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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-first session
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Item 10 (b) of the provisional agenda
Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: criteria for water-reactivity

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals
Twenty-third session
Geneva, 4–7 July 2012
Item 2 (a) of the provisional agenda
Updating of the Globally Harmonized System of Classification and Labelling of Chemicals: physical hazards

Test N.5

Transmitted by the expert from France[1]

Background

1. Following the discussions at the last meeting of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG Sub-Committee) and the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS Sub-Committee) and the invitation expressed to produce more material associated to this test, the expert from France would like to submit results available in France to assess the problems related to the N.5 test. Those have been published in the article reproduced in informal document INF.4 and are summarized hereafter.

I. Summary of the study

2. A systematic study of the influence of important parameters relevant to the UN N.5 test protocol has been performed. The test results show that some of these parameters may greatly influence final data obtained from current procedure in vigour (Manual of Tests and Criteria, fifth revised edition).

[1] In accordance with the programme of work of the Sub-Committee for 2011-2012 approved by the Committee at its fifth session (refer to ST/SG/AC.10/C.3/76, para. 116 and ST/SG/AC.10/38, para. 16).

(a) Sample mass

The sample mass must be sufficient to obtain a significant and easily measurable gas release, but not too great as to exceed the capacity of the gas volume measurement system. The tests show that a mass of 10 g is appropriate in most cases.

(b) Temperature

Given the importance of this factor on the results, if there is a possibility of self-heating when the material is transported in bulk, it seems pertinent to perform another test at a higher temperature. This should also be applied if the product is transported in a hot environment. In any case, reporting results as a function of ambient temperature or using efficient temperature regulation would help achieving more consistent results between laboratories. This remark is all the more important as division 4.3 classification shall prevail against 4.2 in case of both criteria apply.

(c) Free volume of the glassware

The free volume of the glassware is likely to influence the measured gas flow due to thermal expansion of gases when the ambient temperature varies throughout the test. Indeed, in the worst cases, the thermal expansion of gases alone creates an uncertainty which can exceed the classification threshold criterion. Free volume of the glassware should then be reduced as much as possible. Moreover, the conical flask volume influences, as well as the powder/liquid mass ratio, the quality of the powder wetting. Thus, defining the overall volume of the test apparatus would help in limiting the scattering of results between laboratories.

(d) Wetting efficiency of sample

There is a strong link between the quality of wetting and the measured flow release rate. The two substances tested showed very different behaviours according to their actual wettability. Indeed, intimate contact between water and aluminum was not very easy to obtain, while magnesium and water mix very well in all cases. As the best compromise, we suggest to use a 100 ml conical flask in combination with a 25 ml dropping funnel. Moreover, the most efficient sample/liquid mass ratios observed proved to be 1/2 and 1/4.

(e) Nature of the water liquid phase (sea, distilled, …) and pH

Given the influence of composition and pH of the liquid, it seems important to specify the pH of the distilled water used during the test. Moreover, in the case of maritime transport, it appears also pertinent to perform an additional test using seawater. Indeed, seawater can either stop the reaction or magnify it depending on the sample.

The results obtained with an acid and a base raise the question of the influence of the thickness of the oxide layer or the coating layer on the surface of the sample tested. If such a layer is likely to be affected by the conditions of transport or of storage, an additional test with an acid or a base would be suitable, if an acidic or caustic environment may affect accident scenarios.

3. More details about all these results can be found in:

A. JANES – G. MARLAIR - D. CARSON – J. CHAINEAUX, Towards the improvement of UN N.5 test method relevant for the characterization of substances which in contact with water emit Flammable Gases, Journal of Loss Prevention in the Process industries, Volume 25, Issue 3, May 2012, Pages 524-534.

4. From this work, the following principles can be considered to move forward and to propose a more robust test protocol.

II. Proposal

5. The experts from France suggest the following modification principles in the subsequent UN N.5 test protocol.

(a) It appears important to define some experimental conditions which are not specified in the standardized protocol, e.g.:

(i) The use of a 100 ml conical flask and a 25 ml dropping funnel;

(ii) The use of a sample mass of 10 g and a sample/liquid mass ratio of 1/2 or ¼;

(b) It is recommended that other factors not mentioned in the current protocol be taken formally into account, depending on the conditions of storage or transport (further work needed):

(i) Bulk transport, substances capable of self-heating in contact with water would be tested with a thermostatic bath at 40 °C;

(ii) Maritime shipment: test with seawater;

(iii) In case of possible destruction of oxidation layer or coating layer: test with an acidic or a basic solution;

(c) Finally, the work group should encourage complementary work on the issue of water solubility of gases.