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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

Forty-third session
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Item 11 (b) of the provisional agenda
Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: criteria for water-reactivity

N.5 Test for Water Reactive Materials that emit flammable or toxic gas – Status of the HM-14 Project "Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials"

Transmitted by the expert from the United States of America[1]

1. During previous sessions of the Sub-Committee, the expert from the United States presented information related to work underway that relates to the development of criteria and relevant test methods for the classification of materials that in contact with water evolve toxic and/or flammable gases (see informal document INF.40 of the 42nd session in December 2012. Discussion of this topic has been ongoing for some time, and has its origins in GHS discussions on OECD proposals related to classification of these substances. Both the GHS and TDG Sub-Committee members agreed that improvements in Test N.5 of the Manual of Tests and Criteria should be developed prior to the adoption of criteria for substances that in contact with water emit toxic gases. The general consensus is that while draft criteria previously discussed and presented to both Sub-Committees reflected broad consensus support, the test method needed to be updated and improved before the criteria could be finalized and adopted by both Sub-Committees. The purpose of this paper is to provide an update of efforts to date and to summarize efforts that will be undertaken in advance of the forty-third session of the Sub-Committee. Delegations interested in collaborating in this work are invited to contact the principal investigator directly as the work is not managed by the expert from the United States but rather by the

[1] In accordance with the programme of work of the Sub-Committee for 2013-2014 approved by the Committee at its sixth session (refer to ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

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2. In early January 2013 a summary of the HM-14 project was sent to those who had previously asked to be included on distribution for project updates. The update included:

- An updated test plan for the experimental phase of the project; and
- A draft proposal on classification criteria for water reactive materials.

Note: It is recognized that the development of classification criteria for water reactive materials can't be completed until an improved test for the rate of evolution of gasses from substances which in contact with water emit gasses has been agreed and that the classification criteria is a task for the United Nations Committee of Experts on the Transport of Dangerous Goods and Globally Harmonized System of Classification and Labelling of Chemicals. The draft proposal relies heavily upon a proposal transmitted to the Sub-Committee of Experts on the GHS during 2008 by the expert from France (ST/SG/AC.10/C.4/2008/10).

3. Based on a review of existing test methods and results the following principles and information were adopted to guide the development of an improved N.5 test method:

- Highly reproducible and able to yield consistent results between laboratories;
- Using basic apparatus that is simple to use in most laboratory environments and is not unreasonably expensive;
- Must be safe and not pose unreasonable risk to personnel. Materials of construction must tolerate the gases evolved (e.g. HX and other corrosive materials). The test method needs to address the fact that reactive materials will be involved that pose significant hazards if not properly controlled;
- Must account for the fact that the evolved gases may be highly soluble in water. Any method that relies upon manometric methods must address the issue of gas dissolving in the test fluid;
- Needs to address the dynamic range of results possible, ranging from more highly reactive materials such as SiCl4 (as an example of a candidate water reactive material) or substances such as AlH3 (a water reactive substance) currently or likely to be classified as PG I materials, to materials with lower reactivity that belong in PG II or III. The method should be capable of measuring the volume of gas produced, both in total and as a function of time;
- Precision and repeatability will be most important for materials or substances where test results lie near the threshold for a classification, or alternatively for cases such as where the evolved gas is both highly toxic and forms at a slow rate or is extremely volatile with low or moderate toxicity. The test must be sufficiently sensitive and have the ability to take account of competing issues of reactivity and toxicity to ensure appropriate classification; and
- The test must accommodate water reactive materials or substances in the form they are presented for transport and should yield data that reflects intrinsic properties of the materials as presented for transport.

4. The work to develop an improved N.5 test will take place in three phases:

Phase I: Feasibility;

Phase II: Refinement and preliminary validation; and

Phase III: Validation, reproducibility and accuracy.

In phase I, work will be aimed at establishing viable methods for improving the N.5 test method by testing and exploring varying options guided by the principles and information addressed in paragraph 3 and comparing results to those in the literature. The feasibility study will carefully evaluate alternative methods of combining the water reactive material and water, evaluating scenarios both with water limiting and the water reactive material limiting, and exploring whether and how results from these approaches can be reconciled. The suitability of a range of gas measuring techniques will be evaluated. The utility of procedures such as sequential or step-wise mixing of aliquots for characterizing reactivity or for establishing whether there is any initial absorption of evolved gas by solvents or components within the system will be evaluated and the gross impact of increasing the temperature will be assessed. Provisions for management of safety, such as the use of blocks with cylindrical recesses to contain the reaction vessel, and likely pressures for venting will be evaluated. At the end of Phase I, a single, preferred approach will be identified.

Work in Phase II will focus on testing a range of known water reactive materials with the preferred method selected in Phase I. The objective will be to establish that the method works effectively, is accurate and reproducible and to allow for refinement of the test method.

Work in Phase III will focus on establishing the statistical validity of the method, using a small set of test materials in repetitive testing to establish:

- Intra-test variability
- Inter-test variability
- Typical test precision
- Accuracy of method (detection of expected amounts of gas)
- Results for a validation test material that can be used by test labs to qualify their test methods

5. The test plan includes (a) an extensive review of general considerations and thoughts (developed in advance of actual experimentation) intended to guide experimental work, and (b) all defined stages and deliverables, but sufficient flexibility to allow exploration of options and for the work to be guided by experimental findings as they become available. It is the intent of the HM-14 principle investigator and his team to provide a significant level of transparency and to invite participation and input by all concerned parties. The plan was influenced by, and will build upon, prior work at INERIS in France and BAM in Germany both of which have participated and will continue to participate in the effort.

6. Upon completion of this work it is anticipated that an improved test method will be available for consideration by the TDG and GHS Sub-Committees. The test method will include diagrams along with recommended equipment and materials sufficient to let a typical testing lab reproduce the results from this effort. Additionally experimental results reporting, including statistically valid estimates of accuracy and precision for compounds evaluated in Phase III will be presented along with a method validation protocol that can be used by test labs to establish their competence in conducting this test.

7. Depending on the progress made additional information may be provided to members of the Sub-Committee in the form of an information paper.