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SELF SUSTAINING DECOMPOSITION OF AMMONIUM NITRATE CONTAINING FERTILISERS

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Le degré de risque associé à la décomposition auto-entretenue dans une masse d'engrais est lié à la vitesse de propagation, l'importance de la perte de masse, la toxicité des gaz libérés et la sensibilité au déclenchement. Le test classique du pétrin a été modifié par Kemira Agro pour obtenir davantage d'information. Dans la comparaison des vitesses de perte de masse les produits contenant plus de nitrate d'ammonium libèrent plus de gaz durant la décomposition. En utilisant une limite de comparaison de 15 cm par heure pour un produit comme le 15-15-15, la même conséquence est obtenue pour le 25-5-15 avec des taux de combustion inférieurs à 5cm/h qui est la limite avec la classe B dans le test du pétrin. Quand on essaie de diminuer le taux de décomposition de telles formules, le produit peut brûler avec un taux plus faible de décomposition, mais la température d'ignition a baissé d'environ 50°C. Une telle marge de sécurité dans la production est significative et doit être appliquée.

Summary

The degree of hazard associated with self-sustaining decomposition in a mass of fertiliser is related to the velocity of propagation, the extent of mass loss, the toxicity of the gases released and the sensitivity to initiation. The classical trough test has been modified by Kemira Agro to obtain more information. Comparing the mass loss rates the products containing higher amounts of ammonium nitrate release more gases during decomposition. Using a comparison limit of 15 cm/h for a product such as 15-15-15 the same consequence is obtained for 20-5-15 with burning rates less than 5 cm/h which is borderline Class B in terms of the trough test. When attempting to decrease the rate of decomposition of such grades the formulation may burn with a reduced rate of decomposition, but the ignition temperature has decreased by e.g. 50 °C. Such a safety margin in production is significant and should be applied.

1 INTRODUCTION

The demand for more concentrated compound fertilisers originates from the 1950's. This trend led to a group of compound fertilisers being moved into a region of concentrations where the hazard of self-sustaining decomposition appeared. Due to the large quantities involved, past accidents/incidents (Appendix 1) activated a number of studies concerning the factors governing self-sustaining decomposition. Furthermore, international rules were developed for transport and storage of fertilisers (Appendix 2). Since the 1960's and 1970's fertiliser formulations have slowly changed towards those known as cigar burners due to environmental discussion on phosphorous. Hence a completely new set of fertilisers with low contents of phosphorous has been widely developed.

Shortly after the fertiliser deflagration at Delta Chemie at Vlaardingen in November 1963 the Director General of Labour in the Netherlands installed a working group with the appointed task of drawing up prescriptions for the safe storage and transport of fertilisers. Method development took place as the IMCO- subcommittee on the carriage of dangerous goods (AN fertilisers, standards and tests) realised that the existing test methods were not adequate. Huygen and Perbal developed the gauze trough test, which was internationally accepted to assess the possibility of deflagration of fertilisers^{11, 12}.

As a nitrophosphate producer Kemira has studied the safety aspects of commercial fertilisers since the 1960's. All products are tested at a frequency from once per shift to once per production run. The classification of fertilisers¹⁵ clearly states that all fertilisers below 70 % ammonium nitrate are B- class fertilisers if not proven to be Class C. This emphasises the importance of testing materials during production and additionally before delivery. Since 1965 new features to the classical gauze trough test have been applied in Kemira. These are to improve the data handling and interpretation of the test results. The classical test itself gives a lot of information related to the ignition temperature, energy related to ignition, thermal conductivity, mass loss and chemical reactions occurring during the decomposition. The improved test methodology can now be used to estimate the consequences and probabilities of an accident.

The new Seveso II directive 96/082/EEC¹⁶ requires the operator to produce a safety report for the purposes of demonstrating that major accident hazards have been identified and the necessary measures have been taken to prevent such accidents and to limit their consequences for man and environment.

This paper presents some developments, which have taken place during the last decade to emphasise the importance of safety in fertiliser manufacturing.

2 SELF SUSTAINING DECOMPOSITION

2.1 Definition

A fertiliser capable of self-sustaining decomposition is defined as one in which decomposition initiated in a localised area will spread throughout the mass.

Self-sustaining decomposition (zonal decomposition) is a phenomenon in which a decomposition front, initiated locally, will spread gradually throughout the mass. The decomposition is accompanied by evolution of fumes containing toxic gases and a considerable loss in weight of the fertiliser¹⁵.

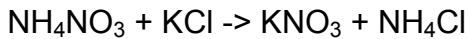
2.2 Self sustaining decomposition

The following conditions are needed^{11, 13}

1. Redox components (NH_4^+ and NO_3^-)
2. A catalyst (Cl, Mn, Co, Cu, ...)
3. All components (1) – (2) concentrated in a narrow zone (e.g. granule)
4. Matrix which is present or formed during decomposition (heat conveyor)

5. Sufficient heat with good conductivity and poor dissipation of heat

Several authors have presented triangular diagrams illustrating the hazardous zones^{7, 11, 12, 18}. These diagrams are difficult to use in computers and therefore for convenience some of the diagrams are presented in Figure 1 based on the molar nutrient ratios. The area for cigar burning ability is within a range of 0.35 to 0.55 as $Cl/(Cl+NO_3)$ and $K/(K+NH_4)$ for a system of NH_4NO_3 - KNO_3 - NH_4Cl - KCl . Chloride is needed as a catalyst, and the solid matrix is a result of the conversion:



Typical formulations are on the diagonal between ammonium nitrate and potassium chloride. The ammonium nitrate rich formulations tend to melt in the test and therefore the probable thermal risk is related to fume off¹².

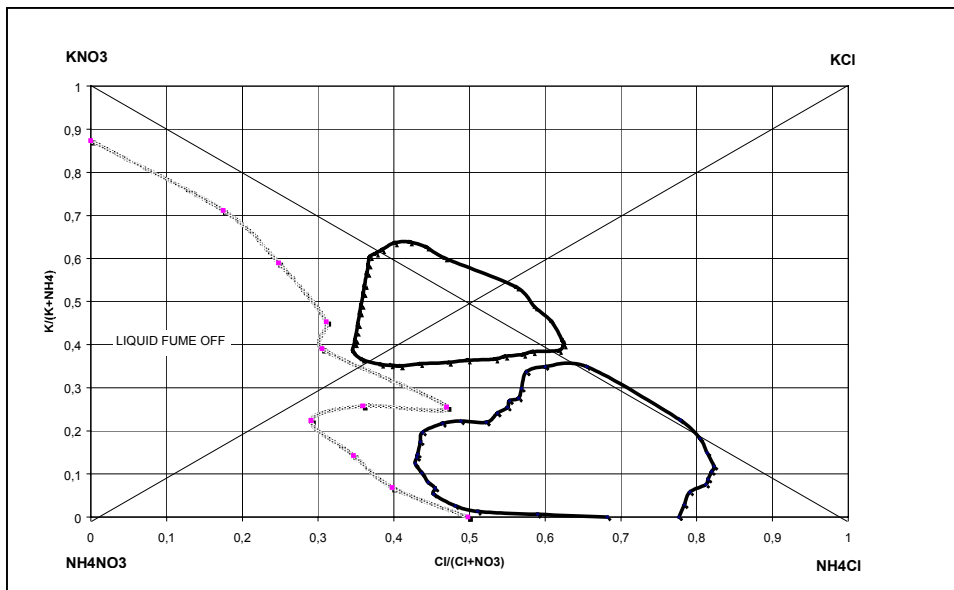


Figure 1: The area of SSD expressed in Jänecke- diagram on the system $(NH_4, K)(NO_3, Cl)$

Addition of phosphorous in a water-soluble form extends the area of decomposition (Figure 2). A similar effect was reported by Perbal^{11, 14} with sulphate. A **solid matrix** at the decomposition temperature is an important factor in governing whether and at what rate the self-sustaining reaction will propagate^{7, 11, 18}.

The greater the tendency for the fertiliser to become molten, or to contain large amounts of liquid phase, before the decomposition temperature is reached, the less likely is the material to propagate the decomposition reaction. Excess and/or the fineness of potassium chloride, the presence of water-insoluble phosphate and specific diluents can form the necessary solid matrix. Calcium sulphate, especially from superphosphates is effective in this way.

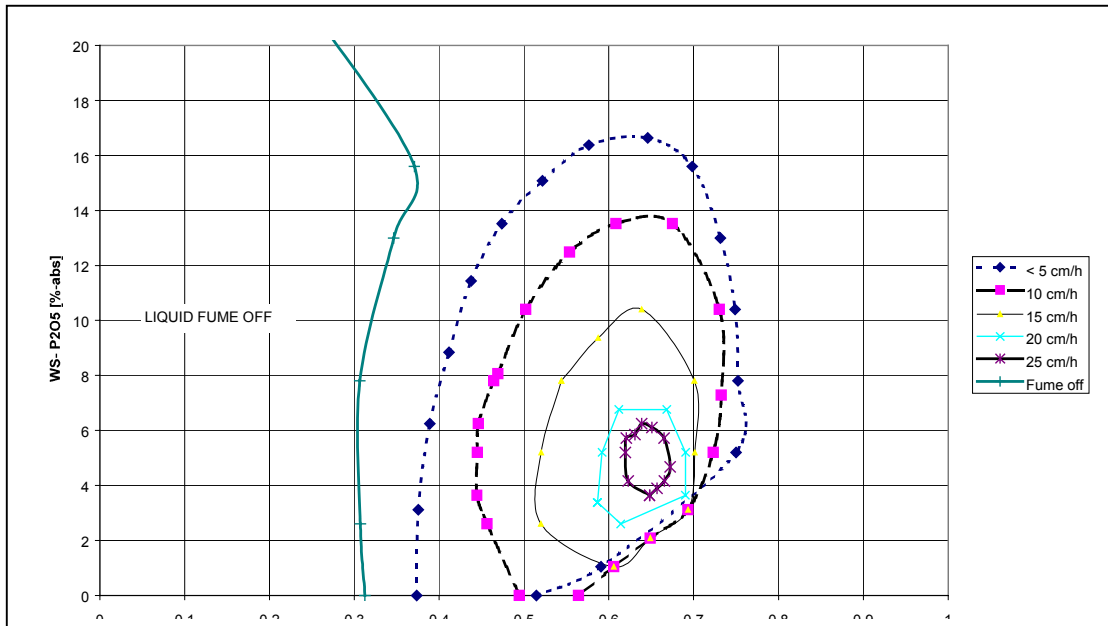


Figure 2: The SSD area expressed as the function of the $\text{Cl}/(\text{Cl}+\text{NO}_3)$ ratio and P2O5 content in the system $\text{NH}_4\text{H}_2\text{PO}_4\text{-NH}_4\text{NO}_3\text{-KCl}$.

2.3 Decomposition reactions

The decomposition reactions do have a complex nature. A schematic representation of the chain reactions is presented.

2.3.1 Non catalysed decomposition reaction

In ammonium nitrate based fertilisers which do not contain chlorides, the decomposition reaction mechanism is a reaction chain, which is completed. The reaction proceeds only if there is enough energy available to maintain the decomposition. In a slow decomposition the gases are mainly nitrogen (N_2) and dinitrogen oxide (N_2O). Traces of other nitrogen oxides (NO_x , NO_xCl) exist. The main features (figure 3) are^{1, 6, 8, 9, 13}

1. Ammonium nitrate melts,
2. Ammonium nitrate dissociates to ammonia and nitric acid,
3. Nitric acid decomposes, and
4. The main gaseous components are N_2O and N_2

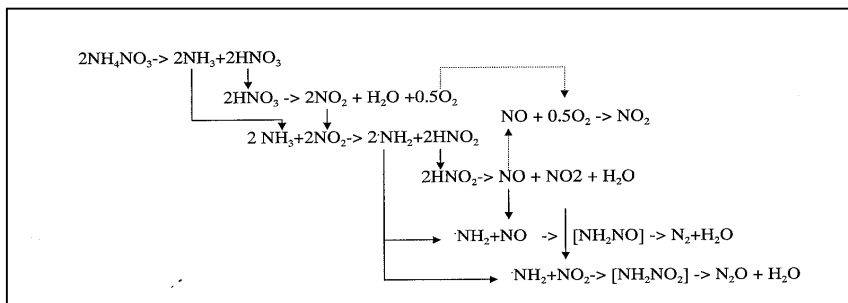


Figure 3: The non-catalysed decomposition reaction

2.3.2 Chloride catalysed decomposition reaction

The chloride catalysed decomposition reaction is the main mechanism involved in the self-sustaining thermal decomposition. The matrix is acidified with hydrochloric and nitric acid, and catalyses the chain reaction. The chloride is mainly from the ammonium chloride present in the fertiliser and the decomposition is actually a decomposition of nitric acid.

As the primarily nitrate source is potassium nitrate it must convert back to potassium chloride. This is possible in the presence of hydrochloric acid and ammonium chloride¹⁹. This reaction forms the chlorine gas analysed in the decomposition gases.

The chlorine gas reacts with ammonia, if present in the matrix, and as a result more hydrochloric acid is formed. The decomposition gas would then consist of nitrogen and water vapour.

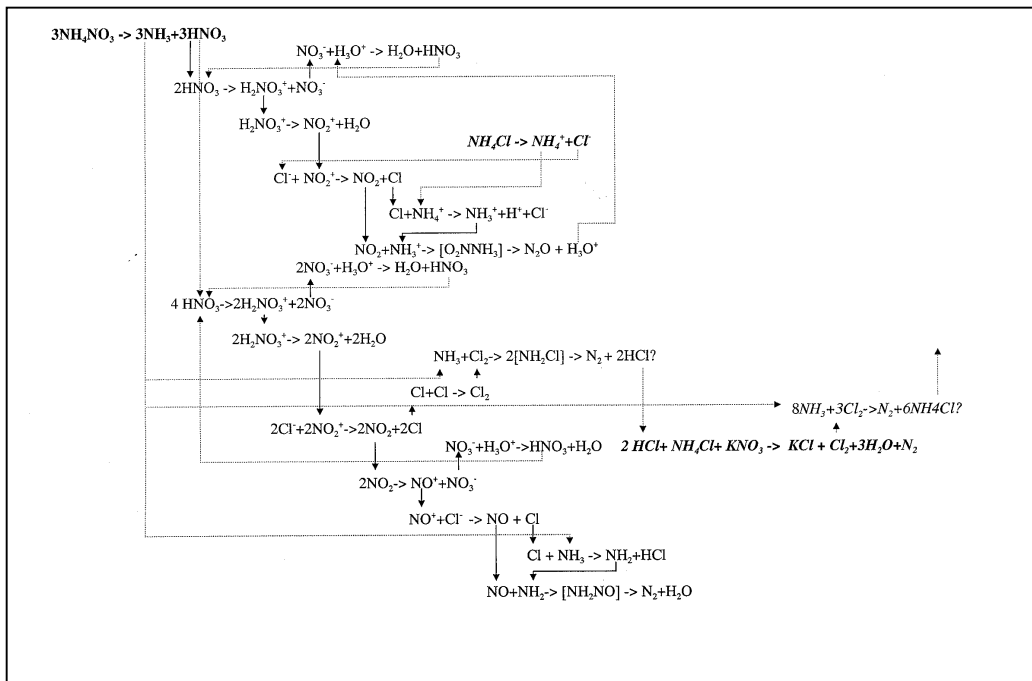


Figure 4: The chloride catalysed decomposition reaction.

In the mechanism the main features (Figure 4) are;

1. The formation of nitric and hydrochloric acids,
2. Chain reaction with ionic and radical steps; chlorine amine is an intermediate stage in which the chloride concentration does not affect the kinetics but is merely having a catalytic affect,
3. The conversion of potassium nitrate into potassium chloride, and
4. The temperature during the decomposition must be above 300 °C to be able to convert the potassium nitrate.

3 TEST METHODOLOGY

The degree of hazard associated with self-sustaining decomposition in a mass of fertiliser is related to: a) velocity of propagation, b) the extent of weight loss, c) the toxicity of the gases released, and d) the sensitivity to initiation^{12, 15, 17}.

3.1 Trough test at ambient temperature

A typical apparatus in figure 5 comprises a trough of internal dimensions 150x150x500 mm, open at the top and constructed from square meshed gauze (preferably stainless steel) with a mesh width of approximately 2.5 mm and a wire thickness of 1.5 mm.

The trough is supported at each corner by a frame constructed from 10-mm diameter metal bars. The bottom of the trough is 150 mm from the ground, allowing free convection of decomposition gases.

The requirement during initiation is that sufficient heat to establish a uniform front should be provided. A steel plate (1- 3 mm) thick is placed inside one end of the trough and in contact with the wire mesh. The plate is heated by means of an electrical heating element or two suitable gas burners (e.g. Teclu or Mekker) which are fixed to the trough support frame. The burners should be capable of maintaining the plate at temperatures between 400- 800 °C (dull red heat)

To prevent heat transmission along the outside of the trough, a steel plate (2 mm thick) heat shield should be installed at approximately 50 mm from the end of the trough at which the heat is applied. It is advisable to use stainless steel for all the components of the apparatus, especially the trough, to achieve better resistance to chemical attack and prolonged life.

3.2 Procedure

The apparatus must be set-up in a fume hood or fume cupboard so that the toxic decomposition gases can be removed. Although there is no explosion risk, it is advisable to use a transparent shield when performing the test.

The trough is filled evenly with granular fertiliser. Decomposition of the fertiliser should be initiated at the one end of the trough by using a gas burner or by using a 250 watt electrical heater. The rate of heating should be adjusted to ensure that the temperature adjacent to the heating plate reaches 300- 400 C within 45 minutes.

Heating should continue until the propagation of the decomposition front (indicated by the change in colour of the granules from brown to off-white) has been observed to move 30 to 50 mm. In the case of thermally stable fertiliser it may be necessary to continue heating for more than one hour to achieve the propagation of the decomposition front.

Fertilisers, which show a tendency to melt readily, must be heated carefully i.e. using a small flame.

The position of the decomposition front should be checked 20 minutes after the discontinuation of heating and subsequently at regular intervals.

If the fertiliser to be tested has a particle size distribution such that a significant amount falls through the mesh of the trough, a gauze with a finer mesh should be used to line the trough.

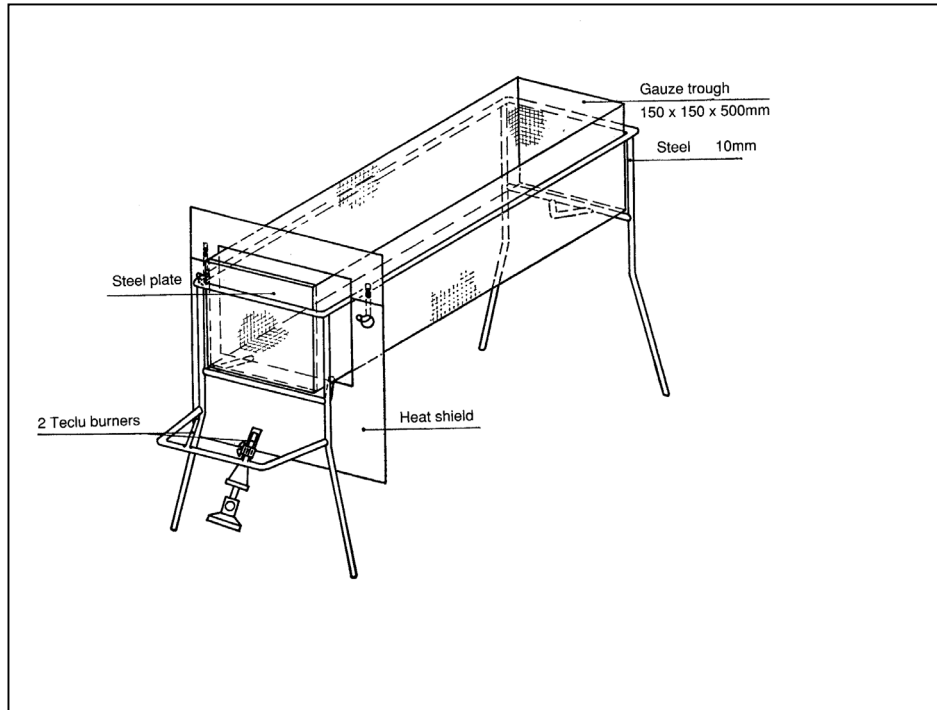


Figure 5: The classical trough test.

3.3 Results

Fertilisers can be placed into one of two categories:

- a) Propagation of the decomposition front continues along the whole length of the trough. => **The fertiliser is capable of showing self-sustaining decomposition.**
- b) Propagation of the decomposition stops almost as soon as the initiating heat source is turned off. => **The fertiliser does not show self-sustaining decomposition in the test.**

In cases where the propagation of the decomposition continues for some time after the initiating heat source is turned off, but stops before the end of the trough is reached the hazard presented by the fertiliser is intermediate between a) and b). If the propagation continues for a distance of 150 mm or more, for the sake of safety, it may be advisable to recommend taking safety precautions against self-sustaining decomposition risk, particularly in production.

3.4 Improved test methodology

The classical trough test has been modified by Kemira Agro to collect the data on thermocouples placed with a fixed interval inside the trough. The temperature is measured as a function of time ($T = f(t)$) (Figure 6). The dT/dt [$^{\circ}\text{C}/\text{min}$] curves (Figures 7 and 8) are recorded for further analysis. In addition the equipment is placed on a balance to record the mass loss during a determination (Figure 9). As a result a lot of information is obtained on

- a) ignition temperature,
- b) energy required to initiate a decomposition,
- c) mass loss rate,
- d) total mass loss,
- e) thermal conductivity of the fertiliser and decomposing matrix, and
- f) a thermogram for identification of the chemical reaction involved.

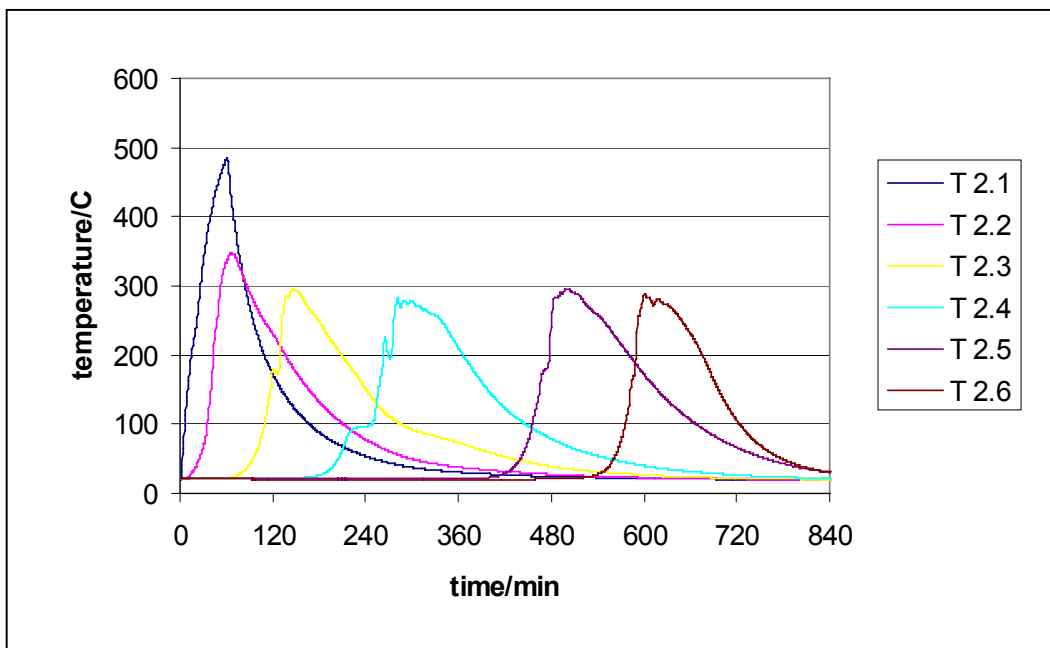


Figure 6: The temperatures as a function of time ($T=f(t)$) in the trough test

4 IGNITION AND ACTIVATION TO DECOMPOSITION

4.1 Ignition temperatures

Before the decomposition reaction can take place the product must be raised to a state of higher potential energy. In the activated state the product thermally decomposes to form a thermally stable composition.

The self-sustaining decomposition is initiated with a heating plate, with an energy input to the fertiliser of 250 W (Figure 7). The temperature increase decreases linearly until the fertiliser mass is initiated for decomposition. After initiation the mass releases heat which is seen

as an increase in temperature. The temperature increases until the mass reaches the maximum temperature caused by the decomposition. The temperature increase rate decreases as the thermocouple can detect only the temperature increases caused by the heat plate, which in case of the example was cut off at 482 °C.

There are significant differences in the ignition temperatures among the studied grades (Appendix 3). The lowest ignition has occurred at 210 °C and the highest at 310 °C. The products made by blending have in some cases significantly higher ignition temperatures, although it can not be given as a general rule. The higher ignition temperatures give some additional safety margin as e.g. 210 °C can be relatively close to the drier inlet air temperature.

The products which are not progressing in the test, it means they do not exhibit self-sustaining decomposition, but do indicate an ignition temperature. This temperature is likely to be the temperature where the solid fume off would take place. For proper (safe) temperature settings in the production unit this information is most valuable.

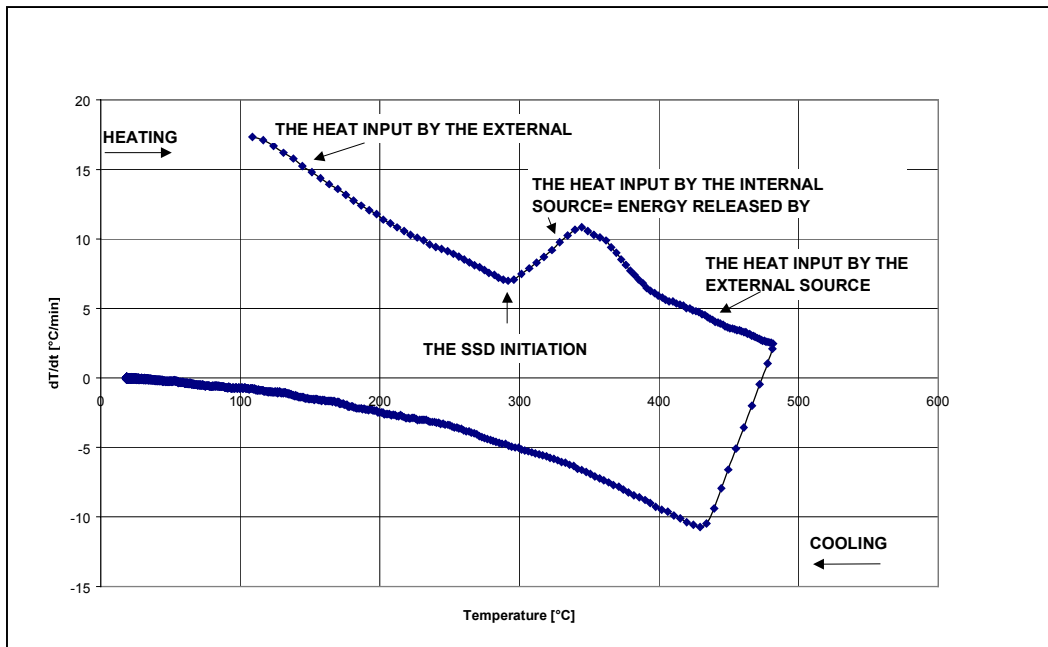


Figure 7: The heating plate temperature (T 2.1) as dT/dt vs. temperature indicating the initiation temperature.

4.2 Energy

As the heat input from the heating plate and the time for initiation are both known it is possible to calculate how much energy is needed to initiate decomposition.

$$\text{Energy} = \text{Heat rate [J/sec]} * \text{Time [sec]} = 250 \text{ [J/sec]} * \text{Time [sec]} \text{ Equation 1}$$

The energy needed varies depending on the fertiliser formulation. The products studied in appendix 3 have a range from 255 to 616 kJ. Based on these values a 40 watt electric light

bulb may be buried in a fertiliser pile for $620 \text{ kJ}/40 \text{ W} = 4$ hours, and for 250 kJ for 2 hours to supply the energy needed for ignition. These results can be used as a relative measure.

4.3 Thermal conductivity

The thermal conductivity of a substance is defined as the rate of heat transfer by conduction across a unit area, through a layer of unit thickness, under the influence of a unit temperature difference, the direction of heat transmission being normal to the reference area.

$$dq/dt = -\kappa \cdot A \cdot d\theta/dx$$

Equation 2

q= heat

t= time

A= area

θ = Temperature

x= length

$\kappa = \text{cal/s} \cdot \text{cm}^2 = \text{W/mK}$

4.4 Reactions and kinetics

The dT/dt graph from thermocouples placed in the trough test indicates what chemical reactions and phase transformations are occurring during the test. This information can be rather difficult to interpret, as the heating rate is not constant like it is in typical commercial devices such as DTA and DSC. Several reactions indicating melting and cooling exist in the heat curve.

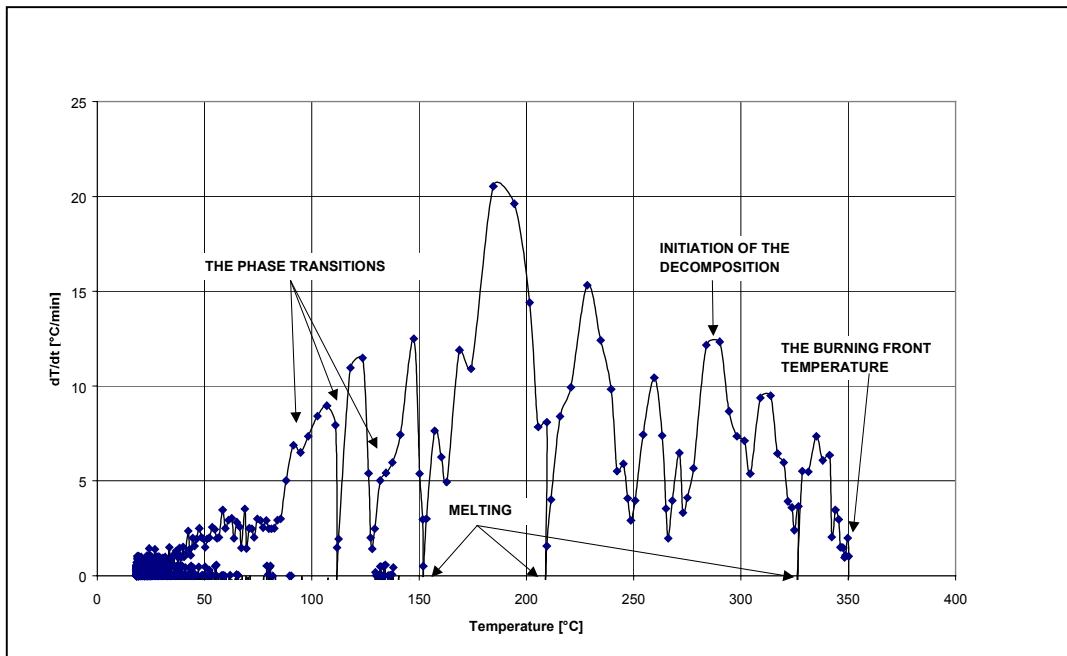


Figure 8: The typical dT/dt graph (T 2.3) as a function of temperature indicating the phase transitions and melting occurring during the test.

5 MASS LOSS AND THE RATE OF MASS LOSS

Although the hazard associated with SSD relates also to the extent of mass loss the only method to measure it is the initial and final mass in the trough. There are no guidelines for interpretation of the mass loss. In the liquid fume off tests the mass loss is normally measured with the so called Beaker test which is appropriate to liquid fertilisers or solid fertilisers which melt and can be stirred.

The mass loss rates and total mass loss has been measured simultaneously with interesting results (Appendix 3). Comparing samples with a rate of 10,5 (30 % mass loss) and 5,6 cm/h (mass loss 55 %) the difference in mass loss is 25 % (Figure 9). For a consequence analysis the product with higher velocity could therefore be considered as safe due to the same amount of gases released per time unit.

The relationship between mass loss and linear rate of decomposition was compared for fertilisers with similar nitrogen content with good regressions ($R^2 = 0,776- 0,992$). Therefore the rate of mass loss correlates with the rate of decomposition when the nitrogen content is taken into account. The mass loss rate ($R^2 = 0.9183$) is obtained as follows;

$$\text{Adjusted rate} = \text{Rate of decomposition [cm/h]} * \text{Total- N} \quad \text{Equation 3}$$

$$\text{Mass loss rate [g/h]} = 8,324 * \text{Adjusted rate} - 171,9 \quad \text{Equation 4}$$

In addition the total mass loss correlates well with the nitrogen content. The correlation is good ($R^2 = 0.824$), although clearly indicates a presence of other variables in the mass loss.

$$\text{Total mass loss [\%]} = 3,887 * \text{Total- N [\%]} - 15,25 \quad \text{Equation 5}$$

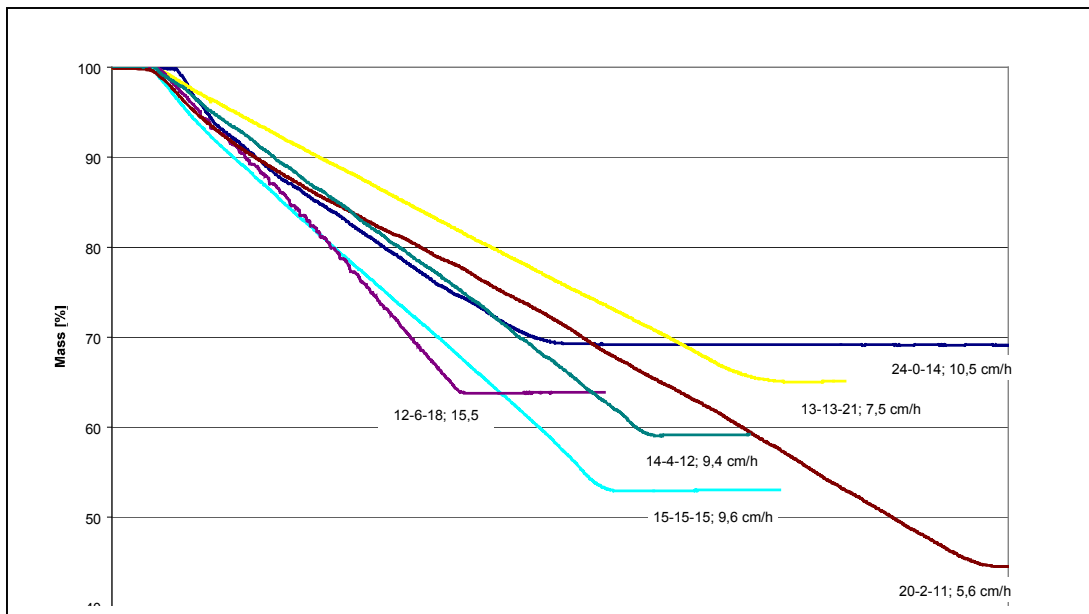


Figure 9: The total mass loss, and the rate of decomposition for different fertiliser formulations.

6 FRONT TEMPERATURE

The burning front temperature correlates well ($R^2 = 0,784$) with the mass loss rate [g/h], which is due to the amount of material creating the decomposition (Figure 10). This relation has been reported in the literature. There is no correlation with the rates of decomposition [cm/h]¹⁸.

In the trough test the maximum temperature in the burning front was around 500 °C for mineral fertilisers. The highest ever obtained was with an organo-mineral fertiliser with more than 800 °C (thermocouple melted). The difference of 100 °C is significant and indicates higher mass loss, more material decomposes during a thermal decomposition and therefore more energy is released.

The temperature of the exit gases has an effect on their toxicity, and in addition it affects the plume rise.

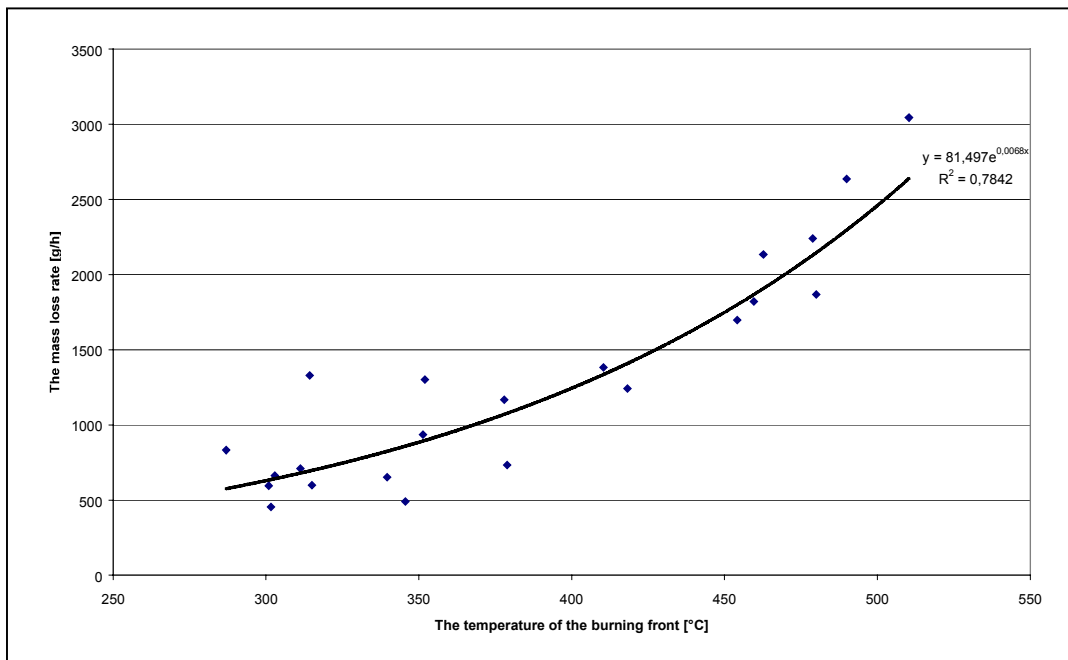


Figure 10: The relation with mass loss rate and the temperature of the burning front.

7 DISCUSSION

7.1 Interpretation of the results

The rates of decomposition varied in the grades studied from 4 to 23 cm/h. For a complete interpretation a reader has a difficult conclusion to make

a) Velocity of propagation-> 12-6-18 (15,5 cm/h) burns faster than 12-6-20 (5,6 cm/h)

b) The extent of weight loss-> 20-4-7 (61 %, 15,8 cm/h) can be considered to be more dangerous than 12-6-18 (36,2 %, 15,5 cm/h)

c) The toxicity of the gases released-> there are no significant differences

d) The sensitivity to initiation-> 20-2-11 (5,6 cm/h, 55,3 %) is ignited at 227 °C where as 20-4-7 (11,4 cm/h, 62 %) ignites at 276 °C.

In all cases the safety margins in the production process must be carefully considered. All the products will decompose if e.g. a lamp is buried to a fertiliser pile- it's only a matter of time. In many processes such as fertiliser drying where there is a built-in heat source in the form of a burner, then the required safety margins will have a significant effect on how the unit should be operated.

7.2 Reliability of the results

The accuracy of the test was studied with a homogeneous sample for total of 11 replications. The rate of decomposition can be reproduced by ± 0.3 cm/h, mass loss by ± 1.3 %. The ignition temperature was ± 10.9 °C with the data measurement interval of once per 30 seconds. This can be improved by reducing the interval to once per 10 seconds. The reliability of the induction period and energy calculation will improve with the increased data collection rate.

Table 1: The statistics of the SSD test methodology.

	Ignition temperature [°C]	Induction period [min]	Energy [kJ]	Front temperature [°C]	Mass loss [%]	Rate [cm/h]
Average	251,6	22,8	342,3	491,9	58,5	17,6
Standard deviation	10,9	1,2	18,0	1,4	1,3	0,3
Relative standard deviation [%]	4,3	5,2	5,2	0,3	2,2	1,6

7.3 Consequence analysis

The consequence analysis on a self-sustaining decomposition has given more respect to small decompositions. It has also confirmed that personal protective equipment must be available over the whole plant area. Proper ventilation is valuable as the gases can be diluted.

It is obvious that new plants should be equipped in such a manner that the suction from the drier will take the decomposition gases, and shall be operable also in difficult conditions. Fume Off conditions are the most dangerous of situations due to the large mass being involved in such a short time. The main parameters there are to avoid overheating around the drier by proper temperature and feed interlocks, proper control of the process especially the pH, a general awareness of the formulation and grade changes and lastly, reworking of reject materials. The procedures related to operation and shutdowns and start-ups should be clearly defined.

Self-sustaining decomposition has major consequences for the storage and shipment of fertilisers. The prevention of such fires mainly involves prevention of the heat sources. Accidents in the past have been caused by buried electrical light bulbs, hot work performed in warehouse, etc. The use of fluorescent lights and hot work permits do provide good precautions. Warehouses equipped with N₂O detectors will give an early warning of decomposition. Firefighting must begin in an early stage before the decomposition spreads too widely thus decreasing the visibility. Much attention is been paid in the production locations, but also persons involved in the storage and distribution of fertilisers should be aware of the consequences and protective measures needed.

8 CONCLUSIONS

The slightly modified trough test, together with modern-day technology being used for treatment of the data, gives a lot of information. The related investments are small compared to the information obtained. Due to the nature of the test method some of the results are qualitative rather than quantitative. The information on the ignition temperatures may give a great deal of help on defining the proper temperature interlocking of a drier, but it is essential to obtain more data for a deeper understanding of self sustaining decomposition.

The measurement of the mass loss clearly identifies that the degree of hazard associated with self-sustaining decomposition in a mass of fertiliser is related to;

- a) Velocity of propagation,
- b) The extent of weight loss,
- c) The toxicity of the gases released, and
- d) The sensitivity to initiation.

9 REFERENCES

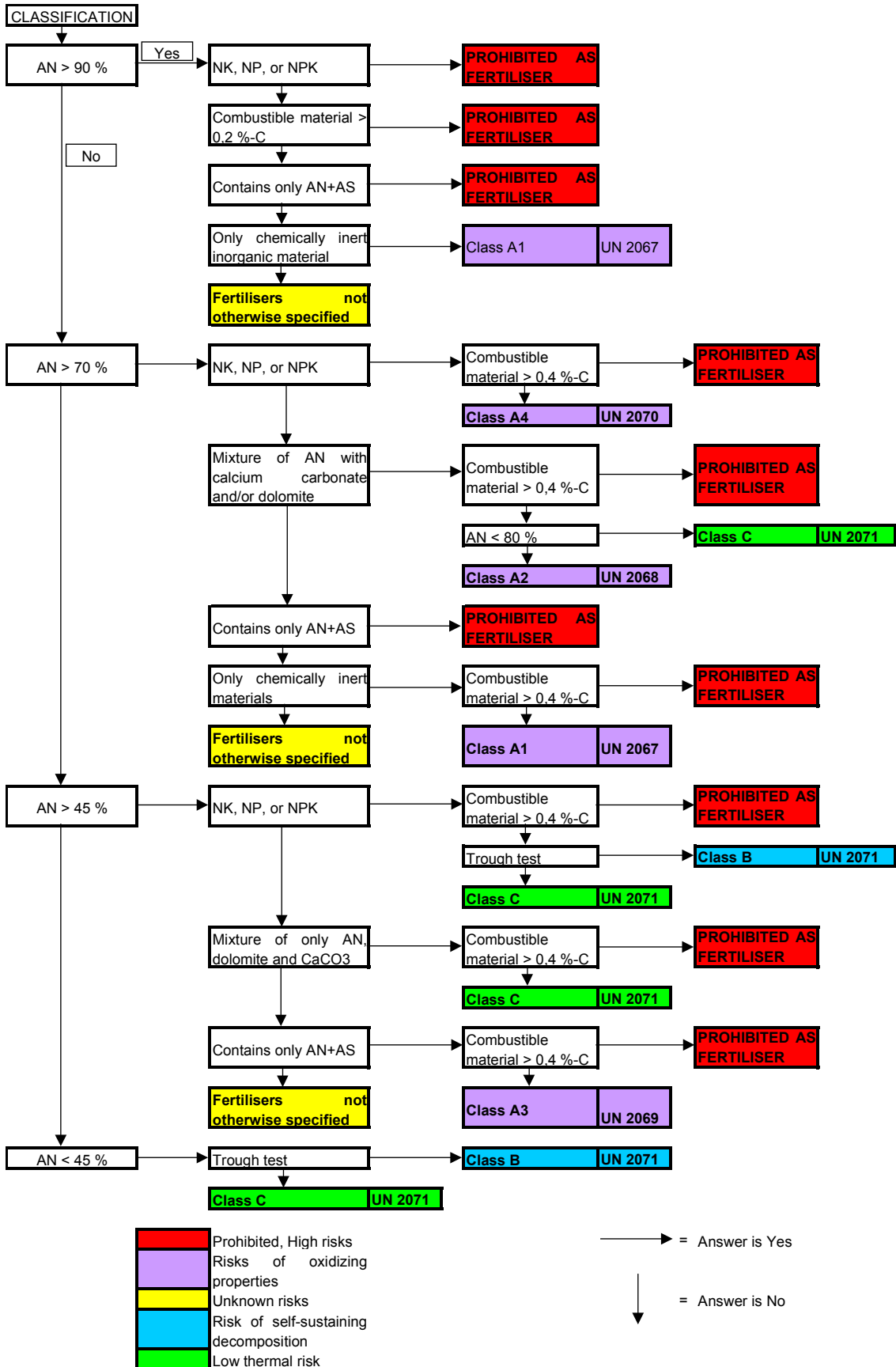
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APPENDIX 1: MAJOR DECOMPOSITIONS

Accident	Cause	Amount of stored material	Damage to the environment	Consequences
The Netherlands, November 1963	Not established	4000 te of 12:12:12 compound fertiliser	Vast amount of dense toxic fumes and a fire.	No one injured.
M.V. Sophocles, Atlantic ocean near the Azores, 1965	Initiation by an electric bulb	5.300 t NPK fertiliser	Boat capsized and sank	3 men drowned
Austria, Dec 1966	overheating due to a mechanical failure	Decomposition in 15 te of 13:13:19 NPK fertiliser in a spherodiser		Release of fumes killed 7 and poisoned 22.
Germany, 1975	Welding spark			1000 evacuated, 67 in hospital
March 1978 Finland	When the plant was shut down for cleaning the drier, material that spilled back into the chamber between drier and furnace started decomposing. The decomposition spread to the contents of the drier.	Material capable of SSD, about 70 te involved. Temperature of gases in the drier reached 250-300°C.	A large gas cloud, 100 m wide, travelled 3-4 km above the nearby sea. Decomposition brought under control in about 2 hours by water addition.	No one injured.
Salzburg, Austria, 6.2.1982	Welding spark	400 tons of fertiliser and pesticides	Large cloud which burned and dispersed	None because of good weather conditions

Ipswich, Suffolk, UK, 14.10.1982	Welding spark, neglect of safety precautions	1380 ton fertiliser including ammonium nitrate, 35 tons potassium nitrate, 150 tons charcoal	Nitrogen oxides, corrosion in buildings in surrounding area	1000 evacuated
Nantes, France, 29.10.1987	Burning material among fertiliser or fault in electrical equipment	1450 tons fertilisers, 750 tons ammonium nitrate, 200 tons urea	Cloud 250 m* 5 km * 15 km	25 000 evacuated
Yugoslavia, September, 1988	An electric lamp fell from the roof	17.000 t NPK capable of SSD.		12.000 evacuated
Lithuania, 87?	External fire caused by ammonia fire	20.000 t NPK	Cloud	7 dead, none evacuated
Humberside coast, UK, 1993	A halogen lamp was buried in a fertiliser	3.000 t NPK	Local residents were advised to close doors and windows.	



APPENDIX 3: THE RESULTS FROM VARIOUS COMMERCIAL FERTILISERS.

Grade	Producer	SSD [cm/h]	LENGTH [cm]	Tot-N [%]	NO ₃ ⁻ [%]	N MASS LOSS [%]	MASS LOSS RATE [g/h]	TEMPERATURE [°C]	ACTIVATION FRONT	
									ENERGY [kJ]	TEMPERATURE [°C]
12-6-18+3MgO	G	15,5	50	12	5	36,2	1381	276	376	410
12-6-20+2MgO+17SO ₃	H	5,6	50	12,6	5,3	34,4	491	255	308	346
12-8-16+3MgO+5CaO+6SO ₃	G	22,5	50	11,9	5,3	25,0	1302	234	307	352
13-13-21	C	7,5	50	13,4	5,2	34,9	599	277	375	315
14-10-20+4S	C	6,7	50	14	5,3	36,8	596	261	397	301
14-10-20+4S	F	6,9	50	14	5,1	37,9	662	246	337	303
14-4-12	E	9,4	50	13,1	5,7	40,9	936	211	255	351
15-15-15	D	6,6	50	15,3	5,7	37,3	652	280	405	340
15-15-15	C	9,6	50	14,6	6,4	53,0	1168	246	324	378
15-15-15+1S	A	4,3	50	15,5	6,3	42,6	455	241	315	302
15-15-15+8CaO	B	11,5	50	15,2	6	56,2	1329	245	300	314
16-5-24	G	10,3	50	16,3	7,3	46,1	1242	258	323	418
17-13-13	I	10,5	50	16,7	8,2	34,4	733	262	300	379
18-3-5 +3SO ₃	J	11,5	50	17,9	8	56,4	1697	263	353	454
20-2-11	K	5,6	50	19,9	9,1	55,3	710	227	302	311
20-2-12+3SO ₃	A	14,7	50	20,2	9,7	61,7	2241	265	345	479
20-2-12+3SO ₃	L	13,9	50	19,6	8,9	59,4	2134	269	383	463
20-3-9 +3SO ₃	A	11,5	50	19,7	9	60,8	1821	250	368	460
20-3-9 +3SO ₃	L	18,7	50	19,5	8,7	60,5	3044	255	375	510
20-4-7 +3SO ₃	A	11,4	50	19,9	9	62,0	1867	276	383	480
20-4-7 +3SO ₃	L	15,8	50	19,5	8,6	61,0	2636	261	331	490
24-0-14+8SO ₃	M	10,5	47	24,3	10,7	30,8	832	310	616	287