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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

Forty-fifth session

Geneva, 23 June – 2 July 2014

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

Transmitted by the expert from the United States of America¹

Introduction

- 1. This working paper and accompanying informal paper (INF.4, 27th session GHS, INF.7, 45th session TDG) follows several papers submitted to the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS Sub-Committee) and the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG Sub-Committee) proposing that pyrophoric gases be included in the flammable gases hazard category of the GHS. The paper reflects work performed by experts from Germany, Sweden, United Kingdom, Canada, the European Industrial Gases Association (EIGA), the Compressed Gas Association (CGA), and the United States of America. A summary of the submittals regarding this hazard is presented in paragraphs 2 through 4 for the Sub-Committee's reference.
- 2. An informal paper submitted to the twenty-fifth session of the GHS Sub-Committee and the forty-third session of the TDG Sub-Committee proposed that pyrophoric gases be included in the flammable gases hazard category of the GHS (informal document INF.51 (TDG,43rd session) INF.15 (GHS, 25th session). The GHS Sub-Committee provided

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¹ In accordance with the programme of work of the Sub-Committee for 2013–2014 approved by the Committee at its sixth session (see ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

general support for addressing pyrophoric gases in the GHS and suggested that a working paper be prepared that addressed whether the hazard be included as a separate hazard class or sub-category within the flammable gases hazard class. Experts also requested that the paper address whether classification of flammable mixtures containing 1% or more of pyrophoric components and whether specific precautionary statements should be developed.

- 3. A follow-up working paper and corresponding informal paper was submitted to the 26th session of the GHS Sub-Committee and the 44th session of the TDG Sub-Committee proposing that pyrophoric gases be included in the flammable gases hazard category of the GHS. The paper provided responses to comments from various experts at the twenty-fifth session of the GHS Sub-Committee (see ST/SG/AC.10/C.3/2013/69–ST/SG/AC.10/C.4/2013/9 and informal document INF.8 (TDG, 44th session)–INF.3 (GHS, 26th session)).
- 4. In response to the working and informal papers submitted at the twenty-sixth session of the Sub-Committee and the forty-fourth session of the TDG Sub-Committee referenced in paragraph 2, the European Industrial Gases Association (EIGA) submitted an informal paper containing comments and suggestions on the above proposal (INF.42, TDG 44th session, INF.14 GHS, 26th session).

Additional work on the proposed amendments

- 5. During the margins of the 26th session of the GHS Sub-Committee, several experts met to discuss how to address the concerns and suggestions raised by EIGA and other Sub-Committee experts. Although there was general support for the proposal to include pyrophoric gases as a hazard within the flammable gases hazard class, experts still had questions about:
 - (a) whether the proposed hazard class should be a separate hazard category or a sub-category within the flammable gases hazard class;
 - (b) the applicability of the 1% cut-off value for gas mixtures;
 - (c) the proposed value in the definition for the auto-ignition temperature; and
 - (d) the concepts of "spontaneous" or "delayed" ignition for pyrophoric gases.

The experts agreed to do some additional research and meet again via teleconference.

6. Experts from Germany, Sweden, United Kingdom, Canada, EIGA, CGA, and the United States of America met via a follow-up teleconference after the twenty-sixth session of the GHS Sub-Committee to discuss the information gathered on the hazard. The experts reached agreement on the following proposal.

Proposed amendments to the GHS

7. Experts are invited to review and comment on the proposed following amendments.

Amendments to Chapter 2.2

- 8. Amend GHS Chapter 2.2 as follows:
 - (a) Amend the chapter title to read: "Flammable gases"
 - (b) In section 2.2.1:
 - renumber current paragraph 2.2.1.2 as 2.2.1.3;
 - Insert a new paragraph 2.2.1.2 to read as follows:
 - "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."
 - (c) In section 2.2.2:
 - renumber current paragraph 2.2.2.2 as new 2.2.2.3 (current table 2.2.2 becomes table 2.2.3)
 - Insert a new paragraph 2.2.2.2 to read as follows:
 - "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).".

- (d) In section 2.2.3:
 - Renumber current paragraph as 2.2.3.1.
 - Amend current table 2.2.3 to read as follows:

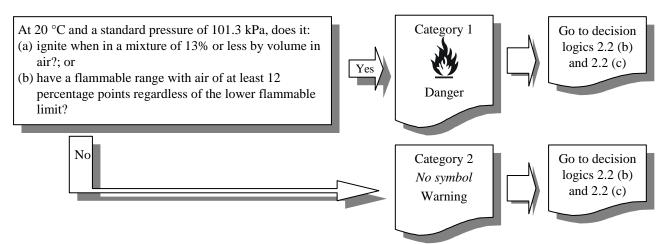
"Table 2.2.3: Label elements for flammable gases

			Additional sub-categories		
	Flammable gas		Pyrophoric gas	Chemically unstable gas	
	Category 1	Category 2	Pyrophoric gas	Category A	Category B
Symbol	Flame	No symbol	Flame	No additional symbol	No additional symbol
Signal word	Danger	Warning	Danger	No additional signal word	No additional signal word
Hazard statement	Extremely flammable gas	Flammable gas	May ignite spontaneously if exposed to air	May react explosively even in the absence of air	May react explosively even in the absence of air at elevated pressure and/or temperature

- Insert a new paragraph 2.2.3.2 to read as follows:
 - "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."

(e) In section 2.2.4:

 In decision logic 2.2 (a), insert two additional boxes with the text "Go to decision logics 2.2 (b) and 2.2 (c)" immediately to the right of the existing Category 1 and Category 2 boxes, as follows:

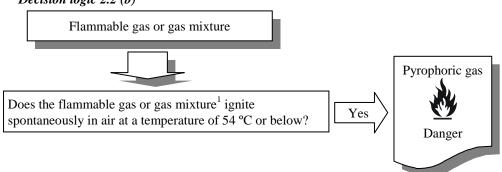


• Insert a new paragraph 2.2.4.2 to read as follows:

"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)."
- Current paragraph 2.2.4.2 becomes new paragraph 2.2.4.3 and current decision logic 2.2 (b) becomes decision logic 2.2 (c).
- Current 2.2.4.3 and 2.2.4.3.1 become new 2.2.4.4 and 2.2.4.4.1.

- Insert two new paragraphs 2.2.4.4.2 and 2.2.4.4.3, to read as follows:
 - "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 $54\,^{\circ}\text{C}$ or below.".
- Current paragraph 2.2.4.3.2 ("Chemical instability...classification purposes") becomes new paragraph 2.2.4.4.4.

Amendments to Annex 1

- 9. In Table A1.2:
 - Amend the title to read: "Flammable gases (see Chapter 2.2 for classification criteria)".
 - In the hazard class column, amend the text in the column to read "Flammable gases".
 - Insert a new row for pyrophoric gases, before the row for "A (chemically unstable gases)" as follows:

Class	Classification Labelling				Hazard statement	
		Pictogram			!	codes
Hazard class	Hazard category	GHS	UN Model Regulations ^a	Signal word	Hazard statement	
Flammable gases	Pyrophoric gas			Danger	May ignite spontaneously if exposed to air	H232

Amendments to Annex 3

- 10. Amend Annex 3 as follows:
 - (a) In Section 1, Table A3.1.1:
 - Insert a new row to reads as follows:

Code	Physical hazard statements	Hazard class (GHS chapter)	Hazard category
(1)	(2)	(3)	(4)
H232	May ignite spontaneously if exposed to air	Flammable gases (chapter 2.2)	Pyrophoric gas

• For H230 and H231 amend the name of the hazard class in column (3) to read: "Flammable gases (Chapter 2.2)"

(b) In Section 2, Table A3.2.2:

P233 and P280

Insert a new row for the hazard class "Flammable gases (chapter 2.2)" (column 3) and hazard category "Pyrophoric gas" (column 4).

P222

Insert a new row for the hazard class "Flammable gases (chapter 2.2)" (column 3) and hazard category "Pyrophoric gas" (column 4), with the same condition for use currently applicable to pyrophoric liquids and pyrophoric solids (column 5).

(c) In Section 3, section A3.3.5:

In the three tables for "Flammable gases (including chemically unstable gases) (chapter 2.2)", amend the first line in the headings to read: "FLAMMABLE GASES".

Add a new matrix applicable to pyrophoric gases as follows:

FLAMMABLE GASES (CHAPTER 2.2)

(Pyrophoric gases)

Symbol Flame

Hazard category Signal word Hazard statement

Pyrophoric gas Danger 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.				
P233 Keep container tightly closed.				
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.