

**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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**Sub-Committee of Experts on the
Transport of Dangerous Goods**

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Item 10 (c) of the provisional agenda

**Issues relating to the Globally Harmonized System
of Classification and Labelling of Chemicals:
pyrophoric gases**

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

Twenty-seventh session

Geneva, 2 – 4 July 2014

Item 3 (g) of the provisional agenda

**Classification criteria and related hazard
communication: miscellaneous**

**Proposal to include pyrophoric gas as a hazard
category in the flammable gases hazard class of
the GHS (track-changes)**

Transmitted by the expert from the United States of America

1. This document contains the text of GHS Chapter 2.2, Annex 1 and Annex 3, as amended in accordance with the proposed list of amendments in document ST/SG/AC.10/C.3/2014/54-ST/SG/AC.10/C.4/2014/5. Amendments are shown in visible mode (“track-changes”).
2. Where no change is proposed for certain hazard or precautionary statements assigned to flammable gases in Annex 3, Sections 1 and 2, the text is highlighted for the convenience of the Sub-committee of Experts on the GHS. Experts are invited to consider whether the full title of the hazard chapter should be included in the assignment.

Annex

Amendments to Chapter 2.2

“CHAPTER 2.2

FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE 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

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 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 gases 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 auto-ignition temperature, a flammable gas mixture is classified as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

2.2.2.23 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 UN Manual of Tests and Criteria according to the following table:

Table 2.2.23: 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
B	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 2.2.34: Label elements for flammable gases (including chemical unstable gases)

			<u>Additional sub-categories</u>		
	Flammable gas		<u>Pyrophoric gas</u>	Chemically unstable gas	
	Category 1	Category 2	<u>Pyrophoric gas</u>	Category A	Category B
Symbol	Flame	No symbol	<u>Flame</u>	<i>No additional symbol</i>	<i>No additional symbol</i>
Signal word	Danger	Warning	<u>Danger</u>	<i>No additional signal word</i>	<i>No additional signal word</i>
Hazard statement	Extremely flammable gas	Flammable gas	<u>May ignite spontaneously if exposed to air</u>	May react explosively even in the absence of air	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 sub-categories, 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.

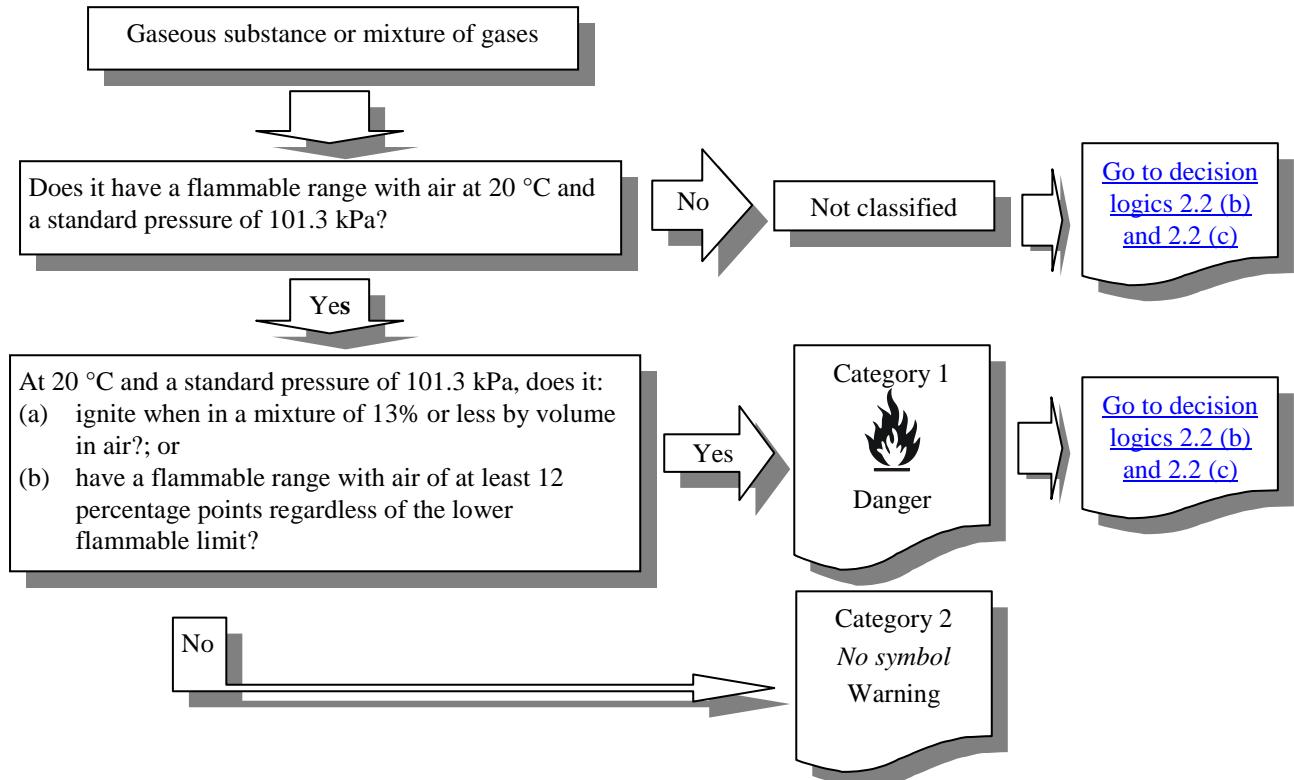
2.2.4 Decision logic and guidance

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 are required. The classification is according to decision logic 2.2 (a).

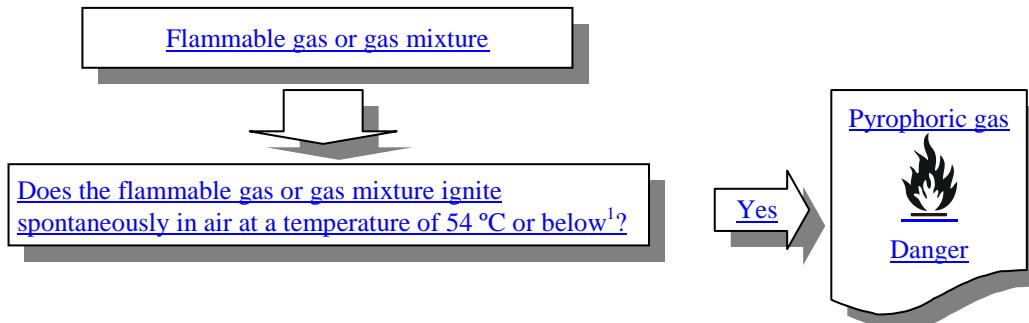
Decision logic 2.2 (a)



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)

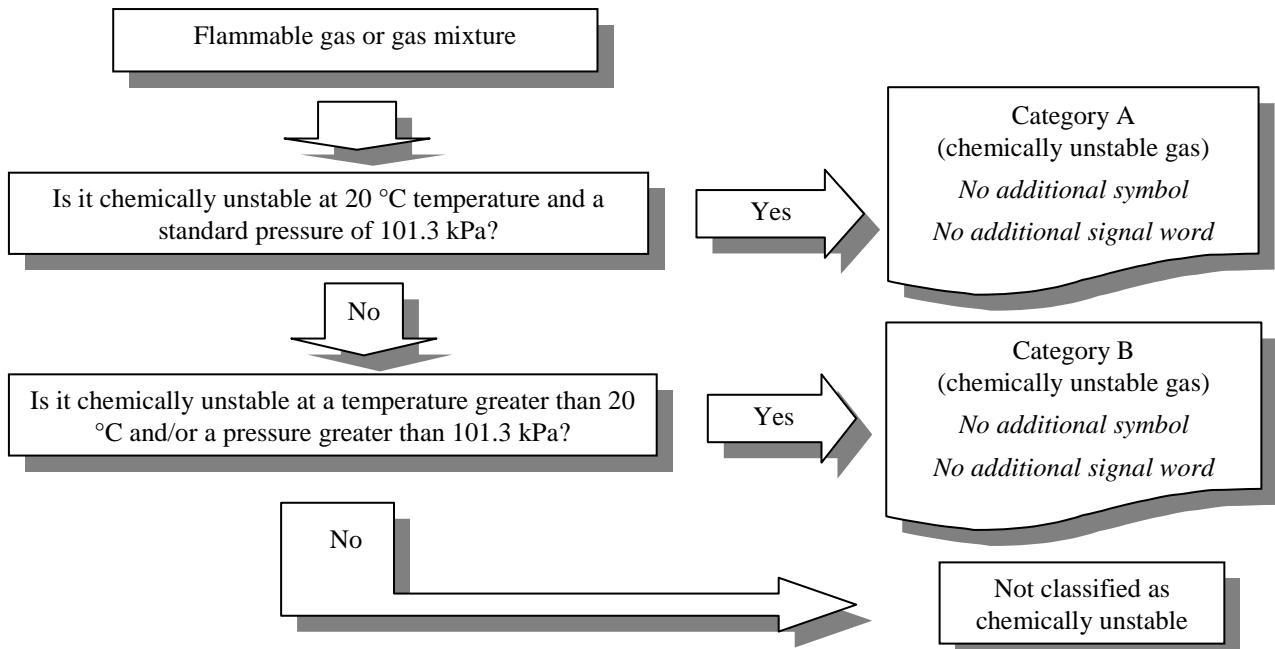


¹ In the absence of data on its auto-ignition temperature, a flammable gas mixture is classified as a pyrophoric gas if it contains more than 1% (by volume) of pyrophoric component(s).

2.2.4.32 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^b](#)).

Decision logic 2.2 ([c^b](#))



2.2.4.43 Guidance

2.2.4.43.1 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”). 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 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 or mixture does not ignite spontaneously on coming into contact with air at a temperature of 54 °C or below.

2.2.4.3.24.4 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 *[The example in 2.2.5 remains unchanged]*

Amendments to Annex 1, Table A1.2

A1.2 FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE 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	1			Danger	Extremely flammable gas	H220	
	2	No pictogram	Not required	Warning	Flammable gas	H221	
	<u>Pyrophoric gas</u>			<u>Danger</u>	<u>May ignite spontaneously if exposed to air</u>	<u>H232</u>	
	A (chemically unstable gases)	No additional pictogram	Not required	No additional signal word	Additional hazard statement: May react explosively even in the absence of air	H230	
	B (chemically unstable gases)	No additional pictogram	Not required	No additional signal word	Additional hazard statement: 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."

Amendments to Annex 3, Table A3.1.1

Code (1)	Physical hazard statements (2)	Hazard class (GHS chapter) (3)	Hazard category (4)
H230	May react explosively even in the absence of air	Flammable gases (including chemically unstable gases) (chapter 2.2)	A (Chemically unstable gases)
H231	May react explosively even in the absence of air at elevated pressure and/or temperature	Flammable gases (including chemically unstable gases) (chapter 2.2)	B (Chemically unstable gases)
H232	<u>May ignite spontaneously if exposed to air</u>	Flammable gases (chapter 2.2)	<u>Pyrophoric gas</u>

(The remainder of the table remains unchanged)

Amendments to Annex 3, Section 2, Table A3.2.2

(Only the rows containing amendments are reproduced here. The remainder of the tables remain unchanged)

Table A3.2.2: Codification of prevention precautionary statements

(1)	Prevention precautionary statements (2)	Hazard class (3)	Hazard category (4)	Conditions for use (5)
P202	Do not handle until all safety precautions have been read and understood.	Flammable gases (including chemically unstable gases) (chapter 2.2)	A, B (chemically unstable gases)	
		Germ cell mutagenicity (chapter 3.5)	1A, 1B, 2	
		Carcinogenicity (chapter 3.6)	1A, 1B, 2	
		Reproductive toxicity (chapter 3.7)	1A, 1B, 2	
P222	Do not allow contact with air.	Flammable gases (chapter 2.2)	Pyrophoric gas	<i>– if emphasis of the hazard statement is deemed necessary</i>
		Pyrophoric liquids (chapter 2.9)	1	<i>– if emphasis of the hazard statement is deemed necessary.</i>
		Pyrophoric solids (chapter 2.10)	1	
P233	Keep container tightly closed.	Flammable gases (chapter 2.2)	Pyrophoric gas	
		Flammable liquids (chapter 2.6)	1, 2, 3	<i>– if the liquid is volatile and may generate an explosive atmosphere.</i>
		Pyrophoric liquids (chapter 2.9)	1	
		Pyrophoric solids (chapter 2.10)	1	
		Acute toxicity, inhalation (chapter 3.1)	1, 2, 3	<i>– if the chemical is volatile and may generate a hazardous atmosphere.</i>
		Specific target organ toxicity, single exposure; respiratory tract irritation (chapter 3.8)	3	

(1)	Prevention precautionary statements (2)	Hazard class (3)	Hazard category (4)	Conditions for use (5)
P280	Wear protective gloves/protective clothing/eye protection/face protection.	Explosives (chapter 2.1)	Unstable explosives and divisions 1.1, 1.2, 1.3, 1.4, 1.5	Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.
		Flammable gases (chapter 2.2)	Pyrophoric gas	
		Flammable liquids (chapter 2.6)	1, 2, 3, 4	
		Flammable solids (chapter 2.7)	1, 2	
		Self-reactive substances and mixtures (chapter 2.8)	Types A, B, C, D, E, F	
		Pyrophoric liquids (chapter 2.9)	1	
		Pyrophoric solids (chapter 2.10)	1	
		Self-heating substances and mixtures (chapter 2.11)	1, 2	
		Substances and mixtures which, in contact with water, emit flammable gases (chapter 2.12)	1, 2, 3	
<i>Remainder of P280: unchanged</i>				

Amendments to Annex 3, Section 3, matrix for flammable gases in A3.3.5

FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE GASES) (Chapter 2.2) (Flammable gases)				Symbol  Flame
Hazard category	Signal word	Hazard statement		
1	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 (INCLUDING CHEMICALLY UNSTABLE GASES)

(Chapter 2.2)

(Flammable gases)

Symbol
<i>No symbol</i>

Hazard category	Signal word	Hazard statement	
2	Warning	H221	Flammable gas
Preccautionary 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)****(Pyrophoric gases)****Symbol**

Flame

**Hazard category**

Pyrophoric gas

Signal word

Danger

Hazard statement

H232 May ignite spontaneously if exposed to air

<u>Precautionary statements</u>			
<u>Prevention</u>	<u>Response</u>	<u>Storage</u>	<u>Disposal</u>
<p>P222 <u>Do not allow contact with air.</u> <i>- if emphasis of the hazard statement is deemed necessary.</i></p> <p>P233 <u>Keep container tightly closed.</u></p> <p>P280 <u>Wear protective gloves/protective clothing/eve protection/face protection.</u> <u>Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.</u></p>			

Note: This table lists only the precautionary statement that is 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 (INCLUDING CHEMICALLY UNSTABLE GASES)

(Chapter 2.2)

(Chemically unstable gases)

Symbol
No additional symbol

Hazard category	Signal word	Hazard statement
A	<i>No additional signal word</i>	H230 May react explosively even in the absence of air
B	<i>No additional signal word</i>	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.

