UN/SCETDG/35/INF.47
UN/SCEGHS/17/INF.10

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

Thirty-fifth session
Geneva, 22 - 26 June 2009
Item 10 of the provisional agenda

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

Seventeenth session
Geneva, 29 June - 1 July 2009
Item 2 (a) of the provisional agenda

Physical hazards

Work 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 the last meeting the informal working group on chemically unstable gases presented an informal document (UN/SCETDG/34/INF.45 and UN/SCEGHS/16/INF.19) reporting about the progress of its work. This document contains further refined drafts and questions to the Sub-Committee.

Inclusion of chemically unstable gases in the GHS

2. In the Annex to the above mentioned document a draft proposal for the inclusion of chemically unstable gases into the GHS was given. **Annex 1** to this document contains a refined draft proposal of amendments to chapter 2.2 of the GHS. The Sub-Committee is invited to consider this draft so that based on the comments received the informal working group could draft an according working document.

3. As presented during the last meeting, the working group agreed not to propose to create a new hazard class but to include additional categories for chemically unstable gases in the hazard class of flammable gases (because most chemically unstable gases are flammable gases as well). Sectors that implement the GHS, such as the transport of dangerous goods, could choose not to implement these GHS categories, by making use of the building block approach.

Test method for determining whether a gas is chemically unstable

4. **Annex 2** to this document contains the draft of the test method for determining whether a gas is chemically unstable or not. The Sub-Committee is invited to consider this draft so that based on the comments received the informal working group could draft an according working document.

5. During the last meeting the group did not make a proposal where to incorporate the agreed test method. Two options were under discussion in the informal working group:

(a) Inclusion into the UN Manual of Tests and Criteria;

(b) Amendment of ISO 10156 (the test method is based on the methods given in this standard and chapter 2.2 of the GHS already refers to this standard).

6. The informal working group seeks advice from the Sub-Committee with regard to the question of where to include the test method. The informal working group would prefer to include the test method into the UN Manual of Tests and Criteria. Furthermore, specific concentration limits shall be added into ISO 10156 (into the tables with data for specific gases that are already part of ISO 10156) in the future.

7. However, since it might take longer to actually include the test method in either or since it might take longer to actually have a revised version of either available, the informal working group would like to propose to refer to a working document (produced in accordance with paragraph 4 above) in the meantime and until a permanent place for inclusion of the test method is available. This would be done as shown in paragraph 2.2.4.3 of Annex 1 to this document.

Concentration limits

8. The draft of the test method contains also a proposal for a generic concentration limit which is supposed to limit the amount of testing. Gas mixtures containing a chemically unstable gas below this concentration are considered as chemically stable and do not have to be tested.

9. Furthermore, this generic concentration limit is supposed to be amended by specific concentration limits for certain gases in order to further limit the necessary amount of testing in the future.

Open issues

10. In the current proposal, testing of gases in the liquid phase is not considered because this is an issue that will need more consideration (and might not be solved during this biennium).

11. The informal working group would be grateful for any comments and suggestions on the drafts and questions. It especially would like to have receive:

(a) Guidance on where to include the test method;

(b) Agreement on the proposed interim solution according to paragraph 7;

(c) Comments on the draft proposal for inclusion into the GHS (Annex 1);

(d) Comments on the draft proposal for the test method (Annex 2);

12. The informal working group would then try to produce working documents as proposed above taking into consideration the comments received.

Annex 1

Draft for chapter 2.2

(proposed amendments are underlined and in red)

"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 Some flammable gases in addition may be *chemically unstable gases* and may 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 chemically unstable flammable gas 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

Additional category of chemically unstable gas	Criteria
1	Gases which are chemically unstable at ambient temperature and pressure
2	Gases which are chemically unstable at 65 °C and the corresponding pressure

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)

	Flammable gas		Chemically unstable gas	
	Category 1	**Category 2**	**Additional category 1**	**Additional category 2**
Symbol	Flame	*No symbol*	*No symbol*	*No symbol*
Signal word	Danger	Warning	*No signal word*	*No signal word*
Hazard statement	Extremely flammable gas	Flammable gas	May decompose explosively at ambient temperature and pressure	May decompose explosively at elevated temperature and/or pressure

2.2.4 Decision logic and guidance

The decision logics 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).

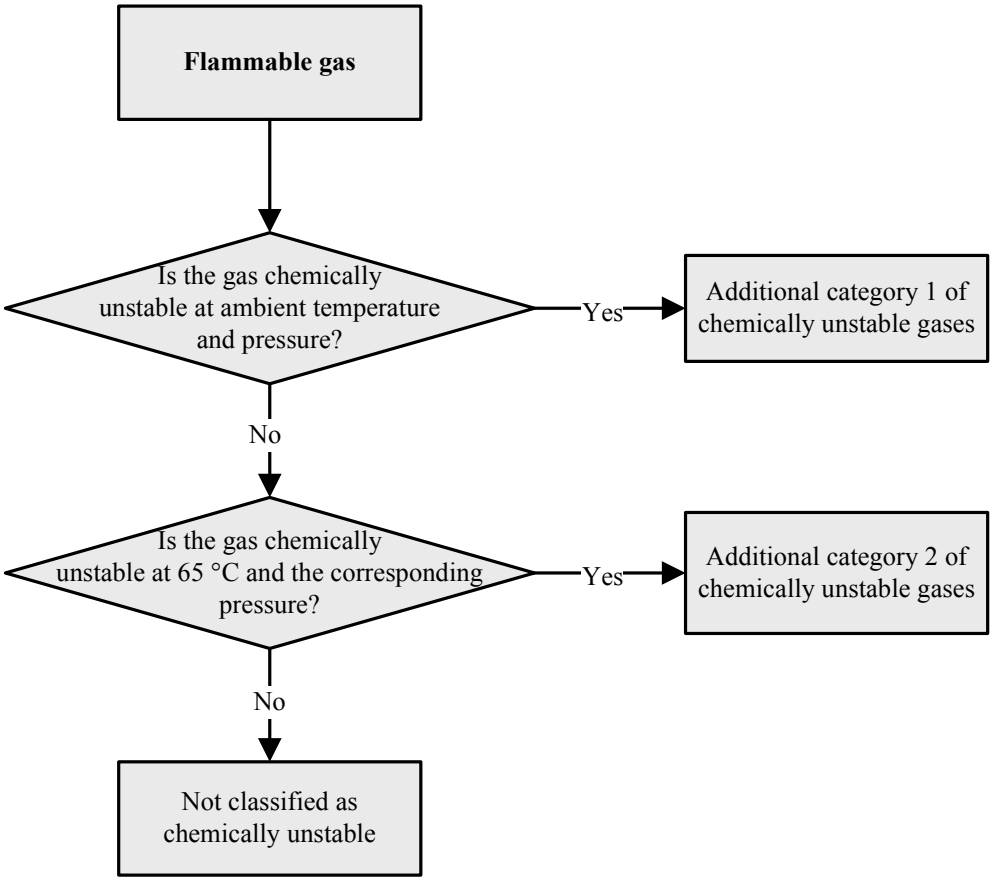
Decision logic 2.2 (a) for flammable gases

<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 by tests in accordance with the test method described in ST/SG/AC.10/C.4/2009/xx.

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>"

Annex 2

with draft of the test method

1 Scope

1.1 This test method covers the determination of chemical instability of gases or gas mixtures by ignition tests in a closed vessel at ambient and elevated temperature and pressure because the ability of dangerous decomposition depends strongly on pressure, temperature and in case of gas mixtures on the concentration of the chemically unstable component. The possibility of decomposition reactions shall be evaluated at conditions which are relevant for transport and handling and use. Therefore two types of tests shall be performed:

a) at ambient temperature and pressure,

b) at 65 °C and the corresponding pressure.

1.2 The test method does not cover gas decomposition under process conditions in chemical plants and possible dangerous reactions between different gases in mixtures.

1.3 Gas mixtures containing a chemically unstable gas in concentrations of 3 mole% or less are considered as chemically stable and therefore do not have to be tested.

1.4 Notwithstanding the above generic concentration limit, for gases listed in the following table the respective specific concentration limits may be applied:

<Comment: Table with specific concentration can be added>

> *Note:* Mixtures of gases, where the components can react dangerously with each other, e.g. flammable and oxidizing gases, are not regarded as unstable in the sense of this test method.

2 Definitions

2.1 For the purposes of this test method the following definitions apply:

Chemical instability:

Ability of a gas or gas mixture to react dangerously even in the absence of any reaction partner by decomposing and thereby causing a temperature and/or pressure increase.

Flame propagation:

In the context of this test method, a decomposition reaction that produces a pressure rise which amounts to more than 20 % of the initial absolute pressure.

Test substance:

Gas or a mixture of gases to be evaluated by this test method.

3. Classification procedures for chemically unstable gases

3.1 Chemically unstable gases or gas mixtures containing unstable components shall be classified as “chemically unstable at ambient temperature and pressure” or “chemically unstable at elevated temperature and/or pressure” according to the test result as follows:

(a) The test substance is classified as “chemically unstable at ambient temperature and pressure” if the test shows flame propagation at 25 °C and 101 kPa.

(b) The test substance is classified as “chemically unstable at elevated temperature and/or pressure” if the test shows flame propagation of the gaseous phase at 65 °C and the corresponding pressure but no flame propagation at 25 °C and 101 kPa.

3.2 The test substance is not classified according to this test method (meaning it is chemically stable) if the mixture shows no flame propagation in the tests.

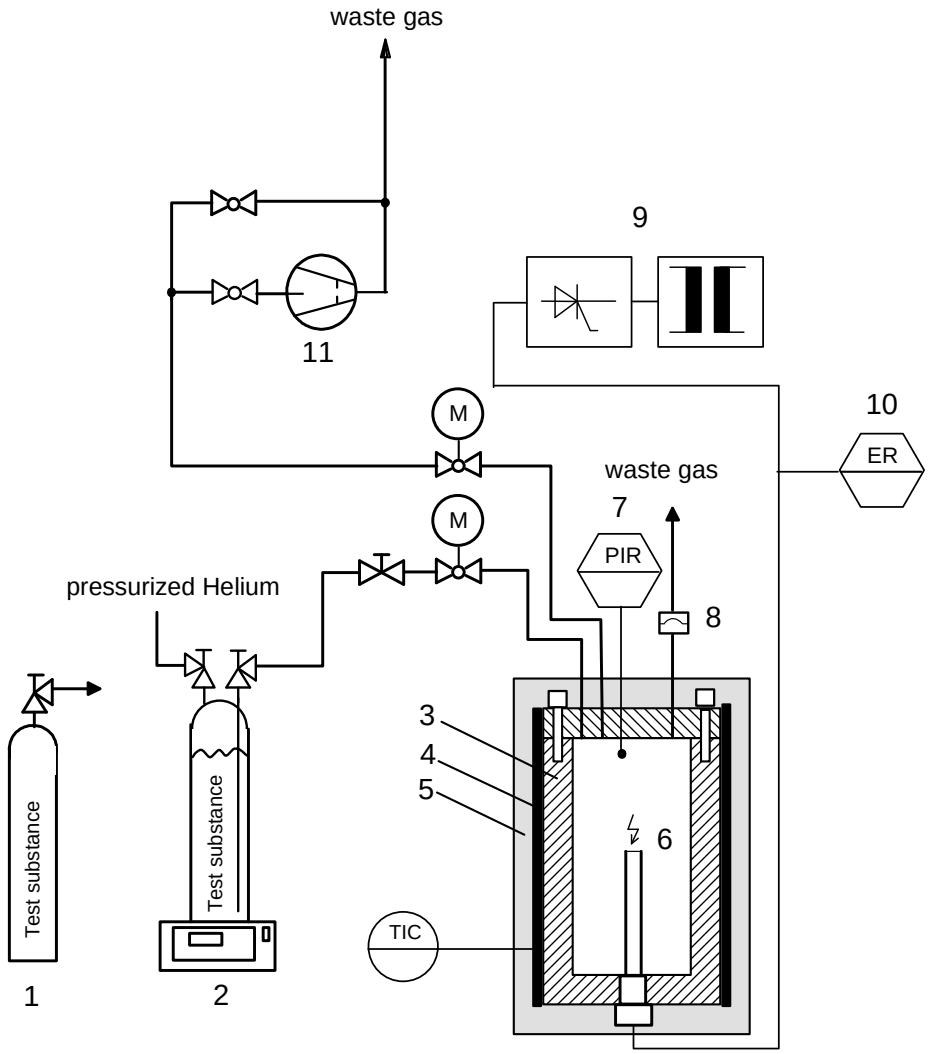
4 Test method

4.1 Abstract

4.1.1 The test substance is charged into a pressure resistant stainless steel vessel at controlled temperature and pressure. The vessel is equipped with a rupture disk. Ignition of the mixture is attempted with an exploding wire igniter. Whether flame propagation has occurred is deduced from the pressure rise produced. If two phases are existent at transport conditions, ignition shall be performed in both, the gaseous and the liquid phase.

4.2 Apparatus and material

4.2.1 The test apparatus is shown in Fig. 1.



(1) Test substance supply (gaseous)
(2) Test substance supply (liquefied)
(3) Pressure resistant test vessel
(4) Regulated electric heater
(5) Thermal insulation
(6) Exploding wire igniter
(7) Pressure sensor, pressure indication and registration
(8) Rupture disk
(9) Electronic ignition device
(10) Ignition energy registration
(11) Vacuum pump

Figure 1: Schematic diagram of test apparatus

4.2.2 The main parts of testing device are:

(a) Heatable ignition vessel made of stainless steel,
(b) Ignition source,
(c) Measuring and recording system to record the pressure inside the ignition vessel,
(d) Gas supply,
(e) Venting system with rupture disk,
(f) Additional piping, fitted with remote-controlled valves and cocks.

Heated ignition vessel

The ignition vessel is a cylindrical stainless steel vessel with an inner volume of about 1 dm^3 and an inner diameter of 80 mm. An exploding wire ignition source is screwed into the bottom of the vessel. The heating jacket is connected to a temperature control unit that heats the outer vessel wall with an accuracy of ± 2 K. The ignition vessel is insulated by temperature resistant insulation material to avoid heat loss and temperature gradients. The vessel shall be pressure resistant up to 50 MPa (500 bar).

Ignition source

The ignition source is an exploding (fusing) wire igniter similar to that described in ASTM E 918 and EN 1839. The igniter consists of two insulated electrodes at 3 mm to 6 mm distance, holding a nickeline wire of 0.12 mm diameter on its ends. The ignition energy is provided by a 1.5 kVA/230 (115) V insulating transformer, which is switched for a short time period to this igniter. The wire melts and then an electrical arc burns between the electrodes for a period extending in maximum to half a period of the supply voltage (10 (8.3) ms). An electronic control unit allows switching different time periods of the mains voltage half wave to the igniter. The corresponding energy delivered shall be in the range of 15 J ± 3 J. The energy can be measured by recording the current and voltage during ignition. A holder for the fuse wire can be made by modifying a 14-mm car spark plug which has a continuous metal contact to the center terminal. By using a steel rod of 3 mm diameter the electrodes of the spark plug can be extended so that the fusing wire can be positioned 20 mm above the bottom of test vessel.

Pressure and temperature recording equipment

The pressure inside the ignition vessel shall be measured using a calibrated piezoresistive pressure transducer. The measuring range shall be 20 times higher than the initial pressure. The sensitivity shall be at least 0.1 % of full scale and the accuracy shall be better than 0.5 % of full scale.
The temperature of the ignition vessel shall be measured and controlled by using a 3 mm thermocouple type "K" (NiCr/NiAl) mounted inside the wall of the autoclave 50 mm below the top.
The digitized pressure signal after ignition shall be recorded by a computer. The starting pressure (p_0) and the highest value of the pressure/time curve (p_{ex}) are calculated from the raw data.

Gas supply

Two different types of gas supply are necessary, one for gaseous test substances and one for liquefied substances. The latter one shall be located on a scale for metering the test substance.

Pressure relief device

The pressure relief device is supposed to protect the test vessel. It is connected by a waste gas pipe. The free diameter of the rupture disk is recommended to be at least 10 mm, the inner diameter of the pipe at least 15 mm. The set pressure of the rupture disk shall amount to 25 MPa (250 bar).

Additional piping, valves and cocks

The piping, valves and cocks which are fitted directly to the test vessel, shall be pressure resistant up to 50 MPa (500 bar). The test equipment shall be operated by remotely operated cocks.

4.3 Test procedure

The tests shall be executed in the following chronological sequence:

4.3.1 Test at ambient temperature and pressure

4.3.1.1 For the tests at 25 °C and 101 kPa (1.01 bar) the exploding wire igniter shall be arranged in the middle of the test vessel. The test vessel and the manifold are evacuated. The test substance is filled by using the remotely operated valves until the final pressure is reached. After closing the valves the igniter is fired. The ignition energy should be limited to about 15 J to avoid an over-initiation in the test vessel at this relatively low pressure. Criterion of a reaction is a pressure rise of more than 20 % after ignition ($f = p_{ex}/p_0 > 1.20$). If no flame propagation is observed two further re-tests shall be carried out.

4.3.1.2 If the test substance fulfils the criterion it is to be classified as “chemically unstable at ambient temperature and pressure”. No further tests are required.

4.3.2 Test at elevated temperature and pressure

4.3.2.1 If in the tests according to 4.3.1 no flame propagation was observed, further tests with gaseous substance at 65 °C and the corresponding pressure shall be performed. Therefore it can be necessary to pressurize the cylinder with the liquefied test substance by helium or to use an air driven compressor. The procedure is the same as in section 4.3.1 but care should be taken with potentially unstable gases under pressure. The ignition energy shall be about 15 J. If no flame propagation is observed two further re-tests shall be carried out.

4.3.2.2 If the test substance fulfils the criterion it is to be classified as “chemically unstable at elevated temperature and/or pressure”. No further tests are required.

5 Safety precautions

5.1 Adequate shielding must be provided to prevent injury in the event of equipment rupture. The apparatus is set up so that the operator is separated by a blast proof barrier or better by a separate room while the vessel contains a charge of test substance. Activation of the ignition source should be possible only from a position shielded from the test vessel.

5.2 The test vessel shall be fitted with a rupture disk vented outside any enclosed area to prevent forming an explosive mixture in a large space.

5.3 The gas cylinder with test substance shall be equipped with a reflux valve and shall be separated from the experimental set-up before the igniter is fired to avoid backfiring into the cylinder. The cylinder valve has to be closed immediately after finishing the filling.

5.4 Some chemical unstable gases can explode with high severity. Therefore it is strongly recommended to start with the experiments at atmospheric pressure.

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