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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

Fiftieth session

Geneva, 28 November-6 December 2016 Item 7 (c) of the provisional agenda

Issues relating to the Globally Harmonized System of Classification criteria and related hazard communication: Classification and Labelling of Chemicals:

classification criteria for flammable gases

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

Thirty-second session

Geneva, 6-9 December 2016 Item 2 (b) of the provisional agenda

work of the TDG Sub-Committee on matters of interest to

the GHS Sub-Committee

Proposal for modification of the classification criteria and hazard communication for flammable gases

Transmitted by the experts from Belgium and Japan on behalf of the informal working group on classification criteria for flammable gases¹

During the December 2015 sessions of the Sub-Committee of Experts on the Transport of Dangerous Goods and the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals, the joint TDG-GHS informal working group on classification criteria for flammable gases presented the results of its work consisting of new classification criteria to be used for dividing flammable gases. As noted in the report², there was full support for the criteria in option 3 in informal documents INF.15 (TDG forty-eighth session) - INF.4 (GHS thirtieth session) i.e., allowing for a change in categorization of current category 1 into Category 1A and Category 1B, with Category 1B addressing gases with a lower flammability limit greater than 6% or a fundamental burning velocity of less than 10 cm/s. It was noted that the new category 1B would allow the classification of gases and gas mixtures with a lower burning velocity developed by the refrigeration and foam plastics industries following the phasing down of high global warming potential substances. It was also noted that the criteria in option 3 would not entail any change in classification for transport purposes.

¹ In accordance with the programme of work of the Sub-Committee for 2015–2016 approved by the Committee at its seventh session (see ST/SG/AC.10/C.3/92, paragraph 95 and ST/SG/AC.10/42,

Refer to the report of the GHS Sub-Committee on its thirtieth session (ST/SG/AC.10/C.4/60, paras. 4 to 8).

- 2. During the June/July 2016 sessions of the TDG Sub-Committee and GHS Sub-Belgium and Japan brought forward working (ST/SG/AC.10/C.4/2016/4 - ST/SG/AC.10/C.3/2016/17) and informal documents INF.9 (thirty-first session) and INF.31 (forty-ninth session). The working document was discussed during the joint meeting and it was decided that this document should be used by the GHS Sub-Committee for further discussion on the communication elements. During the GHS Sub-committee session, different opinions were emitted and a group of experts met during a break to resolve the remaining issues. A consensus was achieved and reported in an informal document INF.28 (thirty-first session). The following was accepted by the GHS Sub-Committee.
 - (a) The proposal in ST/SG/AC.10/C.4/2016/4, as amended by informal document INF.23, with the additional modification needed to address the questions raised during the discussion;
 - (b) Hazard communication elements for 1B flammable gases:

• Symbol: flame

· Signal word: danger

· Hazard statement: flammable gas

• Hazard statement code: H221

The experts from Belgium and Japan volunteered to prepare a revised proposal which has been circulated to all interested parties for comments and is now submitted to the December 2016 session.

- 3. This document contains the following annexes:
 - Annex 1: Proposed amendments to Chapter 2.2 of the GHS
 - Annex 2: Consequential amendments to Annex 1, Table A1.2, of the GHS
 - Annex 3: Consequential amendments to Annex 3 (Sections 1, 2 and 3) of the GHS
 - Annex 4: Consequential amendments to Annex 4, Section 9, of the GHS
- 4. The TDG and GHS sub-committees are invited to consider the proposal as contained in annexes 1 to 4 to this document.

Annex I

Proposed amendments to Chapter 2.2 of 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 $20\,^{\circ}$ C and a standard pressure of $101.3\,^{\circ}$ kPa.
- 2.2.1.2 A *pyrophoric gas* is a flammable gas that is liable to ignite spontaneously in air at a temperature of 54 °C or below.
- 2.2.1.3 A *chemically unstable gas* is a flammable 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 Category 1A, 1B or 2 according to the following table. Flammable gases that are pyrophoric and/or chemically unstable gases are always classified in Category 1A.

Table 2.2.1: Criteria for categorisation of flammable gases

Category		Criteria			
1A	Flammable gas	(a) and (b) h	which at 20 °C and a standard pressure of 101.3 kPa: re ignitable when in a mixture of 13% or less by volume in air; or ave a flammable range with air of at least 12 percentage points egardless of the lower flammability limit.		
	Pyrophoric gas	Flammable gases that ignite spontaneously in air at a temperature of 54 °C o below			
	Chemically Unstable gas	A B	Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa		
1B	Flammable gas	Gases which meet the flammability criteria for Category 1A, but which are not pyrophoric, nor chemically unstable, and which have at least either: a) A lower flammability limit of more than 6% by volume in air; or b) A fundamental burning velocity of less than 10 cm/s;			
2	Flammable gas	Gases, other than those of Category 1A or 1B, 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.
- **NOTE 3:** In the absence of data allowing classification into Category 1B, a flammable gas that meets the criteria for Category 1A is classified per default in Category 1A.
- **NOTE 4:** Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.
- **NOTE 5:** In the absence of data on its pyrophoricity, a flammable gas mixture should be classified as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

2.2.3 Hazard communication

2.2.3.1 General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 1 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.

	Category 1A	Gases categorized as 1A by meeting Pyrophoric or Unstable Gas A/B Criteria			Category 1B	Category 2
		Pyrophoric gas	Chemically unstable gas Category A	Chemically unstable gas Category B		
Symbol	Flame	Flame	Flame	Flame	Flame	No Symbol
Signal word	Danger	Danger	Danger	Danger	Danger	Warning
Hazard statement	Extremely flammable gas	Extremely flammable gas May ignite spontaneously if exposed to air	Extremely flammable gas May react explosively even in the absence of air	Extremely flammable gas May react explosively even in the absence of air at elevated pressure	Flammable gas	Flammable gas

Table 2.2.2: Label elements for flammable gases

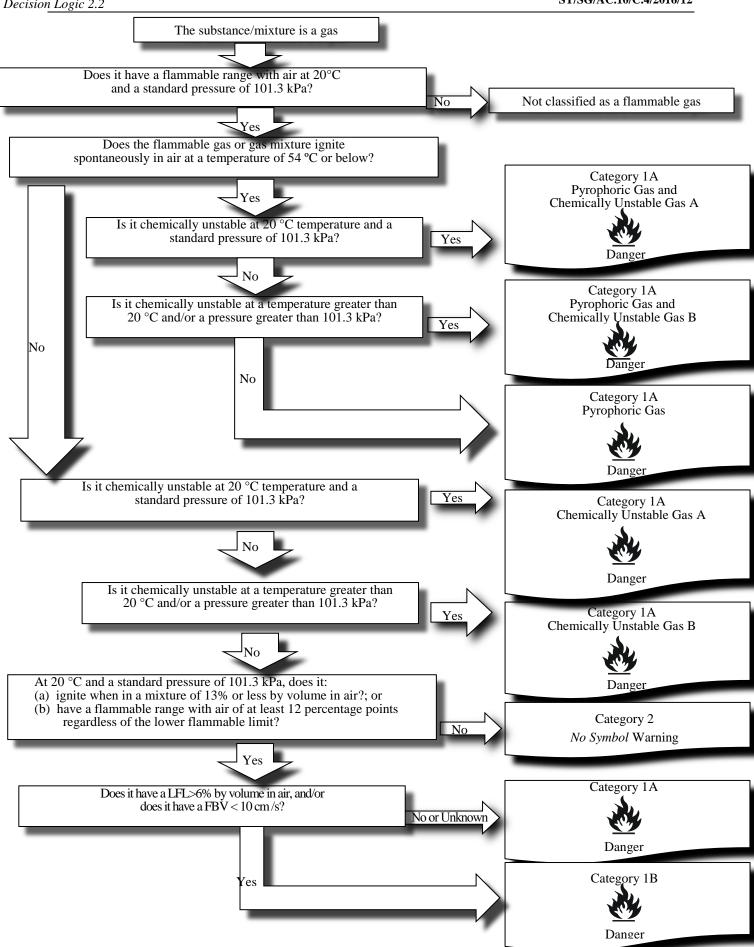
2.2.3.2 If a flammable gas or gas mixture is classified as pyrophoric and/or chemically unstable, then all relevant classification(s) should be communicated on the safety data sheet as specified in Annex 4, and the relevant hazard communication elements included on the label.

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 flammable gases

To classify a flammable gas, data on its flammability, on its ability to ignite in air and on its chemical instability are required. In case of categorisation in Category 1B, data on its lower flammability limit or its fundamental burning velocity is required. The classification is according to decision logic 2.2.



 $^{^{1}}$ In the absence of data on its pyrophoricity, a flammable gas mixture should be classified $\,$ as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

2.2.4.2 Guidance

- 2.2.4.2.1 Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010 "Gases and gas mixtures Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets" and, if using fundamental burning velocity for Category 1B, see ISO 817:2014 "Refrigerants-Designation and safety classification, Annex C: Method of test for burning velocity measurement of flammable gases"). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.
- 2.2.4.2.2 Pyrophoricity should be determined at 54°C in accordance with either IEC 60079-20-1 ed1.0 (2010-01) "Explosive atmospheres Part 20-1: Material characteristics for gas and vapour classification Test methods and data" or DIN 51794 "Determining the ignition temperature of petroleum products".
- 2.2.4.2.3 The classification procedure for pyrophoric gases need not be applied when experience in production or handling shows that the substance does not ignite spontaneously on coming into contact with air at a temperature of 54 °C or below. Flammable gas mixtures, which have not been tested for pyrophoricity and contain more than one percent pyrophoric components, should be classified as a pyrophoric gas. Expert judgement on the properties and physical hazards of pyrophoric gases and their mixtures should be used in assessing the need for classification of flammable gas mixtures containing one percent or less pyrophoric components. In this case, testing need only be considered if expert judgement indicates a need for additional data to support the classification process.
- 2.2.4.2.4 Chemical instability should be determined in accordance with the method described in Part III of the Manual of Tests and Criteria. If the calculations in accordance with ISO 10156:2010 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 10156:2010

Formula

 $\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}}$

where:

V_i% = the equivalent flammable gas content;

 T_{ci} = the maximum concentration of a flammable gas in nitrogen at which

the mixture is still not flammable in air;

i = the first gas in the mixture; n = the nth gas in the mixture;

 K_i = the equivalency factor for an inert gas versus nitrogen;

Where a gas mixture contains an inert diluent other than nitrogen, the volume of this diluent is adjusted to the equivalent volume of nitrogen using the equivalency factor for the inert gas (K_i) .

Criterion

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}} > 1$$

Gas mixture

For the purpose of this example the following is the gas mixture to be used

$$2\% (H_2) + 6\% (CH_4) + 27\% (Ar) + 65\% (He)$$

Calculation

1. Ascertain the equivalency factors (Ki) for the inert gases versus nitrogen:

$$Ki (Ar) = 0.55$$

$$Ki (He) = 0.9$$

2. Calculate the equivalent mixture with nitrogen as balance gas using the Ki figures for the inert gases:

$$2\%(H_2) + 6\%(CH_4) + [27\% \times 0.55 + 65\% \times 0.9](N_2) = 2\%(H_2) + 6\%(CH_4) + 73.35\%(N_2) = 81.35\%$$

3. Adjust the sum of the contents to 100%:

$$\frac{100}{81.35} \times [2\%(H_2) + 6\%(CH_4) + 73.35\%(N_2)] = 2.46\%(H_2) + 7.37\%(CH_4) + 85.2\%(N_2)$$

4. Ascertain the Tci coefficients for the flammable gases:

Tci
$$H_2 = 5.5\%$$

Tci
$$CH_4 = 8.7\%$$

5. Calculate the flammability of the equivalent mixture using the formula:

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}} \qquad \frac{2.46}{5.5} \qquad +\frac{7.37}{8.7} = 1.29 \qquad \qquad \textbf{1.29} > \textbf{1}$$

Therefore the mixture is **flammable** in air."

Annex II

Consequential amendments to Annex 1, Table A1.2 of the GHS

"A1.2 Flammable gases (see Chapter 2.2 for classification criteria)

	Classification Hazard Hazard category class				Labo	elling	Hazard	
			Picto GHS	ogram UN Model Regulations ^a	Signal word	Hazard statement	statement codes	
	Flammable gas				Danger	Extremely flammable gas	H220	
		Pyrophoric ;	gas		See note b	Danger	Extremely flammable gas May ignite spontaneously if exposed to air	H220 H232
Flammable	Category 1A		A		See note b	Danger	Extremely flammable gas May react explosively even in the absence of air	H220 H230
gases		Chemically Unstable gas	В		See note b	Danger	Extremely flammable gas May react explosively even in the absence of air at elevated pressure and/or temperature	H220 H231
	Category 1B					Danger	Flammable gas	H221
	Category 2		No pictogram	Not required	Warning	Flammable gas	H221	

^a Under the UN Recommendations on the Transport of Dangerous Goods, Model Regulations, the symbol, number and border line may be shown in black instead of white. The background colour stays red in both cases."

^b Pyrophoric and chemical unstable gases are covered differently under the UN Recommendations on the Transport of Dangerous Goods, Model Regulations

Annex III

Consequential amendments to Annex 3 of the GHS

Section 1, Table A3.1.1

For H220

In column 4, under "hazard category", replace "1" with "1A".

For H221

In column 4, under "hazard category", replace "2" with "1B, 2".

Section 2, Table A3.2.2

For P210

In column (4), under "hazard category", for "flammable gases" replace "1, 2" with "1A, 1B, 2"

Section 2, Table A3.2.3

For P377

In column (4), under "hazard category", for "flammable gases" replace "1, 2" with "1A, 1B, 2"

For P381

In column (4), under "hazard category", for "flammable gases" replace "1, 2" with "1A, 1B, 2"

Section 2, Table A3.2.4

For P403

In column (4), under "hazard category", for "flammable gases" replace "1, 2" with "1A, 1B, 2"

Section 3, paragraph A3.3.5

Amend the matrix tables for flammable gases as follows and move the tables of flammable gases of Category 1B and Category 2 after the tables dealing with pyrophoric gases and chemically unstable gases as these gases are always flammable gases of Category 1A:

FLAMMABLE GASES (CHAPTER 2.2)

Symbol Flame

Hazard category Signal word Hazard statement

1A Danger H220 Extremely flammable gas



Precautionary statements						
Prevention	Response	Storage	Disposal			
P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.	P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition sources.	P403 Store in a well-ventilated place.				

FLAMMABLE GASES (CHAPTER 2.2)

Symbol Flame

Hazard category Signal word Hazard statement

1A, Pyrophoric gas Danger H220 Extremely flammable gas

H232 May ignite spontaneously if exposed to air



Precautionary statements						
Prevention	Response	Storage	Disposal			
P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P222 Do not allow contact with air. - if emphasis of the hazard statement is deemed necessary.	P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition sources.	P403 Store in a well-ventilated place.				
P280 Wear protective gloves/protective clothing/eye protection/face protection. Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.						

Note: This table lists only precautionary statements that are assigned due to the flammability and the pyrophoricity of the gas. For the other precautionary statements that are assigned based on chemical instability, see the respective table for Chemically Unstable Gases A and B.

FLAMMABLE GASES (CHAPTER 2.2)

Symbol

Flame

Hazard category	Signal word	Hazard statem	ent
1A, Chemically Unstable gas A		H220	Extremely flammable gas
	Danger	H230	May react explosively even in the absence of air
1A, Chemically Unstable gas B		H220	Extremely flammable gas
	Danger	H231	May react explosively even in the absence of air at
			elevated pressure and/or temperature



Response		
Kesponse	Storage	Disposal
P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition sources.	P403 Store in a well-ventilated place.	
I S P I	P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition	P2377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition

Note: This table lists only the precautionary statement that is assigned due to the flammability and the chemical instability of the gas. For the other precautionary statements that are assigned based on pyrophoricity, see the respective table for Pyrophoric Gas.

FLAMMABLE GASES (CHAPTER 2.2)

Symbol Flame

Hazard category Signal word

Hazard statement

1B

Danger

H221 Flammable gas



Precautionary statements					
Prevention	Response	Storage	Disposal		
P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.	P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely.	P403 Store in a well-ventilated place.			
	P381 In case of leakage, eliminate all ignition sources.				

FLAMMABLE GASES **(CHAPTER 2.2)**

Symbol No symbol

Hazard category Signal word Hazard statement 2

Warning	H221	Flammable gas

Precautionary statements						
Prevention	Response	Storage	Disposal			
P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.	P377 Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381 In case of leakage, eliminate all ignition sources.	P403 Store in a well-ventilated place.				

Annex IV

Guidance on the preparation of Safety Data Sheets (SDS)

In paragraph A4.3.9, table A 4.3.9.2, amend the text in column 3 for the row applicable to chapter 2.2 as follows:

Chapter	Hazard class	Property/Safety characteristic/Test result and Remarks/Guidance
2.2	Flammable gases	 for pure flammable gases: no data on the explosion / flammability limits is needed because these are indicated based on Table A4.3.9.1 indicate the T_{Ci} (maximum content of flammable gas which, when mixed with nitrogen, is not flammable in air, in %) as per ISO 10156 indicate the Fundamental Burning Velocity (FBV) if the gas is classified as Category 1B based on FBV, generally determined by ISO 817:2014, Annex C
		 for flammable gas mixtures: indicate the explosion / flammability limits, if tested or indicate whether the classification and category assignment is based on the calculation as per ISO 10156. indicate the Fundamental Burning Velocity (FBV) if the gas mixture is classified as Category 1B based on FBV, generally determined by ISO 817:2014, Annex C

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