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Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 2 (b) of the provisional agenda
Explosives and related matters:
improvement of test series 8

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

Thirty-seventh session

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Item 2 (a) of the provisional agenda

Classification criteria and related hazard communication: work of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG) on matters of interest to the GHS Sub-Committee

Explanatory text about applicable temperature limits in Appendix 6 of the Manual of Tests and Criteria

Transmitted by the European Chemical Industry Council (CEFIC)*

Introduction

- 1. Appendix 6 "Screening Procedures" of the Manual of Tests and Criteria contains a set of useful criteria to identify the need for testing for classification purposes.
- 2. Section 3.3 (c) in that appendix stipulates that for organic substances containing chemical groups associated with explosive properties the Class 1 acceptance procedure does not have to be applied:
 - (a) When the exothermic decomposition energy is less than 500 J/g, or
 - (b) When the onset of exothermic decomposition is $500~^{\circ}\text{C}$ or above as indicated by Table A6.2.
- 3. This text was adopted at the forty-third session of the Sub-Committee (June 2013) as a result of a proposal submitted by Sweden (see ST/SG/AC.10/C.3/2013/8) with the intention of clarification. Unfortunately, in this context an important information in the original text was deleted with respect to the temperature limit of 500 °C: "The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g".

^{*} In accordance with the programme of work of the Sub-Committee for 2019-2020 approved by the Committee at its ninth session (see ST/SG/AC.10/C.3/108, paragraph 141 and ST/SG/AC.10/46, paragraph 14).

4. CEFIC is of the opinion that it would be helpful to re-introduce this sentence into the screening procedures for purposes of clarification.

Discussion

- 5. Currently, the second column of table A6.2 only mentions the decomposition onset but does not specify any upper limit for the evaluation of the measurement. According to the third line of table 6.2, the Class 1 acceptance procedure should be performed in cases where a substance has a decomposition energy of $\geq 500~\text{J/g}$ in combination with a decomposition onset below 500 °C.
- 6. In case a substance has several decomposition peaks in the DSC measurement for example 400 J/g in the range of 200-350 $^{\circ}$ C and 150 J/g in the range of 480 to 700 $^{\circ}$ C this could be interpreted as having a total of 550 J/g with an onset below 500 $^{\circ}$ C and thus establishing the need to test for Class 1.
- 7. According to the original explanatory text above, such interpretation would not be correct. In the example above, only the first exotherm of 400 J/g should count, and the class 1 acceptance procedure should be waived.
- 8. It is commonly known that all energetic organic molecules are decomposed up to 500 °C; only slow secondary reactions between inorganic compounds may take place at or above such temperatures. These reactions do not contribute to a rapid explosive decomposition and thus are of no relevance for the evaluation with respect to explosive properties.
- 9. Therefore, it would be helpful to clarify that the upper range for the evaluation of the decomposition energy should be 500 °C. Substances with a decomposition energy less than 500 J/g in a temperature range up to 500 °C should not be classified as explosive of Class 1.

Proposal

- 10. Reintroduce the explanatory text about the temperature limit in the Manual of Tests and Criteria, Appendix 6, section 3.3 (c) to read (new text is <u>underlined</u>; deleted text is <u>erossed out</u>):
 - "(c) For the organic substance or a homogenous mixture of organic substances containing chemical group (or groups) associated with explosive properties:
 - when the exothermic decomposition energy is less than 500 J/g, or
 - when the onset of exothermic decomposition is 500 °C or above as indicated by Table A6.2.

Table A6.2 DECISION TO APPLY THE ACCEPTANCE PROCEDURE FOR CLASS 1 FOR AN ORGANIC SUBSTANCE OR A HOMOGENOUS MIXTURE OF ORGANIC SUBSTANCES

| Decomposition energy (J/g) | Decomposition onset temperature (°C) | Apply acceptance procedure for Class 1? (Yes/No) |
|-------------------------------|---|--|
| < 500 | < 500 | No |
| < 500 | ≥ 500 | No |
| ≥ 500 | < 500 | Yes |
| ≥ 500 | ≥ 500 | No |

The temperature limit is to prevent the procedure being applied to a large number of organic molecules which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g. The exothermic decomposition energy should therefore be evaluated with an upper temperature limit of 500 °C and may be determined using a suitable calorimetric technique (see 20.3.3.3); or"