



Letter to the Editor

Some comments on the paper of H. Fierz: Influence of heat transport mechanisms on transport classification by SADT-measurement as measured by the Dewar-method

We would like to comment on a paper by Fierz [1], recently published in the *Journal of Hazardous Materials*.

Fierz [1] draws some conclusions concerning the scale-up applicability of the H.4 Dewar test method [2] to solid self-reactive substances. His main points are:

- The SADT-test using a 500 ml Dewar vessel correctly predicts the thermal behaviour of a 500 l package filled with a liquid, but it will only be representative for an 8 l package filled with a solid.
- The UN-test H.4 was obviously designed to make a direct scale-up to a predetermined package size possible. This does not work for solids. Extrapolated package sizes for solids are dramatically different from those for liquids.
- For solids, the UN-test H.4 errs grossly on the unsafe side and should therefore not be used.
- The concept of time constants and specific heat losses for cooling of solids is misleading and should be abandoned. For solids, the cooling characteristics of the bulk in its packaging should be determined individually in each case or even better: the theory of Frank–Kamenetzki should be applied.

To avoid misunderstanding of the applicability of the UN H.4-test, our objections are as follows:

There is some evidence from experiments referring to the problem that the small-scale “Wärmestau”-test (UN H.4) is in good agreement with the US-SADT test (UN H.1), where one-to-one samples are used. Table 1 summarises the SADT values for six solid self-reactive substances and organic peroxides, obtained from the H.1 large-scale test as well as the H.4 small-scale test. Besides the SADT, the sample mass, the packaging and in the case of the H.4 test also the half-time of cooling (for water) and the calculated average Dewar heat loss is listed. The SADT values obtained with these different test methods show satisfying agreement. The maximum temperature difference is 5 K which is the typical temperature increment of the test procedure in the H.4 test. Some of these results are published in the UN book [2], however, they were not discussed in Fierz’ paper. These examples clearly show to our opinion that the H.4 Dewar test is very well suited for the scale-up to larger volumes than the proposed 8 l.

A further example was given by Steensma in an internal paper [3], who investigated a specific solid organic peroxide with both the US-SADT test and the UN H.4-test. The key conclusion was that for 90 l of that peroxide (43 kg, bulk density of 465 kg/m³), the

Table 1
Comparison of test results of the UN-tests H.1 and H.4 for solids and pastes

Substance	Test H.1 (US-SADT)			Test H.4 (heat accumulation storage test)				Remarks
	Sample mass (kg)	Packaging	SADT (°C)	Sample mass (kg)	Dewar heat loss (mW/kg K)	Half-time of cooling (H ₂ O) <i>t</i> _{1/2} (h)	SADT (°C)	
Di-(4- <i>tert</i> -butylcyclohexyl)-peroxydicarbonate	43	1G	40	0.19	79	10.2	45	UN manual
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (66%)	30	1G (50 l)	50	0.25	58	13.9	45	UN manual
Didecanoyl peroxide, 97%	45.4 (100 lb)		35	0.17	75	10.7	40	Technical pure
2,4-Dichlorobenzoyl peroxide, 50% in dibutylphthalate (as a paste)	15.9–34 kg (35–75 lb)		43	0.535	75	10.7	40	
Dibenzoyl peroxide, 50% in tricresylphosphate (as a paste)			54	0.50	75	10.7	60	50% in a Phthalic acid ester
Dilauroyl peroxide			49	0.25	80	10.0	45	

Table 2
SADT values for 2,2'-AIBN derived from different test methods

Pack size (kg)	SADT (°C)		
	ARC	US	Dewar
50	60	50	50
1	67	60	

deviation in the SADT between the two methods is visible but still acceptable, a few degrees K.

Another work in which different experimental methods have been used to estimate the SADT of self-reactive substances, is published by Whitmore and Wilberforce [4]. Besides many liquids, some solids have been investigated as well. Table 2 shows the results for 2,2'-azodiisobutyronitrile (AIBN), a solid substance of some importance in chemical industries. Again the temperatures do not show a significant difference. This can be taken as another evidence that the results from the H.4 test are on the safe side when extrapolating to larger quantities.

A theoretical treatment of the Dewar test was given by Grewer [5]. Grewer compared the theories of Semjonov and Frank–Kamenetzki and derived the following relations for the characteristic length (r_0) of a package of a self-reactive substance exhibiting the same heat loss as a Dewar flask:

$$\frac{c_p \rho}{k_w} r_0 = \frac{3}{e} \tau_{ad} \quad (\text{Semjonov}) \quad (1)$$

$$\frac{c_p \rho}{\lambda} r_0^2 = \delta_{cr} \tau_{ad} \quad (\text{Frank–Kamenetzki}) \quad (2)$$

with c_p being the specific heat capacity in J/(kg K), ρ the bulk density in kg/m³, k_w the heat transfer coefficient of the Dewar flask in J/(s m² K), λ the heat conductivity of the self-reactive solid in J/(s m K), δ_{cr} the critical Frank–Kamenetzki parameter and τ_{ad} the adiabatic induction time in s.

The difference between Eqs. (1) and (2) lies in the power of the characteristic length. While in Semjonov's approach, the characteristic length is directly proportional to τ_{ad} , in Frank–Kamenetzki's approach r_0 is proportional to the square root of τ_{ad} . Note, that the dependence of r_0 on τ_{ad} implies a dependence of r_0 on the storage temperature T_0 , since the adiabatic induction period is the shorter the higher the storage temperature is.

For the case of the Dewar vessel, Grewer gives a relation between τ_{ad} and the half-time of the temperature decay $t_{1/2}$. As Grewer showed (see Ref. [5, pp. 34–35])

$$\frac{\tau_{ad}}{t_{1/2}} = \frac{e}{\ln 2} = 3.92 \quad (3)$$

An example calculation given by Grewer for

$$a \text{ (m}^2\text{/s)} = \frac{\lambda}{\rho c_p} = 2 \times 10^{-7} \quad (4)$$

and $\tau_{\text{ad}} = 1.1 \times 10^5$ s leads for a spherical package ($\delta = 3.32$) to a critical radius of 0.27 m, or a volume of 82 l, respectively. Grewer concludes that for bulk powders “. . . it is estimated that a 500 cm³ Dewar corresponds to a product volume of 100 l . . .”.

For the example given by Fierz in Appendix A of his paper, the application of Eqs. (2) and (3) leads to the following results:

With

$$t_{1/2} = -\tau \ln\left(\frac{1}{2}\right) = -\frac{c_p}{\dot{q}_{\text{loss}}} \ln\left(\frac{1}{2}\right) \quad (5)$$

one obtains

$$r_0^2 = \delta_{\text{cr}} \frac{\lambda}{\rho c_p} \times 3.92 \left(-\frac{c_p}{\dot{q}_{\text{loss}}}\right) \ln\left(\frac{1}{2}\right) \quad (6)$$

Inserting the values for λ , ρ , c_p and \dot{q}_{loss} given by Fierz, one obtains $r_0 = 0.15$ m. This refers to the volume of a sphere of about 14 l.

These calculations show a strong dependence of the characteristic length on the material properties, especially on the thermal diffusivity a . Suppose, the volume of a package is a function of the third power of its characteristic length (sphere, cylinder with height = diameter, cube), then the critical volume to avoid self-decomposition depends on a with the power of 1.5. As e.g. the bulk density may vary for different solids over about one order of magnitude, the critical volumes of different self-reactive substances may vary for a factor of about 30.

The value for the bulk density of 1000 kg/m³ as given by the model calculation of Fierz is close to the particle density of organic solids and thus comparatively high as a bulk density. Bulk densities for self-reactive substances are typically between 200 and 600 kg/m³ leading to higher values for r_0 . According to Eq. (6), a bulk density of 430 kg/m³ would correspond to a volume of about 50 l. The calculation Fierz presented in his paper leads to a volume of 50 l if a bulk density of 290 kg/m³ is assumed. These examples show the very strong dependence of the critical dimensions on the bulk density.

In addition, the adiabatic induction period is the lowest possible value for a runaway reaction to occur at a given storage temperature. Induction times under non-perfect conditions will be higher and thus result in a further increase of the critical characteristic length according to Eq. (2).

This theoretical treatment suggests the conclusion that a more detailed investigation of the influence of the physical and chemical parameters is needed. We are currently working on that problem and will present the results as soon as possible. Besides the theoretical treatment, the experiments suggest to our opinion that the H.4 Dewar test is very well suited to predict at least the behaviour of a 50 l sized package without insulation.

References

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