

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

21 June 2010

Sub-Committee of Experts on the
Transport of Dangerous Goods

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

Thirty-seventh session

Geneva, 21–30 June 2010

Item 10 of the provisional agenda:

**Issues relating to the Globally Harmonized System of
Classification and Labelling of Chemicals (GHS)**

Nineteenth session

Geneva, 30 June–2 July 2010

Item 2 (a) of the provisional agenda

Physical hazards

Classification of chemically unstable gases and gas mixtures

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

Background

1. During the sessions in July 2009 an informal document about the status of developing criteria and a test method for the classification of chemically unstable gases was submitted to the Sub-Committee TDG and the Sub-Committee GHS. Both noted the progress made with satisfaction and the Sub-Committee TDG agreed that the test method should be included into the UN Manual of Test and Criteria.

Amendments to the GHS

2. The Annex to this document contains the proposal for including the classification of chemically unstable gases into the GHS, chapter 2.2 as presented in principal during previous sessions. Proposed amendments to chapter 2.2 are shown **in red and underlined**.

3. According to the proposal, no new hazard class is added to the GHS but chemically unstable gases are incorporated into the hazard class of flammable gases (because most chemically unstable gases are flammable gases as well). The proposed hazard statements for both categories of chemically unstable gases are the same because it is most important to raise awareness for the chemical instability of the gas (details should be given in the SDS). There are also other categories in the GHS for which the hazard statements are the same (e.g. for three of the categories of gases under pressure, for self-reactives and organic peroxides, type C, D, E and F, for substances which in contact with water release flammable gases, category 2 and 3 and for oxidizing liquids and solids, category 2 and 3). A symbol and signal word are not assigned because they are already assigned based on the classification as flammable gas.

4. Sectors that implement the GHS, such as the transport of dangerous goods, may choose not to implement these GHS-categories, by using the building block approach.

* In accordance with ST/SG/AC.10/C.3/70, para. 85 and ST/SG/AC.10/C.4/34, para. 17 to 19.

Test method for determining chemical instability of gases

5. Document UN/SCEGHS/19/INF.26 and UN/SCETDG/37/INF.63, respectively contains in its Annex a proposal for a method for determining whether a gas is chemically unstable. This method is supposed to be included into the UN Manual of Tests and Criteria and is referred to in the UN-GHS, chapter 2.2.
6. However, since it will take longer to include the test method into the UN Manual of Tests and Criteria, the respective reference in the UN-GHS will be to UN/SCEGHS/19/INF.26 (as shown in clause 2.2.4.3 in the Annex below) until the UN Manual of Tests and Criteria is amended accordingly.
7. The expert from Germany (together with other interested experts) would prepare a working document proposing the respective amendment of the UN Manual of Tests and Criteria once the proposal as outlined below is accepted by the Sub-Committees.

Concentration limits

8. The draft of the test method contains also a proposal for a generic concentration limit and for specific concentration limits which are supposed to limit the amount of testing. Gas mixtures containing a chemically unstable gas below the respective concentration limits are considered as chemically stable and do not have to be tested.
9. The specific concentration limits for acetylene given in the method for determining chemical instability of gases and gas mixtures are mainly based on data from the following literature taking into account a safety margin:
 - Holtappels, K.; Schönbucher, A.: Inert gas and fuel gas influence on the pressure limits of stability of acetylene; Chem. Eng. Tech. 26 (2003) No. 11, p. 1142 – 1146.
 - Schendler, T.; Schulze, H.-P.: Stabilitätsgrenzdrücke von Acetylen/Gas-Gemischen; Chem.-Ing.-Tech. 62 (1990) Nr.1, S. 41-43.
10. Further specific concentration limits may be added if appropriate data are available. It is the intention to add specific concentration limits for acetylene in nitrogen at a pressure of 200 bar and specific concentration limits for ethylene oxide gas mixtures until the next meeting in December 2010.

Proposal

11. Both Sub-Committees are asked to consider the proposed amendments to the GHS as shown in the Annex to this document and to the method for determining chemical instability of gases and gas mixtures as described in UN/SCEGHS/19/INF.26 and UN/SCETDG/37/INF.63, respectively. Based on the comments received working documents will be prepared for the December meetings.

Annex

Proposed amendments to the GHS

“Chapter 2.2

Flammable gases

2.2.1 Definitions

2.2.1.1 A flammable gas is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa.

2.2.1.2 A chemically unstable gas is a gas that is able to react explosively even in the absence of air or oxygen

2.2.2 Classification criteria

2.2.2.1 A flammable gas is classified in one of the two categories for this class according to the following table:

Table 2.2.1: Criteria for flammable gases

Category	Criteria
1	Gases, which at 20 °C and a standard pressure of 101.3 kPa: (a) are ignitable when in a mixture of 13% or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.
2	Gases, other than those of Category 1, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air.

NOTE 1: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.

NOTE 2: Aerosols should not be classified as flammable gases. See Chapter 2.3.

2.2.2.2 A flammable gas that is also chemically unstable is additionally classified in one of the two categories for chemically unstable gases according to the following table:

Table 2.2.2: Criteria for chemically unstable gasses

<u>Additional category of chemically unstable gas</u>	<u>Criteria</u>
<u>1</u>	<u>Gases which are chemically unstable at ambient temperature and pressure</u>
<u>2</u>	<u>Gases which are chemically unstable at elevated temperature and/or pressure</u>

2.2.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2.2.3: Label elements for flammable gases (including chemically unstable gases)

	<u>Flammable gas</u>		<u>Chemically unstable gas</u>	
	<u>Category 1</u>	<u>Category 2</u>	<u>Additional category 1</u>	<u>Additional category 2</u>
Symbol	Flame	<i>No symbol</i>	<i>No symbol</i>	<i>No symbol</i>
Signal word	Danger	Warning	<i>No signal word</i>	<i>No signal word</i>
Hazard statement	Extremely flammable gas	Flammable gas	<u>May react explosively even in the absence of air</u>	<u>May react explosively even in the absence of air</u>

2.2.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

2.2.4.1 Decision logic for the classification of flammable gases

To classify a flammable gas, data on its flammability are required. The classification is according to decision logic 2.2 (a).

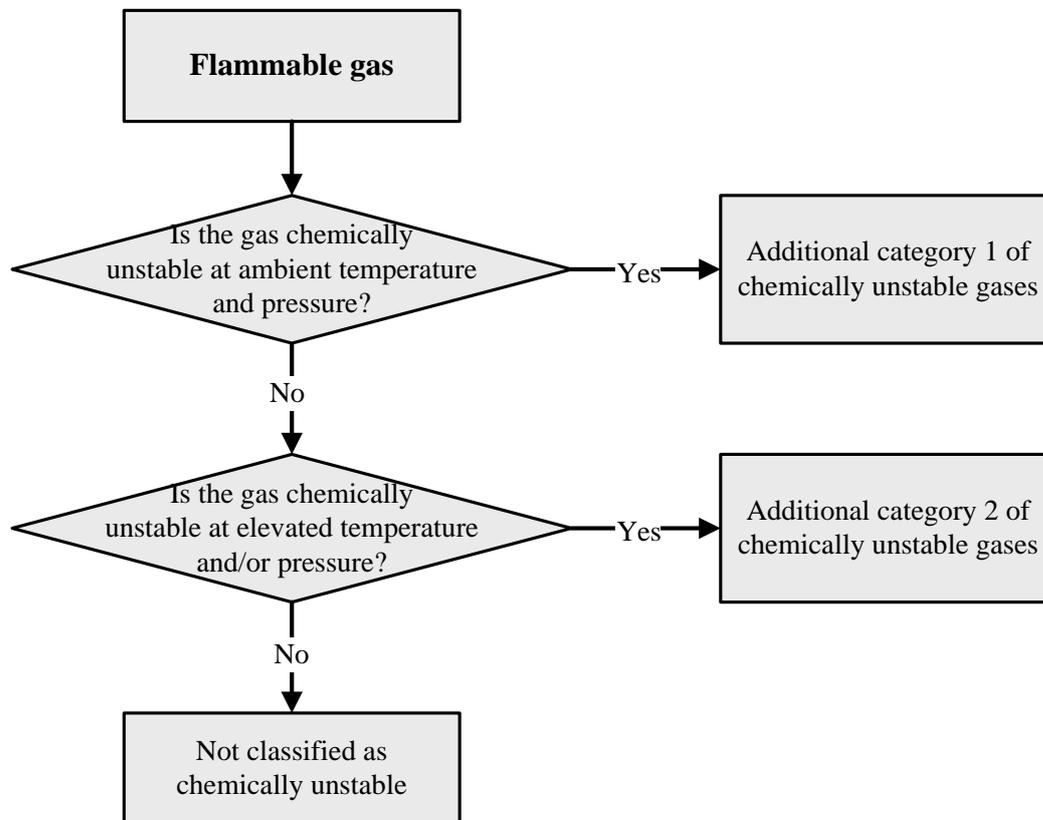
Decision logic 2.2 (a) for flammable gases

<Unchanged decision logic as currently in section 2.2.4.1>

2.2.4.2 Decision logic for the classification of chemically unstable gases

To classify a chemically unstable gas, data on its chemical instability are required. The classification is according to decision logic 2.2 (b).

Decision logic 2.2 (b) for chemically unstable gases



2.2.4.3 Guidance

Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets”). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.

Chemical instability should be determined in accordance with the method described in UN/SCEGHS/19/INF.26. If the calculations in accordance with ISO 10156 show that a gas mixture is not flammable it is not necessary to carry out the tests for determining chemical instability for classification purposes.

2.2.5 Example: Classification of a flammable gas mixture by calculation according to ISO 10156:1996

<Unchanged text as currently in section 2.2.5>