

## Investigating unusual powder decomposition incidents

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In mid-2020, spontaneous decomposition of a bagged powdered product occurred at a manufacturing plant resulting in plumes of white smoke / gas in the product storage area. There were no injuries but the incident was unexplained and external assistance was sought to investigate the occurrence. During the investigation phase, another incident occurred with the same product in a separate manufacturing facility. The incidents were uncannily similar – with neither having a readily discernible cause. The material being dried contained two energetic functional groups and hence energetic decomposition was anticipated.

The manufacturing company had performed thermal safety studies on the material and had identified the onset of decomposition using adiabatic calorimetry (Accelerating Rate Calorimetry (ARC)) to be 130°C. The product was dried in a filter dryer at a maximum temperature of 75°C with material cooled to 40°C before discharge into flexible intermediate bulk containers (FIBC's). Even accounting for the effect of scale and applying a "safety factor" to the onset of decomposition observed in the ARC, it did not appear conceivable that a product at 75°C could undergo self-reaction / decomposition. Repeat testing of material from the "incident batch" confirmed that the underlying self-heating / decomposition behaviour was consistent with all prior studies and the material was thus not fundamentally different.

The investigation process identified a number of factors which confounded conventional wisdom – both incidents occurred with the last batch discharged from the dryer and none of the prior bagged product from the same production batches showed any adverse activity at all. Even more confusing was that the last discharged batches contained only about half of the material that went into all previous bags from the same batch. Additionally, both incidents occurred multiple hours after discharging when material would have had a chance to cool somewhat.

This paper outlines the incident investigation process and the new safety testing which supported it. The paper highlights shortcomings in the manufacturing companies scale-up testing protocols – which are likely mirrored in many other powder drying operations globally. The cause of the incidents is demonstrated together with recommendations for testing protocols for powder drying operations and mitigation / risk minimization strategies for safe operation in the future. The investigation also considered the potential for dust cloud ignition and the potential for electrostatic induced self-heating behaviour of bulked powder which had hitherto not been deeply investigated. Whilst slightly unusual, the incident events were not unforeseeable – had the correct testing protocols been in place.

The key aims of the paper are to highlight some of the complexities of investigating decomposition incidents and also to demonstrate a robust small-scale testing strategy which will enable safe processing conditions to be established and maintained for powder drying operations in general. As Ecclesiastes wrote, "there is nothing new under the sun", but these incidents serve as a timely reminder to consider all potential hazards.

**Keywords:** Decomposition, runaway, thermal stability, incident investigation, oxidation, exothermic reaction

### Introduction

#### Process Information

The substance which is the subject of this paper, which will be referred to as "Product A", is an isolated powdered intermediate in the manufacture of an agrichemical product. The molecule contains two energetic functional groups which are of process safety relevance. Product A is dried in 1500 kg loads at 75°C in a nitrogen-inerted, agitated Nutsche filter dryer before cooling to below 40°C and discharging. In one manufacturing location, the product is discharged into flexible intermediate bulk containers (FIBC's) whilst in the other facility of interest, the material is discharged into 200 L fibreboard drums. Each FIBC contains around 400 kg of product and each fibreboard drum contains around 100 kg of product. Once filled, the containers are placed in a storage area awaiting further processing steps. The process has been in operation for some time without incident. The operating company had obtained thermal stability data on the dried product using Thermal Screening Unit (TSu). The test is a sealed differential thermal analysis (DTA) thermal screening technique designed to identify exothermic decomposition reactions. Testing across a range of batches indicated thermal instability – ascribed to the molecular fragmentation of one or both of the energetic functional groups - from 140°C. Allowing for a safety margin, the company stipulated that the material must be kept below 100°C to avoid decomposition.

#### Incident Descriptions

##### Incident 1: Q3-2020

In mid-2020, a drying cycle of 1700 kg of Product A was completed routinely and material discharged to FIBC's. This was the fourth batch of a five batch campaign. There were no obvious deviations from the normal sequence. Several hours after the discharge, the last FIBC containing the final 200 kg of batch (rather than normal 400 kg), started to emit smoke / fume which became more and more dense. The first four bags containing 400 kg from the same batch remained unaffected despite being in close proximity to the final bag. The fuming event was captured by plant closed-circuit television (CCTV). A snapshot of the incipient stages of the fuming event is shown in Figure 1.



**Figure 1: Incipient stages of the incident event captured from CCTV images.**

On further investigation, there were a couple of small abnormalities associated with the batch. Firstly, about 300 kg from batch 3 failed to empty, and remained in the drier, where it got mixed in and heated for a second time. Secondly, a few times during drying of batch 4 the agitator amperage jumped to a high value. It was also noted that the recorded weight in the incident bag *increased* by 3 – 5 kg during the fuming event. Despite these apparently minor anomalies, batch 5 was subsequently completed normally.

#### **Incident 2: Q4-2020**

In late 2020, at a different manufacturing facility on another continent, the 17<sup>th</sup> batch of Product A manufacture was just being completed. The final bag of product discharged from the dryer was packed into a 200 L fibreboard drum contained in two polyethylene bags. The final discharge contained 35 kg of Product A, slightly less than normal. After nearly two days in the drum storage area, this single drum of the product began to emit fume / smoke. This continued until local fire fighters deluged the drum with water, extinguishing the event. Figure 2 shows the fuming event captured by a witness camera. After the event, a blackened residue was found in the incident drum, but product in surrounding drums, from the same batch, was found to be chemically unchanged / unaffected.



**Figure 2: Image of the drum fuming event captured by witness camera**

## **Method and Initial Results**

### **Incident Investigation**

The operating company initially performed repeat TSu thermal stability testing on the “incident batches” to identify any differences in stability compared with other batches. There was no evidence of any change in fundamental stability. Given that the discharged material was at or below 40°C and the maximum recommended exposure temperature was 100°C, the operating company did not believe it was credible. Although no injuries were sustained by workers in either incident, the potential for future events, propagation to adjacent product and escalation needed to be addressed and measures take to avoid repetition. At this point, external support from an expert process safety company was sought to support the incident investigation and provide additional thermal stability testing data.

The initial phase of the investigation was to identify the nature of the event – and then to examine initiating causes. Examining the data available on the product and the circumstances of the incident, it was soon concluded that the event was not an explosion (either of dust or gas / vapour). The findings / factors which led to this conclusion were:

- There was no airborne dust inside the containers in either incident. The materials had been sat for many hours after filling when any airborne dust formed during discharge will have settled out. The powder has a minimum ignition energy (dust cloud) of 20 – 25 mJ, so is certainly susceptible to electrostatic ignition, but the lack of a dust cloud at the time of the event excludes this as a possibility.
- There is no residual solvent in the dried product which may have increased ignition sensitivity.
- There was no evidence of burning / flames and the events were of long duration (lasting tens of minutes) - not at all consistent with an explosion event.

It was concluded that the event must have involved a thermal event, of some description. It was next considered that the event could have been a thermal decomposition (known to start from between 100 and 140°C) initiated by a hot surface or a high-energy electrostatic spark, however, this was also quickly eliminated, based on the following factors:

- There were no electrical items in the vicinity of the containers in either incident, no heated pipework or systems and no moving mechanical items from which frictional heating could have arisen.
- Under laboratory test conditions, the material was not found capable of propagating a hot spot – even if one had been present.
- Electrostatic ignition was quickly concluded by one of the company's incident investigation teams to be the cause of the incident. However, on closer inspection, there was no evidence to support this. Even for an insulating powder, the time elapsed between filling the bag and the incidents initiating will have allowed charge to dissipate to a greater or lesser extent. Electrostatic discharges would be likely at the point of highest charge (initially on filling) not after a period of hours when some dissipation will have occurred. There is a very low likelihood of there being anywhere near enough charge remaining to initiate a 20-25 mJ discharge. In addition, there is a very low likelihood of a discharge anywhere near as concentrated as the test discharge. It is theoretically possible for a spark discharge to have occurred from the static dissipative bag if it retained charge transferred from the powder and was not earthed. But after 44 hours it is suspected most of the charge will have dissipated and the chances of any type of discharge was bordering on non-credible.
- In the unlikely event that an electrostatic discharge occurred, triggering bulk decomposition or burning of bulk powder from electrostatic discharge is much more difficult than ignition of dust clouds. Attempts were made in the laboratory to initiate layer decomposition using electrostatic discharge without success.

Based on the initial findings of the incident investigation, it was concluded that powder decomposition was the most likely cause of both incidents and a more detailed investigation of thermal stability was initiated.

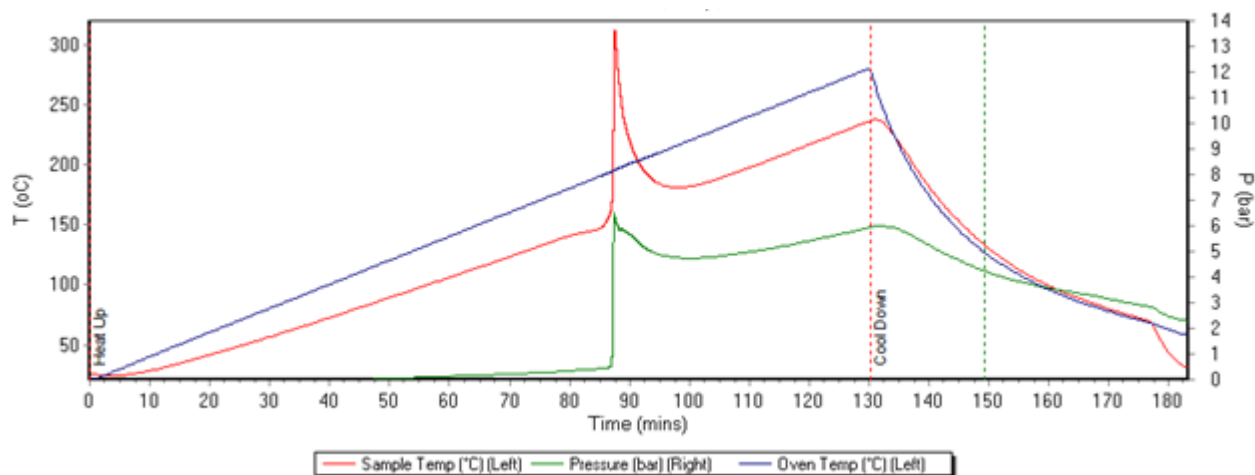
### Further Investigation of Thermal Stability

There were a number of similarities in the two incidents which differentiated these batches, subtly, from routine batch materials. Specifically:

- Both incidents occurred with the last batch discharged from the dryer in the batch campaigns
  - It was inferred that this could have lengthened the time of exposure to elevated temperature for material that remained in the dryer throughout the batch.
- There was evidence of material hold-up in the dryer between batches
  - This again presented the likelihood that materials were exposed to elevated temperature for durations longer than normal. It is also possible that aggregated “chunks” of compacted powder could have been discharged at a higher temperature (or at least the inside could have been hotter than bulk powder discharged). The location of powder temperature sensors also meant that higher temperature hotspots within the dryer may have gone undetected.
- Less material discharged to the final container than standard discharged quantities
  - Subtly, this could lead to a higher surface area / volume ratio of the containers and the inclusion of more air inside the fibreboard drum.

The initial client thermal stability data on the product was obtained from TSu and Accelerating rate Calorimetry (ARC) studies. Critically, these two methods involve the testing of sealed containers of material, with limited air availability.

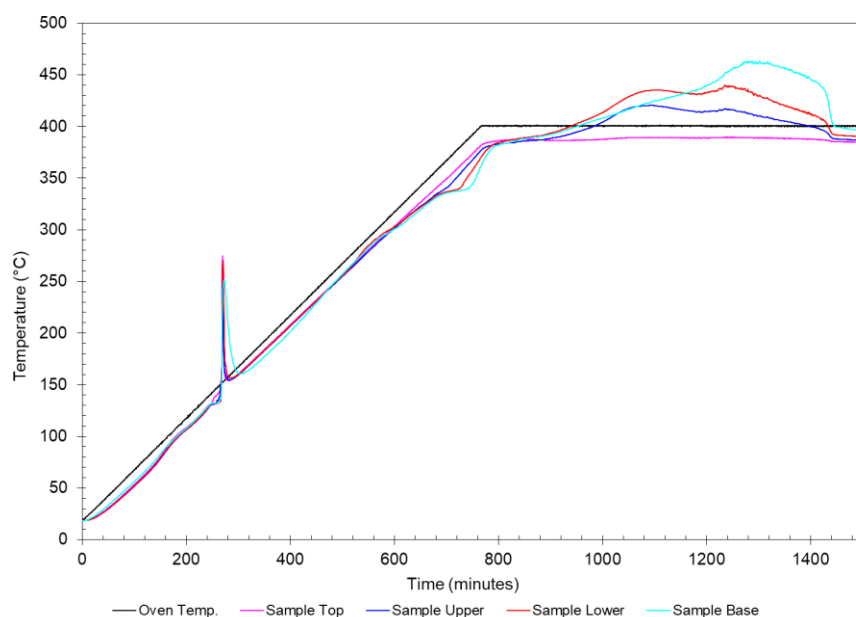
The TSu test result for material taken from the incident batch is displayed in Figure 3. This shows the decomposition reaction occurring from around 140°C – fully consistent with all prior data collected on the material. The operating company applied an industry standard 40 – 50 K safety margin to the measured onset – providing a maximum recommended safe handling temperature of 100°C. As this was above the drying temperature (75°C) and the powder temperature on discharge (40°C), a deeper investigation of thermal stability was initiated.



**Figure 3: TSu test results on sample taken from the incident batch**

TSu is a Differential Thermal Analysis (DTA) screening tool which is neither adiabatic nor thermally efficient – hence large safety margins are typically required to derive approximate maximum safe handling temperatures. More critically, as the test cells are sealed there is little / no oxygen available to support any oxidation events. For powders with a high relative surface area, oxidation must always be considered for elevated temperature operations where air is present. This is particularly true for powder drying operations.

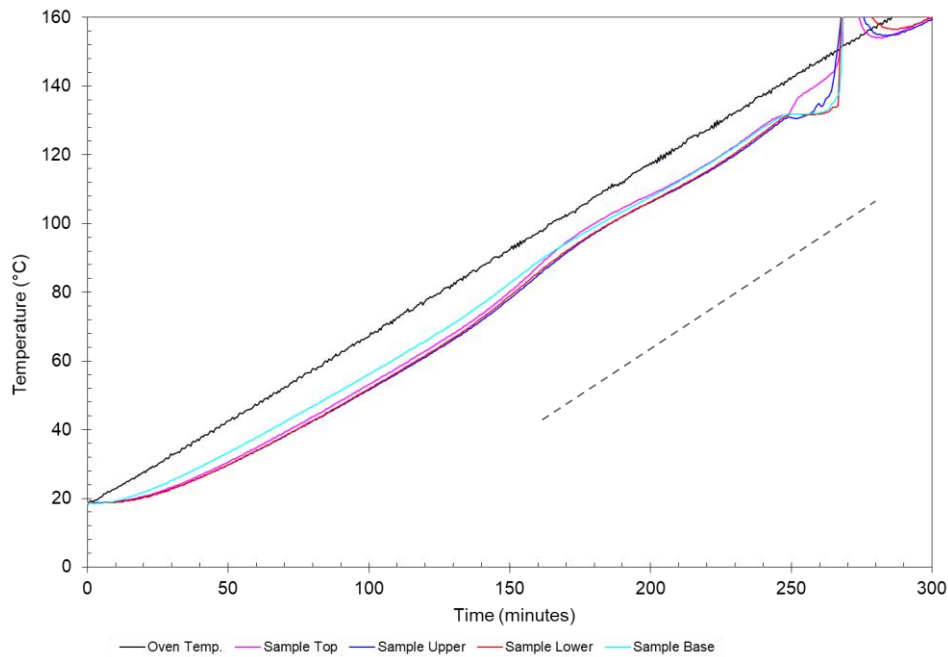
A Diffusion Cell Test (DCT) was conducted on the powder using a temperature ramp profile to examine, in more detail, the effect of abundant air availability on the powder at elevated temperature. The DCT equipment is a cylindrical, open topped glass test cell with a volume of approximately 100 cm<sup>3</sup> that has a sintered glass base allowing the free movement of air through powder from the top and bottom. The test result is shown in Figure 4.



**Figure 4: Diffusion cell thermal stability screening test result**

Examination of the test data initially concluded, consistent with prior thermal stability data from TSu, that the material undergoes significant exothermic reaction from around 140°C. The shape of this event (i.e. very sharp temperature rise) is consistent with a self-decomposition reaction rather than an oxidation reaction (which are normally more prolonged, less sharp, events). Further activity is seen on reaching an oven temperature of 400°C – likely to be consistent with smouldering / combustion of the decomposed product at this high temperature.

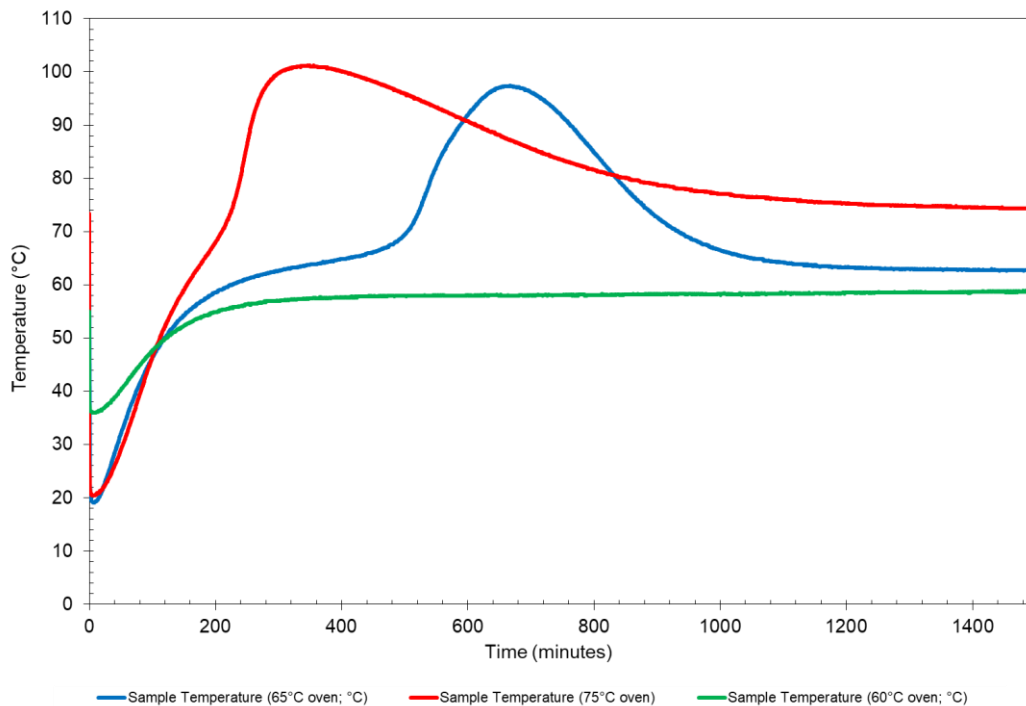
Closer inspection of the period *before* the primary decomposition yielded a very interesting – and ultimately pivotal – finding. Figure 5 depicts a close-up of the initial ramped section of the test from ambient temperature up to 160°C. The dashed grey line indicates the expected trajectory of temperature in the absence of any energetic activity.



**Figure 5: Diffusion cell test – zoom in on initial ramp section from 20 – 160°C**

As can be clearly seen in Figure 5, there is a small, but prolonged upward deviation in sample temperature starting from approximately 60°C. Although the magnitude of this event is small, it suggested that there is some form of energetic activity. The fact that this activity is not observed in the sealed TSu or ARC tests strongly suggests that it is an oxidation event. To further investigate this phenomenon further isothermal tests in wire mesh baskets were performed.

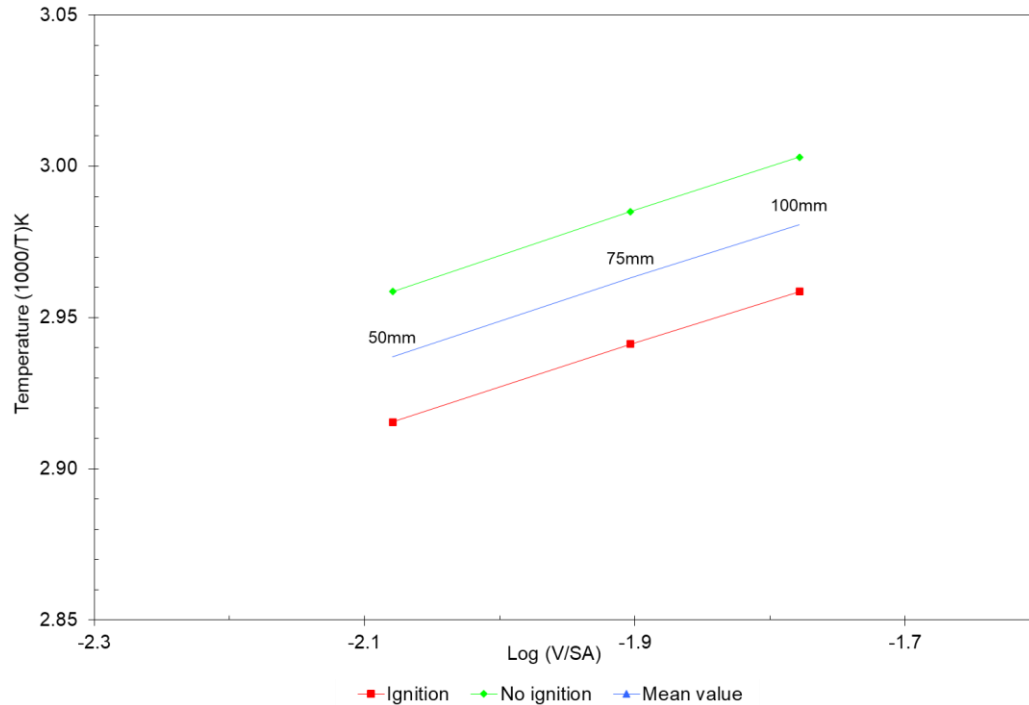
A series of wire mesh basket tests were performed isothermally in three different sizes of baskets. Whilst the magnitude of the heat release was much higher than observed in the DCT, it was (just) insufficient to initiate the primary decomposition. Figure 6 shows the data from isothermal tests at 60, 65 and 75°C using a 100 mm cube basket.



**Figure 6: Basket test results – 100 mm basket isothermal results at 60, 65 and 75°C**

At this scale, the 60°C isothermal test did not propagate the initial reaction whereas the 65°C basket did. Given the much larger scale of the plant storage vessels, it is highly likely that the oxidation events would propagate directly into the primary decomposition.

Testing was repeated at two other basket sizes to provide a relationship between “ignition” trigger temperature and basket size (plotted as  $\log(\text{volume}/\text{surface area})$ ). The relationship is shown in Figure 7.



**Figure 7: Critical ignition temperature extrapolation from three basket sizes**

Extrapolating the mean ignition temperatures to the 1 m<sup>3</sup> FIBC indicated a likely “ignition” temperature of 44°C.

Examination of the product from the 100 mm basket test at 65°C clearly showed chemical changes / browning of the material focused at the centre of the sample (where heat losses are lowest and temperature would be highest). Figure 8 shows a section through the product taken after the 100 mm / 65°C isothermal test. The originally powdered product had all hardened with a brown colouration which was darkest at the centre.



**Figure 7: Post-test sample after the 100 mm basket test at 65°C**

## Discussion

### Incident Cause

The conclusion of the study was that the incidents occurred due to low temperature oxidation reactions which caused material to self-heat to temperatures where the more significant and violent decomposition reaction occurred. These reactions are not detected in sealed cell DTA test methods where air availability is very limited.

Why these reactions were only observed with a very small number of batches was the study of further hypothesis and investigation. It was concluded that:

- Based on the extrapolated critical ignition temperature from the isothermal basket tests (44°C), the discharge temperature (40°C) was very close to the ignition temperature. The material, on discharge, would therefore have been very close to the borderline between ignition / no-ignition. This partially explains why not all batches undergo this behaviour. Representatively measuring temperature within a solid is invariably more complex and less accurate than measuring in a uniform temperature liquid.
- The incidents occurred with the last discharged batch from each campaign. This contributed several aggravating factors which increased the likelihood of ignition:
  - Material would have been exposed to drying temperatures for longer (this would particularly exacerbate any autocatalytic behaviour associated with the self-heating reaction and may have resulted in material reaching a higher temperature).
  - Increases in the dryer agitator amperage were consistent with compacted lumps of powder, possibly adhered to the dryer walls, being displaced. These lumps are likely to have been at a higher temperature than bulk material (due to prolonged close proximity to the heated walls) and due to their compacted nature, it is unlikely that the core of the lumps would have cooled to 40°C prior to discharge. Indeed, it is possible that these heated lumps were the initiating causes of the events when discharged into the storage container and “insulated” inside powder.

Further testing performed during the investigation concluded that the material, if transported, would be classified as a UN Division 4.2 self-heating substance (of packing group II). Under GHS (Globally Harmonized System of Classification and Labelling of Chemicals) the sample would be classified as self-heating substance (of category 1).

### Recommendations for Safe Manufacturing

A wide-ranging number of recommendations were made to the operating company as a result of the investigation. Those relevant to continued manufacture and drying of the material included:

- Temperature monitoring enhanced to ensure that bagged material is below 40°C (or lower if possible). Temperature monitoring of stored material could also be considered to monitor for hotspots.
- Cleaning of the dryer walls between each batch to avoid aggregation and prolonged exposure / overheating of wall deposits.
- Ensuring that bagged material does not contain any lumps of compacted powder which could serve as a “nest” for smouldering / self-heating activity. Sieving at the outlet to the drier was recommended for this purpose with any captured lumps either broken up or set aside / discharged.
- Consider installation of a dedicated water sprinkler / quench system which can be externally activated to avoid the need for personnel to enter an area with hazardous gases.
- In addition, consideration was recommended for either vacuum packing product (to eliminate air in stored bulk material) or inert gas blanketing storage containers.

### Root Cause

The company operating the process has generally very good process safety practices and policies including process safety testing protocols. However, like many other organisations we have worked with – and in many other incidents we have investigated – there can be an over-reliance on test equipment for purposes that it was not designed. In this case, thermal stability screening was performed using TSu and ARC which are both robust techniques for liquid samples. However, in the case of powders, undesirable events can arise through decomposition but also from oxidation / combustion processes. The finer the powder, the higher the potential risk of such behaviour. Even if the dryer was inert gas blanketed, the storage of discharged warm powder into containers which allow air diffusion through the powder can create a risk.

A robust testing program for powder drying should always look at decomposition AND oxidation potential. While one technique can be used for both, some techniques are limited to only examining one property – potentially creating a blind-spot around the other property.

### Conclusions

The two powder fuming incidents described in this paper arose, in all likelihood, due to powder oxidation reactions which commence at (or just above) the powder discharge temperature and well below the powder drying temperature. This behaviour of the powder was not established during scale-up processes – and hence mitigation strategies were not present to address it. Fortunately, the consequences of the two incidents were relatively minor involving no serious injury or fatality – but the potential existed for escalation and much more serious harm had the events not been detected early and intervention action not taken. Had the events happened inside solid vessels potential for over-pressurisation may also have existed, potentially with more serious consequences.

In many ways, process safety is a very complicated, multidisciplinary and often poorly understood subject. However, at its most simple, it is just a process which identifies the hazardous properties of materials, identifies ways in which these

properties can create a risk of harm and then identifies strategies to mitigate risks as far as reasonably practicable creating an acceptable level of residual risk. The cornerstone of strong process safety performance is robust procedures for identifying material and process properties from which risks can then be identified and mitigation strategies implemented. Robust process safety testing programs should be established for all scaled up processes which examine the full range of potential hazards. The incidents described herein occurred, in small part, due to the failure to consider the oxidation potential of powders in drying and storage as well as decomposition. Different techniques are required to assess these two risks. This is observed to be a common short-coming in many companies who over-rely on one or two thermal stability test techniques.

### **Acknowledgements**

The operating company are thanked and praised for allowing the sharing of incident information and process safety data.