaneous self-sustaining decomposition is not likely to occur below 130°C. If special mixtures are made outside the normal commercial range, lower decomposition temperatures can perhaps be experienced. It has long been shown that fertilisers containing no chloride are not susceptible to self-sustaining decomposition. Parker and Watchorn found that a KCl content of only 1% was sufficient to provoke a self-sustaining decomposition. What is your experimental experience in this regard?

Mr. HUYGEN: I agree that with a pH of 6 it is very unlikely that decomposition will occur below 130°C. On the other hand, as you know, there exists a range of fertilisers at a lower pH value. In practice, I would say that discussion of temperatures in the range of 80 - 100°C is rather irrelevant, because, in order to obtain a good quality product, it would normally be cooled to a much lower temperature.

With regard to your question about chloride, we do not have any experimental evidence of decomposition in fertilisers which do not contain chloride at all. Nevertheless, from work in the literature on the decomposition of ammonium nitrate, I think there is good evidence that other catalysts, e.g. cobalt, can be responsible for the evolution of nitrous gases from nitric acid resulting from the decomposition of ammonium nitrate at rather lower temperature.

Dr. P.W. REYNOLDS (Scottish Agricultural Industries Ltd., U.K.): I should also like to congratulate the authors on an excellent

contribution to a very important subject. Obviously, the expensive and dangerous decompositions which occurred at Frankfurt, Cambridge (U.S.A.) and Vlaardingen cannot be too frequently recalled, and if any other boats turn upside down like the "Sophocles", bulk shipment of such fertilisers will become extremely unpopular. S.A.I. and I.C.I. together have worked a great deal on this subject, and, as you have heard, several references have been made to our article published by Parker and Watchorn in the Journal of Science, Food and Agriculture last June. And I wholly agree with Mr. Huygen that, apart from very minor matters, our conclusions are virtually identical.

I should, however, like to ask Mr. Huygen whether inert components may not be more important than his paper suggests. For example, the addition of 30% of Kieselguhr can convert a non-burning composition into a vigorous zonal burner. Similarly, the addition of ground rock phosphate can convert safe mixtures into zonal burners.

As an extension of the same point, may not phosphates of calcium have the same sort of effect. Although chemically these phosphates of calcium may not be involved in the reaction associated with zonal burning, they provide an inert diluent which absorbs the liquids produced during decomposition - liquids which, as Mr. Huygen so rightly states, may easily delay the progress of the burning front and make the mixture less liable to zonal burning. In addition, of course, the presence of phosphate in that form tends to move the ratios of the active ingredients into the dangerous zone for any given total fertiliser composition. For these reasons, a 1-1-1 compound based on the nitro-phosphate process is a vigorous burner, whilst the more concentrated 17-17-17 compound, based on ammonium phosphate, is safe and cannot be made to burn.

The safe handling of compounds containing ammonium nitrate is, I think, vastly helped by this understanding of the cause of the troubles which have already occurred, and also by our ability to determine by experiment and almost to predict the liability of any mixture to undergo this sort of zonal decomposition. In my own opinion, it is even better to make compounds which are free from this risk; and it is perhaps worth emphasising that the compounds which S.A.I. are making in their plant at Leith, which you will visit tomorrow, as well as the corresponding compounds made by I.C.I., based on ammonium nitrate, ammonium phosphates and potassium chloride, are all safe from this particular danger. They are high-analysis 2-1-1, $1\frac{1}{2}$ -1-1, 1-1-1, 1-2-1 and 1-2-2 formulations. The 1-1- $1\frac{1}{2}$ which we make is just on the edge of zonal decomposability. It is safe at ambient temperature, but a heap already heated throughout the mass, e.g. when just freshly produced, is on the verge of zonal combustibility.

Finally, I should like to ask whether Mr. Huygen or anyone else can suggest an additive or a treatment which will transform a marginal burner into a safe product to ship in bulk?

Mr. HUYGEN: With regard to compounds based on ammonium nitrate,

ammonium phosphate and potassium chloride, I can only repeat what I previously said in commenting on the article by Parker and Watchorn: we agree that these formulations are relatively safe, but only if the worst points in the diagram are avoided; and this is also true for other systems. I also agree that if, in this diagram, you select a 1-1-1 ratio, it will not be a burning composition. Moreover, I agree that the same ratio produced by the nitro-phosphate process may give rise to a burner. But there are many different ratios, and although I cannot give specific examples, I feel fairly sure that, with other ratios, the reverse may be true. I should like to stress again, therefore, the importance of the methods of testing, in order to enable anybody to ascertain at what point in the diagram of a system he should select any given formulation so as not to overstep the tolerance limit of decomposability.

I also agree with Dr. Reynolds' remarks on diluents: in some cases they improve the situation, whilst in other cases they can make it distinctly worse. It is unwise to generalise in this respect: in our experience with diluents, one should examine the influence of each material individually.

Mr. M. DETUNCQ (Péchiney-St.Gobain, France): In your trials on rates of decomposition, what is the temperature of the fertiliser mass not subject to direct heat?

Mr. HUYGEN: The ambient temperature.

Mr. DETUNCQ: With a large quantity of fertiliser (e.g. 5,000 tons of 12-13-6,) at what temperature, measured in the core of the pile, would you advise action such as breaking up the pile?

Mr. HUYGEN: We do not measure the temperature of a pile in several places; and you would, in fact, need to measure at a large number of points to make sure that a decomposition had not started. In our experiments, we found that even in the close vicinity of the highest temperatures the surrounding material was practically at ambient temperature. Thus, the taking of a few temperature measurements within the pile would not be likely to be of much help, if you wished to detect a decomposition caused by an external source of heat.

However, if your question refers to the possibility of a spontaneous reaction, I would agree that measurement of temperature at the core of the pile would be useful, although we do not do this ourselves. We rely on the temperature at which the fertiliser leaves the coolers in our plants. But in reply to your question, I would say that a safe temperature would be one that is below the level indicated in our Fig. 12.

Mr. R. ARDOUIN (Union Française d'Engrais, France): The authors have made no mention of a most important factor in this phenomenon

of spontaneous combustion - the presence of organic materials in superphosphate. These organic materials originate from the raw materials used and, more rarely, from the use of residual sulphuric acid, but this would deserve a study in itself. These organic materials are easily oxidised in the presence of nitrate, and this propensity to oxidation varies from one phosphate to another according to its composition, which depends on the formation of the deposits. Thus the proportion of bitumen in the content of organic matter varies from 10 to 20%, and that of humic acid, from 8 to 70%. Moreover, these organic materials contain cellulose and very condensed hydro-carbons. Thus they can also account for spontaneous decomposition.

I also mention the influence of reducing agents such as salts of iron and manganese contained in the slags which are sometimes used in mixtures with nitrates.

I think the best method of stopping a decomposition is not the spraying of water, for -

- the water cannot penetrate into the mass, from which gases are given off through all the fissures. The surface of the mass forms a slope down which the water slips but does not penetrate;

- it favours the decomposition of the nitrate, and the evolution of nitrous gases is intensified.

In my opinion, a good method consists in dispersing and spreading out the product in the reaction zone: it cools rapidly in the open air and the phenomenon is arrested.

Mr. HUYGEN: I agree that it is preferable to break up a pile, if a decomposition has started and if one is still able to do so, i.e. if the phenomenon is detected in time. But in some cases, decomposition proceeds too far for anyone to come near the material, and then a vigorous water jet is, in our opinion, the only means of stopping the process. It would be of great help to be able to determine the exact spot where decomposition started, and we have developed means of doing this.

With regard to your point about organic material, this is a complicated question. Our Fig.12 refers only to the actual decomposition reaction; but it is possible that other reactions interfere with this situation, raising the temperature level, so that the basis of our study is shifted. However, every manufacturer should be aware of what he uses in his process and should take adequate steps to prevent accidents caused by the presence of residual acids or organic material from other sources. Reactions which are not completed at the production stage obviously interfere with the relationship between critical mass and critical temperature.
