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Sub-Committee of Experts on the Transport of Dangerous Goods

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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-first session

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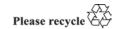
Issues relating to the Globally Harmonized System of Joint work with the Sub-Committee of Experts on the **Transport of Dangerous Goods (TDG Sub-Committee)**

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 group¹ on classification criteria for flammable gases

During the December 2015 sessions of the Sub-Committee of Experts on the 1. 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), 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 Sub-Committee, 48th session) -INF.4 (GHS Sub-Committee, 30th session) i.e., allowing for sub-categorization of current category 1 into category 1A and 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 sub-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

Refer to the report of the GHS Sub-Committee on its 30th session (ST/SG/AC.10/C.4/60, paras. 4 to 8).



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,

also noted that the criteria in option 3 would not entail any change in classification for transport purposes.

- 2. As regards the proposed hazard communication elements in informal documents INF.24 (TDG Sub-Committee, 48th session) INF.7 (GHS Sub-Committee, 30th session) Belgium and Japan agreed to bring forward further information. In addition to this formal proposal the experts from Belgium and Japan submit additional information in an informal document regarding the appropriateness of the signal word and hazard statement (warning/flammable gas) for the proposed category 1B.
- 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. Changes to the current text in the GHS are shown using the "track-changes" function.

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 °C and a standard pressure of 101.3 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 one of the two categories for this class according to the following table:

Table 2.2.1: Criteria for flammable gases

A flammable gas is classified in Category 1 or 2 according to the following table. Pyrophoric and/or chemically unstable gases are always classified in Category 1. Gases classified in Category 1, but which are not pyrophoric and/or chemically unstable, may be further categorized on the basis of the lower flammability limit (LFL) or the fundamental burning velocity (FBV) (see Table 2.2.1).

Table 2.2.1: Criteria for categorisation of flammable gases

Category	Criteria
1 <u>/1A</u>	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 flammability limit.
<u>1B</u>	Gases which meet the criteria of category 1/1A 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	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 is additionally classified as pyrophoric if it meets the criteria in the following table:

Table 2.2.2: Criteria for pyrophoric gases

Category	Criteria
Pyrophoric gas	Flammable gas that ignite spontaneously in air at a temperature of 54 °C or below.

- **NOTE 1:** Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.
- **NOTE 2:** 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).
- 2.2.2.3 A flammable gas that is also chemically unstable is additionally classified in one of the two categories for chemically unstable gases using the methods described in Part III of the Manual of Tests and Criteria according to the following table:

Table 2.2.3: Criteria for chemically unstable gases

Category	Criteria
A	Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa
В	Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa

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.

Table 2.2.4: Label elements for flammable gases

	Flammable gas			l A	Additional sub-categories		
			Pyrophoric gas	Chemically unstable gas			
	Category 1/1A	Category 1B	Category 2	Pyrophoric gas	Category A	Category B	
Symbol	Flame	[Flame]	No symbol	Flame	<u>Flame</u> No additional symbol	<u>Flame</u> No additional symbol	
Signal word	Danger	[Danger]/ [Warning]	Warning	Danger	<u>Danger</u> No additional signal word	<u>Danger</u> No additional signal word	
Hazard statement	Extremely flammable gas	[Flammable gas]/ [Highly flammable gas]	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 and/or temperature	

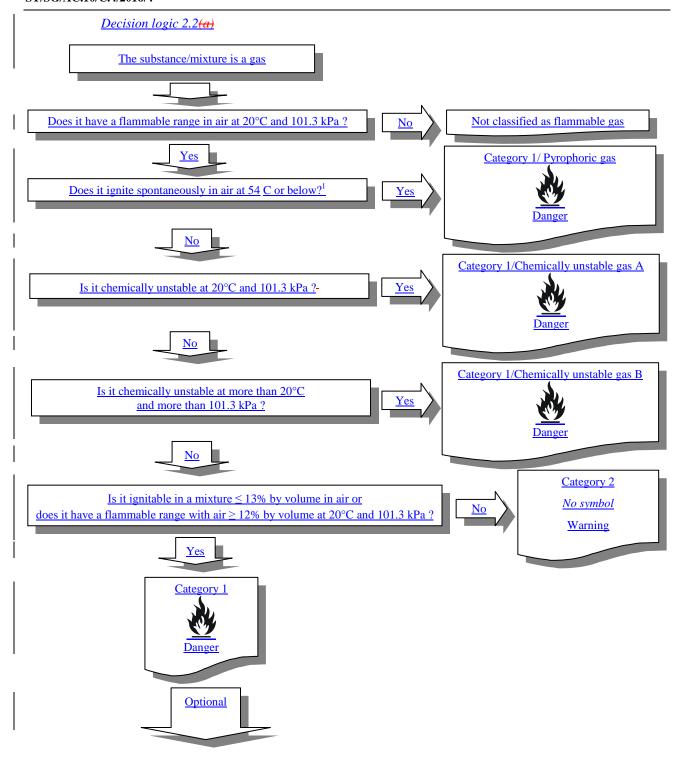
2.2.3.2 If a flammable gas or gas mixture is additionally classified in one or more subcategories, then all relevant classification(s) should be communicated on the safety data sheet as specified in Annex 4, and the relevant hazard communication elements included on the label.

2.2.4 Decision logic and guidance

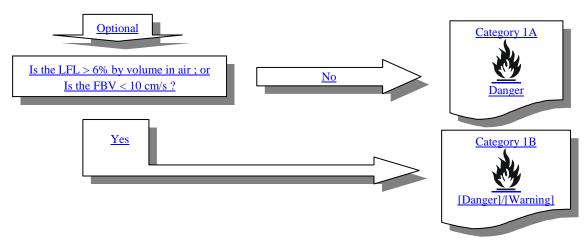
The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

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 further categorisation within category 1, data on its lower flammability limit or its fundamental burning velocity is required. The classification is according to decision logic 2.2_(a).



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



2.2.4.42 *Guidance*

- 2.2.4.42.1 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.
- 2.2.4.42.2 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".
- 2.2.4.42.3 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.
- 2.2.4.42.4 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:

$$Ki (Ar) = 0.5$$

$$Ki (He) = 0.5$$

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

$$2\%(H_2) + 6\%(CH_4) + [27\% \times 0.5 + 65\% \times 0.5](N_2) = 2\%(H_2) + 6\%(CH_4) + 46\%(N_2) = 54\%$$

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

$$\frac{100}{54} \times [2\%(H_2) + 6\%(CH_4) + 46\%(N_2)] = 3.7\%(H_2) + 11.1\%(CH_4) + 85.2\%(N_2)$$

4. Ascertain the Tci coefficients for the flammable gases:

Tci
$$H_2 = 5.7\%$$

$$Tci CH_4 = 14.3\%$$

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

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}} = \frac{3.7}{5.7} + \frac{11.1}{14.3} = 1.42$$
1.42 > 1

Therefore the mixture is <u>flammable</u> in air."

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

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

	Classification		Labelling			Hazard	
-	Hazard		Pictogram				statement codes
		Hazard category	GHS	UN Model Regulations ^a	Signal word	Hazard statement	
		1 <u>/1A</u>			Danger	Extremely flammable gas	H220
		<u>1B</u>		2	[Danger]/ [Warning]	[Flammable gas]/[Highly flammable gas]	<u>H221</u>
		2	No pictogram	Not required	Warning	Flammable gas	H221
	Flammable gases	Pyrophoric gas		2	Danger	Extremely flammable gas May ignite spontaneously if exposed to air	H220 H232
		A (chemically		(<u>Not</u> applicable) ^b	<u>Danger</u> No	Extremely flammable gas Additional hazard statement:	<u>H220</u>
		unstable gases)	No additional pictogram	Not required	additional	May react explosively even in the absence of air	H230
		B (Not		<u>Danger</u> No additional signal word	Extremely flammable gas Additional hazard statement:	<u>H220</u>	
		(chemically unstable gases)	No additional pictogram		May react explosively even in the absence of air at elevated pressure and/or temperature	H231	

^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 Chemically unstable gases are not authorized for transport.

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 "1/1A".

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 "1/1A, 1B, 2"

Section 2, Table A3.2.3

For P377

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

For P381

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

Section 2, Table A3.2.4

For P403

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

Section 3, paragraph A3.3.5

Amend the matrix tables for flammable gases as follows:

FLAMMABLE GASES (CHAPTER 2.2)

(Flammable gases)

Symbol Flame

Hazard category Signal word Hazard statement

1/1A 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)

(Flammable gases)

Symbol Flame

Hazard category Signal word Hazard statement

1B [Danger]/[Warning] H221 [Flammable gas]/[Highly Flammable Gas]



<u>Precautionary statements</u>			
Prevention	Response	<u>Storage</u>	<u>Disposal</u>
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) (Pyrophoric gases)

Symbol Flame

Hazard category Signal word Hazard statement

Pyrophoric gas Danger <u>H220</u> Extremely flammable gas

H232 May ignite spontaneously if exposed to air

*

	Precautionary statements				
Prevention	Response	Storage	Disposal		
P222					
Do not allow contact with air.					
- if emphasis of the hazard statement is					
deemed necessary.					
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 pyrophoricity of the gas. For the other precautionary statements that are assigned based on the flammability, see the respective tables for flammable gases.

FLAMMABLE GASES (CHAPTER 2.2)

(Chemically unstable gases)

Symbol

No additional symbol

Flame

Hazard category	Signal word	Hazard staten	nent
A	No additional signal word	<u>H220</u>	Extremely flammable gas
	<u>Danger</u>	H230	May react explosively even in the absence of air
В	No additional signal word	<u>H220</u>	Extremely flammable gas
	<u>Danger</u>	H231	May react explosively even in the absence of air at
			elevated pressure and/or temperature



Precautionary statements					
Prevention	Response	Storage	Disposal		
P202					
Do not handle until all safety precautions					
have been read and understood.					

Note: This table lists only the precautionary statement that is assigned due to the chemical instability of the gas. For the other precautionary statements that are assigned based on the flammability see the respective tables for flammable gases.

Guidance on the preparation of Safety Data Sheets (SDS)

In paragraph A4.3.9, table .A4.3.9.2, 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 if the gas is classified as Category 1B on the basis of the Fundamental Burning Velocity (FBV), indicate the FBV, as measured by ISO 817:2014 "Refrigerants-Designation and safety classification, Annex C: Method of test for burning velocity measurement of flammable gases" or another scientific validated method. for flammable gas mixtures: indicate the explosion / flammability limits, if tested (if classification as flammable is based on the calculation as per ISO 10156, assignment of cat. 1 is compulsory) if the gas mixture is classified as Category 1B on the basis of the Fundamental Burning Velocity (FBV), indicate the FBV, as measured by ISO 817:2014 "Refrigerants-Designation and safety classification, Annex C: Method of test for burning velocity measurement of flammable gases" or another scientific validated method.