



**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-fourth session**

Geneva, 25 November – 4 December 2013

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-sixth session**

Geneva, 4 – 6 December 2013

Item 2 (g) of the provisional agenda

**Classification criteria and 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 follows an informal paper submitted to the 25th session of the Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS Sub-Committee) and the 43rd session of 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 (informal document INF.51 (43rd session) and informal document INF.15 (25th session)).
2. The GHS Sub-Committee had a robust discussion on the informal paper, and while there was widespread support in principle for the proposal, several suggestions to improve the paper were made (ST/SG/AC.10/C.4/50, paras 30-32). This working paper addresses those concerns.
3. As explained in the informal paper mentioned in paragraph 1, these gases do not appear to be a transport issue since in the United Nations Recommendations on the Transport of Dangerous Goods Model Regulations, they are transported either as flammable gases or flammable liquids and packaged in such way so that they are not exposed to air. Since the TDG Sub-Committee did not have sufficient time to address the

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).

paper and is the focal point for the physical hazards, the expert from the United States of America is also requesting the TDG Sub-committee's views on this proposal.

Hazard classification of pyrophoric gas

4. Pyrophoric gases are gases that ignite spontaneously when exposed to air. They are flammable but do not require an ignition source like other flammable gases.
5. Currently, the United Nations's Recommendations on the Transport of Dangerous Goods – Model Regulations identifies these gases as Class 2, Division 2.1 flammable gases. The hazards of these gases are addressed for transport through TDG packaging requirements and TDG packing instruction P200.
6. Likewise, under the GHS, pyrophoric gases are classified as Category 1 flammable gases, and labels for such chemicals must bear the flame pictogram, the danger signal word, and contain the hazard statement “Extremely flammable gas.”
7. However, these label elements do not provide a warning that the gas will ignite spontaneously when exposed in air. As described in more detail in INF.51 (TDG 43rd session) – INF.15 (GHS, 25th session), a number of workers handling such gases in the workplace have been killed or injured because they did not know of this hazard.
8. Since pyrophoric gases are classified as flammable gases by the TDG Sub-Committee, and to remain harmonized with the TDG, pyrophoric gases are proposed as a separate hazard category within the flammable gases hazard class (GHS chapter 2.2). They are not proposed as a sub-category within the flammable gas hazard class like that of chemically unstable gases.
9. The definition for pyrophoric gases is, “a *pyrophoric gas* is a substance or mixture in a gaseous state that will ignite spontaneously in air at a temperature of 54.4 °C (130 °F) or below.” The use of the term spontaneous in the definition means that ignition begins without an ignition source. The temperature criterion is of longstanding use in the United States of America, and arrived at by agreement of the National Fire Protection Association (NFPA), the U.S. Department of Transportation, and the U.S. Occupational Safety and Health Administration (OSHA). It also represents an upper bound for the hazards associated with gas cylinder filling or other exposures in the workplace.
10. The current approach taken for flammable gas mixtures in the TDG includes a 1% cut-off value for pyrophoric gas mixtures. However, this 1% value establishes packaging requirements for transport and includes elements of risk. This risk-based approach is not appropriate for the workplace, as the GHS is based on hazards. In addition, the GHS physical hazard classes identify the physical effect of substances and mixtures. To remain consistent with the other GHS physical hazard class definitions, this proposal follows that same approach and the 1% cut-off value for pyrophoric gas mixtures is not included.
11. There are gases that are both chemically unstable and pyrophoric, e.g., diborane. Accordingly, paragraph 2.2.2.2 has been updated to indicate that pyrophoric gases can also be classified into one of the chemically unstable categories.
12. Spontaneous ignition for pyrophoric gases may be delayed, depending on the specific conditions of release (e.g., temperature, moisture, velocity of the release). A note about the potential delayed ignition is provided in the proposed amendments to Chapter 2.2 and may be added if appropriate.

Test methods

13. The European Union recommends the use of several methods to test the auto-ignition temperature of liquids and gases, specifically, IEC 79-4 (IEC 60079-4), DIN 51794, ASTM-E 659-78, BS 4056, NF T 20-037. The IEC standard has been withdrawn and replaced by IEC 60079-20-1 ed1.0 (2010-01). Several methods do not address gases; therefore, this proposal proposes the use of IEC 60079-20-1 Ed 1.0 (2010-01) and DIN 51794.

Proposed amendments to GHS

Amendments to Chapter 2.2

14. Amend GHS Chapter 2.2 as follows:

- (a) Amend the chapter title to read: “Flammable gases (including chemically unstable gases) and pyrophoric gases.”
- (b) In Section 2.2.1, Definitions, add a new sub-section 2.2.1.3 and the following corresponding text.

2.2.1.3 “A *pyrophoric gas* is a substance or mixture in a gaseous state that will ignite spontaneously in air at a temperature of 54.4 °C or below.”
- (c) Update the title to Table 2.2.1, to read: “Table 2.2.1: Criteria for flammable and pyrophoric gases”
- (d) In Table 2.2.1, insert a new row at the end to include the following criteria for pyrophoric gases:

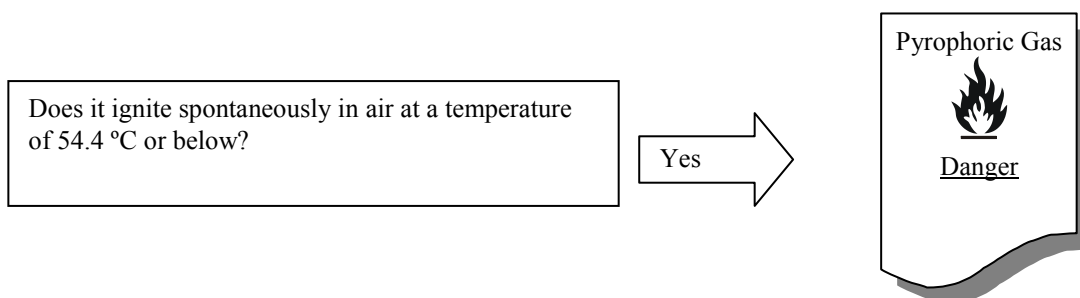
Pyrophoric Gases	Gases which ignite spontaneously in air at a temperature of 54.4 °C or below.
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- (e) Insert a new Note (Note 3) after Table 2.2.1 to read as follows:

“**NOTE 3:** *Pyrophoric gases should not be classified as flammable gases, category 1 or 2. Spontaneous ignition for pyrophoric gases is not always immediate, and there may be a delay.*”
- (f) In paragraph 2.2.2.2 insert “, in category 1 and 2, or pyrophoric gas which” after the words “A flammable gas”.
- (g) Update the title to Table 2.2.3 to read: “Table 2.2.3: Label elements for flammable gases (including chemically unstable gases) and pyrophoric gases”
- (h) Insert a new column for pyrophoric gas in Table 2.2.3, containing the following text:

	Pyrophoric Gas
Category	Pyrophoric Gas
Symbol	Flame
Signal word	Danger
Hazard statement	Catches fire spontaneously if exposed to air

- (i) Update the title to section 2.2.4.1 to read “*Decision logic for flammable and pyrophoric gases*”.
- (j) In the introductory text of Section 2.2.4.1, insert a new sentence after the first sentence that reads: “To classify a pyrophoric gas, data on its ability to ignite if exposed to air is required.”
- (k) Update the decision logic 2.2(a) by inserting an additional decision immediately following “Gaseous substance or mixture of gases”. The inserted logic is presented below.





15. Insert a new paragraph 2.2.4.3.3, to read as follows:
- “2.2.4.3.3 Pyrophoricity should be determined by tests in accordance with any of the following methods:
- IEC 60079-20-1 ed1.0 (2010-01)
DIN 51794

Amendments to Annex 1

16. Amend Annex 1 as follows:
- (a) Update the title of A1.2 by inserting the text “and pyrophoric gases” after the parenthetical phrase “including chemically unstable gases”.
 - (b) In the table A1.2, update the title of the hazard class by inserting the text “and pyrophoric gases” after the parenthetical phrase “including chemically unstable gases”.
 - (c) In the table A1.2, insert a new row to identify the communication elements for pyrophoric gases, as shown below:

Classification		Labelling				Hazard statement codes
Hazard class	Hazard category	Pictogram		Signal word	Hazard statement	
		GHS	UN Model Regulations ^a			

Classification		Labelling			Hazard statement codes
Hazard	Hazard	Pictogram		Signal word	
Flammable gases (including chemically unstable gases) and pyrophoric gases	Pyrophoric gas			Danger	Catches fire spontaneously if exposed to air
					H250

Amendments to Annex 3

17. Amend Annex 3 as follows:

- (a) In Section 1, update the hazard class assignment of hazard statement H250 in Table A3.1.1 to include “Flammable gases and pyrophoric gases (chapter 2.2)”.
- (b) In Section 1, update the hazard category assignment of hazard statement H250 in Table A3.1.1 to include “Pyrophoric gas” and clarify the hazard category assigned to pyrophoric liquids and pyrophoric solids is category 1.
- (c) In Section 2, Table A3.2.2, update the hazard class, hazard category, and conditions for use assignments of precautionary statements P210, P222, P233, and P280. The hazard class for each should be updated to add “Flammable gases and pyrophoric gases (chapter 2.2)”. The hazard category for each should be updated to add “Pyrophoric gas”. The conditions for use for each precautionary statement should be updated to add the same conditions for use as applied to pyrophoric liquids and solids.
- (d) In Section 2, Table A3.2.3, update the hazard class, hazard category, and conditions for use assignments of precautionary statements P370, P378, and P370+P378. The hazard class for each should be updated to add “Flammable gases and pyrophoric gases (chapter 2.2)”. The hazard category for each should be updated to add “Pyrophoric gas”. The conditions for use for each precautionary statement should be updated to add the same conditions for use as applied to pyrophoric liquids and solids.
- (e) In Section 3, Section A3.3.5, update the matrix showing the applicable precautionary statements for pyrophoric gases, to update the title of the flammable gases matrixes to read “FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE GASES) and PYROPHORIC GASES (Chapter 2.2)”
- (f) In Section 3, Section A3.3.5, update the matrix showing the applicable precautionary statements for pyrophoric gases, by inserting a new matrix for pyrophoric gases, as shown in the following:

FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE GASES) AND PYROPHORIC GASES

(CHAPTER 2.2)

(Pyrophoric gases))

Symbol
Flame



Hazard category

Pyrophoric gas

Signal word

Danger

Hazard statement

H250 Catches fire spontaneously if exposed to air

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>P222 Do not allow contact with air. – <i>if emphasis of the hazard statement is deemed necessary.</i></p> <p>P233 Keep container tightly closed.</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection. Manufacturer/supplier or the competent authority to specify the appropriate type of equipment.</p>	<p>P370 + P378 In case of fire: Use ... to extinguish – <i>if water increases risk.</i> ...Manufacturer/supplier or the competent authority to specify appropriate media.</p>		