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EXPLOSIONS PART 3 OF 3: POWDER DECOMPOSITION

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Introduction

When powders are exposed to heat - either deliberately in dryers or inadvertently in process plant - or when powders are packaged whilst warm into large containers, hoppers or silos, many will decompose exothermically.

Two types of decomposition are relatively commonplace:

- Self-heating reactions that are dependent on the presence of oxygen for the reaction to proceed. Coal is a good example of a material that undergoes an oxidative reaction.
- Decomposition reactions that are not dependent on the presence of oxygen and will occur under vacuum and/or in inert atmosphere. 2,2'-azodi-isobutyronitrile is a good example of this type of material.

Decomposition can occur from a relatively low temperature, often leading to smouldering or a fire. Often decomposition reactions will rapidly generate large quantities of gas, and in the extreme, can be evolved at such high rates as to give the powder some explosive properties.

In any risk assessment it is important that the thermal properties of the materials to be handled are identified in the early stages of process design so that appropriate safety measures can be incorporated. However, there are a number of factors that affect the temperature at which the onset of thermal instability can commence for any given material; the thickness of layers or the amount of bulking allowed and the availability of air to the material are fairly important. To give a useful indication of thermal properties in the plant, any test will need to simulate the conditions that are likely to be found there.

A number of laboratory tests have been proposed to cover most situations and these are incorporated in the IChemE guide - Prevention of fires and explosions in dryers (Abbott, 1990).

Screening Tests

The first stage of a thermal hazard study comprises a series of small scale screening tests which can be conducted isothermally, if the plant exposure temperature is specified, or ramped at typically 0.5°C/min. The availability of air in the small scale tests is varied by means of a forced air flow (aerated test) or sintered glass base (diffusion cell). It is noteworthy that the forced air flow should not be too high since this will result in excessive heat loss from the powder. The intention is to increase the availability of air beyond that

available by natural diffusion alone (ie the test is simulating the worst case during a fluid-bed drying cycle when the fan is running down and air is permeating through the bed).

A third screening test is used to simulate layers of product which may build up on ledges or walls within equipment/vessels which are heated.

Availability of air is a crucial factor in cases where the decomposition reaction is driven by oxidation. Many companies test their powdered products with differential scanning calorimetry (DSC) or an accelerating rate calorimeter (ARC) or with Dewar flasks that simulate low heat-loss conditions. These tests may give accurate onset temperatures for decomposition reactions, but for oxygen-dependent reactions, because the amount of air available to the powder is restricted, the reaction will be suppressed. For example, onset temperatures obtain using the methods in the Dryers guide can be as much as 100°C lower than those determined using calorimetric or Dewar techniques.

Safety factors can be applied to the onset temperatures to take into account inaccuracies in plant temperature measurement and bulking effects. However, the safety factors recommended can result in unrealistic safe operating temperatures for the process.

Further testing

Further investigation, using thermal ignition theory, can give more accurate onset temperatures for a given situation.

Powder in bulk can self-heat at lower temperatures than the same material in a smaller volume. Self-heating occurs when the heat generated by the material exceeds the heat lost from the reaction zone. The increased insulation provided by the surrounding powder in bulk situations reduces the rate of heat loss from the reaction zone in the centre of the powder. Since heat generation in the powder is dependent on its temperature, it follows that in bulk the heat generated is greater than the heat lost at lower temperatures.

The relationship between onset temperature and "bulk" size can be represented by the basic equation:

$$\log \left[\frac{\bar{\delta}_c T_i^2}{r^2} \right] = M - \frac{N}{T_i}$$

where $\bar{\delta}_c$ is a dimensionless parameter depending on the shape with radius r ; M and N are constants of the material. This equation can be used to predict the effect of scale on any given material by determining the onset temperature (critical temperature) T_i , of a number of small-scale experiments and extrapolating to a particular bulk situation.

The above equation is cumbersome to use with the temperature being present on both sides of the equation, but it can be solved iteratively. Recent empirical work by Leusche has shown that by plotting

$$\log \left[\frac{\text{volume}}{\text{surface area}} \right] \text{ vs } \frac{1}{T}$$

where the volume and surface area apply to the shape of the material, and T is the onset temperature (in Kelvin), a similar relationship exists. This is easier to use in practice.

Thermal ignition energy theory is the basis of the test for the UN transportation classification for spontaneously combustible material, packaging group 4.2.

Gas Evaluation

Fires and explosions are not the only risk from the drying and thermal decomposition of materials. The release of gas from a decomposition can also lead to a hazard in powder processing operations. There are two scenarios to consider - when the gas is released slowly or when rapid gas evolution occurs.

In certain situations, thermal decomposition can lead to the slow evolution of flammable gases which could accumulate in the dryer system. Once the gas concentration reaches flammable concentrations, the gases could be ignited by another ignition source or by the decomposing materials itself. One example of this phenomenon is in the combustion of coal in bulk where, because of the restricted air availability, carbon monoxide will not necessarily prevent damage from gas evolution.

It is essential to also screen for the evolution of gas when conducting tests on materials to be dried. No one test is accepted as suitable for all situations; however, a good starting point is to screen the materials in a Carius tube apparatus which is principally used to screen chemical reactions for a thermal runaway. This test (described in the IChemE guide - Chemical reaction hazards) can give an indication of when gas evolution occurs, the rate of evolution and the total gas evolved, plus whether the emitted gas is flammable, whereas the methods described earlier do not.

Explosives

Decomposition leading to rapid gas evolution without the involvement of external oxygen is often known as deflagration. In the extreme, decomposition can be so rapid that the reaction propagates through the unreacted substance at the speed of sound. This reaction, known as detonation, is accompanied by a shock wave in the material which can generate extremely high pressures. It is important to screen any materials for potential hazards from these types of reaction.

Tests are available that are well established and are generally used for regulatory purposes, such as the Notification of new substances regulations and the UN Transport of dangerous goods regulations. These sets of regulations examine the material's susceptibility to ignition from friction, heat and impact, with additional tests available in the UN regulations to determine whether the material could deflagrate or detonate.

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