CASE STUDIES ON THE EXPLOSION OF ORGANIC POWDERS IN THE PHARMACEUTICAL INDUSTRY AND IN THE FOUNDRY SAND

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Abstract

The two case histories illustrated in this paper concern (a) the formation of dust clouds, with particular attention paid to the role of fine powder fractions, and (b) the evaluation of ignition energies and corresponding powder characterization. It is believed, or at least hoped, that such studies could stimulate the development of improved containers and associated safety equipment design.

In the first case history the explosion of an organic powder used in the pharmaceutical industry has been studied with the aim to understand the cause of its occurrence. The explosion has occured while a loading phase at the reactor hatch was being completed. It has impacted both internal and external parts of the reactor. Two workers have been injured rather seriously. The reactor contained very little methyl alcohol vapours left from the previous batch production. Nitrogen flow was being sent through the reactor. Various hypotheses have been examined, among which powder ignition caused by an electrostatic discharge from the stirrer shaft, formation of an 'hybrid' mixture and finally the ignition of a cloud of very fine powder floating over the reactor hatch, caused by an electrostatic discharge formed by rubbing among them the two (not sufficiently) anti-static plastic bags which contained the powder. Following experimental tests conducted under controlled conditions, which are illustrated in the paper, the latter hypothesis has proved the more likely.

The second case history concerns the explosion of foundry sand powder during pressure unloading of a pressure-tank made by Al alloy (P-Al Mg 4.4 R

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5000 series) and characterized by a project pressure of 98 kPa. The explosion caused the pressure-frames to collapse and fragment into several parts which impacted the driver-operator and led him to death. The safety valves (PSV) installed on the tank and on the feeding pipe of the air compressor could not operate because the explosive event was instantaneous. Tests made have revealed the presence of over std organic substances in the foundry sand. The internal tank overpressure occurred during the final unloading phase and was apparently caused by the explosion of combustible dust contained in the foundry sand. Progressive enrichment of the combustible fraction of the dust has caused the lower explosivity limit (LEL) to be reached. Likely ignition source has been the mechanical friction between iron materials contained in the powder.

Keywords: dust explosion, fine powder fraction, pressure tank, mechanical friction

Case 1: Introduction

The explosion of a dust cloud formed by an organic intermediate used in the chemical-pharmaceutical industry is illustrated in the following. After the explosion, the reactor in which it had occurred as well as the nearby equipment and walls were covered by a partially burnt, dark organic substance[1]. In the reactor itself a thick layer of semi-fused substance was found under the dark layer. On this basis, the conclusion reached by the local criminal laboratory department was that ignition had occurred inside the reactor. The ignition source had been an electrostatic discharge from the stirrer shaft to the reactor wall. The laboratory stated that grounding of the stirrer shaft was not ensured, during the previous production batch, owing to the defective contact that could often be observed between a rotating shaft and the grounded reactor chassis. As a consequence, an electrostatic charge did accumulate on the insulated stirrer shaft. The ball bearing onto which the shaft was fixed was believed to be responsible for the defective earthing. Oxygen would have entered the reactor together with the organic powder contained in the fiber drums (Figure 1), while the latter was being charged through the open hatch. As a consequence, the plant owner faced

[1] Each production batch began with loading the powderized organic substance contained in four fiber drums through the hatch of a previously emptied 3,000 L reactor. The explosion occurred when the two workers involved in the operation were just finishing loading the second drum, i.e., after 2÷3 minutes.

criminal trial for having caused severe burns to the two workers involved.

The counts of indictment comprised inadequate reactor design and lacking safety measures and training.

Fig. 1 - Fiber drum.

Investigation of the explosion cause

In order to oppose the hypothesis advanced by the criminal laboratory, a series of tests were made in which the passage of continuous current from stirrer shafts (having different diameters) to the ground was verified using ball bearings of different size. Tests were made under stirring. It was found that poor electric contact did sometimes occur with small (1-2 cm diameter) ball bearings. Conversely, the ball bearing which supported the 5 cm diameter shaft installed in the plant reactor allowed permanent passage of electric charge. Furthermore, the stirrer was standing still when the explosion occurred. The hypothesis advanced by the police department could thus be weakened and during the trial, due to pressing questioning on the part of the defendant's lawyer, it was substantially withdrawn. The question remained, however, about the real, or more likely, cause of the explosion.

Finding the 'real' cause proved a rather difficult job. In order to accomplish it, several aspects have been considered, among which:

-powder characterization,

-use of inert (nitrogen) gas, correctness of the loading procedure,

-sources of electrostatic discharge, earthing, atmospheric moisture,

-ignition point,

as well as other variables and the interactions among them. The main points will be illustrated in the following paragraphs.

Fig. 2 - Surface voltage test

Powder characterization

The CHETAH analysis (1) showed that the substance molecule did not present particularly dangerous properties. The Over-all Energy Release Potential was 0,537, i.e., it was 'low'. Measurement of the particle size distribution revealed the presence of a 10% (by volume) fraction of very fine powder (up to 7.8 μm cumulative limit). The measured lower flammability limit (LEL) of the substance was 15 mg/L, i.e., close to the lower limit normally found with powders (10÷60 mg/L).

Loading procedure

Following each production batch the reactor was emptied through the bottom valve while nitrogen was being sent into the reactor, from the top, to compensate vacuum. The final vapour phase contained, besides nitrogen, solvent (methanol) vapour, 26% by volume, which condensed on cooling prior to the subsequent batch in a small (about 200 mL) liquid pool. The latter was completely absorbed by the first amounts of powder poured into the reactor. No hybrid (powder + air + solvent vapour) mixture could be formed or sustained in these conditions, also because the nitrogen flow was continued throughout. Dust clouds could actually be formed when the powder fell into the reactor but not enough oxygen, and no ignition source, were there to give rise to an explosion.

Use of inert gas

The operational procedure required that a precisely metered nitrogen flow be sent into the reactor during the loading step. Accuracy was important as it had been previously shown that such a flow would prevent a large amount of oxygen entering the reactor. As a consequence, the flammability region would not be reached although the hatch was kept open[2]. Measurements shows that after loading the content of the first two drums only 5% (vol/vol) oxygen entered the reactor[3]. The ternary graph that fur-

[2] At present a completely sealed system is used.

[3] The instrument used was the Gas Vision Multiwarn II & PAC III produced by the Dräger Company; readings were taken at about half the reactor length.

nishes the flammability region for the methanol-oxygen-nitrogen mixture shows that the flammability region is never entered with a 5% oxygen content. Also, concerning powder-air mixtures, there is an oxygen concentration limit below which, whatever the ignition energy, explosion can not occur. For most mixtures this limit is usually comprised between 6 and 15% oxygen concentration. Finally, concerning the hybrid mixture, it is known that the presence of a combustible vapour (methanol in this case) can dramatically reduce both the concentration of powder that can give rise to an explosion[4] and its minimum ignition energy (2). However, the mentioned reduction was observed using air as comburent. The presence of nitrogen is likely to produce a less pronounced effect. In any case the formation of an hybrid mixture was not supported, as said above. Also, the worker in charge of the operation admitted that a much greater flow ('*we were running at fully open throttle*', he said later) was being used when the explosion occurred. He felt he had to reduce the loading time in order to catch up with the production program. He also thought that increasing the nitrogen flow would make the operation safer. Alas, in this way he increased the amount of fine powder floating over the hatch and paved the way to the explosion (according to the hypothesis which will be illustrated below).

Sources of electrostatic discharge

Earthing the reactor, the motor chassis and the like was found to comply with best practices. The connection of the entire electric system to the earth had been checked every two years, as required by the Italian law, and found adequate. Workers wore antistatic clothes and shoes. No segments of the loading chain involved plastic, rubber or other insulating materials. So, what could be the cause for a potential electrostatic discharge? A brief remark by Martin Glor, a well known scientist working in this field, was revealing: "..*electrostatic discharges are realized .. when emptying powders from plastic bags or shaking plastic bags near conductive parts such as a reactor hatch..*" (3). This comment stimulated the investigation of the properties of the antistatic plastic bags used at the plant. Preliminary tests showed that some bags were not antistatic at all. It was

[4]The instrument used was the Gas Vision Multiwarn II & PAC III produced by the Dräger Company; readings were taken at about half the reactor length.

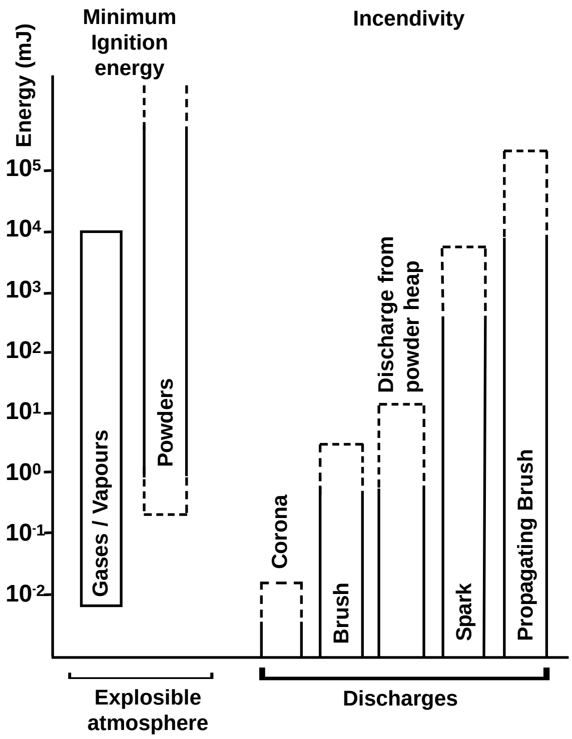

Fig. 3 - Ignition energy

also discovered that in order to quicken the loading operation the two bags placed in the second fiber drum had been vigorously shaken and rubbed one against the other, the day of the explosion, since a certain amount of substance remained trapped inside film pleats that strongly sticked to each other. It was concluded that rubbing could have charged the plastic sheet with a sufficiently strong n electrostatic charge. However, did the corresponding discharge have sufficient energy to ignite the powder? Furthermore, where did ignition happen, inside or outside the reactor? In terms of owner's responsibility the answer to these questions could have made the difference between jail and personal liberty. It was quickly concluded that finding such answers deserved some supplementary investigation. To this aim, an instrument was purchased by which the surface potential of the plastic sheet could be measured (4). Also, sistematic and lenghty tests were performed on the bags.

Tests were made by simply opening the bags and rubbing them inside in order to separate the two sheets (Figure 3). All bags got charged, whatever their antistatic additive content. However, the electrostatic charge disappeared instantaneously from the bags that were truly antistatic. On the contrary, the charge remained on the plastic sheet for a long time, sometimes hours and days, when the bags were not antistatic[5]. It should be remarked that few of them showed this behaviour. The results of the tests were the following:

- the value of the electrostatic potential found on the plastic sheets that were not antistatic varied between +3 and + 16 kV, often reaching values greater than +20 kV;
- an estimate of the ignition energy was obtained through the relation $E = \frac{1}{2} CV^2$, which gives the amount of energy E (mJ) that can be obtained from a body having capacity C (picofarads) brought to a potential V (kV). In the case of a plastic bag the capacity can be estimated as being equal to 100 pF. The surface energy thus varied from 20 to 50 mJ.

Fig. 4 - Fragments of the tank.

[5] This time period ('relaxation time') depends on a few variables, among which the atmosphere humidity content. On the day of the explosion weather was windy and not particularly moist, contrary to what happens most of the time in the Po valley, according to information gained from the local meteorological station.

It can be be noticed that the energy obtainable from the plastic sheet had about the same value as the energy required to ignite a dust cloud (5). In connection to this, the 'powders' and 'spark' segments in Figure 4, taken from M. Glor (ref 7), should also be examined. Antistatic bags showed energy values of the order of 1 mJ (1÷5 kV), too small to ignite the substance. It should also be recalled that the dielectric constant of air would prevent the electrostatic discharge with surface voltage values lower than 5 kV.

Ignition point

Concerning the second question, ignition could not occur inside the reactor because the low oxygen concentration made the required ignition energy much higher than that available on the bags (2). Conversely, the latter was more than sufficient to ignite the small amount of fine powder fraction floating over the hatch. The powder could remain suspended in the air because its settling speed, obtained by Stoke's law, was about 1 cm/s, a value which corresponded, but was opposed to, the nitrogen flow exiting the reactor through the hatch.The mass suspended in the open atmosphere was sufficient[6] to give rise to a deflagration that could ignite other powder fractions and extend itself inside the reactor, in which it pushed a turbulent, oxygen enriched flame front. However, the abundant nitrogen flow that was being sent into the reactor could quickly suppress the flame.

The heat developed in the reactor during the '*rapid fire ball coming from somewhere, but I couldn't see wherefrom*' (as the injured worker said later) was just enough to melt a limited amount of the substance well settled in the reactor.

Conclusion

All the mosaic *tessera* thus seemed to fit well. As a consequence, the conclusion formally put forward in court was that it was very muck likely, although by no means fully established, that defective plastic bags

[6] The substance LEL is 15 mg/L. Shaking the bags could have dispersed in the 50 L volume available over the hatch an amount at least equal to 15 mg/L x 50 L = 750 mg, i.e., the content of a teaspoon.

were the cause of the explosion. In other words, it was by no means matter of poor reactor design. Furthermore, all safety measures, both of technical and managerial nature, were in place. It was finally stated that too many variables, about twenty of them could be identified, have to be properly aligned for an explosion to occur. Therefore the problem at hand was too complex to be completely solved *ex post*. Finally, also since *in dubio pro reo* (5), the owner was acquitted. The worker responsibility was considered a question of utmost delicacy and shadowed. The owner escaped jail and his good reputation was fully re-established, also because a substantial amount of money was paid to the injured workers as 'good-will' compensatory damages. The owner also improved the safety of its process equipment and tried, albeit until now unsuccessfully, to establish a committee for the study of dust explosions within an Italian association of chemical industries.

Case 2: Introduction

The explosion took place while foundry sand was being pneumatically discharged to a cement works silo. The accident caused the front tank to break into various parts (Figure 4) - one of these parts being roughly cut along the plane passing through the symmetry axis - and substantial deformation of the upper part of the back tank in proximity to the front tank (Figure 5). The fragments of the tank were hurled in all directions, some of these fragments hitting the driver who sustained serious injuries all over his body.

Event analysis

The main features characterising the accident which resulted in the tank breaking into various fragments were:
projection of tank fragments in all directions;
occurrence of a flash-flame as evinced from the post-mortem carried out on the driver's body;
occurrence of the accident almost at the end of tank discharge operations, given the limited amount of foundry sand found on the scene of the accident.

Given these elements it was inferred that the event could have been caused by:

explosive or anyway reactive substances,
gas mixture explosion (from gas or vapours),
dust explosion,
hybrid mixtures explosion (gas or vapours and dusts),
fog explosion,
explosion resulting from internal pressure Pmax, generated by air compressor, exceeding tank mechanical resistance threshold.

The first hypothesis was not borne out by the analyses carried out to detect traces of explosive substances nor was any "crater", that is the area where such substances or any manufactures or fragments that could confirm such hypothesis, found.

In theory, a flammable gas mixture could have formed in the tank because of any of the following reasons:
presence of adsorbed gasses,
presence of flammable liquids in the sand,
reaction between foundry sand constituents and water,
reaction of sand constituents (e.g. carbon with the oxygen contained in the air),
reaction of sand constituents (carbon with the carbon dioxide to be found in the air and in the exhaust fumes possibly drawn in by the compressor and sent to the tank),

Fig. 5 - Deformations of the truck

production of hydrogen from acid or basic etches.

The first three of the possible causes for the formation of flammable mixtures were ruled out by the tests carried out on specimens of foundry sand taken from the back tank inasmuch as representative of the foundry sand to be found in the affected tank. It should anyway be borne in mind that even if a flammable mixture had formed, it would have been dispelled by the large amount of air introduced for pneumatic transfer; in other words the explosion would have occurred in the early discharge stage and not in the final stages of the discharge operation.

On the grounds of the tests carried out and given the absence of significant temperature increases, the other two possibilities are highly unlikely, basically because it is difficult to exceed given temperatures even with compression ratios equal to maximum compression ratio and because it was demonstrated there was no fusion or incipient fusion of the plastic fabric (nylon) placed on the bottom plate or of the rubber to be found in the pressure valve and in all the connection hoses.

The formation of hydrogen from basic etch was ruled out because the pH of the solution obtained from the contact of sand with water proved to be only slightly basic (8÷9), both because of the absence of visible traces of corrosion on the internal surfaces of the aluminium plate fragments and because, even if it had formed, it would have been dispelled by the air; in other words the explosion would have taken place in the early discharge stages and not towards the end of the discharge operations.

The specimen of foundry sand proved not to be flammable and so, in theory, we should have ruled out the possibility that an explosible dust-air cloud might have formed inside the tank; however, the tests carried out showed a marked difference in the carbon content to be found in the foundry sand specimen taken from the tank truck and the specimen taken from the adduction pipe leading to the silo, which lends credibility to the hypothesis of a dust explosion having caused tank breakage.

Having, as previously said, ruled out the presence of flammable gases or vapours, the hypothesis of hybrid mixture explosion was also ruled out.

The only possible phenomenon leading to fog formation could be oil blow-by from the compressor lubrication system, this hypothesis too being dismissed because of the small amount of oil used and because of the substantial amount of air introduced.

The hypothesis that tank breakage might have been caused by the fact that material breaking pressure was exceeded was also ruled out following functionality testing of the air compressor, which means that the maximum pressure one can reach before the pressure safety valve (PSV) intervenes is of 225 kPa.

Accident dynamics

In order to understand what might have brought about such violent tank breakage, let us reconstruct the chain of events that is likely to have caused:

it has been demonstrated the foundry sand loaded on the tank truck at the plant contained an abnormally high content of organic substances; this was put down to a specific processing operation or an accidental spillage following which organic substances come to outweigh definitely inert silica sands and rough ferrous materials may be found;

when the tanker tank reached its destination, the driver connected the tank's discharge piping with the silo to be filled and started tank discharge operations by opening the relevant discharge valve causing an influx of air from the compressor;

in such conditions the tank was pressurised at a pressure not exceeding 100 kPa, this provided the safety valve worked, and the massive air flow from below prevented the lighter particles from passing through the gate valve on the tank causing them to build up; said particles kept on moving in an upside-down conical-shaped area which had formed between the flow of air between the bottom of the tank and the pressurised tank walls;

because of the above-described separation, the concentration of organic substances kept on building-up until it reached or exceeded lower explosivity limit; in other words was sufficient 500 grams of said substances (if we take the acceptable value to stand at 50 mg/L);

as is customary, once the discharge operation was almost over, the driver closed and re-opened the discharge valve both to cause said particles, no longer sustained by the gas flow, to fall and to then drive them towards the exit gate; this specific operation led to the formation of mechanical sparks resulting from the friction of the ferrous materials on the bottom of the tank (the generation of electrostatic charges was ruled out as foundry sand is almost conductive, given the relatively slow value of electric resistivity);

the spark triggered the ignition of the flammable dust cloud, which - being at the maximum pressure of 1 bar, could lead to an explosion pressure value of 1.6÷2 MPa, given an explosion pressure value of 0.8÷1 MPa for

dusts under standard conditions;
given a pressure excess of 1.7÷2.1 MPa , the tank membranes ruptured;
the pressure generated found an outlet through the spaces in between the fragments that were hurled in all directions and the resulting turbulence dragged other dust; this fuelled the combustion (flame-thrower effect) which hit the driver engaged in the discharge operations.

Conclusions

Non-flammable dust substances consisting of a mix of two or more components having different granulometry or density, when at least one of the components is flammable, may bring about flame propagation, that is an explosion. This phenomenon can occur because different granulometries or densities can generate a different concentration of the various mixture components at different times and in different places, which may result in the generation of a flammable volume.

The source of ignition for the explosion of the flammable mixture consisting of combustible dust dispersed in the air was put down to sparks from the mechanical friction between the iron materials present in the dust.

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