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INVESTIGATIONS INTO THE INITIATION OF A DETONATION OF MOLTEN AMMONIUM NITRATE BY FALLING OBJECTS.

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SUMMARY

In this paper the results are presented of drop tests simulating falling objects into a melt of ammonium nitrate which may happen in the case of a fire. During such a fire parts of a collapsing building may fall into molten ammonium nitrate. One of the conclusions from investigations performed in Canada was that the impact sensitivity of such a melt would be in the same class of shock sensitivity as nitroglycerine. This caused the concern of the relevant industry and resulted in the execution of the test programme presented here. In the various tests performed no detonation has been observed even under the most severe test conditions. Exposition of pure nitroglycerine to the same conditions would certainly have resulted in a detonation. This test could not be performed for safety reasons. It thus may be concluded that molten AN is less sensitive than nitroglycerine. Additional tests have to show the difference in the initiation behaviour of both substances. It is unlikely that a detonation of molten AN may result from impact forces of collapsing buildings.

REVIEW OF EARLIER WORK AND SOME RELEVANT PROPERTIES OF MOLTEN AMMONIUM NITRATE

During certain stages of the production process of fertilizers ammonium nitrate (AN) will be present in the molten state. The first stage is in the reactor in which the AN is produced. After this stage the AN melt is slightly diluted and stored in a tank at a lower temperature, but still in the molten state. From the storage tank the molten AN is transferred to the fertilizer plant in which the AN may be concentrated again previous to its use in the fertilizer grain.

Next to these normal process stages one undesired situation may exist in which molten AN can be present, viz. in case of a fire. Especially when a fire can reach a store of high strength AN-fertilizer the melt will consist of nearly pure AN. In Table 1 an overview is given of concentrations and temperatures typical for the above-mentioned situations.

Earlier investigations at TNO sponsored by the Dutch government and fertilizer industries [3] led to the conclusion that under certain conditions molten AN can detonate. Such a detonation is a supersonic transmission of a reaction front through a substance. In Figure 1 the results of these investigations are shown.

Table 1 Concentrations and temperatures of molten AN during the production stages and in case of a fire.

Stage	Concentration (%)	Temperature (°C)
AN production (reactor)	96	≤ 182
Storage and transport of molten AN	84-95	145
Production of fertilizer (concentration)	96-98	160-170
Fire in high strength AN	> 98	> 230

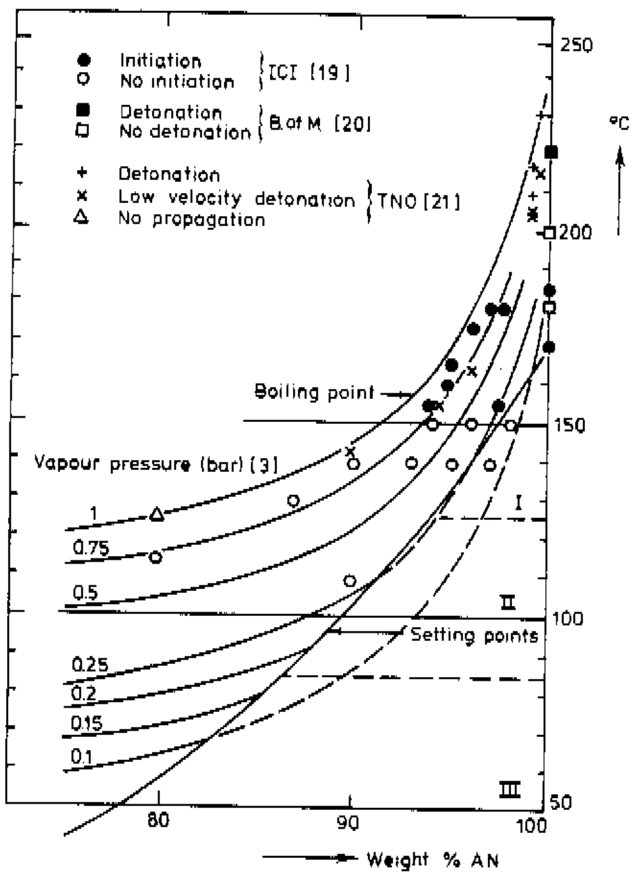


Figure 1 Summary of results of investigations into the detonation of molten AN by ICI [1], Bureau of Mines [2] and TNO [3].

With respect to these results the following remarks have to be made:
The TNO results were obtained by using the TNO 50/70 tube test as recommended by the United Nations [4]. A secondary confinement (reinforcement) was used because of the decreasing strength of stainless steel at higher temperatures. Details of the test are given in Figure 2.

The concentration and temperature limits for a detonation depend on the conditions under which they are determined. At larger diameters of the test set-up a substance can more readily detonate due to decreasing lateral pressure losses and the detonation velocities will increase up to a certain maximum which is substance dependent. In the test set-up only at temperatures higher than 205 °C detonations were observed.

For a low velocity detonation (LVD) it is more complex to translate test results into practical situations since these LVDs can only propagate due to the production of reaction centres caused by rarefaction waves from the steel containment. Due to the absence of wall effects an LVD of molten AN is not possible in tanks, for instance.

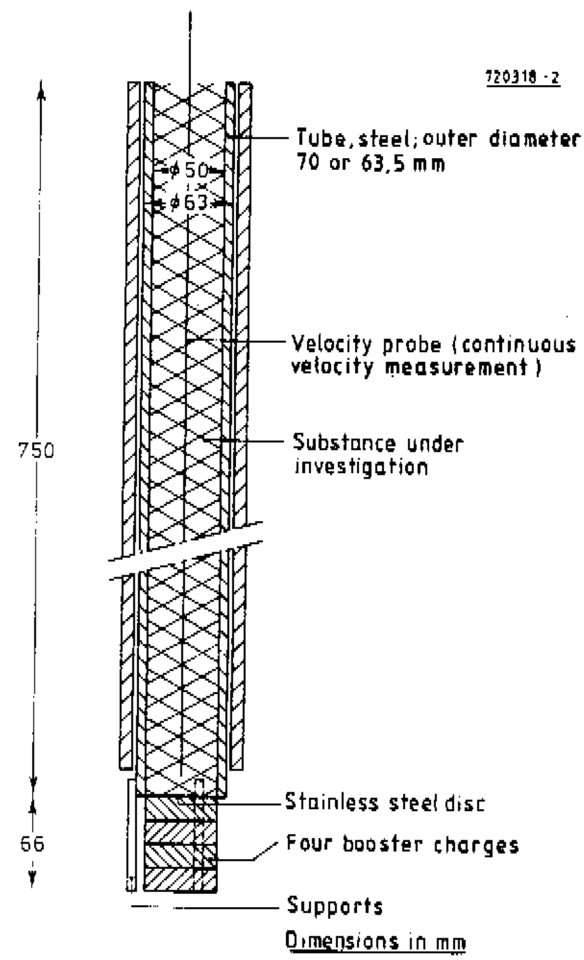


Figure 2 Test set up of the 'reinforced' 50/70 TNO tube test.

SHOCK INITIATION CHARACTERISTICS OF MOLTEN AMMONIUM NITRATE

Part of the extensive research programme of the Queen's University which was sponsered by the Canadian government and fertilizer industries dealt with the initiation of molten AN. Both gap tests [5] and tests using black powder as initiator [6] were performed.

From the gap tests it was concluded that the impact pressure varies from 12500 MPa at 236 °C to 650 MPa at 260 °C, which should be in the same class as nitroglycerine and /or nitroglycerine-based dynamites.

From the black powder initiation tests it was concluded that exploding pipes containing black powder appear to be capable of initiating a detonation in molten AN at certain temperatures and if present in sufficient quantities. The mechanism of such an initiation is a DDT (deflagration to detonation transition) where a deflagration is the subsonic transmission of a decomposition front through the substance without the necessary participation of oxygen from the air.

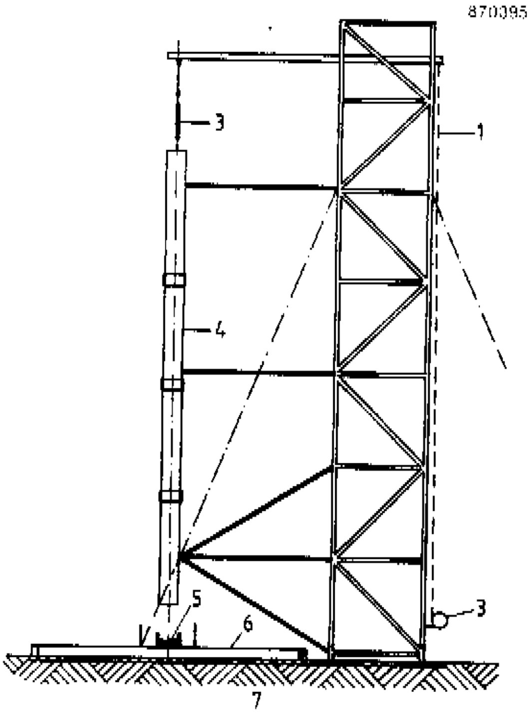
OBJECTIVES OF THE PRESENT PROGRAMME

As a result of the observations mentioned above the International Fertilizer Industry Association (IFA) and the Association des Producteurs Européenne d'Azote (APEA) commissioned the TNO Prins Maurits Laboratory to execute a research programme into the potential initiation of a detonation of molten AN by falling objects as the results observed by the Queen's University could involve initiation of molten AN by falling debris in the case of a fire. After discussions within Subcommittee II of the Working party on the safety of fertilizers of IFA/APEA it was decided to start with the investigation whether a detonation of molten AN could be initiated by falling objects. In the following paragraphs the investigations will be reported.

TEST SET-UP

A drop-tower (Figure 3) has been erected from which weights could be dropped into a beaker containing molten AN. The drop-tower which is constructed from scaffolding has a height of about 14 m, while one meter below the top a horizontal jib is fitted. The projection of this jib at the front of the tower is about 3.5 m. Two pulleys situated at either end of the jib guide the load cable for the drop-weight. The beaker with molten AN is situated on a heavy construction consisting of steel plating, concrete, sand and gravel. This construction of the area of impact maximizes the elasticity of the strike.

The opening of the beaker through which the drop-weight must fall to hit the molten AN has a diameter of 200 mm. Great aiming accuracy is therefore required, the diameter of the weight being 160 mm. In order to guide the drop-weight accurately into the



1. Tower construction (scaffolding)
2. Electric winch
3. Electro-magnetically operated hook
4. PVC guide-tube
5. Beaker
6. Steel plate
7. Sandwich bed.

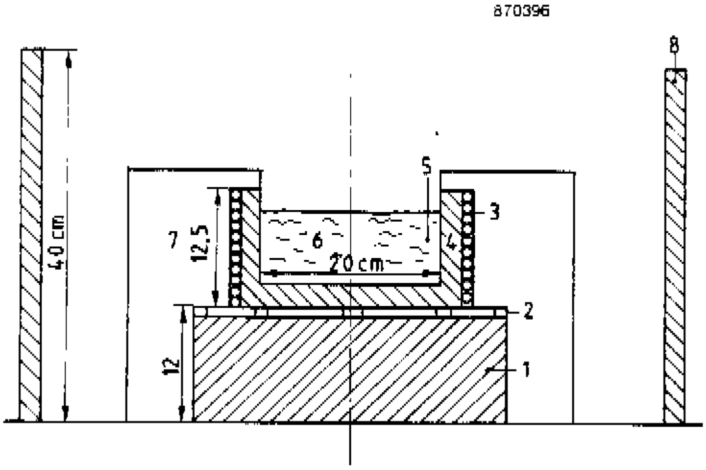
Figure 3 Drop-tower test set-up.

beaker the drop weight travels for most of its fall through a vertical PVC tube with an inner diameter of 190 mm.

The beaker configuration (Figure 4) consists of a stainless steel container (the beaker) with an inner diameter of 200 mm and a height of 100 mm, containing between 3 and 3.3 kg of molten AN during nearly all tests. The beaker can be heated by an electric heating wire closely wound around the beaker. Insulation and measuring equipment (thermocouples and blast gauges) were present during the tests. The blast gauges were installed for the detection of a possible detonation.

Confinement of the molten AN could be obtained by introducing a rigid disc (thickness 3 mm, made from glass fibre or stainless steel) in the beaker immediately above the liquid. The degree of confinement is proportionate to the diameter of this disc. Disc diameters of 175, 196 and 198 mm have been applied in the experiments. In the paragraph on test results this confinement will be reported as follows:
- None, indicating that no disc was used.
- 175, 196 or 198, representing the diameter of the disc.
- None - 198, indicating the limits of confinement. In such a series in fact no confinement and the disc of 198 mm have been applied, with the possible use of intermediate discs of 175 and 196.

At a later stage also a disc providing concave confinement has been applied.

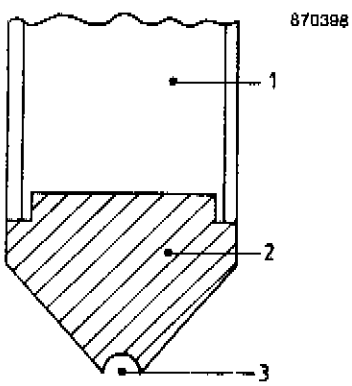


1. Steel anvil
2. Concrete insulation
3. Heating wires
4. Beaker
5. Thermocouple
6. Molten AN
7. Glass-wool insulation
8. Protecting ring.

Figure 4 Beaker configuration

Several heating procedures have been applied during the experiments, the most adequate being a separate preheating up to 50 °C below the required temperature and a subsequent heating in the preheated beaker. During this heating in the beaker the liquid could periodically be stirred in order to keep the temperature distribution uniform within 2 °C.

For safety reasons in most of the tests a drop-weight was applied composed of a PVC tube which was closed at the bottom and filled with small lead balls, since such a weight would scatter in case of a detonation of the AN. At a later stage both a drop-weight of solid steel and a wedge-shaped weight (see Figure 5) were used.



1. PVC tube, filled with lead balls
2. Wedge
3. Nick

Figure 5 Wedge-type lead ball drop-weight

In Figure 6 measurements are given of the pressure on the bottom of the beaker during and after impact of four types of drop-weights. In these tests water was used instead of molten AN and the mass of the steel weights differed from those used in the AN tests. From these tests it can be seen that the peak pressures are essentially no function of the mass but of the drop-height [7].

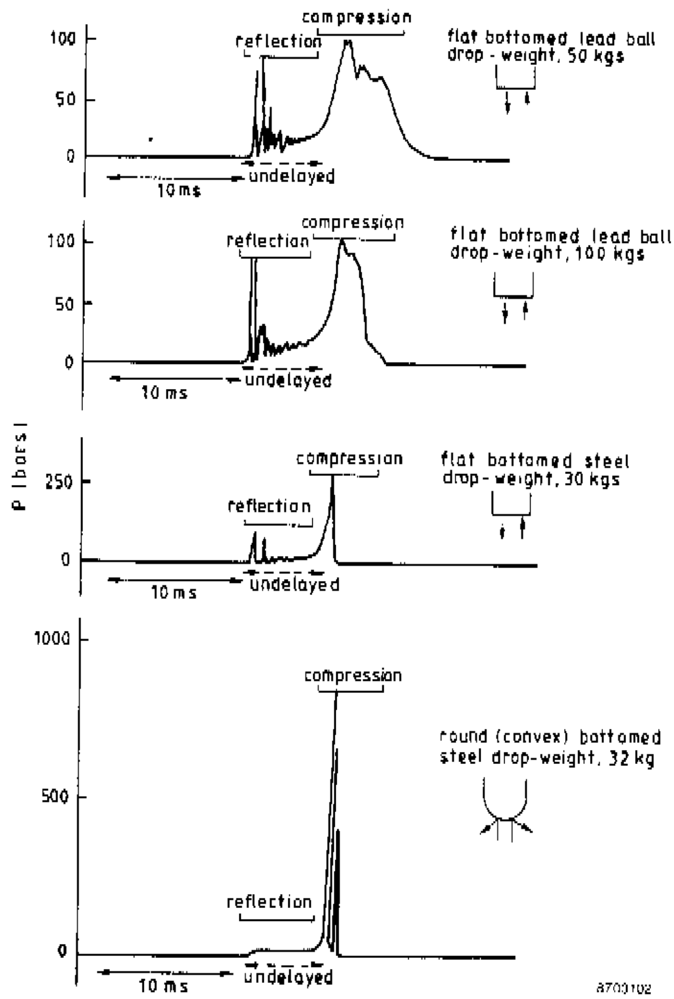


Figure 6 Pressure-time curves measured at the bottom of the beaker corresponding with the fall of a drop-weight on water.

After the drop-tests with pure AN also tests have been performed with contaminated AN. Sand (as a source for hard particles which can sensitize substances), coke (as a reducing agent), micro bubbles (little glass spheres used for sensitizing explosives) and nitrogen bubbles (flow 240 l/h), commonly used to sensitize liquids in tests for the determination whether a cavitated liquid can propagate a detonation [4], were used as contaminants.

For all tests one quality of very pure AN (laughing gas quality) has been used with the following (typical) technical specifications:

- AN content calculated on a water-free basis	99.99 %
- water content	0.20 %
- ashes after decomposition	0.002 %
- chlorine content	< 5 ppm
- iron content	< 1 ppm
- organic material in total	max. 10 ppm
- pH	4.8

Some physical properties of the molten AN have been measured prior to each drop.

- The density has been determined by sucking 25 ml of the hot AN into a preheated pipette, the volume of which has been calibrated at 220 ° C. By weighing this pipette an indication of the density of the liquid could be obtained. Further, the density has been calculated from the sample mass introduced and the known volume of the completely filled beaker.
- The pH has been measured in a 10 % solution of AN in water and the moisture content by the Karl-Fischer method.

TEST RESULTS

In total 47 drop-tests have been carried out without any detonation. The conditions under which these tests were performed can be summarized as follows:

Series 1:	Effect of temperature (5 tests).
Drop-weight:	Lead ball, 50 kg, height 6 - 11.5 m,
Sample:	AN pure, 200 - 262 °C, density 1390 - 1410 kg/m^3, pH 2.93 - 3.63, moisture content 0.05 - 0.28 % w/w,
Confinement:	None.
Result:	No explosion, only blue/grey fumes, brown NO_x gases and smell of ammonia.

Series 2:	Effect of confinement (4 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN pure, 232 - 285 °C, density 1130 - 1400 kg/m^3, pH 2.86 - 3.77, moisture content 0.10 - 0.56 % w/w,
Confinement:	175 - 198 mm.
Result:	No explosion, only blue/grey fumes.

Series 3:	Effect of sand addition to AN (4 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN with sand, 230 - 263 °C, density 1030 - 1400 kg/m^3, pH 2.74 - 3.61, moisture content 0.12 - 0.54 % w/w,

Contaminant:	Sand, 5-10 g,
Confinement:	none - 196 mm.
Result:	No explosion.

Series 4:	Effect of coke addition to AN (6 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN with coke, 230 - 273 °C, density 880 - 1310 kg/m^3, pH 2.76 - 3.26, moisture content 0.40 - 0.56 % w/w,
Contaminant:	Coke 3 - 150 g,
Confinement:	None - 198 mm.
Result:	No explosion, only blue/grey fumes. With high content (83 and 150 g.) of coke self-ignition occured before the actual drop-test could be performed.

Series 5:	Effect of addition of microbubbles to AN (8 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN with microbubbles, 200 - 275 °C, density 840 - 1390 kg/m^3, pH 2.85 - 6.36 (microbubbles can react slightly alkaline with water), moisture content 0.19 - 0.61 % w/w,
Contaminant:	Microbubbles 100 - 170 g (type Fillite 200/7). and 125 - 135 g (type 3M C15/250), the bursting pressure of the latter being approx. 17 bars,
Confinement:	None - 196 mm.
Result:	No explosion, only blue/grey fumes.

Series 6:	Effect of cavitation of AN by nitrogen bubbles (4 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m, 4 tests,
Sample:	AN pure, 230 - 278 °C, density 1170 - 1360 kg/m^3, pH 2.74 - 3.36, moisture content 0.05 - 0.57 % w/w,
Confinement:	None - 196 mm.
Result:	No explosion, only blue/grey fumes.

Series 7:	Effect of concave confinement (2 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN pure, 230 - 260 °C, density 1350 kg/m^3, pH 2.81 - 3.78, moisture content 0.14 - 0.60 % w/w,
Confinement:	196 mm.
Result:	No explosion, only blue/grey fumes.

Series 8:	Effect of a wedge type drop-weight (4 tests).
Drop-weight:	Lead ball, 50 kg, height 11.5 m,
Sample:	AN pure, 230 - 260 °C, density 1240 - 1400 kg/m^3, pH 2.77 - 3.62, moisture content 0.14 - 0.69 % w/w,
Confinement:	None - 196 mm.
Result:	No explosion, only blue/grey fumes.

Series 9:	Effect of 100-kg drop-weight (4 tests).
Drop-weight:	Lead ball, 100 kg, height 9 m,

Sample: AN pure, 230 - 260 °C, density 1240 - 1400 kg/m³, pH 2.77 - 3.62, moisture content 0.14 - 0.69 % w/w,
Confinement: None - 196 mm.
Result: No explosion, only blue/grey fumes.

Series 10: Effect of a steel drop-weight (5 tests).
Drop-weight: Steel, 58.5 kg, height 11.7 m,
Sample: AN pure, 260 - 263 °C, density 980 - 1090 kg/m³, pH 2.73 - 2.86, moisture content 0.44 - 0.67 % w/w,
Confinement: None - 196 mm.
Result: No explosion, only blue/grey fumes.

Series 11: Effect of addition of glass microbubbles to AN in combination with a steel drop-weight (1 test).
Drop-weight: Steel, 58.5 kg, height 11.7 m,
Sample: AN pure, 218 °C, density 1220 kg/m³, pH 4.86, moisture content 0.39 % w/w,
Contaminant: Microbubbles 117 g (type 3M C15/250), bursting pressure approx. 17 bars,
Confinement: 196 mm.
Result: No explosion, only blue/grey fumes.

CONCLUSIONS

From the drop-tests the following can be concluded:

- Neither a densely packed lead ball drop weight of 50 kg nor a solid steel drop-weight of 60 kg did initiate a detonation of molten AN in the temperature range 180 - 270 °C after a drop from a height of 11.5 m.
- The introduction of sand particles into AN did not influence the impact results.
- Addition of reducing materials like coke particles resulted in a swift ignition. It has not been tested if an initiation could be obtained under these conditions. With minor additions of coke no ignition was observed. In this case the mixture could neither be initiated by the drop-weight.
- Also after inclusion of glass microbubbles in the AN the mixture could not be initiated.
- Since pure nitroglycerine will be initiated under the test conditions it can be concluded that molten AN is less sensitive than nitroglycerine.
- As a consequence it is unlikely that a detonation of molten AN may result from the impact forces of collapsing buildings.

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

Q - Mr. N. ROBINSON, Hydro Fertilizers Ltd., UK

I understand that organic matter catalyses the ammonium nitrate decomposition. Can you comment on what type of organic matter is the most harmful ? Am I right in assuming the most harmful things are graphite, or does it not matter as long as it is organic matter ?

A - In our investigations, we did not change the type of organic matter. Coke was used only. Also in the Canadian work coke was used. In previous work, we performed some thermal stability tests where oil was added to the molten ammonium nitrate, however at lower temperatures. At the surface of the liquid a reaction was observed, but no self ignition. Since the addition of organic matter has not been investigated systematically by us, I cannot really answer your question.

Q - Mr. P. ORPHANIDES, Duetag, France.

My question is not addressed to you, but to Mr. Ormberg as Chairman of the Safety Working Party. What are the conclusions you have drawn out of the work done and the conclusions presented concerning the detonation of ammonium nitrate ?

A - Mr. S. ORMBERG, Norsk Hydro, Norway.

For new projects, as for existing stores, the authorities frequently put forward questions like: What happens with AN if the warehouse burns and the roof falls in ? Existing papers and reports have mainly evaluated sensitivity to high energy impacts (bullets, boosters,etc.). The present project was initiated to get results from simulated scenarios, like falling debris onto molten and overheated AN.

The conclusion of the work is just as Mr. Groothuizen said at the end of his paper. The probability of detonation of molten AN during a fire in a storage by falling debris is very unlikely to happen, as long as you use the knowledge and experience we have today for production and storing.

A - Perhaps I can comment on this. The weights we have used compared with parts of building constructions are perhaps a little low, but, in theory, the pressures are the same. The pressures which come into the molten ammonium nitrate by a dropweight, are not dependent on the weight itself. They depend on the velocity at which the weight strikes the molten ammonium nitrate and they depend on the impedence of both the dropweight and the molten ammonium nitrate. So if you have a weight, say 1000 kg, then the pressure will be the same as for the weight of 50 kg.

Mr. Groothuizens's presentation ended with this conclusion: It can be concluded that molten ammonium nitrate is less sensitive than nitroglycerine. As a consequence of this research project it is unlikely that a detonation of molten ammonium nitrate may be initiated by falling debris from a collapsing building.