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An Alternative Way to Determine the Deflagration Behaviour

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This paper presents a new test set-up in a closed autoclave for testing the deflagrative behaviour of substances is presented. Several substances are tested in the Time/pressure test (UN test C.1) and in the closed autoclave. It is first shown that the results of the tested substances in the Time/pressure test (UN test C.1) stay in an good accordance with the tabled values in the UN Recommendation on the Transport of Dangerous Goods (hereinafter UN Transport Regulation). The testing of these substances in the closed autoclave and the comparison of the values show a good very good repeatability. When comparing the results of the closed autoclave with the tabled results in the UN Transport Regulation and the results of the Time/pressure test (UN test C.1) performed it is pointed out, that well-known deflagrative substances like ammonium nitrate which show no deflagrative behaviour in the Time/pressure test (UN test C.1) can be brought to deflagration in the closed autoclave. It therefore can be maintained that the test set-up presented here is more sensitive than the Time/pressure test and can be used as an alternative for the deflagration testing.

1. Introduction

Pharmaceutical agents, plant protecting agents, pigments of dye, distillation residues and other chemical products are produced in large amounts with a high standard in aspects of process safety and risk management. In many cases, the potential risk of a substance is correlated to specific chemical reactive groups, which reduces the thermal stability of the substance (like azide or nitro groups). Many risks are correlated to the mean temperature of the package of the product, like self-heating or self-reactivity. A special kind of risk is given, if the decomposition of a substance is triggered by a local hot spot and the complete package decomposes exothermically. This decomposition propagates like a combustion zone for which, however, no air or oxygen is necessary. This process is called “deflagration”.
In a production process this deflagration behaviour is a special risk, because one of the class protection methods against gas or dust explosions, the inertisation of the production step, does not work here. The risk of deflagration, however, has to be taken into account not only for the production, but also in the UN Transport Regulation for the classification of explosive substances (class 1), self-reactive substances (division 4.1) and organic peroxides (division 5.2).

2. Experimental

State of the art testing for deflagrative behaviour is performed according to:

- VDI2263 sheet 1: Test Methods for the Determination of the Safety Characteristics of Dusts, Test 1.6.
- UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 2003) section 23, test C.1: Time/pressure test and test C.2: Deflagration test.

2.1 Deflagration testing according to VDI2263 sheet 1

The test described in VDI2263 sheet 1 consists of a cylindrical glass tube. The tube stands on its circular end. Thermocouples are positioned at varying levels alongside the vertical orientation of the tube. The sample is filled into this tube. The ignition of the sample is carried out by using a glow coil, a micro burner or an ignition

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mixture and can be performed from the top or bottom side of the tube. The temperatures of the thermocouples inside the substance and the time are recorded.

2.2 UN test method C.1: Time/pressure test

The UN test C.1 consists of a cylindrical steel pressure vessel with 89 mm length and 60 mm external diameter. A pressure transducer is positioned at the side of the pressure vessel. The autoclave is positioned with an angle of 60° to its circular end. At the bottom side the ignition system, consisting of an electrical fusehead together with an 13 mm square piece of primed cambric is positioned. The autoclave is filled with 5 g of the sample. The top side of the autoclave is closed with an rupture disc with an bursting pressure of approx. 22 bar_g. The ignition system is fired and the pressure in the autoclave and the time are recorded.

2.3 UN test method C.2: Deflagration test

The UN test C.2 consists of a Dewar vessel with an volume of about 300 cm³ and an internal diameter of 48 mm with an vertical observation window. Two thermocouples are positioned in the Dewar vessel in horizontal orientation 50 mm and 100 mm from the top of the Dewar vessel. The Dewar vessel is filled with 265 cm³ of sample and ignited by the use of a gas burner. The temperatures of the thermocouples inside the substance and the time are recorded.

2.4 Deflagration testing in the closed autoclave

The test set-up presented here for testing the deflagration ability of a sample is based on a test setup according to Grewer and Klais (1987). The test set-up consists of a high-pressure autoclave made of stainless steel. The inner diameter of the autoclave is 55 mm and it has a height of 79 mm. In this autoclave, a glass cylinder with an inner diameter of 45 mm and an inner height of 67 mm and a nominal inner volume of approx. 140 mL, is positioned. The top end side of the autoclave consists of a closure head and a lock nut. The upper part of the closure head with a diameter of 55 mm has the three G1/8” threads. These threads are positioned uniformly in cylindrical orientation. The length of the closure head up to the G1/8” threads is 85 mm. The inner diameter of every drilling is approx. 5 mm. One of the threads is connected to a NiCr-Ni thermocouple (also known as Type K) with a mantle with an outer diameter of 1.5 mm and an inert mantel material like Inconel. The second thread is connected to a piezoelectric pressure sensor. The third threads lead to the ignition system. This consists of a glow plug. The coil of the glow plug is cut and replaced by a coil which consists of a 1.0 mm diameter platinum wire. This platinum wire coil has approx. 6 - 9 windings and is connected to the glow plug by brass or copper wires. For the test set-up see also Figure 1.

The test item is filled into the glass cylinder and weighed. Thereafter an igniting mixture (silicon/lead dioxide at a weight ratio 1.5:1) is placed on top of the test item. The platinum wire coil extends into the ignition mixture. For liquid or pasteous substances the ignition mixture is covered by a thin layer of PVC-sheet or equivalent. The glass cylinder is transferred to the autoclave, which is closed and can be heated if required (for example in an oven). After the sample has been prepared in the autoclave the ignition mixture is fired by using an electrical impulse of approx. 8 V DC and 10 A. The pressure in the autoclave, the temperature in the sample, the voltage applied to the ignition system and the time are recorded.

2.5 Substances

The substances used for the tests are summarised in Table 1. The tabled results of the UN Transport Regulation for the outcomes of the Deflagration test (UN test C.2) and the Time/pressure test (UN test C.1) for the substances used are shown in Table 2.

Table 1: Substance used for testing

Substance	Structural Classification	State of matter at room temperature
2,2′-Azobis(2-methylpropionitril) (AIBN)	Azo compound	Solid
Dicumyle peroxide	Organic peroxid	Solid
Pigment	Azo compound	Solid
Ammonium nitrate	Salt	Solid
tert-Butyl peroxy-2-ethylhexanoate	Organic peroxide	Liquid
Azodicarbonamide	Azo compound	Solid
Blend of a flammable solid (division 4.2) with an oxidising substance (division 5.1)	Blend	Solid
Tetrazol derivate		Solid

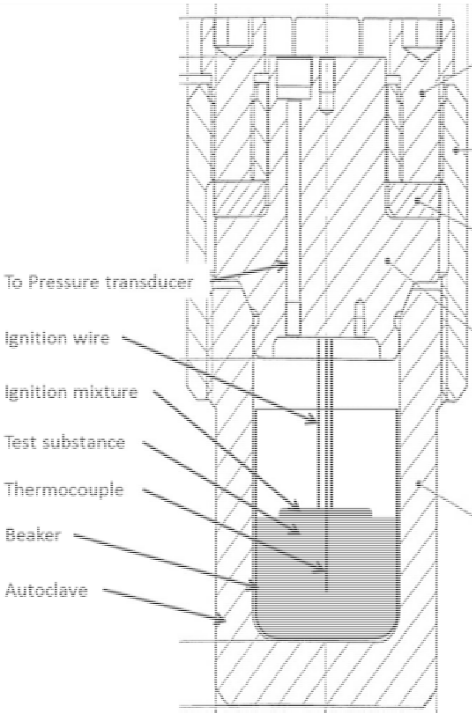

Figure 1: Schematic drawing of the test set-up

Table 2: Values documented in the UN Transport Regulation for the outcome of the Deflagration test (UN test C.2) and the Time/pressure test (Un test C.1)", for the other substances noted in Table 1 no data is documented in the UN Transport Regulation

Substance	Time/pressure test (C.1)		Deflagration test (C.2)
	Maximum pressure	Time for pressure rise from 690 kPa to 2070 kPa	Propagation rate
2,2′-Azobis(2-methylpropionitril) (AIBN)	> 2070 kPa	68 ms	"No stable propagation"
Dicumyl peroxide	< 690 kPa	-	"No ignition"
Pigment	No data available		No data available
Ammonium nitrate	< 2070 kPa	-	No data available
tert.-Butyl peroxy-2-ethylhexanoate	> 2070 kPa	384 ms	0.74 mm/s
Azodicarbonamide	> 2070 kPa	63 ms	0.35 mm/s
Blend of a flammable solid (division 4.2) with an oxidising substance (division 5.1)	No data available		
Tetrazol derivate	No data available		

2.6 Evaluation of the data

The evaluation of the data of the Time/pressure test is performed according to UN Transport Regulation: The time for the pressure rise from 690 kPa to 2070 kPa was taken. For each substance three tests were performed and the mean value of the pressure rise of these three tests is used. In addition to this, the maximum pressure is noted.

In the test in the closed autoclave the maximum pressure and maximum temperature and the corresponding times to reaching these maximum values are recorded. An exemplary course of a deflagration test is shown in Figure 2. Based on the pressure course, the first derivative of the pressure in dependency of the time (pressure rise rate) is calculated and plotted as a function of the pressure. This pressure rise rate can be plotted in a double logarithmic graph as function of the pressure as shown in Figure 3. In this graph a linear dependency of the pressure rise rate to the pressure can be found in the case of a deflagration. The slope of the linear pressure rise rate normalised to the sample mass and the free head space in the autoclave, as shown in column 7 in Table 4 is used, when comparing the results of the same substance.

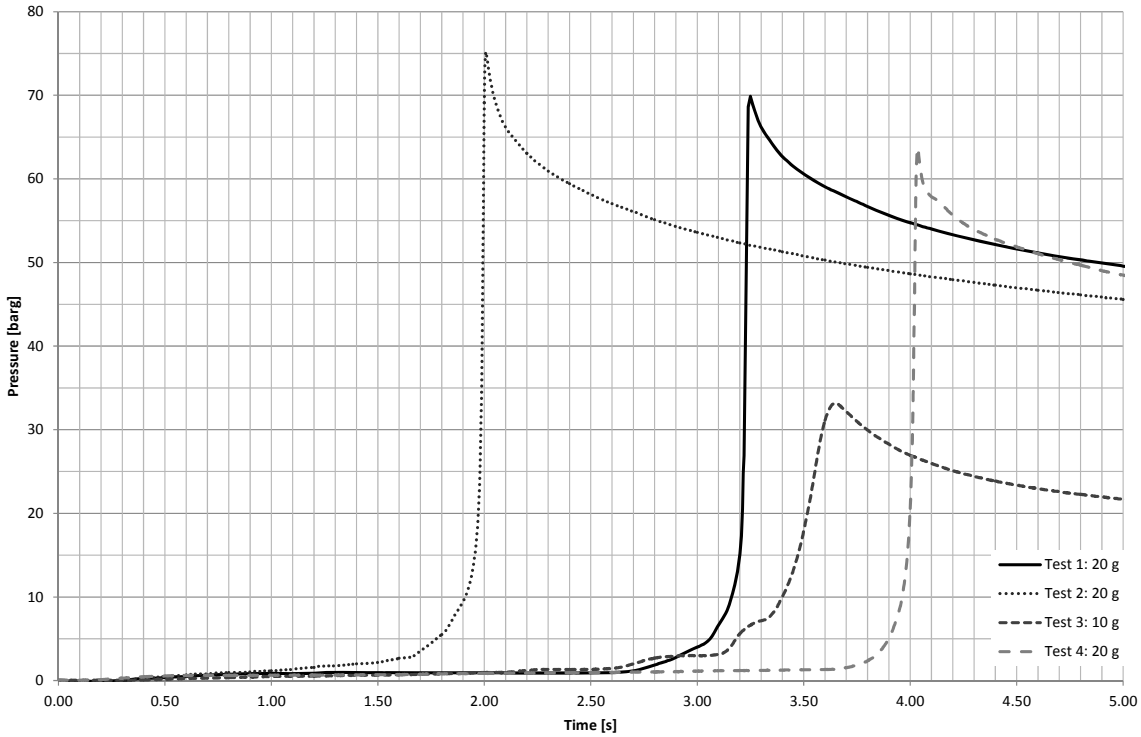

Figure 2: Exemplary courses for the experiments performed with AIBN. The ignition for all four tests was performed at a testing time of 0 s.

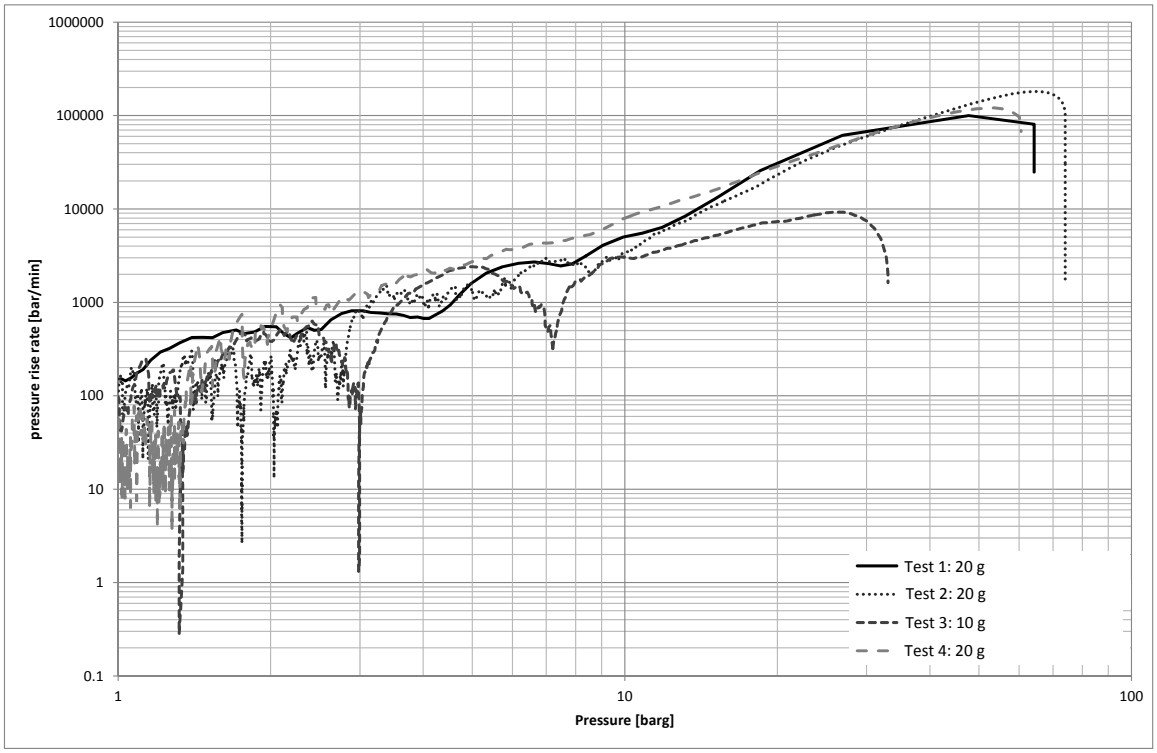

Figure 3: Evaluation of the four pressure courses of the testing of AIBN.

3. Results

With the above mentioned substances tests in the time/pressure test and the in the closed autoclave were carried out. The results of the time/pressure test are summarized in Table 3. The results of the tests in the closed autoclave are summarized in Table 4.

Table 3: Results of the testing in the Time/pressure test (UN test C.1)

Substance	Time for pressure rise from 690 kPa to 2070 kPa	Maximum pressure
Dicumyle peroxide	-	< 690 kPa
Pigment	145 ms	> 2070 kPa
Ammonium nitrate	-	< 690 kPa
tert-Butyl peroxy-2-ethylhexanoate	1240 ms	> 2070 kPa
Blend of a flammable solid (division 4.2) with an oxidising substance (division 5.1)	-	< 2070 kPa
Tetrazol derivate	-	< 690 kPa

Table 4: Results of the testing in the closed autoclave

Substance	weight	Max. pressure	Time to max. Pressure	Max. temperature	Max. pressure rise rate	Normalised slope of the pressure rise rate
	[g]	[kPa]	[ms]	[°C]	[10^6 bar/s]	[L/(s g)
2,2′-Azobis(2-methylpropionitril) (AIBN)	20 g	69900	3250	340	6.73	0.278
2,2′-Azobis(2-methylpropionitril) (AIBN)	20 g	75000	2008	340	12.25	0.232
2,2′-Azobis(2-methylpropionitril) (AIBN)	10 g	33000	3658	340	5.61	0.269
2,2′-Azobis(2-methylpropionitril) (AIBN)	20 g	64000	4034	345	7.50	0.170
Dicumyl peroxide	32 g	570	790	55	0.01	-
Pigment	10 g	97200	5870	> 1000	1.16	0.329
Pigment	20 g	255800	7432	915	25.95	0.163
Ammonium nitrate	44 g	18400	15200	22	0.01	0.016
Ammonium nitrate	46 g	26900	13538	68	0.01	0.013
tert.-Butyl peroxy-2-ethylhexanoate	42 g	40000	56810	70	0.17	0.157
tert.-Butyl peroxy-2-ethylhexanoate	47 g	41100	19220	140	0.07	0.110
Azodicarbonamide	20 g	109600	2690	410	0.50	0.143
Blend of division 4.2 and division 5.1	29 g	51200	8640	955	0.21	0.114
Tetrazol derivate	38 g	43800	92715	385	0.01	0.044
Tetrazol derivate	38 g	105000	87618	535	0.02	0.052

Additionally, for the blend of a flammable solid (division 4.2) with an oxidising substance (division 5.1) the Deflagration test (UN Test (C.2)) was performed. The result of this test is a propagation rate of 1.3 mm/s.

4. Discussion of the results

On the basis of the test results, it can be pointed out that the obtained results of the Time/pressure test (UN test C.1) stay in an good accordance with the tabled values in the UN Transport Regulation.
A comparison of the results of the deflagration test in the closed autoclave showes a very good accordance, when testing the same substance under comparable conditions (sample mass and the resulting free head space of the autoclave). Therefore, it can be stated that the repeatability in the closed autoclave is given.

A comparison of the results of the deflagration test in the closed autoclave with the results of the Time/pressure test (UN test C.1), shows that at least all substances that deflagrate in the Time/pressure test (UN test C.1), also show a deflagration in the closed autoclave. In the closed autoclave a deflagration is indicated by linear dependency of the pressure rise rate as function of the pressure in a double logarithmic plot. It is also shown that well-known deflagrative substances like ammonium nitrate which display no deflagration behaviour in the Time/pressure test (UN test C.1), show a deflagration in the closed autoclave.
It therefore can be assumed that the deflagration test in the closed autoclave presented can be used as an alternative for the deflagration testing in the Time/pressure test (UN test C.1).

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