

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 Globally Harmonized System of Classification and Labelling of Chemicals

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UPDATING OF THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

Physical hazards

Report of the 2nd meeting of the informal working group on chemically unstable gases

Transmitted by the expert from Germany on behalf of the informal working group

Introduction

1. During its twelfth session the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals agreed on the terms of reference for an informal working group that shall address the classification of chemically unstable gases.
2. The second meeting of the informal working group took place on November 19, 2007. Experts from CGA (Compressed Gas Association), EIGA (European Industrial Gases Association), JIMGA (Japan Industrial and Medical Gases Association) and Germany (BAM) attended the meeting.

Report of the Meeting

3. Two alternative test methods were discussed during the meeting. These test methods are:
 - Accelerating Rate Calorimetry
 - Test method based on ISO 10156 and ASTM E 918

Accelerating Rate Calorimetry (ARC)

4. Prior to the meeting CGA had sent information about ARC (Accelerating Rate Calorimetry) which might be an alternative test method for determining chemical instability of gases. This method is based on recording the pressure and temperature of a vessel which is slowly heated, thereby deducing information about the reaction rate.
5. ARC was proposed as an alternative because it would meet CGA's concerns about the reproducibility of the ignition source and the insufficient division into degrees of hazards of chemically unstable gases with regard to the test method based on ISO 10156 and ASTM E 918.
6. The participants of the working group have no experience whether ARC is applicable to gases as well. CGA provided a list of publications relating to ARC which also includes a reference on measurements using ethylene oxide.

Test method based on ISO 10156 and ASTM E 918

7. A draft of a possible flow chart for classifying gases according to the test method based on ISO 10156 and ASTM E 918 was presented by BAM. Depending on the outcome of the tests between one test and a maximum of nine tests (3x3 tests) is necessary for the complete procedure. The performance of a complete test procedure consisting of nine tests is possible within one day.
8. The autoclave used for the proposed test method is the one described in ASTM E 918. The reason for proposing this autoclave is that it should be globally available already.
9. BAM has carried out a sequence of tests in order to determine the reproducibility of the energy provided by the ignition source (exploding wire). It turned out that sufficient reproducibility is given. Furthermore, the tests showed that the ignition energy in the proposed test method was low enough in order not to increase the pressure above the pressure rise criterion of 10 % without that actually a self-sustaining decomposition is initiated.
10. Division into degrees of hazard would be achieved by distinguishing between
 - gases that are chemically unstable at ambient conditions,
 - gases that in themselves are normally stable but that can become unstable at elevated temperatures and pressures and
 - a further division might be gases that are unstable in the liquid phase only.

Further proceeding

11. The two alternative test methods also differ with regard to the underlying principle for distinguishing between hazard categories. ARC is not based on intrinsic properties under different conditions but the results are based on the ease of ignition. The test method based on ISO 10156 and ASTM E 918 determines whether a gas is unstable at the respective conditions, e.g. ambient or transport conditions.
12. The participants agreed that a test procedure that just differentiates between "chemically stable" and "chemically unstable" is not useful and does not provide enough information. A suitable test method should be able to discriminate between acetylene and nitrous oxide and possible distinctions could be "chemically unstable at ambient conditions", "chemically unstable at elevated conditions" and "chemically unstable but difficult to ignite".
13. It was agreed that nitrous oxide is a special case which might be difficult to classify appropriately according to the hazard it presents (considering the difficulty with which it is ignited). It therefore might be necessary to have a special note for nitrous oxide if a test method shows for other gases to result in an appropriate division into categories.
14. The participants agreed that actual test results according to both test methods would have to be available in order to make a reasonable decision which test method is the most suitable for the classification of chemically unstable gases.
15. The following gases were selected as bench mark for these tests:
 - Acetylene (ethyne)
 - Ethylene (ethene)
 - Ethylene oxide
 - Butadiene-1,2
 - Butadiene-1,3
 - Nitrous oxide

16. BAM will carry out the tests with these gases according to the proposed test method based on ISO 10156 and ASTM E 918 until end of March, 2008. Elevated conditions were fixed to be 65 °C and the corresponding vapor pressure.

17. CGA will find out whether they have the possibility to carry out tests using ARC. In case that is possible they will have the same gases tested by ARC and provide a date until when that is possible.

18. In addition to the test method, the terms of references require that criteria for the classification of gas mixtures have to be worked out. These criteria should indicate below which concentrations of a chemically unstable gas in a gas mixture testing is considered to be not necessary and a mixture does not have to be classified as unstable. The participants are asked to consider this subject for the next meeting.

19. The terms of references for this informal working group require that not only a suitable test method is developed but that also a proposal how the issue of chemical instability of gases could be included into the GHS based on the test method and that a proposal for suitable hazard communication elements for chemically unstable gases is developed. Therefore the participants are asked to consider a possible classification scheme and wording as well as possible solutions for positioning such a procedure in the GHS until the next meeting.

Next meeting

20. A further meeting will be necessary after the test results using the "bench mark" gases are available. Therefore it was agreed to have the next meeting in connection with the next meetings of the UN-Sub-Committees TDG and GHS in Geneva.

21. Proposed date: July 7 (p.m.) and July 8 (a.m.), 2008
