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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

Thirty-eighth session
Geneva, 29 November–7 December 2010
Item 3 of the provisional agenda
Explosives and related matters

Changes to screening test for substances that may have explosive properties

Transmitted by the expert from Japan and by the International Council of Chemical Associations (ICCA)[1]

1. As a result of discussions at the thirty-first session (ST/SG/AC.10/C.3/2007/10, informal document INF.45), thirty-second session (informal document INF.35) and thirty-third session (ST/SG/AC.10/C.3/2008/40) at the Sub-Committee, screening procedures were specified in Appendix 6 of the Manual of Test and Criteria to judge whether large-scale classification tests; i.e., Test Series 1 or 2, need to be performed for substances that may have explosive properties.

2. According to the NOTE in section 3 of the screening procedures, tests 1 (a) and 2 (a) are not required if the exothermic decomposition energy of organic materials is less than 800 J/g.

3. In subsection 20.3.3.3 of the Manual of Tests and Criteria, it is stated that the exothermic decomposition energy may be estimated using a suitable calorimetric technique such as differential scanning calorimetry (DSC) or adiabatic calorimetry.

4. This statement is based on the condition that the exothermic decomposition energies of the very same sample measured by two different methods; i.e., DSC and adiabatic calorimetry, will agree within an allowable error.

5. However, such condition is not necessarily valid because these two types of calorimetries are based upon different measuring principles.

[1] In accordance with the programme of work of the Sub-Committee for 2009-2010 approved by the Committee at its fourth session (refer to ST/SG/AC.10/C.3/68 para. 118(a) and ST/SG/AC.10/36, para. 14).

6. In practice, as shown in Annex of this document, test measurements over 11 kinds of chemical substances show considerable disagreements between Q_{DSC} and Q_{adia}, which are the exothermic decomposition energies measured by DSC and adiabatic calorimetry, respectively.

7. Moreover, observed values of Q_{adia} have a tendency to be lower than those of Q_{DSC} suggesting that the adiabatic calorimetry tends to underestimate the exothermic decomposition energy.

8. This finding is not surprising but can be scientifically explained: Main factors are the heat loss and the response time of the equipment (i.e. the method is only near adiabatic).

9. Therefore, it is suggested that the adiabatic calorimetric techniques should not be used to determine the thermal decomposition energy of substances and mixtures.

Proposal

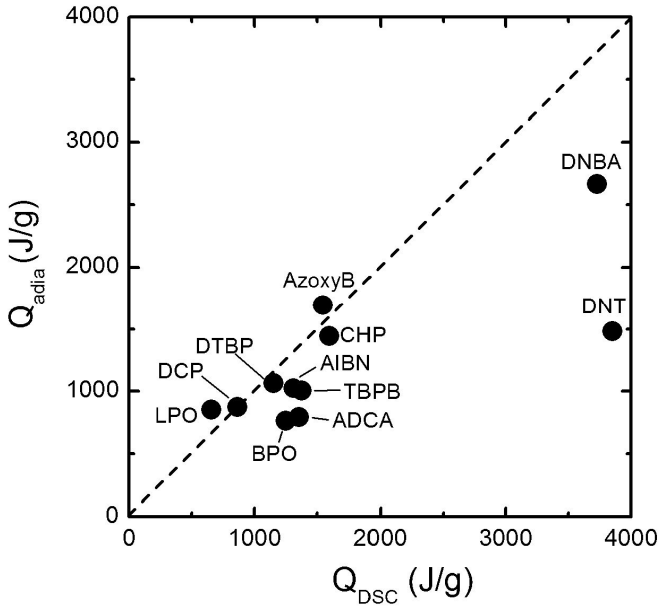
10. We propose that the Sub-Committee consider exclusion of the adiabatic calorimetric techniques from the methods to determine the thermal decomposition energy of substances and mixtures in the next biennium. Possible amendments to subsection 20.3.3.3 of the Manual of Tests and Criteria are as follows:

"Thermal stability and exothermic decomposition energy may be estimated using ~~a suitable calorimetric technique such as~~ differential scanning calorimetry ~~or adiabatic calorimetry~~. ~~In using such techniques, special~~ Special care should be taken in interpreting the results when:

- Sampling and testing mixtures;
- The material of the sample vessel may influence the result;
- Endotherms immediately precede exotherms;
- Evaporation of constituents will lower the exothermicity (sealed sample vessels should normally be used);
- The presence of air may critically affect the measured decomposition energy;
- There is a large difference between the specific heats of the reactants and products; and
- Using rapid heating rates (~~when differential scanning calorimetry is used,~~ the heating rates should normally be in the range of 2 to 5 K/min).

"~~If differential scanning calorimetry is used, the~~ The extrapolated onset temperature is defined as being the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline.".

Annex



ADCA	azodicarbonamide	DNBA	dinitro benzoic acid
AIBN	2,2-azobisisobutyronitrile	DNT	2,4-dinitrotoluene
AzoxyB	azoxybenzene;	DTBP	tert-butyl peroxide
BPO	benzoyl peroxide	LPO	lauroyl peroxide
CHP	cumyl hydroperoxide	TBPB	tert-butyl perbenzoate
DCP	dicumyl peroxide		

Comparison of the exothermic decomposition energies measured by DSC (Q_{DSC}) and adiabatic calorimetry (Q_{adia}) over 11 kinds of chemical substances. ARC type instrument was used for adiabatic calorimetry.