

UN/SCETDG/49/INF.78 UN/SCEGHS/31/INF.23

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

4 July 2016

Sub-Committee of Experts on the Transport of Dangerous Goods

Forty-ninth session

Geneva, 27 June – 6 July 2016

Item 10 (c) of the provisional agenda

**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-first session

Geneva, 5– 8 July 2016

Item 2 of the provisional agenda

**Joint work with the Sub-Committee of Experts on the
Transport of Dangerous Goods (TDG Sub-Committee)**

Proposal for modification of flammable gases, GHS Chapter 2.2

Transmitted by the expert from the United States of America

Introduction

1. At the 29th session of the UNSCEGHS, the U.S. submitted an informal paper presenting comments expressing concern about the changes being proposed for the flammable gases chapter, GHS Chapter 2.2. In particular, the U.S. noted that the changes proposed for the chapter may cause confusion or misinterpretation of the existing classification criteria, hazard communication, and decision logics and guidance agreed upon for chemically unstable gases and pyrophoric gases. The informal paper also requested that the Joint TDG-GHS Informal Working Group not only address categorization of flammable gases of Category 1 gases, but review how a new Category 1b would interact with the other criteria (e.g., Pyrophoric gases and Chemically Unstable gases) of the chapter to ensure that the classification criteria, hazard communication, and decision logics and guidance of the flammable gases addressed by this chapter are not compromised and are presented in a clear, concise manner (informal documents INF.58 (47th session) and INF.16 (29th session)).

2. At the 30th session of the UNSCEGHS, the United States of America offered to support the efforts of the Informal working group in drafting of GHS Chapter 2.2. This document is the result of these drafting efforts and is submitted to supplement the work done by the Joint TDG-GHS Informal Working Group and the experts from Belgium and Japan, presented in working paper ST/SG/AC.10/C.3/2016/17 – ST/SG/AC.10/C.4/2016/4.

Comments

3. As the U.S. reviewed the draft chapter provided in the working paper, we evaluated how various implementing countries may apply the proposed classification scheme of category 1/1A and category 1B. If the intention of this work is to provide a harmonized classification approach, then we do not see that happening as some countries may continue to assign flammable gas category 1, while others may choose to use the flammable gas category 1A and 1B classification scheme. The U.S. believes that the use of providing an

option did not help to simplify the classification approach for this hazard class. Therefore, the U.S. suggests that the option to classify a flammable gas as either a category 1 or 1A be removed. Instead, we suggest that the chapter only support classification into category 1A or category 1B, in addition to the pyrophoric gases, chemically unstable gases and category 2 categories.

4. The U.S. also notes that with regard to classifying a flammable gas as either a category 1A or a category 1B, a substance or mixture classified into category 1A flammable gas can only be classified as a category 1B flammable gas when there is sufficient additional data to support the category 1B classification. A similar approach was taken for eye irritation categories 2A and 2B.

5. The U.S. also notes that the paper submitted by the Joint TDG-GHS Informal Working Group does not account for the classification of a flammable gas that is both a pyrophoric gas and chemically unstable. This is also the case with the paper submitted by Germany, EIGA and CEFIC. In the attached proposal, the U.S. proposes a decision logic that captures the classification of gases into more than one category.

Proposal

6. Using the working paper submitted by the experts from Belgium and Japan as a base document, and taking the above comments into account, the U.S. drafted a flammable gases chapter that attempts to

- (a) Clearly state the classification criteria,
- (b) Identify all the hazard communication elements, including when the substance or mixture is classified into more than one hazard category, and
- (c) Provide a decision logic that lead the classifiers to the proper hazard classification assignment(s).

7. The Joint Sub-committee is invited to consider this proposal and provide further comments for clarification or improvement of the GHS chapter 2.2, Flammable Gases.

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 into one or more categories according to the following table:

Table 2.2.1: Criteria for flammable gases

Category	Criteria
<u>Pyrophoric gas</u>	<u>Flammable gas that ignite spontaneously in air at a temperature of 54 °C or below.</u>
<u>Chemically Unstable Gas A</u>	<u>Flammable gases which are chemically unstable at 20°C and a standard pressure of 101.3 kPa</u>
<u>Chemically Unstable Gas B</u>	<u>Flammable gases which are chemically unstable at a temperature greater than 20°C and/or a pressure greater than 101.3 kPa</u>
<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 <u>flammability limit.</u>
<u>1B</u>	<u>Gases which meet the criteria of category 1A and which have at least either:</u> <u>a) A lower flammability limit of more than 6% by volume in air; or</u> <u>b) A fundamental burning velocity of less than 10 cm/s.</u>
<u>2</u>	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.

NOTE 3: Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.

NOTE 4: 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).

NOTE 5: Pyrophoric and/or chemically unstable gases are always considered classified into Category 1A. See Table 2.2.2 for the appropriate label elements for flammable gases classified into one category and Table 2.2.3 for flammable gases classified into more than one category.

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Table 2.2.2: Criteria for pyrophoric gases¶
Category ...

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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 2.2.2: Label elements for flammable gases

	<u>Category 1A</u>	<u>Category 1B</u>	<u>Category 2</u>	<u>Pyrophoric Gas</u>	<u>Chemically Unstable Gas A</u>	<u>Chemically Unstable Gas B</u>
<u>Symbol</u>	<u>Flame</u>	<u>Flame</u>	<u>No symbol</u>	<u>Flame</u>	<u>Flame</u>	<u>Flame</u>
<u>Signal word</u>	<u>Danger</u>	<u>[Danger]/ [Warning]</u>	<u>Warning</u>	<u>Danger</u>	<u>Danger</u>	<u>Danger</u>
<u>Hazard statement(s)</u>	<u>Extremely flammable gas</u>	<u>[Flammable gas]/ [Highly flammable gas]</u>	<u>Flammable gas</u>	<u>Extremely flammable gas</u> <u>May ignite spontaneously if exposed to air</u>	<u>Extremely flammable gas</u> <u>May react explosively even in the absence of air</u>	<u>Extremely flammable gas</u> <u>May react explosively even in the absence of air at elevated pressure and/or temperature</u>

Deleted: 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

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2.2.3.2 If a flammable gas or gas mixture is classified into more than one category, then all relevant classifications should be communicated on the safety data sheet as specified in Annex 4, and the relevant hazard communication elements included on the label as specified in Table 2.2.3.

Table 2.2.3: Label elements for flammable gases classified into more than one category

	<u>Pyrophoric Gas & Chemically Unstable Gas A</u>	<u>Pyrophoric Gas & Chemically Unstable Gas B</u>
<u>Symbol</u>	<u>Flame</u>	<u>Flame</u>
<u>Signal word</u>	<u>Danger</u>	<u>Danger</u>
<u>Hazard statements</u>	<u>Extremely flammable gas</u> <u>May ignite spontaneously if exposed to air</u> <u>May react explosively even in the absence of air</u>	<u>Extremely flammable gas</u> <u>May ignite spontaneously if exposed to air</u> <u>May react explosively even in the absence of air at elevated pressure and/or temperature</u>

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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 to category 1B, data on its lower

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flammability limit or its fundamental burning velocity is required. The classification is according to decision logic 2.2.

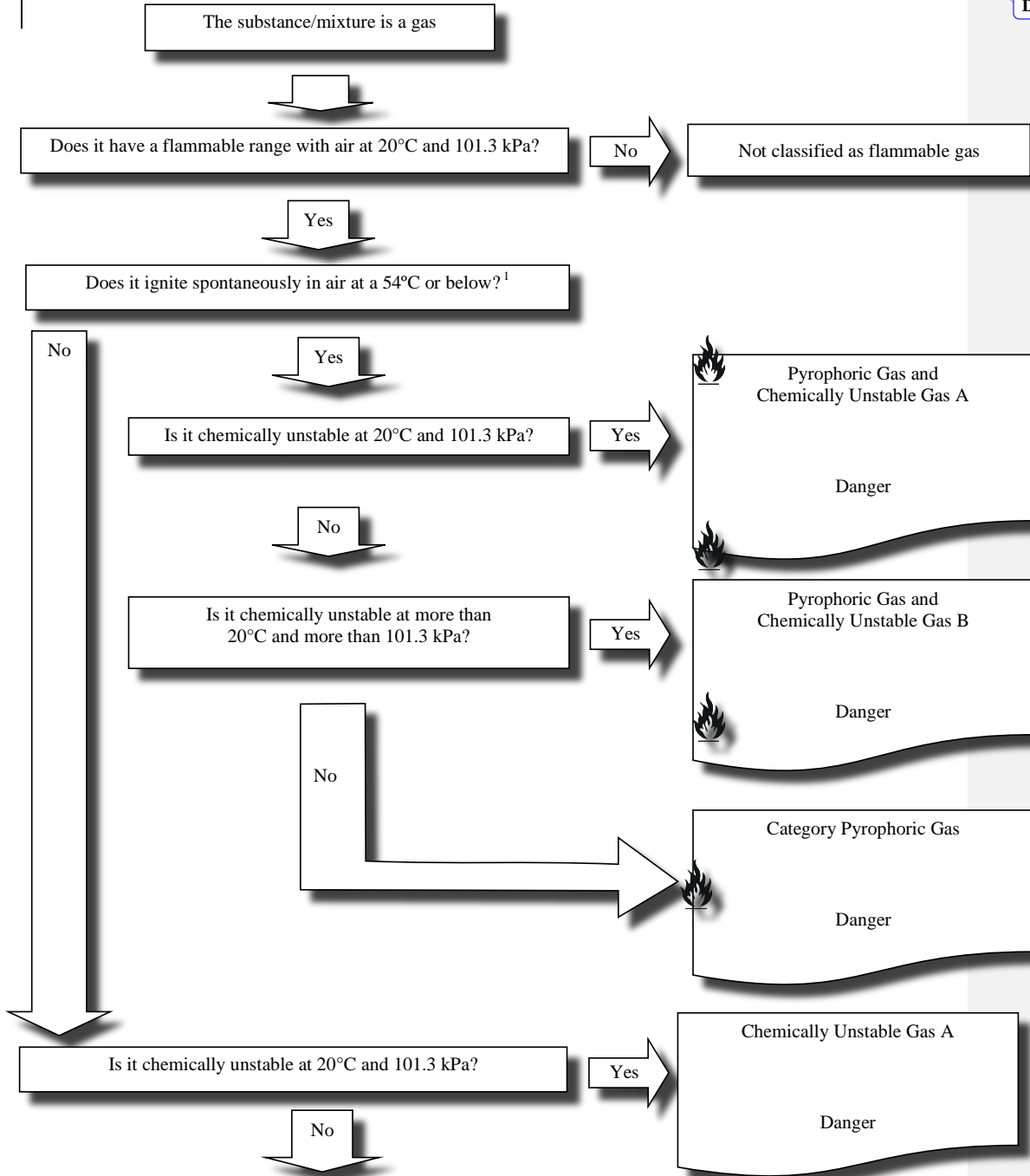
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Decision logic 2.2.

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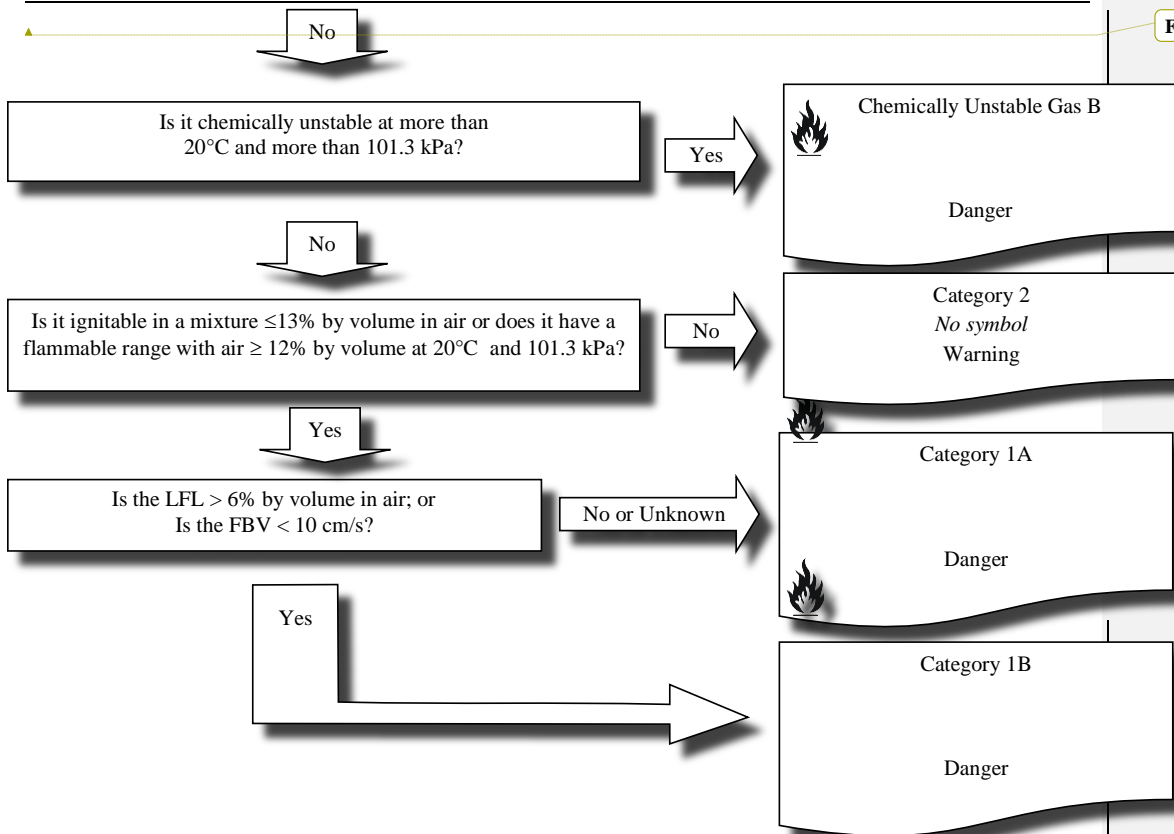
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¹ In the absence of data on its pyrophoricity, a flammable gas mixture should be classified as pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

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2.2.4.2 Guidance

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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.

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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”.

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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.

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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.

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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 n^{th} gas in the mixture;
 K_i = the equivalency factor for an inert gas versus nitrogen;

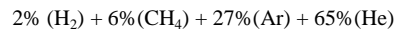
Where a gas mixture contains an inert diluent other than nitrogen, the volume of this diluent is adjusted to the equivalent volume of nitrogen using the equivalency factor for the inert gas (K_i).

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



Calculation

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

$$K_i (\text{Ar}) = 0.5$$

$$K_i (\text{He}) = 0.5$$

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

$$2\% (\text{H}_2) + 6\% (\text{CH}_4) + [27\% \times 0.5 + 65\% \times 0.5] (\text{N}_2) = 2\% (\text{H}_2) + 6\% (\text{CH}_4) + 46\% (\text{N}_2) = 54\%$$

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

$$\frac{100}{54} \times [2\%(\text{H}_2) + 6\%(\text{CH}_4) + 46\%(\text{N}_2)] = 3.7\%(\text{H}_2) + 11.1\%(\text{CH}_4) + 85.2\%(\text{N}_2)$$

4. Ascertain the Tci coefficients for the flammable gases:

$$\begin{aligned} \text{Tci H}_2 &= 5.7\% \\ \text{Tci CH}_4 &= 14.3\% \end{aligned}$$

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









$$\sum_i^n \frac{V_i\%}{T_{ci}} = \frac{3.7}{5.7} + \frac{11.1}{14.3} = 1.42 \qquad \mathbf{1.42 > 1}$$

Therefore the mixture is flammable in air.

Annex 2

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 statement codes
Hazard class	Hazard category	Pictogram		Signal word	Hazard statement	
		GHS	UN Model Regulations ^a			
Flammable gases	Pyrophoric gas			Danger	Extremely flammable gas May ignite spontaneously if exposed to air	H220 H232
	Chemically unstable gas A		<i>(Not applicable)^b</i>	Danger	Extremely flammable gas May react explosively even in the absence of air	H220 H230
	Chemically unstable gas B		<i>(Not applicable)^b</i>	Danger	Extremely flammable gas May react explosively even in the absence of air at elevated pressure and/or temperature	H220 H231
	1A			Danger	Extremely flammable gas	H220
	1B			[Danger]/ [Warning]	[Flammable gas]/[Highly flammable gas]	H221/[Hxx x]
	2	No pictogram	<i>Not required</i>	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 Chemically unstable gases are not authorized for transport.

Annex 3

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:

**FLAMMABLE GASES
 (CHAPTER 2.2)
 (Flammable gases)**

Symbol
 Flame

Hazard category	Signal word	Hazard statement
1A	Danger	H220 Extremely flammable gas



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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



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Hazard category

1B

Signal word

[Danger]/[Warning]

Hazard statement

H221 [Flammable gas]/[Highly Flammable Gas]

Precautionary statements

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

FLAMMABLE GASES
 (CHAPTER 2.2)
 (Pyrophoric gases)

Symbol
 Flame



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Hazard category	Signal word	Hazard statement
Pyrophoric gas	Danger	H220 Extremely flammable gas H232 May ignite spontaneously if exposed to air

Precautionary statements			
Prevention	Response	Storage	Disposal
P222 Do not allow contact with air. <i>– if emphasis of the hazard statement is deemed necessary.</i> 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)

Hazard category	Signal word	Hazard statement	Symbol
A	<u>Danger</u>	H220 <u>Extremely flammable gas</u> H230 May react explosively even in the absence of air	
B	<u>Danger</u>	H220 <u>Extremely flammable gas</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.*

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FLAMMABLE GASES
(CHAPTER 2.2)
(Pyrophoric and Chemically unstable gases)

Symbol

Flame

<u>Hazard category</u>	<u>Signal word</u>	<u>Hazard statement</u>
<u>Pyrophoric and Chemically unstable gases A</u>	<u>Danger</u>	<u>H220</u> Extremely flammable gas <u>H230</u> May react explosively even in the absence of air
<u>Pyrophoric and Chemically unstable gases B</u>	<u>Danger</u>	<u>H220</u> Extremely flammable gas <u>H231</u> May react explosively even in the absence of air at elevated pressure and/or temperature



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<u>Precautionary statements</u>			
<u>Prevention</u>	<u>Response</u>	<u>Storage</u>	<u>Disposal</u>
<u>P202</u> <u>Do not handle until all safety precautions have been read and understood.</u> <u>P222</u> <u>Do not allow contact with air.</u> <i><u>– if emphasis of the hazard statement is deemed necessary.</u></i> <u>P280</u> <u>Wear protective gloves/protective clothing/eye protection/face protection.</u> <u>Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.</u>			

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

Annex 4

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	<p><u>for pure flammable gases:</u></p> <ul style="list-style-type: none"> – no data on the explosion / flammability limits is needed because these are indicated based on Table A4.3.9.1 – indicate the T_{Cl} (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. <p><u>for flammable gas mixtures:</u></p> <ul style="list-style-type: none"> – 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.