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Testing strategy for classifying self-heating substances for transport of dangerous goods

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Abstract

A testing strategy for the classification of self-heating substances for transport of dangerous goods is proposed. The strategy was developed based on the tests described and correlations used in the UN Recommendations. It was demonstrated that the value of activation energy of the exothermic reaction has a significant impact on the extrapolation of test results with regard to different container sizes and temperatures. Based on a combination of the Grewer Oven test screening, the 25 mm cube test at 140 °C, and the determination of the activation energy of a specific material, a flowchart is presented for classifying chemicals as self-heating. The presented approach allows predicting chemical stability in large containers more accurately and eliminates the need to perform hazardous large-scale tests of energetic chemicals in a laboratory.
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Keywords: Tests; Correlations; Activation energy; Critical temperature; Predictions; Container sizes

1. Introduction

The recommended testing scheme [1,2] for classification of substances as self-heating (Division 4.2) begins with the testing of a 100 mm cubic mesh container filled with the test substance in a recirculating air oven at 140 °C for 24 h. Depending upon the outcome of the test (at least a 60 °C temperature rise), the scheme provides for more testing at different temperatures or in a smaller cube [1,2]. Because of the nature (high energy, fast reaction rate, significant gas evolution) of the chemicals that need to be classified, it may be not safe to perform the 100 mm cube test in a laboratory.

The goal of this project was to develop a more cost efficient and less time consuming method for classifying substances as self-heating. This can be achieved by developing correlations between different test scales and temperatures, so that the tests recommended (100 mm cube at 140, 120, and 100 °C) could be either substituted by smaller scale tests (25 mm cube) at higher temperatures or could be predicted based on the determined properties of the substances.

The basis of the tests in the Recommendations is that, according to the Frank–Kamenetskii (F–K) model of thermal ignition [3], the self-heating temperature of charcoal at 50 °C in a 27 m^3 container correlates to a self-heating temperature at 140 °C in a 100 mm cube. Therefore, if a substance does not demonstrate self-heating in a 100 mm cube at 140 °C for 24 h, with a temperature rise of at least 60 °C, it will not self-heat in a 27 m^3 container at 50 °C. It is also indicated in the Recommendations that in a 450 l container a material can be exempt from Division 4.2 self-heating if a negative result is obtained in a 100 mm cube at 100 °C. In a 3 m^3 container, a material can be exempt from Division 4.2 self-heating if a negative result is obtained in a 100 mm cube at 120 °C.

2. Results and discussion

The relationships between the critical temperatures in different container sizes established in the Recommendations allow the values of activation energy to be calculated that support these relationships. The F–K plots are presented in Fig. 1.

An activation energy of ∼90 kJ/mol was determined when correlating the 27 m^3 container at 50 °C to the 100 mm cube

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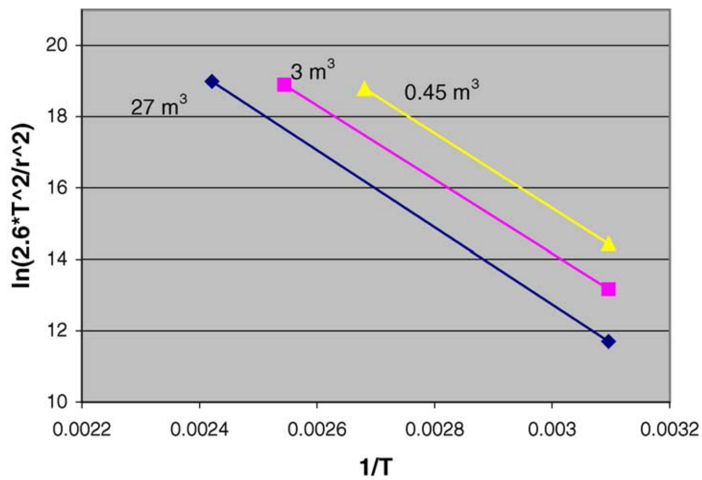

Fig. 1. F–K plots that relate 27, 3, and 0.45 m^3 at 50 °C to 100 mm cube at 140, 120, and 100 °C, respectively.

at 140 °C and ∼87 kJ/mol was determined when correlating the 3 m^3 container at 50 °C to the 100 mm cube at 120 °C and 0.45 m^3 container at 50 °C to the 100 mm cube at 100 °C. Similar results were obtained in references [4,5]. After these activation energies were determined, the results could be extrapolated to smaller cube sizes for all three relationships (Table 1). Also a screening test (Grewer Oven) that is specified in the Recommendations [6] is included in Table 1 for comparison. The requirement for the screening test is for the onset temperature to be at least 80 °C above the critical temperature for a volume of 1 l (100 mm cube).

The relationships between the critical temperatures in different container sizes established in the Recommendations are valid only if a material under investigation has an activation energy of ∼87–90 kJ/mol. If a material has an activation energy that differs from 87–90 kJ/mol (either higher or lower), different critical temperatures in a 100 mm cube will correlate to the stability at 50 °C in 27, 3, or 0.45 m^3 containers. Calculations were performed for a material with a higher (∼123 kJ/mol), as well as a lower, activation energy (∼75 kJ/mol). The results are summarized in Table 2.

For an activation energy of 123 kJ/mol, the recalculated test temperatures in a 100 mm cube that correlates to 50 °C in three different container sizes described in the Recommendations will be 110 °C (instead of 140 °C) for a 27 m^3 container, 95 °C (instead of 120 °C) for a 3 m^3 container, and 83 °C (instead of 100 °C) for a 0.45 m^3 container. As we can see for higher activation energies, the test temperatures at which chemical stability should be determined are significantly lower than the test temperatures in the Recommendations, determined for an activation energy of 87–90 kJ/mol. If a material with a lower activation energy is used, an opposite result is obtained. For an activation energy of 75 kJ/mol, the recalculated test temperatures in a 100 mm cube that correlates to 50 °C in three different container sizes described in the Recommendations will be 167 °C (instead of 140 °C) for a 27 m^3 container, 135 °C (instead of 120 °C) for 3 m^3 container, and 110 °C (instead of 100 °C) for a 0.45 m^3 container. It is clear from the above that the activation energy of a specific material must be determined to accurately predict the temperature and the test cube size that would correlate with the stability at 50 °C in a larger container.

One of the smaller cube size tests that is specified in the Recommendations is a 25 mm cube test at 140 °C. If a positive result is obtained in this test, the material is classified as Packing Group II. If a negative result is obtained, more testing is recommended to exempt the material for transportation in packages of no more than 3 m^3 containers or no more that 0.45 m^3 volume. An alternative approach to conducting more testing would be to correlate the stability in this test to the stability at 50 °C in the 3 container sizes of interest and calculate the activation energy from each correlation. The activation energy values obtained from these correlations are summarized in Table 3.

Table 1
Critical temperatures in smaller cubes that correlate to 27, 3, and 0.45 m^3 containers at 50 °C

Container size (m^3)	Critical temperatures in 100, 50, 25 mm cubes and Grewer Oven (°C)			
	100 mm[a]	50 mm	25 mm	Grewer Oven[a]
27	140	165	195	220
3	120	143	169	200
0.45	100	121	145	180

[a] From the Recommendations.

Table 2
Critical temperatures in 100/50/25 mm cubes that correlate to 27, 3, and 0.45 m^3 containers at 50 °C as a function of chemical activation energies

Container size (m^3)	Critical temperatures in 100/50/25 mm cubes for different activation energies (°C)		
	123 kJ/mol	90 kJ/mol	75 kJ/mol
27	110/125/141	140/165/195	167/202/245
3	95/109/124	120/143/169	135/165/200
0.45	83/96/110	100/121/145	110/137/168

Table 3
Activation energies that correlate critical temperature of 140 °C in a 25 mm cube to 27, 3, and 0.45 m^3 containers at 50 °C

Container size (m^3)	27	3	0.45
Activation energy (kJ/mol)	124	106	90

These activation energy values can be used as breakpoints for classifying chemicals as:

(1) not self-heating substance of Division 4.2 (if the determined activation energy of a chemical is higher than 124 kJ/mol and the chemical is stable in a 25 mm cube at 140 °C),
(2) exempt for transportation in packages of not more than 3 m^3 volume (if the determined activation energy of a chemical is higher than 106 kJ/mol and the chemical is stable in a 25 mm cube at 140 °C),
(3) exempt for transportation in packages of not more than 0.45 m^3 volume (if the determined activation energy of a chemical is higher than 90 kJ/mol and the chemical is stable in a 25 mm cube at 140 °C).

In order to use this approach for classifying chemicals, the activation energy of the exothermic reaction would need to be determined. The activation energy can be determined from a DSC test in air using the isothermal DSC method previously developed [7] or any other existing method for developing kinetics. The DSC test should be used for determining the activation energy only when the exotherm onset temperature in the Grewer Oven test is not significantly different from the one in the DSC test to confirm that the same reaction occurs in both tests.

The described approach is summarized in a flowchart presented in Fig. 2. A screening test that is specified in the Recommendations (Grewer Oven test with an onset temperature 80 °C above the reference temperature for a volume of 1 l) is also added to the flowchart.

- If the onset temperature in the Grewer Oven test is higher than 220 °C, the material should be classified as a not self-heating substance of Division 4.2.
- If the onset temperature in the Grewer Oven test is higher than 200 °C, the material should be exempt for transportation in packages of not more than 3 m^3 volume.
- If the onset temperature in the Grewer Oven test is higher than 180 °C, the material should be exempt for transportation in packages of not more than 0.45 m^3 volume.

If the onset temperature in the Grewer Oven test is lower than 180 °C, or if larger than 0.45 m^3 or 3 m^3 volume containers need to be transported, a test in a 25 mm cube at 140 °C for 24 h should be performed. If the test result is positive (exotherm with temperature rise more than 60 °C), the material is classified as Packing Group II. If the test result is negative, the activation energy of the exothermic reaction should be determined. Based on the activation energy determined, the material should be classified as specified in Table 4.

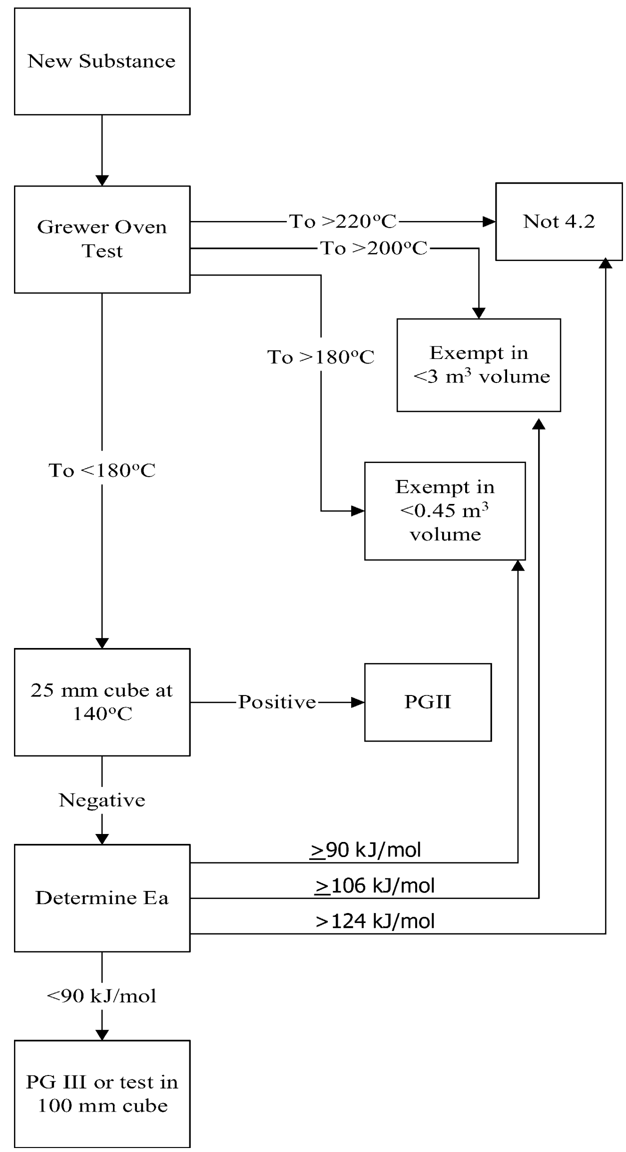

Fig. 2. Flowchart for classification of self-heating substances.

The following additional considerations may be taken into account when classifying chemicals as self-heating. The intent of the regulation is to determine whether self-heating can occur at 50 °C in the containers in which chemicals are transported. If chemicals are transported in smaller containers, the test temperature in a 25 mm cube can be determined from a

Table 4
Chemical classification for transportation based on the value of activation energy determined

Activation energy (kJ/mol)	Material classification
$E_a > 124$	Not self-heating substance of Division 4.2
$124 > E_a \geq 106$	Exempt for transportation in packages of not more than 3 m^3 volume
$106 > E_a \geq 90$	Exempt for transportation in packages of not more than 0.45 m^3 volume
$E_a < 90$	PG III or test in 100 mm cube

correlation between the specific container size at 50 °C and the 25 mm cube using the activation energy value determined for the specific material. If the test substance demonstrates no self-heating at that temperature, it should be safe to transport it in the specified container size.

3. Conclusions

It was demonstrated that the critical temperatures in small test cubes that correlate to the chemical stability in various large container sizes at 50 °C are dependent upon the activation energy of the chemical of interest. Activation energy breakpoints that allow predictions of chemical stability in 27, 3 and 0.45 m^3 containers at 50 °C have been calculated.

This approach allows predicting chemical stability in large containers more accurately and eliminates the need to perform hazardous large-scale tests of energetic chemicals in a laboratory.

The presented information is purely theoretical and is based on correlations of tests required by the regulations. Experimental work is needed to confirm the described approach.

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