Determination of Spontaneous Ignition Behaviour of Calcium Stearate Dust Accumulation

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Abstract. The self-ignition of combustible dusts depends on their chemical composition, on the properties of the substances in the composition, on the granulometry and geometry of the mass of the material and, last but not least, on the ambient temperature. Self-ignition is a complex process that takes place in three successive or simultaneous stages of development. These stages influence each other and are the following: self-heating, evaporation of moisture, and self-ignition itself. The underlying cause of self-heating (or possibly self-ignition) is that molecules on the surface of combustible dust particles are subjected to exothermic reactions with oxygen in the air transported in the free volume between particles, even at normal temperatures. Any amount of heat released will then cause an increase in temperature in the reactive dust-air system, thus accelerating the reaction of other dust molecules with oxygen. Calcium stearate is a carboxylate of calcium, classified as a calcium soap. It is a component of some lubricants, surfactants, as well as many foodstuffs. Due to its large utilization, it was considered important to analyze the flammability properties at bulk depositing to ensure proper safety regulations to avoid unwanted events such as fires or explosions. This paper aims to describe/present the self-ignition behaviour of combustible dust as a function of volume by evaporation tests under constant temperature conditions. The obtained results showed the maximum quantity that can be stored in bulk and the time until an ignition could take place, so that protective measures can be taken to avoid incidents (fires, explosions).

1. Introduction
NFPA 68 [1] defines dust as any finely divided particle having a diameter of 420 µm or less. More than 70% of the powders processed in the industry are combustible [2]. This makes most industrial applications that process dust susceptible to explosions [3].

"Dust" is the well-known notion for materials obtained by crushing solids beyond a certain degree of fineness. This notion therefore also includes materials commonly known as powder, flour powder, etc. Dust consists of a lot of solid particles, whose main property, which distinguishes them from other fragmented solids, is their very low rate of fall in gases in general and in the air in particular. Dust particles in a volume of air, without touching each other, form a mixture of powder - air. In this case, the air is the dispersing agent, and the powder particles are called the dispersed phase. Such mixtures have in some respects similarities to gaseous mixtures. When powder particles are at rest on a substrate and touch each other, it is referred to as "powder layers" or "powder deposits". In this state, the dust can be compared to some extent with a porous body [4].
In order to occur, explosions of powder and hybrid mixtures require five basic components [5]:
1. Fuel;
2. Oxidant (air);
3. Source of initiation;
4. Mixing fuel in the air;
5. A certain degree of closure.

The most explosion-type events take place inside process equipment (e.g., mills, silos, cyclones, pipes) [3].

Additionally, one or more explosions may occur after the pressure wave of the first explosion. These strong pressure waves can disperse the dust deposited in the area, forming a new cloud of dust that can be initiated by the energy released by the first explosion. Secondary explosions can be even stronger than the first explosion due to the larger amount of powder or hybrid mixture.

The assessment of the self-ignition hazard of bulk materials requires the experimental determination of self-ignition temperatures as a function of volume. For this purpose, there are two standardized methods, namely the determination of the self-ignition temperature of the dust samples in the oven and the measurement of the self-ignition temperature of a layer of dust deposited on a hot surface. Sometimes, depending on the behavior of the sample during these tests makes the second method is more difficult to apply [6, 7].

Vulnerable industries to fire or dust explosion include, but are not limited to, agriculture, chemicals, food (sugar, candy, spices, starch, flour, and feed), cereals, fertilizers, tobacco, plastics, wood, forest, paper, pulp, rubber, furniture, textiles, pesticides, pharmaceuticals, tire, and rubber manufacturers, dyes, coal, metalworking (aluminum, chromium, iron, magnesium, and zinc), recycling and coal operations. Given this long list of vulnerable industries, combined with the fact that many companies cannot adequately identify a fuel dust threat, OSHA suggests completing a thorough dust hazard assessment covering the following areas:

- Materials that can be combustible;
- Processes that use any combustible dust;
- Open and especially hidden areas, where dust can collect;
- Opportunities that can cause air dust in the air;
- Any ignition source.

The self-ignition of combustible dusts depends on several factors such as chemical composition, properties of the substances in the composition, particle size and geometry of the mass of the material, and last but not least on the ambient temperature. The underlying cause of self-heating (or possibly self-ignition) is that molecules on the surface of combustible dust particles are subjected to exothermic reactions with oxygen in the air transported in the free volume between particles, even at normal temperatures. Any amount of heat released will then cause the temperature in the reactive dust-air system to rise, thus accelerating the reaction of other dust molecules with oxygen. The thermal balance between the heat produced inside the dust mass (quantity and surface area of surface reactive molecules, calorific value) and the heat loss from the environment (thermal conductivity and dust mass size, heat transfer coefficient on the outer surface of the dust mass and size are decisive for the evolution of the system, either towards reaching a thermal equilibrium at a slightly higher temperature level or towards increasing the temperature of the dust mass until self-ignition, in case of insufficient heat dissipation from the system (in this case, heat production is superior to the overall heat loss) [6,7].

The basic experimental principle used to describe the self-ignition behavior of dust is to determine the self-ignition temperature of dust masses with different volumes, by steaming experiments in isoperibolic conditions (storage at constant oven temperatures) inside a heating oven. The dust sample
is placed freely in baskets made of wire mesh of different sizes with a spatula, without compressing and leveling on top. The baskets are open at the top and closed at the bottom. The mesh size was chosen so that the dust could not fall through the net, but at the same time prevents the diffusion of oxygen from the air supply system of the oven inside the dust sample. The volumes used for this study were: 8 cm$^3$, 125 cm$^3$, 343 cm$^3$, and 1000 cm$^3$. These chimneys were placed in the center of the preheated oven at the test temperature [6,7].

When a layer of dust is lit, a fire breaks out. A dust fire can turn into a dust explosion. On the other hand, the ignition of a cloud of dust can lead to an explosion that, unlike a fire, is associated with pressure changes (generally very rapid) and the sudden development of heat. This exceptionally violent reaction is responsible for the specific hazards associated with a dust explosion.

Calcium stearate is a carboxylate of calcium, classified as a calcium soap. It is a component of some lubricants, surfactants, as well as many foodstuffs. It is a white waxy powder [8].

Calcium stearate is produced by heating stearic acid and calcium oxide:

$$2C_{17}H_{35}COOH + CaO \rightarrow (C_{17}H_{35}COO)2Ca + H_2O$$

(1)

It is also the main component of soap scum, a white solid that forms when soap is mixed with hard water. Unlike soaps containing sodium and potassium, calcium stearate is insoluble in water and does not lather well [8]. Commercially it is sold as a 50% dispersion in water or as a spray-dried powder. As a food additive, it is known by the generic E number E470. Calcium stearate is a waxy material with low solubility in water, unlike traditional sodium and potassium soaps. It is also easy and cheap to produce and exhibits low toxicity. These attributes are the basis of many of its applications. Related applications exist for the magnesium stearate [8].

- Calcium stearate is used as a flow agent and surface conditioner in some candies such as Smarties, jawbreakers, and Spreees.
- It is a waterproofing agent for fabrics.
- A lubricant in pencils and crayons.
- The concrete industry uses calcium stearate for efflorescence control of cementitious products used in the production of concrete masonry units i.e. paver and block, as well as waterproofing [9].
- In paper production, calcium stearate is used as a lubricant to provide good gloss, preventing dusting and fold cracking in paper and paperboard making [10].
- In plastics, it can act as an acid scavenger or neutralizer at concentrations up to 1000ppm, a lubricant, and a release agent. It may be used in plastic colorant concentrates to improve pigment wetting. In rigid PVC, it can accelerate fusion, improve flow, and reduce die swell.
- Applications in the personal care and pharmaceutical industry include tablet mold release, anti-tack agent, and gelling agent.
- Calcium stearate is a component in some types of defoamers.
- Anticaking agent.

Being combustible dust, in order to be able to take the proper measures for preventing unwanted events such as fires or explosions, a characterization is required. This paper aims to describe/present the self-ignition behaviour of calcium stearate combustible dust as a function of volume by evaporation tests under constant temperature conditions. The obtained results showed the maximum quantity that can be stored in bulk and the time until an ignition could take place, so that protective measures can be taken to avoid incidents (fires, explosions).
2. Materials and methods

Were performed tests to determine the self-ignition temperature for the calcium stearate dust. The sample used was representative, obtained under normal operating conditions of the process.

The experimental setup used to perform the tests is performed in accordance with the requirements of the standard SR EN 15188: 2008 and is shown in figure 1. Thermocouples with a protective coating with an outer diameter of approximately 1 mm and a data acquisition system corresponding to the recording of signals from thermocouples were used to measure and record the temperature of the sample and the oven.

To determine whether or not self-ignition occurs, there are two methods:

a) When the temperature in the center of the sample rises by at least 60 K above the oven temperature;

b) When the temperature in the center of the sample shows an inflection point, relative to time if it appears above the oven temperature.

If working at significantly lower temperatures, the sample temperature will approach asymptotically the oven temperature (curve A).

At higher oven temperatures, significant reactions with oxygen take place in the dust mass, the sample temperature will be temporarily higher than the oven temperature and the self-heating process will start, without igniting the sample. Thereafter, the sample temperature decreases to the oven temperature (curve B).

The heat production in the sample has reached a point where it continuously exceeds the heat loss (through heat conduction, convection and radiation). After an induction time, the sample temperature rises rapidly until self-ignition occurs (curve C).

The self-ignition temperature is between the furnace temperatures of curves B and C.

For each test, the time interval between placing the sample in the oven and reaching the steaming temperature and the total steaming time was recorded. In addition, the time interval between reaching the steaming temperature and ignition was recorded, i.e. reaching the maximum temperature.
Figure 1. Experimental assembly for hot steaming tests

1 - heating oven; 2 - inner enclosure; 3 - air outlet, diameter = 10 mm air inlet (preheated air, flow); 4 - thermocouple for temperature measurement; 5 - thermocouple for measuring the sample temperature; 6 - wire mesh cylinder, with dust sample; 7 - deflector

3. Results and discussion

Following the analysis, the results presented in table 1 below were obtained, as well as the graphs in figure 2-3.

Table 1. Results obtained at calcium stearate oven test.

| Characterization of the sample | Dust volumes tested (cm³) | Auto-ignition temperature (°C) | Induction time (hours) |
|-------------------------------|--------------------------|-------------------------------|-----------------------|
| Name: Calcium stearate        | 375                      | 270                           | 1,5                   |
| Bulk density: 2,38 g/cm³      | 745                      | 250                           | 3,2                   |
| Moisture: 0,20 %              | 1500                     | 240                           | 5,4                   |
In Figure 2, ignition temperatures are presented. The figure shows the variation of ignition temperature (1/Tsi) as a function of the logarithm of the volume to area ratio (lg (V/A)). The legend indicates that V represents the volume of the test sample, and A represents the area of the test sample. The line that crosses the Tsi values separates the equilibrium regions from the unstable regions for the dust volumes. Self-ignition occurs in the region above the curve. For calcium stearate sample, it can be seen that for a volume of 5 m³, the minimum ignition temperature is 10 °C.

In Figure 3, the induction times, required for the critical ignition for different dust volumes, were plotted as lg(t1/1h) function of lg(V/A). From this figure, the induction time for the self-ignition of the dust samples deposited at temperatures over the ignition temperature can be deduced.
As an example, a cylindrical volume of 1 m³ of dust, has a self-ignition temperature higher than 36°C. If this volume of calcium stearate dust is stored at this constant temperature, it will be 40 days before an ignition could occur.

Combining the two graphs one can know the maximum time that a certain volume of dust can be deposited so that it doesn’t reach the self–ignition temperature. Based on that values the safety manager can take the proper measures in order to avoid unwanted events.

In general, self-ignition or spontaneous combustion is limited to the contact of solids with high specific surfaces. Oxygen can react on surfaces in the entire amount, as long as the air exchange is large enough. The oxidation process can begin at room temperature depending on the substance.

4. Conclusions
Although all precautions are taken in the dust industry, there are often situations that lead to loss of life and significant material damage. Thus, in the drying processes, self-ignition, respectively fires of dust accumulations are considered as the main cause for such incidents.

Self-ignition is a common source of ignition in the storage of bulk materials, such as dust and dust. The assessment of this ignition hazard takes into account the manufacturing or storage conditions and requires the experimental determination of critical self-ignition temperatures as a function of volume.

The experimental results showed that the calcium stearate dust is combustible and based on the graphs obtained the safety measures can be taken such that unwanted fires and explosions can be avoided.

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