

Self-triggering reaction kinetics between nitrates and aluminium powder

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Abstract

During the night between the 19 and 20 September 2003, a loud explosion occurred at about 3 km from the town of Carignano that was clearly heard at a distance of some tens of kilometres. The explosion almost completely destroyed most of the laboratories of the Panzera Company that were used for the production of fireworks.

The results of the research activities that were carried out using a differential scanning calorimeter (DSC) on the same raw materials that made up the pyrotechnical mixture that exploded are reported in this paper. This activity was carried out to identify the dynamics of the accident. It proved possible to verify how the event was produced because of a slow exothermic reaction which, after about 8 h, caused the self-triggering of 120 kg of finished product.

The detonation can therefore be put down to a runaway reaction in the solid phase, whose primogenial causes can be attributed to a still craftsman type production system, not conformed to the rigorous controls and inspections as those required by a safety management system for major risk plants, as the Panzera Company was.

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1. Introduction

A loud explosion occurred during the night between the 19 and 20 September at 3.15 a.m. at about 3 km from the town of Carignano (near Turin, in Italy) which was clearly heard at a distance of some tens of kilometres. In reality three distinct explosions occurred a few seconds after each other. These almost completely destroyed most of the labs in the Panzera Company that were used for the production of fireworks. From the first controls that were made, it clearly emerged that the first two detonations were responsible for the complete destruction of the parts of the premises known as Labs 10 and 11 and for the damage that was caused to the other buildings.

On the contrary of what happened in a number of analogous accidents [1–3], nobody was injured, but all the windows of the other low buildings and factory offices were shattered. Numerous houses on the outskirts of Carignano also suffered from shattered windows.

Lab 11 was where the chemical products were mixed. It was divided into two sections: one was set up for the mixture of components to obtain a product with a white colour effect, named “Bianco Luce (White Light)”; the other section was used to store raw materials, closed in their containers (25 kg of magnesium, about 25 kg of perchlorate potassium and about 25 kg of gum-arabic). In another small separated room of the same lab there was also a container with about 14 kg of a “Flash” mixture, made up of about 10 kg of potassium perchlorate and 4 kg of aluminium.

The day before the accident, 6 mixtures of 20 kg each (for a total of 120 kg) were prepared and then transported into Lab 10. In view of the work of the following day, another 4 mixtures of the same composition had been prepared, but these were not complete as they lacked 1 kg of aluminium and they were still at the dry state (with a total amount of pyrotechnic material of 76 kg).

The 120 kg of material taken from Lab 11 had been changed into pellets during the day of the 19 September in Lab 10. These handmade articles were kept in a specific storeroom for a first drying; they would then have been dried in another room.

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Lab 10 was also divided into two sections: the pellet press from which the so-called “Comets” (small cylinders with a diameter of about 2.5 cm and a thickness of 2 cm) are obtained from the “White Light” mixture and a trolley on which 10 wooden frames with metallic grids used as supports for the final product were placed. In this latter room, apart from the trolley, there was also a container of “gunpowder” which was proportioned in very small quantities to act as a trigger for the Comets.

2. State of the site

With reference to the lay-out in Fig. 1, the entity of the damage can be synthetically summarised as follows.

From an inspection of the sites it was observed that two labs for the mixing of pyrotechnical products (no. 10, Photograph 1 and no. 11, Photograph 2) and a pillbox destined for the storage of finished products (no. 4 (Photograph 3)) exploded. The surrounding buildings were also all damaged to various degrees in relation to their distance from the origin of the accident (Photograph 4).

All the glass panes of the other low factory buildings and the offices were shattered. Most of the roofs of the buildings suffered damage both as a consequence of the fragments that had fallen

Table 1
Location of some projectiles (concrete blocks)

No.	Dimensions [cm]	Approximate weight [kg]	Distance from lab	
			10 [m]	11 [m]
1	73 × 26 × 45	213	–	83
2	20 × 20 × 45	23	–	97
3	70 × 26 × 90	205	55	65
4	55 × 26 × 36	128	35	–
5	60 × 26 × 60	234	61	–
6	40 × 30 × 24	72	69	–

on them and because of the air displacement. Some pine trees that had been planted near the explosion location had been cut off or knocked down (Photograph 5).

Apart from the photographs, that are considered more significant than a detailed description, the dimensions, weights, and distances of some fragments are shown in Table 1 to help understand the power of the explosions that occurred. The positions of the fragments are also reported in Fig. 1.

The planimetry of a typical lab is shown in Fig. 2 in order to better understand the state of damage to the structure. These were smaller premises (small storerooms) that were used to store the raw materials, the partially prepared products and the final products. Some of these small rooms were completely open on one

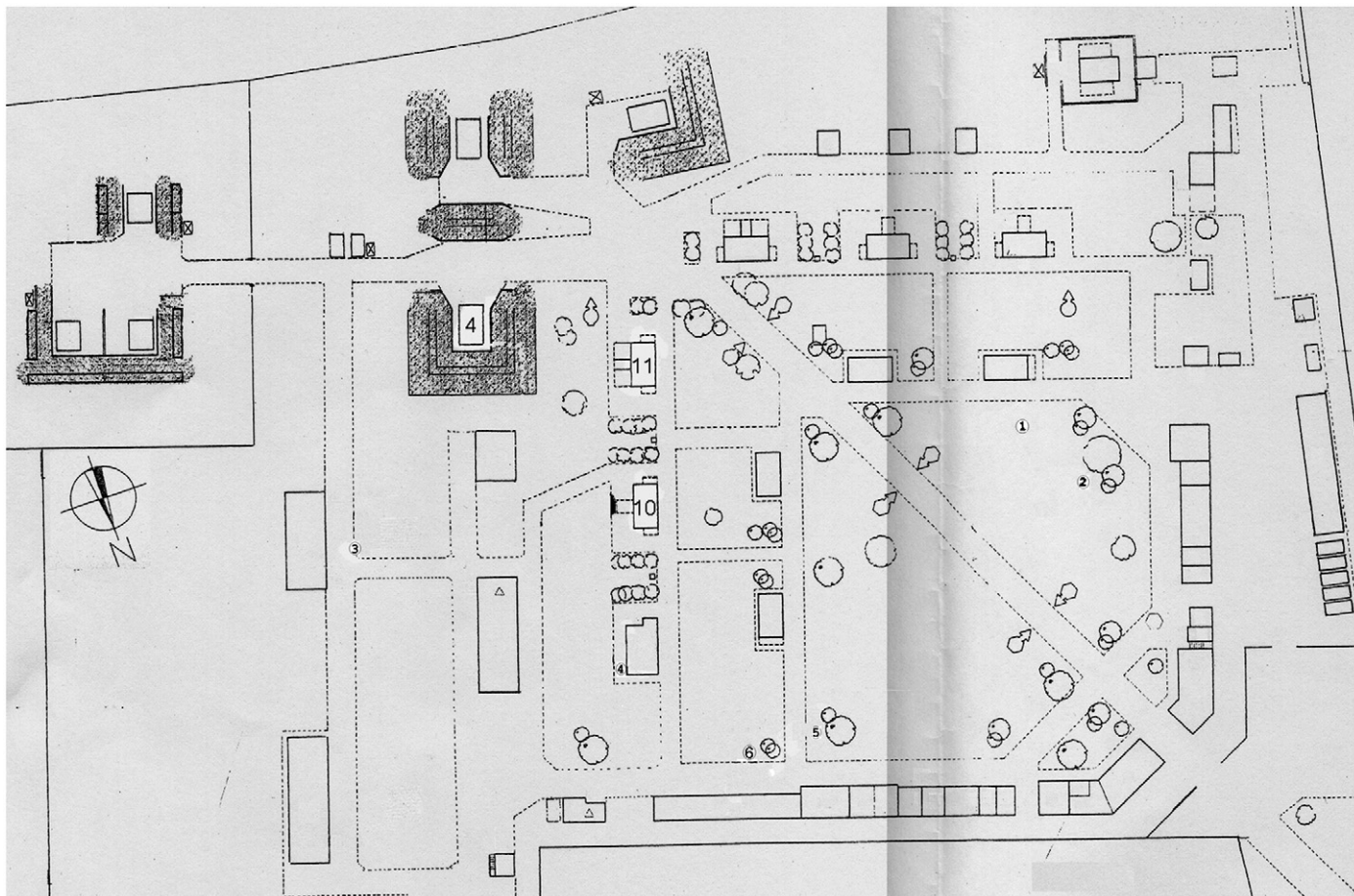


Fig. 1. Lay-out of the company site (numbered buildings are the ones completely destroyed by the explosion; circled numbers represent the projectiles listed in Table 1).



Photograph 1. Lab 10.



Photograph 2. Lab 11.

or two sides. Some equipment, e.g. mixers or sieving machines, were kept in these open spaces.

From a structural point of view, the aforementioned labs were made of masonry (concrete) and sometimes covered in face bricks; the roof structures were always light: layers of asbestos cement or polymeric material.

Apart from the labs, there were other buildings on the company site close to the entrance that were used as offices, storerooms, the guardian quarters etc. On the other side there were the pillboxes, which were even simpler buildings than the labs and were made in not very resistant masonry (sink blocks

of cement) with very light covering. These were used to store the final packed products.

3. The production process

The production activities of the Panzera company were of a craftsman type and were divided over some tens of labs inside which only one worker usually worked. The equipment these workers used were very simple: scales, sieves, buckets, bailers and mixers.



Photograph 3. Pillbox 4.



Photograph 4. Damages in the surroundings.

Each batch of work was of the order of 20 kg. In short, the work that was carried out in each single lab was similar to that of a baker, as will become clearer from the brief description of the working procedures that is here given.

The Panzera's production process for the preparation of a pyrotechnical mixture can be summarised as follows:

- The different components that made up the formulation, all under form of weighed and dry sieved powders were first premixed and placed in a container.
- The mixture was then placed in a mixer with stirrer.
- A modest and predefined amount of water was added and the mixture was blended for some minutes.
- The wet mixture was then passed through a sieve to make it more uniform and then divided into two different containers of about 10 kg each.
- After that the mixture was prepared in small cylinders onto which a small quantity of gunpowder is placed for triggering purposes.

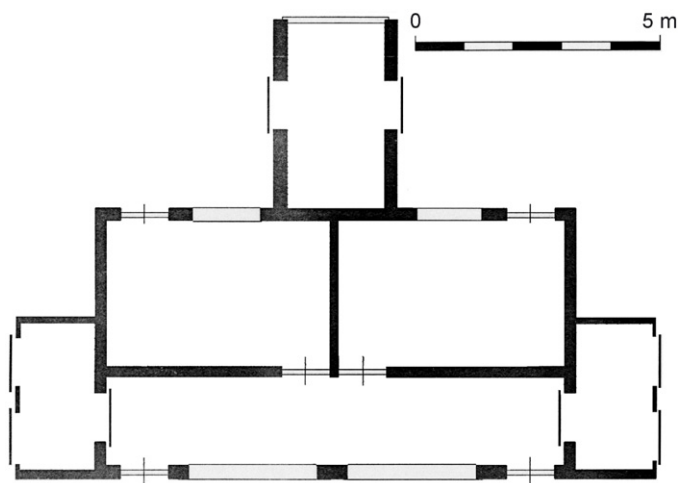


Fig. 2. Planimetry of the Labs 10 and 11.

- The thus made fireworks are left to dry in open spaces and aired for 24 h and then completely dried in dedicated rooms at a moderate temperature of 35 °C.

The evening before the explosion, the mixture used in Lab 10, where the first explosion occurred, had the composition that is shown in Table 2.

4. Chemistry and thermal stability of fireworks

A great deal of literature exists on pyrotechnics: books, specialised reviews, congress proceedings, etc.; the text by Cokling should be considered for reference [4].

The reactions that are involved in pyrotechnics are above all oxide-reduction reactions that occur in the absence of external oxygen (the oxidising agent, e.g. barium nitrate, already contains

Table 2
Composition of the detonated mixture

Substance	Quantity [kg]	%
Barium nitrate	12.4	60.8
Sulphur	2.6	12.8
Aluminium (powder)	3.6	17.6
Gum-arabic	0.6	2.9
Water	1.2	5.9
Total	20.4	100

With these quantities of raw material, 1000 “Comet” fireworks, each of about 21 g, can be obtained. The firework cylinders are 2 cm in height and 3 in diameter.

the necessary oxygen to react with the reducer, usually an easily oxidizable substance such as aluminium).

The reaction velocity can vary from a slow combustion (opportunistically dosing the components) to an instantaneous detonation, according to the preparation method and the work conditions.

Water is used during the preparation to favour cohesion between the powders for the subsequent preparation of the pellets.

Various accidents caused by the presence of water or humidity in mixtures containing aluminium and nitrates have been dealt with in literature [1].

As known, the reaction of aluminium with water is very exothermic and can cause a rise in temperature in the mass, up to its ignition.

Sulphur has a particularly low fusion point (119 °C) and it plays the role of “fire starter” in a pyrotechnical composition: in a liquid phase, it suffers from exothermic reactions at low temperatures with different oxidants and the heat that is generated is used to trigger more energetic reactions in the other combustible materials that are present.



Photograph 5. Explosion effects on the pine trees.

It is worthwhile recalling that, once the mixture has been prepared with the components in the desired proportions according to the effects one wishes to obtain and also in the desired shape (cartridges, catherine wheels, etc.), this mixture, in “normal” conditions (environmental temperature and pressure, the absence of humidity and heat sources, etc.) remains stable in time [5]. In order to perform its pyrotechnical action, it must be triggered by a specific fuse.

The thermal stability of the main products of Table 2 [4] is known and summarised in Table 3.

5. Experimental activities

A research activity was carried out, using the same raw materials that made up the “White Light” pyrotechnical mixture, which was still available in the company storeroom, in order to identify the cause of the accident.

The experiments that were carried out using a DSC 820 scanning differential calorimeter of the TA8000 Mettler thermoanalysis station were programmed with the objectives of evaluating:

- The thermal stability (reactivity) of the finished pyrotechnical mixture.
- The thermal stability of the binary and ternary mixtures of the various components in order to ascertain their respective roles in the reaction.
- The reactivity of the aluminium with water and the role played by this reaction in the reaching of the ignition temperature.
- The time that is necessary for a sample of the mixture involved in the accident, reacting with the water, to provoke a rise in the temperature up to the ignition one, through a kinetic analysis.

Only the most important results, which were obtained analysing the finished product or mixtures of its components, are shown here, with the purpose of compare the thermal effects; the data relative to gunpowder is not shown, as this has not been considered to be responsible for the accident that occurred.

All the experiments were carried out using a closed, sealed steel crucible with air on the inside; the heating velocity of the sample was always 2 °C/min [6].

5.1. DSC on “White Light”

Fig. 3 shows an example of the results that were obtained on samples of the dried final product. Apart from a series of endothermic effects due to fusion and transition of the different components, two exothermic effects can be seen, between 205 and 259 °C for the first ($\Delta H_{\text{EXO}} = -120 \text{ J/g}$) and between 265 and 295 °C for the second ($\Delta H_{\text{EXO}} = -215 \text{ J/g}$).

5.2. DSC on mixtures of barium nitrate and other components

The results that were obtained with mixtures of only two components, as $\text{Ba}(\text{NO}_3)_2$ and sulphur, showed a series of endothermic effects due to fusion and transition of the various components and an exothermic effect between 255 and 300 °C ($\Delta H_{\text{EXO}} = -80 \text{ J/g}$).

The results of the mixtures of barium nitrate and the specific aluminium powders that were used have not been shown, as no measurable thermal effects were encountered up to the explored temperatures (300 °C) and they are therefore not of interest.

5.3. DSC on aluminium powder and water

Fig. 4 shows an example of the results that were obtained. An exothermic effect can be observed between 145 and 275 °C ($\Delta H_{\text{EXO}} = -3815 \text{ J/g}$).

5.4. DSC on aluminium, barium nitrate and water

Fig. 5 shows an example of the results that were obtained. An exothermic effect can be observed between 60 and 120 °C ($\Delta H_{\text{EXO}} = -620 \text{ J/g}$).

5.5. DSC on the complete formulation, including the addition of water

The solid mixture was prepared according to the proportions shown in Table 2.

The water (18% in weight) was added directly to the sample already in the crucible. In this way the mixing between the powder and water was kept to a minimum.

Table 3
Summary of the stability of the components that make up the “White Light” mixture

Component	Stability
<i>Sulphur</i>	The heating curve shows a series of endothermic effects due to the transition of the crystalline phases (rhombo-monoclinical), fusion and fragmentation of the S8 molecule (liquid)
<i>Potassium nitrate</i>	The heating curve shows a series of endothermic effects due to the transition of the crystalline phases (rhombo-trigonal) and fusion
<i>Gunpowder</i> (mixture of potassium nitrate 75%, carbon 15% and sulphur 10%)	The heating curve shows endothermic peaks due to the solid–solid transition and fusion of the sulphur and to the solid–solid transition of the potassium nitrate and a violent exothermic effect starting from 330 °C
<i>Potassium nitrate–sulphur–aluminium mixture</i>	The heating curve shows endothermic peaks due to the solid–solid transition and fusion of the sulphur and the solid–solid transition of the potassium nitrate. An exothermic effect can be observed close to the fusion temperature of the potassium nitrate (334 °C). A reaction between the oxidant and the combustible material and a successive ignition of the mixture can be hypothesised

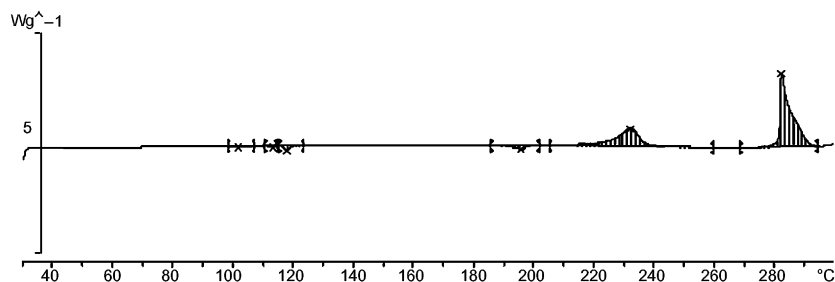


Fig. 3. DSC on 4.75 mg of the “White Light” mixture.

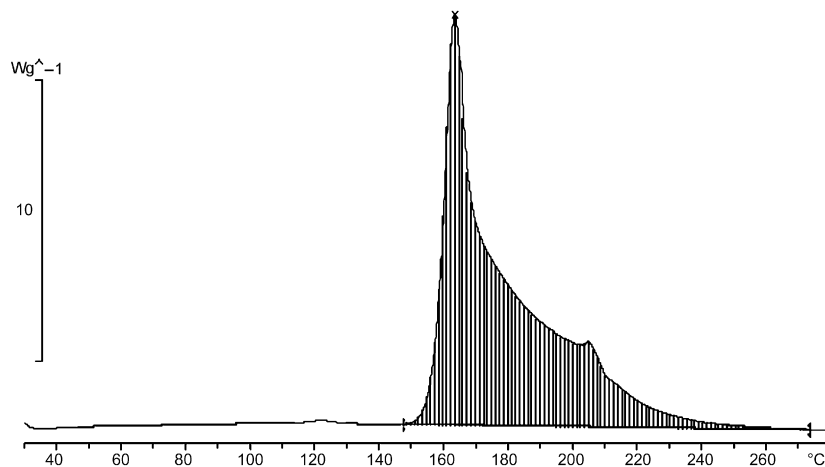


Fig. 4. DSC on 4.49 mg of aluminium powder and water in the proportions shown in Table 2.

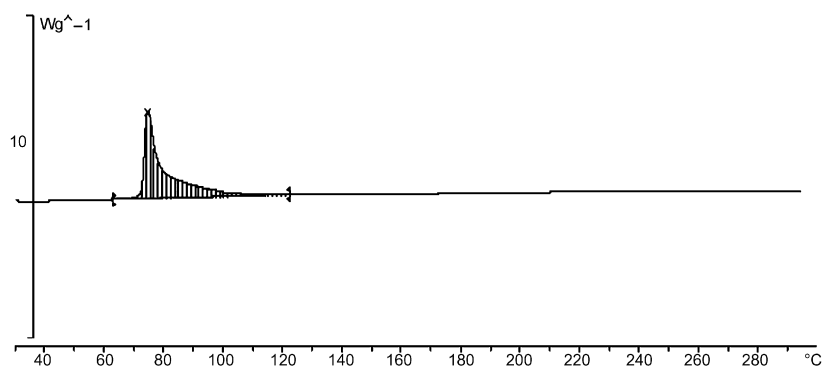


Fig. 5. DSC on 4.93 mg of a mixture of aluminium, water and barium nitrate according to the proportions shown in Table 2.

Fig. 6 shows an example of the results that were obtained. Two exothermic effects can be observed, the first between 80 and 165 °C ($\Delta H_{\text{EXO}} = -115 \text{ J/g}$) and the second between 170 and 260 °C ($\Delta H_{\text{EXO}} = -183 \text{ J/g}$).

A second test was performed mixing the solids with an excessive amount of water (55% in weight).

Fig. 7 reports the results that were obtained after immediately analysing the prepared sample. An exothermic effect can be observed between 70 and 135 °C ($\Delta H_{\text{EXO}} = -710 \text{ J/g}$).

Fig. 8 reports the results that were obtained after having left a similar sample to the previous one for some hours. The absorption of water and a change in the aspect of the mixture were noted. Apart from a series of endothermic effects due to fusion

and transition of the individual components, two exothermic effects were also observed in the DSC, the first between 210 and 255 °C ($\Delta H_{\text{EXO}} = -60 \text{ J/g}$) and the second between 255 and 300 °C ($\Delta H_{\text{EXO}} = -35 \text{ J/g}$).

Three samples with 50% water were then analysed at three different heating velocities (2, 5 and 10 °C/min) in order to estimate the time necessary to complete the ignition reaction of the mixture. Fig. 9 shows the results that were obtained.

A $\ln(K_0) = 15.23$ and an activation energy of 63.96 kJ/mol was calculated from an elaboration of the DSC data, obtained using the standardised ASTM E698 method and assuming a first order reaction.

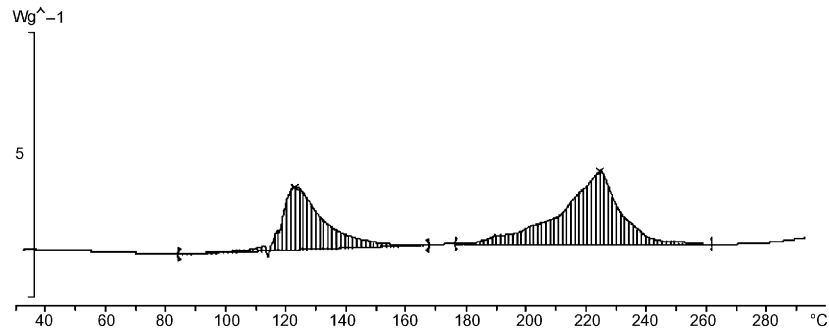


Fig. 6. DSC on a sample with a composition equal to that of Table 2 with the gunpowder trigger and water at 18% in weight being added directly to the crucible.

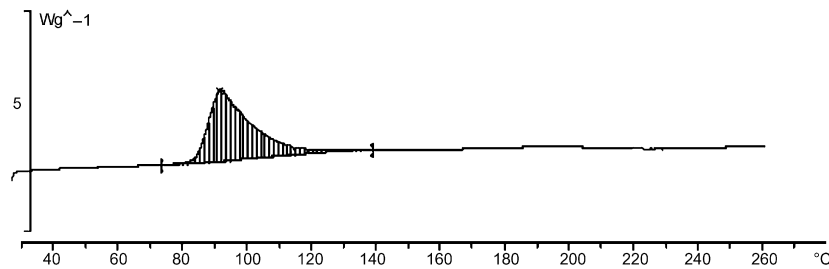


Fig. 7. DSC on a sample with a composition equal to that of Table 2 plus the gunpowder trigger, mixed with water at 55% in weight and immediately analysed.

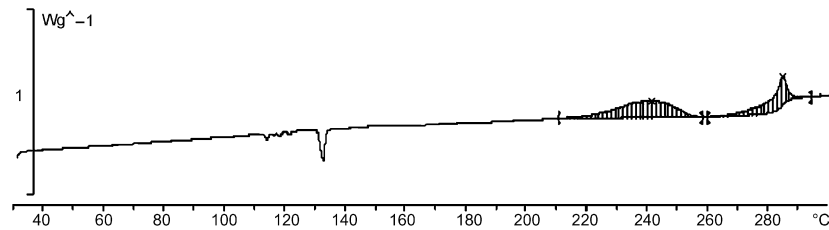


Fig. 8. DSC on a sample with a composition equal to that of Table 2, plus the gunpowder trigger mixed with water at 55% in weight left to rest for 2 h.

From these parameters it is possible to calculate, for example, a 90% conversion in isothermal conditions at 80 °C after 27 min, that is, the mixture, kept at 80 °C, reacts up to 90% in 27 min. In order to confirm the reliability of this kinetic model, a DSC test was carried out on a sample with the same characteristics but in isothermal conditions at 80 °C (Fig. 10). A conversion was measured, in these conditions, at 80 °C of 90%

after 28 min, a result that is in close agreement with the kinetic previsions.

As the model was thus confirmed, it is possible to observe, that in order to have a conversion of 90% at 40 °C, about 433 min are necessary (equal to about 7.30 h), a time that was estimated to be very close to that which had passed between the end of the mixing of the “White Light” mixture and its detonation.

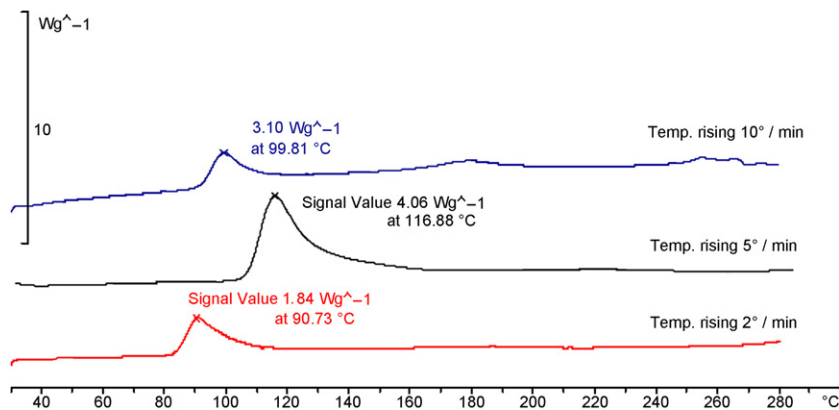


Fig. 9. DSC graph of the “White Light” mixture with 50% of water for different heating velocities.

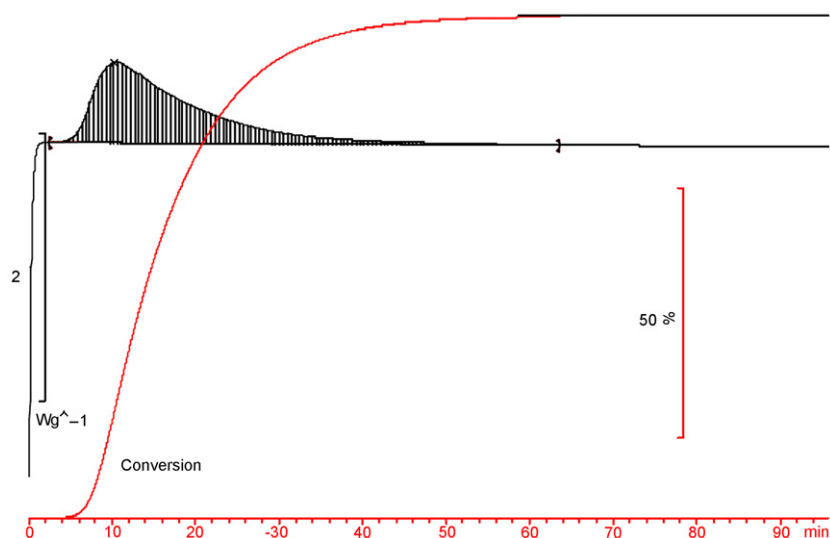


Fig. 10. DSC graph for the “White Light” mixture with 50% of water in isothermal conditions.

5.6. Conclusion from the DSC analysis

The experimentation that was carried out allowed the following conclusions to be drawn:

1. The sample taken from the already dried pellet (and without gunpowder), thermally decomposes at the temperatures and ways foreseen in literature, just like a sample of gunpowder on its own. As this reacts at a lower temperature than the sample without it, its triggering function can be confirmed, that is, that its addition helps lower the ignition temperature of the mixture.
2. The DSC curve of the barium nitrate/sulphur binary mixture shows the foreseen exothermic effect of oxidation of the sulphur by the nitrate, while the barium nitrate/aluminium mixture does not show any exothermic effects, since it was not possible to use the instrument at temperatures above 300 °C. It is most likely that oxidation occurs at higher temperatures.
3. The test relative to the reactivity of aluminium with water in the proportions used in the company is very interesting. It is known that aluminium reacts with water to form H_2 and $Al(OH)_3$ freeing 418 kJ/mol_{Al} which correspond to about 15 kJ/g_{Al}. A reaction heat (ΔH) of 3.815 kJ/g of mixture that corresponds to about 12 kJ/g_{Al} is obtained from the test. This remarkable quantity of heat is able to increase the temperature of the reagent mass by some hundreds of degrees and to exceed the ignition temperature of the studied pyrotechnical mixture.
4. The tests clearly show the role played by water in the reactivity of the system. It is not so much the quantity of water that is present (much more that is used in the foreseen formulation was used during the experiments) that counts, but rather the possibility of being absorbed and being distributed in a more or less homogeneous way. If the water is not in fact distributed in a uniform way, reactions can occur in one or more points of the mixture resulting in an undesired increase

in temperature. If the water instead is uniformly distributed in the reaction mass, the velocity of the heat release is low and the system does not self-heat according to a runaway reaction process in that it is able to lose the reaction heat through simple dissipation.

5. The kinetic analysis made it possible to evaluate the time necessary for a pyrotechnical mixture of the same composition as that which caused the accident to react with water and to free the quantity of heat that is necessary to raise the temperature of the mass to that of ignition. This was therefore a runaway reaction in the solid phase.

6. Dynamics of the accident

6.1. Identification of the sequence of events

The relevant damage to the buildings that was ascertained inside the large area (5.8 ha) in which they are located are the result of not only the initial detonation but also the two immediately following domino effects. From an examination of the site, it can be stated that the first detonation occurred in the storeroom on the right of Lab 10 and after a few seconds the storeroom on the right of Lab 11 also exploded. Then, after another few seconds, the explosion inside pillbox no. 4 occurred (Photograph 3) followed by a severe fire, seeing the quantity of finished products that were stored there.

The part of the rooms where the initial explosion occurred was determined in order to identify the aetiology of the damage. From an inspection of the site, it unequivocally results that the events occurred in the aforementioned sequence. The way the trees were broken, their position on the ground and the finding of parts of the trunks inside Lab 10 all show that this had already been destroyed when the explosion occurred in Lab 11, an explosion which was much stronger than the first. As an example, the trunk of a tree on the ground can be seen in the forefront of Photograph 6; this is also visible in Photograph 7, where, on the right, in the background, the only fragment of masonry still



Photograph 6. Detail of the effect of the explosion on the trees.

standing from Lab 11 can be seen. If we look back at [Photograph 6](#), it is obvious how the metallic section became wrapped around the trunk when this was still standing, having been projected by the initial explosion that occurred in Lab 10, which was located on the left.

It can clearly be seen from the craters on the ground, which both sites show, that both detonations occurred in the storerooms on the right of the two labs.

The reason for the two domino effects can be put down to the projection of numerous heavy fragments of masonry to even great distances. The projectiles from Lab 10 triggered the explosion in Lab 11 and the projectiles from here triggered the explosion in pillbox 4.

6.2. Aetiology of the initial explosion

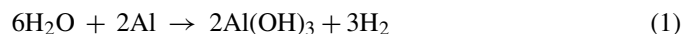
As clearly emerged from the experiments, the cause of the initial explosion can be put down to the self-heating of a rather modest quantity, perhaps even just one “comet” of the “White Light” mixture, with the addition of the water foreseen in the formulation. There are different possible reasons for the self-heating, one according to the quantity and arrangement of a little of the mixture being prepared (Case 1) or another where all the mixture had already been transformed into pellets and these were resting on the screens placed in the storeroom on the right of Lab 10 and left to dry (Case 2).



Photograph 7. Position of the damaged trees with respect to Lab 11.

Case 1. The addition of water at the end of the preparation of the mixture allows the powders to agglomerate thanks to the gum-arabic, and after sieving, the product has the aspect of small lumps of 2–5 mm in diameter.

At this point, the water inevitably begins to react with the Aluminium powders according to the well known exothermic reaction:



The development of hydrogen is not a problem in itself in that, being much lighter than air, it rapidly disperses as it forms.

The reaction heat instead tends to slowly increase the temperature of the quantity (10 kg) of the mixture kept in a plastic bucket for the subsequent mixing.

In normal circumstances, the loss of heat does not create a problem as:

- (a) It is sufficient to occasionally stir the product to cool it and therefore to avoid a possible run-away reaction. This procedure was part of the normal procedures for loading the pellet press and was therefore performed by default; in short, the product being worked had automatically cooled probably without the worker even having realised it.

It can be noted how the passing of time, during the pellet pressing operations, leads to a reduction in heat produced per mass unit in that the slow procedure of reaction (1) leads to:

- (b) Favour the evaporation of the non reacted water; this being an endothermic process, it tends to cool the mass under reaction.
- (c) Diminish the quantity of water available for the reaction, which, in this way, tends to extinguish. If, instead, some kilograms of raw material had, for organisational or temporal reasons, remained on the bottom of the bucket to be transformed into pellets the following day, the situation would be different. The aforementioned phenomena would have occurred just the same, without the cooling due to the product being stirred, therefore the product on the bottom of the bucket would have continued to heat up, though very slowly.

Case 2. In the hypothesis that all the contents of the bucket had been changed into pellets at the end of the day, the only possible explanation is that at least one of these had a higher water content than usual.

This does not seem very likely seeing the way the preparation is prepared for mixing.

- After the first mixing of the powders that make up the formulation (~20 kg) in the mixer, the water is added (1.2 kg weighed separately) and the mixing is continued for 1' 30". Everything is then transferred onto a large mesh-vibrating screen that makes the product even more uniform and changes it into the aforementioned small lumps. From what has been mentioned, it is possible to imagine that there is no precise guarantee on the exact division of water on the powder mass,

therefore the possibility of some of the product that is wetter than it should be remaining on the bottom of the bucket should not be considered as a rare event.

- At this point, a few pellets, or even just one, instead of cooling according to what is stated in points (b and c), tend to heat slowly. It can in fact be noted how the mechanism of point (c) should be very reduced seeing the very unfavourable relationship between the surface and the mass of the mixture, compared to the lumps of the product at the start.

In short, even in this case the gradual and initially very slow increase in temperature (even of just one pellet) would have led to a run-away reaction.

7. Conclusions

The relevant damage to the buildings that was ascertained inside the large area in which the Panzera Company is located, were the result of not only the initial detonation but also of two immediately successive domino effects. An examination of the premises has made it possible to establish how the first detonation can be traced to 120 kg of finished product manufactured in cylinders of about 21 g. The two domino effects were due to the projection of numerous masonry fragments to a certain distance (up to about 100 m).

The reasons of the initial explosion, which occurred in the middle of the night (3.15 a.m.), that is, at about seven and a half to 8 h after work stopped, were identified through the experimentation.

A reaction heat equal to 3.815 kJ/g of mixture being prepared was found during the experiments due to the addition of water to the mixture.

This remarkable quantity of heat is able to increase the temperature of the reactive mass by some hundreds of degrees and to exceed the ignition temperature of the tested pyrotechnical mixture. The experimental tests clearly showed the role the water played of the reactivity of the system; it is therefore not so much the quantity of water that is present that influences the situation but rather the possibility of being absorbed and of being distributed in a more or less homogeneous way.

If the water were not distributed in a uniform way, reactions could in fact occur in one or more points of the mixture with undesirable increases in temperature. If, instead, the water were uniformly distributed throughout the reaction mass, the heat release velocity would be low and the system would not self-heat in that it is possible to dissipate the reaction heat simply by stirring the substance being prepared with a bail.

The kinetic analysis made it possible to evaluate the time that is necessary for the pyrotechnical mixture to react with the water and free a quantity of heat that is able to raise the temperature of the mass to that of ignition. This time resulted to be compatible with that which led to the explosions (7.30–8 h). The cause of the initial explosion can therefore be put down to the self-heating of a rather modest quantity, perhaps even just one pellet or some kilograms of mixture left to be mixed the following day. The reasons behind the self-heating have been

analysed in detail in the text. It was however a runaway reaction in the solid phase whose primogenial causes can be attributed to a still craftsman type of production which did not conform to the rigorous control and inspection criteria it should have set up according to a safety management system where these controls have been introduced.

The production of pyrotechnical material is in fact usually performed not only according to craftsman methods but also with care being entrusted more to good sense and habits rather than a systematic safety procedure, as can be seen from the numerous catastrophic accidents that periodically occur, even in companies known to be careful about safety. In the present case, the safety management system, even if required by the laws in force, had not been implemented.

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