

Modified Setup of 20-L-Sphere for the Determination of Safety Characteristics of Nano Powders

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This paper describes a modified experimental setup for the test apparatus 20-L-Sphere (also known as 20-L Siwek Chamber), that enables the test samples to be kept under inert atmospheric conditions nearly until ignition. This setup was designed to allow the determination of safety characteristics of nanopowders under most critical circumstances (e.g. minimisation of the influence of oxidation before the test itself). The aim of this modification was to determine, whether or not the current setup and procedures underestimate the explosion violence and ignitability of nanopowders. The work includes experimental results of micrometer dusts to validate the modified setup. Moreover first results of nanometer iron and aluminium dusts are presented, which were kept at inert conditions until shortly before the ignition. The tested nano iron was found to react pyrophoric, as soon as it gets in contact with air, while the tested nano aluminium did not generally show such behaviour.

1. Introduction

Nanotechnology is one of the fastest growing industries at present and probably will be for the next decades. This development particularly results from the modified properties of materials within the nanometer range. The different types of behaviour of such substances and the lack of knowledge about their interaction with the environment require intensive investigation for risk assessment. For this reason health effects of nanoscale materials on the human organism for example are examined in numerous studies and research projects. Conversely in depth experience and knowledge of fire and explosion risks in the production, handling and transport of nanoscale materials and particles with sizes below one micrometer are not widely available. Based on experience of dusts with particle sizes in the micrometer range it is well known that dusts are classified more critically with decreasing particle size, as their explosion severity and ignition sensitivity increase.

Explosion properties of combustible dusts are described with safety characteristics. Experimental data about determination of safety characteristics of nanometer powders published for example by Holbrow et al. (2010) or Bouillard et al. (2010) – which are the basis for risk assessment and design of prevention and protection measures – are still limited. Furthermore existing studies were carried out in accordance to international standards like EN 14034 series (2011) or ASTM E1226-10 (2010) for the determination of safety characteristics of combustible dusts in general. However it was not verified whether or not these standardised test methods are also suitable for a reliable evaluation of the combustion and explosion behaviour of nano powders. For example surface passivation may however result in a decrease of ignition sensitivity and reactivity before the test itself. Such processes are already well known for metallic micrometer dusts. The effect could be increased by the greater specific surface area of nanoscale powders. This would complicate a direct comparison of safety characteristics of micro- and nanopowders without taking the oxide content into account. Available safety characteristics do usually not contain information about the oxide content of investigated powders. Published explosion characteristics and studies like those from Eckhoff (2012) and Worsfold et al. (2012) on the explosion behaviour of nanodusts

did not consider that subject. This paper shows a possible experimental approach to evaluate the oxidation effect on the explosion behaviour of nanodusts. The test results could be used for the development of new test equipment for the determination of safety characteristics of nanodusts or the modification of standard equipment and procedures.

2. Experimental

According to EN 14034 series (2011) and ASTM E1226-10 (2010) the 20-L sphere (Figure 1) is used for the determination of the safety characteristics maximum explosion pressure P_{max} , maximum rate of pressure rise $(dp/dt)_{max}$ or explosibility index (K_{St}) and lower explosion limit (LEL). It consists of a hollow sphere of 20 litres internal volume made of stainless steel. For testing, a dust sample is placed in the storage chamber, pressurised and then dispersed into the sphere via the outlet valve and the rebound nozzle. Therefore the explosion chamber must be evacuated to 0.4 bar absolute while the dust container is filled with 21 bar absolute of compressed air. The evacuation of the explosion chamber is necessary to ensure ambient pressure after the dispersion process.

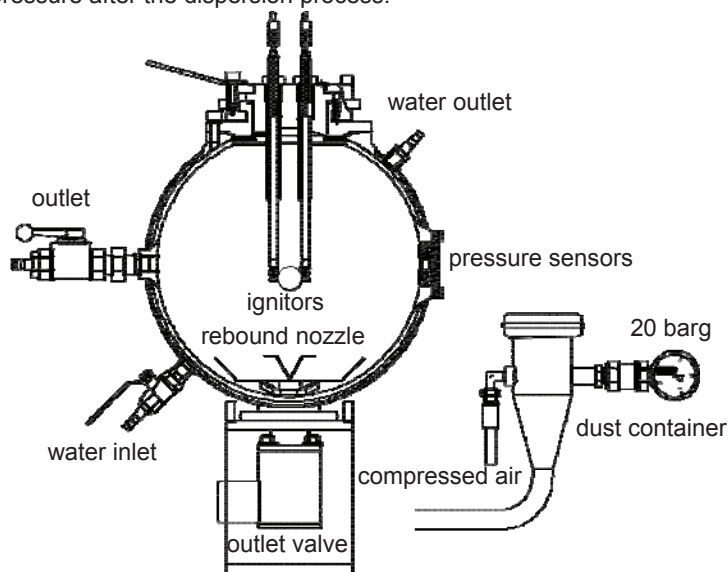


Figure 1: Schematic of standard 20-L sphere (edited from VDI 2263-1, 1990)

2.1 Modified experimental setup

For the determination of the most critical behaviour of nanopowders it is necessary to test powders which were produced and transported, without or with only a minimum of oxygen. To minimize the influence of oxygen passivation during testing it is in addition to that necessary to handle such samples under absence of oxygen until the time of ignition. A suitable experimental setup to implement that is placing test equipment and sample preparation into an enclosure with controllable gas atmosphere. Thus a special glovebox system operated with nitrogen has been developed in which test equipment such as the 20-L sphere and the sample preparation were integrated. For each test also the test chamber of the 20-L sphere is flushed with nitrogen.

Especially metallic nanopowders can ignite spontaneously during the injection process into the explosion chamber. Main reasons for that are the high ignition sensitivity of such substances and high shear forces that can occur during the dispersion process into the explosion chamber (Wu et al., 2010). This behaviour may lead to increased wear of parts of the test apparatus (e.g. outlet valve). Moreover, these uncontrolled early ignitions do not allow obtaining reliable safety characteristics of respective.

Therefore - contrary to the standard test procedure - the samples were directly placed into the explosion chamber. In order to disperse the dust adequately, a special mushroom nozzle was used. This nozzle is shown in Figure 2.

With this method and the inerted explosion chamber the dust sample gets in contact with oxygen only shortly before ignition (approximately 60 ms). In order to ensure ambient oxygen concentration at time of ignition the test gas, which is injected from the dust container through the outlet valve into the explosion chamber, had to be enriched with oxygen. The increased oxygen content of the test gas was calculated on basis of the ideal gas law.

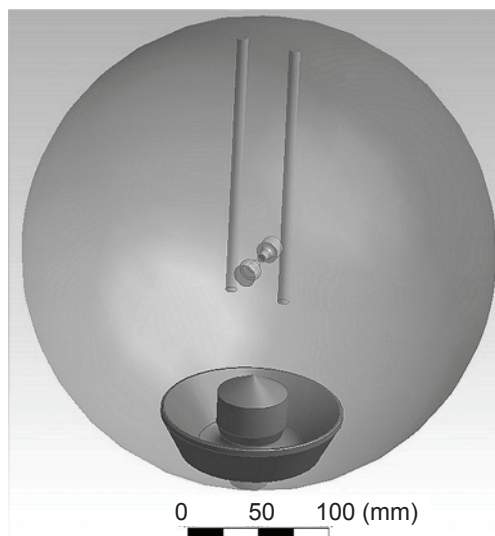
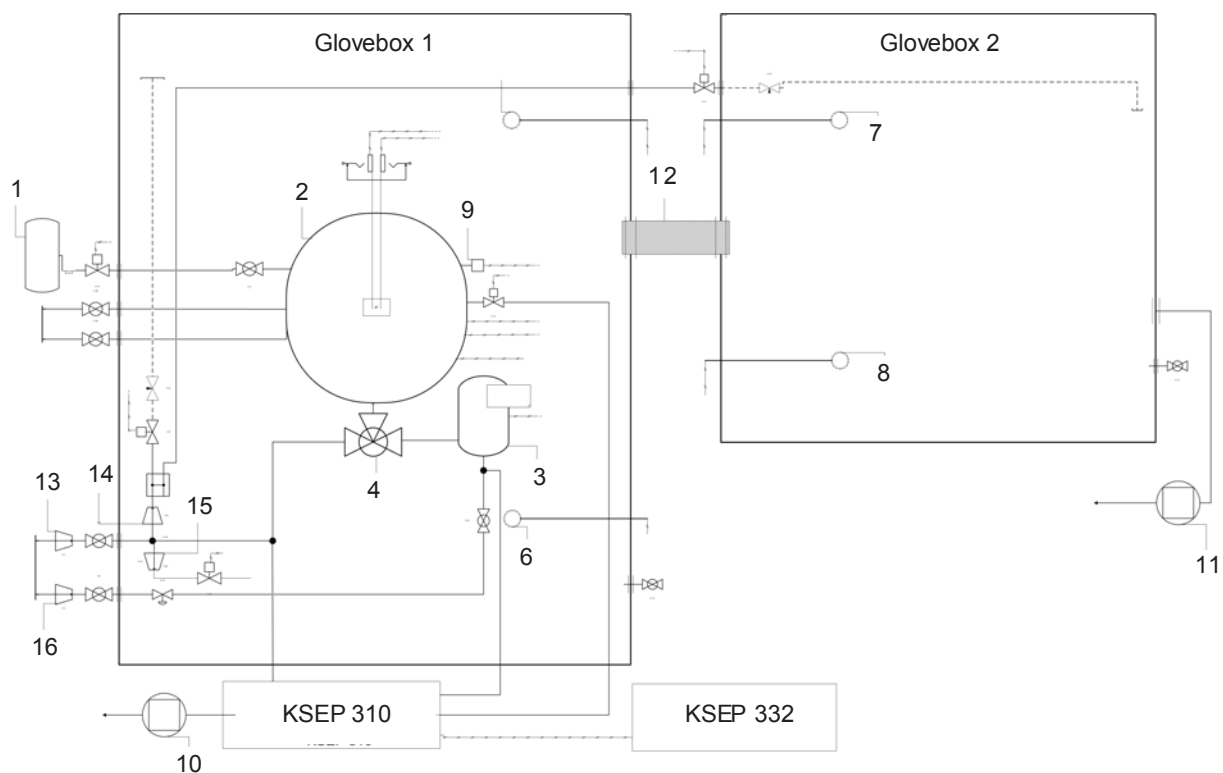


Figure 2: Image of the so called mushroom nozzle within the explosion chamber of the 20-L sphere



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|---------------------------|---|
| 1. exhaust gas cleaner | 9. safety switch |
| 2. 20-L explosion chamber | 10. vacuum pump for explosion chamber |
| 3. dust storage container | 11. vacuum pump for preparation chamber |
| 4. outlet valve | 12. antechamber |
| 5. oxygen sensor 1 | 13. nitrogen pressure reducing valve |
| 6. oxygen sensor 2 | 14. glove box inerting pressure reducing valve |
| 7. oxygen sensor 3 | 15. glove box inerting pressure reducing valve
(during operating vacuum cleaner) |
| 8. oxygen sensor 4 | 16. oxygen pressure reducing valve |

Figure 3: sketch of the modified setup

A sketch of the modified experimental setup is shown in Figure 3. The modified experimental setup consists of two separated work stations. Glove box 2 is used for storage and preparation (e.g. weighing of the sample), while the 20-L sphere (or any other test apparatus) is placed into glove box 1. Both work stations are linked by an antechamber (12), which can be locked on both sides. This gives the opportunity to operate both glove boxes independently from each other under inert conditions. Especially the box for sample preparation needs to be kept under inert conditions constantly. Otherwise the total amount of powder to be examined would be exposed to oxygen.

In order to monitor the oxygen content inside the glove boxes and to ensure an inert atmosphere two oxygen sensors are installed in each box (5-8). The test gas is premixed in the dust container before each test. For this purpose, first oxygen is injected into the dust container. The pressure is controlled by a fixed pressure reducing valve (16). The gas supply is manually regulated by a diaphragm valve. An additional ball valve is used to limit the volume of the dust container to the standardized 0.6 L (otherwise the volume of the dust container would be enlarged by the volume of the pipes). It also prevents the backflow of the test gas, when the dust reservoir is fully loaded with 21 bar absolute. Nitrogen is supplied to both glove boxes with 21 bar absolute. The inlet pressure is reduced by another pressure reducing valve (14) to avoid sudden overpressure inside. Nitrogen is injected into the glove boxes by perforated stainless steel tubes. The supply is controlled by solenoid valves and can additionally be accurately dosed via needle valves.

3. Validation

To validate the modified setup, tests with two different dust samples have been conducted. A lignite and a maize starch dust were chosen for these tests. The tested lignite dust has a median value of 37.7 μm and a specific surface area of 4.9110 $\text{m}^2\cdot\text{g}^{-1}$ (BET surface area), while the median value of maize starch amounts to 13.5 μm and the specific surface area is 2.4857 $\text{m}^2\cdot\text{g}^{-1}$ (BET surface area).

Table 1: Validation results for lignite and maize starch

Characteristic		lignite		maize starch	
		Standard test	Modified setup	Standard test	Modified setup
P_{max}	[bar]	8.7	8.3	8.4	8.7
dp/dt_{max}	[$\text{bar}\cdot\text{s}^{-1}$]	793	883	614	596
K_{St}	[$\text{bar}\cdot\text{m}\cdot\text{s}^{-1}$]	215	240	167	162
LEL	[g m^{-3}]	30	30	30	30
P_{max}	maximum explosion overpressure				
dp/dt_{max}	maximum pressure rise				
K_{St}	dust explosion constant				
LEL	lower explosion level				

The validation results for both dusts are shown in Table 1. It can be seen that tests with modified setup and standard method delivered mostly comparable results within the margin of uncertainty that is usually reached in dust explosion tests. The values for P_{max} are really close to each other. While for lignite the maximum overpressure determined with the modified setup is a little bit lower (8.3 bar instead of 8.7 bar with standard test method) it is vice versa for maize starch (8.7 bar with modified setup and 8.4 bar with standard test method). But values for P_{max} are still within the tolerance level (10 % for P_{max}).

The results for the pressure rise (614 $\text{bar}\cdot\text{s}^{-1}$ with standard method and 596 $\text{bar}\cdot\text{s}^{-1}$ with modified setup) and K_{St} -value respectively for maize starch show a good agreement as well. Only for lignite the K_{St} -value determined with the modified setup (883 $\text{bar}\cdot\text{s}^{-1}$) is higher than the result of the standard test (793 $\text{bar}\cdot\text{s}^{-1}$). Although this value is considerably higher, it is still within the tolerance level. Results for the lower explosion level are for all dusts and methods the same.

This preliminary validation has shown that modified setup and standard test method deliver comparable results for the tested dusts. For a final validation a much higher amount of different dust samples needs to be tested.

4. Results of first tests with nano dusts

For first tests with dusts produced in the nanometer range, nano iron and nano aluminium were chosen. Properties of both dusts are listed in Table 2. Although particles of both dusts are produced in the upper nanometer range, laser diffraction analysis has shown, that these primary particles form agglomerates in the lower micrometer range. While iron seems to form smaller agglomerates (about 1.4 μm) than the tested aluminium (about 4 μm) it has a much smaller specific surface area (7.6 $\text{m}^2\cdot\text{g}^{-1}$) than the aluminium which has a specific surface area of 18.3565 $\text{m}^2\cdot\text{g}^{-1}$.

Table 2: Properties of tested dusts produced in the nanoscale

	nano aluminium	nano iron
Median value (laser diffraction)	4.028 μm	1.493 μm
BET surface area	18.3565 $\text{m}^2\cdot\text{g}^{-1}$	7.6036 $\text{m}^2\cdot\text{g}^{-1}$
Median primary particle size (supplier information)	90 – 110 nm	90 – 110 nm
Oxide content	9 mass-%	4 mass-%

Both dusts were furthermore examined with a Scanning Electron Microscope (SEM). Figure 4 shows two SEM images of nano aluminium. The left picture illustrates the agglomerate of a lot of smaller primary nanoparticles. On the first view there seems to be no difference to particles within the smaller micron range. But a closer look (picture on the right side of Figure 4) reveals that there are a lot of cavities and pores which increase the specific surface area. For a better comparison BET measurements of an aluminium dust, consisting of spherical primary particles with a median diameter of about 4 μm , have been carried out. These measurements with micrometer aluminium resulted in a specific surface area of 1.9981 $\text{m}^2\cdot\text{g}^{-1}$. Hence, although the nano particles formed agglomerates within in the micrometer range, even these agglomerates have a much higher specific surface area than comparable micrometer particles. It needs to be further investigated, whether or not this trend is generally applicable to even smaller nanoparticles and if or how this higher surface area affects the explosion behaviour.

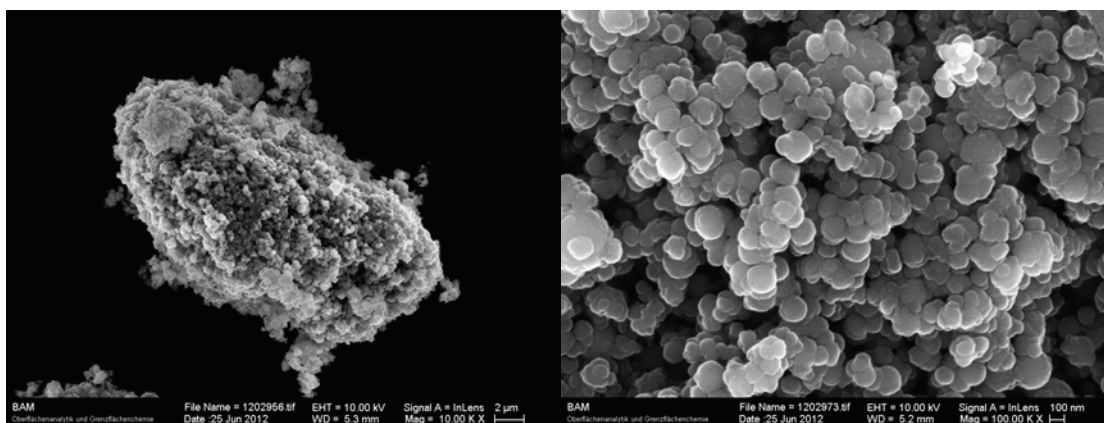


Figure 4: SEM images of nano aluminium at different resolutions

Results of first tests in the 20-L-Sphere with nano aluminium and nano iron are presented in Table 3. Nano iron has shown pyrophoric behaviour. Thus it was not possible to determine explosion characteristics with the standard test method. With the modified setup it was possible to handle this dust until dispersion within the explosion chamber. Nevertheless the results cannot be considered as real explosion characteristics, because first of all iron ignited spontaneously, as soon as the oxygen/nitrogen-mixture was injected into the explosion chamber (that means before the ignition was triggered). The second problem is that the mentioned spontaneous ignition occurred when the pressure inside the explosion chamber was still below ambient conditions. This means, that the dust ignited below 1 bar absolute, at a much lower oxygen concentration and when the outlet valve was still open. The latter leads to the problem of a bigger volume of the test apparatus. Unfortunately these tests with nano iron needed to be aborted already at a concentration of 250 $\text{g}\cdot\text{m}^{-3}$ because the damage to the outlet valve was too high.

It can be furthermore seen that maximum overpressure and lower explosion level of nano aluminium are comparable or equal. However measured values with the modified setup for the pressure rise are lower than the results with the standard test method. One could assume that oxidation of the test sample before ignition does not influence safety characteristics because of these results. This is not necessarily the case, because aluminium needs to be oxidised partially after manufacturing in order to be safer for transport. Although the manufacturer tried to reduce the oxide content to a minimum, measurements have shown that the dust was already partially oxidised (Table 2). Responsible for the lower values with the modified setup is thus probably the weaker dispersion by the bowl nozzle of very heavy dusts like metallic dusts. For those heavy dusts (which can be dispersed weakly) further tests with passivated samples under

variation of the ignition delay time need to be conducted, in order to verify whether or not comparable results with the standard test method are possible.

Table 3: Test results of nano aluminium and nano iron

Test result		nano aluminium		nano iron	
		Standard test	Modified setup	Standard test	Modified setup
P_{\max}	[bar]	9.7	9.1	-	3.4 (only until 250 g·m ⁻³)
dp/dt_{\max}	[bar·s ⁻¹]	1806	1267	-	525 (only until 250 g·m ⁻³)
K_{St}	[bar·m·s ⁻¹]	490	344	-	143 (only until 250 g·m ⁻³)
LEL	[g m ³]	30	30	-	60

5. Conclusion/Final Remarks

The aim of this paper was first of all to introduce a new approach to investigate the influence of oxide content to safety characteristics of dusts consisting of primary nano particles. Therefore a modified setup was designed. It has been shown that there are still some problems that need to be solved. Even though with the modified setup it is possible to investigate, how the higher oxide content influences test results, because oxidation before the test itself can be avoided. It is furthermore able to get rough information about the explosion behaviour of pyrophoric dusts, which cannot be tested in general with the standard procedure so far.

To fully understand the influence of oxygen on explosion behaviour of nano dusts further research will be done. It is therefore first of all necessary to determine the oxygen content of the sample to be tested. Besides the determination of the specific surface area this is crucial for the characterisation of the sample and for a proper clarification of the determined characteristics.

The next research steps will include the improvement of the modified setup to ensure comparable results with the standard setup even for heavier dusts like metal dusts. In addition to that more dusts with different oxide contents and particle sizes will be tested.

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