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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

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Issues relating to the Globally Harmonized System of 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, 7–9 (morning) December 2016 Item 2 (b) of the provisional agenda Classification criteria and related hazard

communication: work of the TDG Sub-Committee on matters of interest to the GHS Sub-Committee

Classification criteria and hazard communication for flammable gases: "track-changes" version of the proposal in document ST/SG/AC.10/C.3/2016/58-ST/SG/AC.10/C.4/2016/12

Transmitted by the experts from Belgium and Japan

This document shows the text of Chapter 2.2 of the GHS and its annexes 1 and 3, as amended by the proposal in ST/SG/AC.10/C.3/2016/58–ST/SG/AC.10/C.4/2016/12 for consideration of both sub-committees.

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 °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 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 <u>categorisation of flammable gases</u>

C	Category		teria		
	Flammable gas 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.		
1 <u>A</u>		unle	ess data shows them to meet the criteria of category 1B		
	Pyrophoric gas	Fla	Flammable gases that ignite spontaneously in air at a temperature of 54 °C or belo		
	Chemically Unstable gas	<u>A</u>	Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa		
		<u>B</u>	Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa		
<u>1B</u>	Flammable gas	Gases which meet the flammability criteria for Category 1A, but which are pyrophoric, nor chemically unstable, and which have at least either:			
		<u>(a)</u>	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		ses, other than those of Category 1, which, at 20 °C and a standard pressure		
		of 1	01.3 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 14:** Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.

NOTE 52: 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).

2.2.2.2 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.

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 2.2.42: Label elements for flammable gases

	Category 1A		Gases categorized as 1A by meeting pyrophoric or unstable gas A/B criteria			
		Pyrophoric gas	Chemically unstable gas Category A	Chemically unstable gas Category B		
Symbol	<u>Flame</u>	<u>Flame</u>	No additional symbol Flame	No additional symbol Flame	<u>Flame</u>	No symbol
Signal word	<u>Danger</u>	<u>Danger</u>	<u>No additional signal</u> word <u>Danger</u>	<u>No additional signal</u> word <u>Danger</u>	<u>Danger</u>	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 and/or temperature	Flammable gas	Flammable gas

2.2.3.2 If a flammable gas or gas mixture is <u>additionally</u> classified <u>in one or more sub categoriesas pyrophoric and/or chemically unstable</u>, 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.

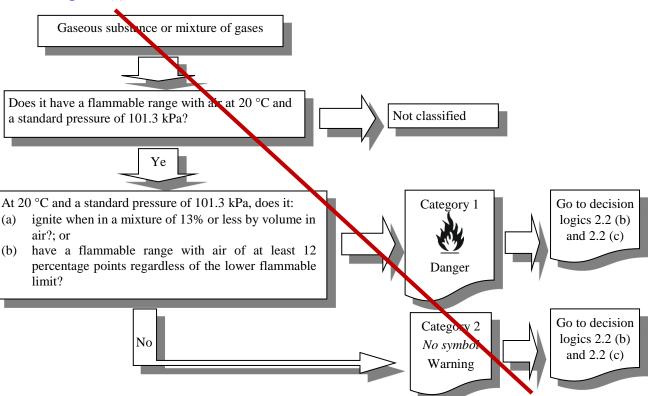
2.2.4 Decision logic and guidance

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-(a).

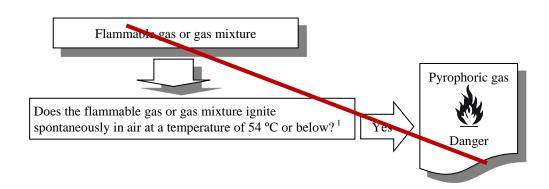
Decision logic 2.2 (a)



2.2.4.2 Decision logic for pyrophoric gases

To classify a flammable gas as a pyrophoric gas, data on its ability to ignite in air are required. The classification is according to decision logic 2.2 (b).

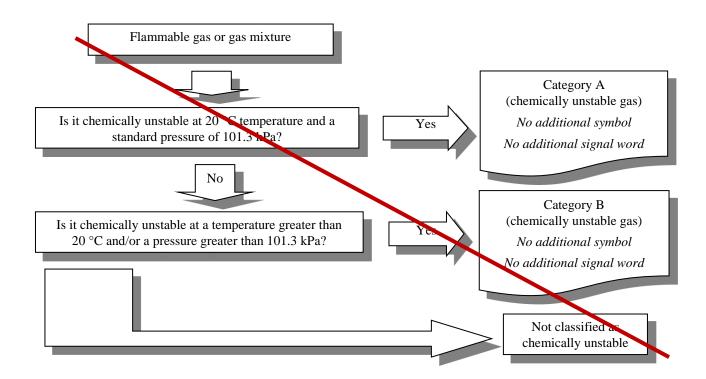
Decision logic 2.2 (b)

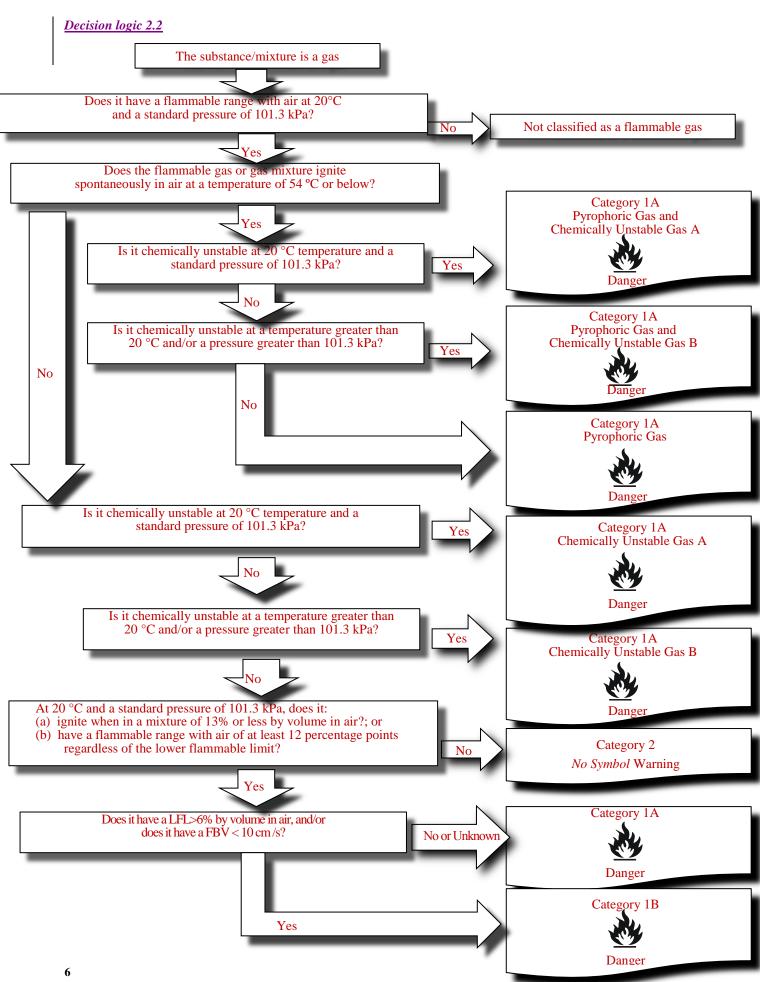


2.2.4.3 Decision logic for chemically unstable gases

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

Decision logic 2.2 (c)





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).

2.2.4.4 *Guidance*

- 2.2.4.4.1 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.
- 2.2.4.4.2 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".
- 2.2.4.4.3 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.
- 2.2.4.4.4 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) = 0.59

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

$$2\%(H_2) + 6\%(CH_4) + [27\% \times 0.5\frac{5}{5} + 65\% \times 0.5\frac{9}{2}](N_2) = 2\%(H_2) + 6\%(CH_4) + 46\frac{73.35}{5}\%(N_2) = 54\frac{81.35}{5}\%(N_2) = 54\frac{81.35}\%(N_2) = 54\frac{81.35}{5}\%(N_2) = 54$$

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

$$\frac{100}{54} \times [2\%(H_2) + 6\%(CH_4) + \frac{4673.35}{5}\%(N_2)] = \frac{3.72.46}{5}\%(H_2) + \frac{11.17.37}{5}\%(CH_4) + \frac{85.2\%(N_2)}{5}$$

4. Ascertain the Tci coefficients for the flammable gases:

Tci
$$H_2 = 5.75\%$$

Tci $CH_4 = 14.38.7\%$

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

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

$$\sum_{i}^{n} \frac{V_{i}\%}{T_{ci}} = \frac{2.46}{5.5} + \frac{7.37}{8.7} = 1.29$$
1.42 > 1

Therefore the mixture is <u>flammable</u> 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			Labelling			<u>Hazard</u>			
<u>Hazard</u> class	<u>Haza</u>	ard category		GHS	Pictogram UN Model Regulations	Signal word	Hazard statement	statement codes	
	category	Flammable :		gas		2 2	<u>Danger</u>	Extremely flammable gas	<u>H220</u>
		Pyrophoric :			See note b	<u>Danger</u>	Extremely flammable gas May ignite spontaneously if exposed to air	H220 H232	
1A Pyropho egas A (chemica y unstable gases) Flammable B	Pyrophori e-gas A (chemicall y-unstable gases) B	1A Pyrophori egas A (chemicall y unstable gases) B (chemicall	<u>A</u>	No additional pictogram	<u>See note b</u> Not required	Danger No additional signal word	Extremely flammable gasAdditional hazard statement: May react explosively even in the absence of air	H220 H230	
gases	<u>y unstable</u>		No additional pictogram	See note b Not required	Danger No additional signal word	Extremely flammable gasAdditional hazard statement: May react explosively even in the absence of air at elevated pressure and/or temperature	H220 H231		
	<u>c</u>	eategory 1B			2	<u>Danger</u>	Flammable gas	<u>H221</u>	
	<u>C</u>	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)

(Flammable gases)

Symbol

Flame

Hazard category Signal word Hazard statement

1<u>A</u> Danger H220 Extremely flammable gas



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

FLAMMABLE GASES (CHAPTER 2.2)

(Pyrophoric gases)

Symbol Flame

Hazard category Signal word Hazard statement

<u>1A, Pyrophoric gas</u> Danger <u>H220</u> <u>Extremely flammable gas</u>

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. P280 Wear protective gloves/protective clothing/eye protection/face protection. Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.	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.			

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

FLAMMABLE GASES (CHAPTER 2.2)

(Chemically unstable gases)

Symbol

No additional symbol
Flame

Hazard category	Signal word	Hazard statement
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<u>1A, Chemically Unstable gas A</u> *No additional signal word* <u>H220</u> <u>Extremely flammable gas</u>

<u>Danger</u> H230 May react explosively even in the absence of air

<u>1BA, Chemically Unstable gas B</u> 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			
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	P403 Store in a well-ventilated place.				
P202 Do not handle until all safety precautions have been read and understood.	In case of leakage, eliminate all ignition sources.					

Note: This table lists only the precautionary statements that <u>are is</u> assigned due to the <u>flammability and the</u> chemical instability of the gas. For the other precautionary statements that are assigned based on the <u>pyrophoricity flammability</u> see the respective tables for <u>Pyrophoricflammable</u> gases.

FLAMMABLE GASES (CHAPTER 2.2)

Symbol flame

<u>Hazard category</u> <u>Signal word</u> <u>Hazard statement</u>

<u>1B</u> <u>Danger</u> <u>H221</u> <u>Flammable gas</u>



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

FLAMMABLE GASES (CHAPTER 2.2)

(Flammable gases)

Symbol No symbol

Hazard category Signal word Hazard statement

Warning H221 Flammable gas

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

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:

Chapt er	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: