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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

#### Fifty-eighth session

Geneva, 28 June-2 July 2021

Item 3 of the provisional agenda

#### Listing, classification and packing

## Proposal to create UN Numbers for pyrophoric gases and add criteria for pyrophoric gases in Division 2.1

### Transmitted by the Compressed Gases Association (CGA) and European Industrial Gases Association (EIGA)\*,\*\*

## Background

1. In 2017, CGA and EIGA submitted document ST/SG/AC.10/C.3/2017/43 for consideration by the Sub-Committee at its December session. The proposal aimed to create a UN number for disilane and UN numbers for pyrophoric gases as well as to add criteria for pyrophoric gases into Division 2.1 of the UN Model Regulations.
2. There was general support for the proposal, and it was agreed that an amended proposal would be submitted to the Sub-Committee. This document revises the original proposal taking into account technical and editorial amendments received during the 2017 session.
3. Whilst packing instruction P200 (5) q on *gas specific provisions* and (5) z on *requirements for N.O.S. descriptions and for mixtures* make reference to pyrophoric gases, pyrophoric gases are not identified in the Dangerous Goods List of the UN Model Regulations.
4. Furthermore, pyrophoric gases are not defined in Chapter 2.2 on *Class 2-Gases* and were only recently defined in Chapter 2.2 on *flammable Gases* of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).
5. CGA and EIGA members and others have become increasingly concerned that the pyrophoric hazard for pyrophoric gases and gas mixtures together with disilane are not identified in the UN Model Regulations.

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\* A/75/6 (Sect.20), para. 20.51

\*\* This document was scheduled for publication after the standard publication date owing to circumstances beyond the submitter's control.

6. Disilane (Chemical Abstracts Service Registry Number 1590-87-0) is a pyrophoric liquefied gas under pressure. At atmospheric pressure, it boils at -14.3 °C and its vapour pressure at 20 °C is 2.3 bar. Furthermore, it is spontaneously flammable in air.
7. A generic number is used for the transport of disilane, (UN 3161). The proper shipping name is Liquefied Gas, Flammable, N.O.S. (Disilane) as there is no specific UN number for disilane. This generic UN number only partially reflects its flammability properties. As with silane (UN 2203), disilane is pyrophoric, and silane is forbidden for transport by air freight, both in cargo and passenger aircraft. All other pyrophoric materials in the UN Model Regulations are forbidden for transport by air freight, in cargo and passenger aircraft.
8. As there is no identification for pyrophoric gases at the present in the Dangerous Goods List, for mixtures that are flammable and pyrophoric, they can be classified as UN 1954 COMPRESSED GAS, FLAMMABLE, N.O.S. and may thus be transported by cargo aircraft.
9. CGA and EIGA wish to see the hazard identification of disilane, and pyrophoric mixtures clarified so that there is no possibility of these products being transported by air.
10. CGA and EIGA propose to introduce in Chapter 2.2 the criteria adopted in the GHS for pyrophoric gases and to create the necessary new N.O.S. entries for the pyrophoric mixtures transported and for pure pyrophoric gases not yet listed in the Dangerous Goods List. In addition, add a subsidiary hazard of Division 4.2 on *substances liable to spontaneous combustion* to UN 1911, Diborane, UN 2199, Phosphine and UN 2203, Silane.
11. There are six proposals:
  - (i) Add into Chapter 2.2 of the UN Model Regulations the criteria for pyrophoric gases as adopted in the GHS;
  - (ii) Modify 2.4.3.1, Definitions and properties;
  - (iii) Add in 2.4.3.2, Classification on Division 4.2 a new paragraph;
  - (iv) Add into the Dangerous Goods List new entries for disilane and N.O.S. entries for gases that are pyrophoric which are currently not listed;
  - (v) Add into the packing instruction P200 new entries for disilane and N.O.S. entries for gases that are pyrophoric which are currently not listed;
  - (vi) Add a subsidiary hazard of Division 4.2, Substances liable to spontaneous combustion to UN 1911, Diborane, UN 2199, Phosphine and UN 2203, Silane.

## Proposal 1

12. The original proposal 1 has been modified to include a sentence, taken from 2.2.4.2.2 of the GHS aimed at easing the determination of pyrophoricity, as follows:

In 2.2.2.1 (a) add after the existing text the following paragraph:

“A flammable gas is additionally classified as pyrophoric if it ignites spontaneously in air at a temperature of 54 °C or below. Pyrophoricity should be determined at 54 °C in accordance with either IEC 60079-20-1 ed 1.0 (2020-01) “Explosive atmospheres – Part 20-1: Material characteristics for gas and vapor classification – Test methods and data” or DIN 51794 “Determining the ignition temperature of petroleum products”. 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).”

## Proposal 2

13. In 2.4.3.1, Definitions and properties, amend 2.4.3.1.1 (a) as follows (new text is underlined):

“(a) Pyrophoric substances, which are substances, including mixtures and solutions (liquid or solid), which even in small quantities ignite within five minutes of coming in contact with air. Pyrophoric substances are also gases that meet the requirements for pyrophoricity, see 2.2.2.1 (a). These are the Division 4.2 substances the most liable to spontaneous combustion; and”

## Proposal 3

14. In 2.4.3.2, Classification on Division 4.2, add a new paragraph 2.4.3.2.3 (new text underlined) as follows and renumber the existing 2.4.3.2.3 as 2.4.3.2.4:

“2.4.3.2.3 Gases are considered pyrophoric gases which shall be classified in Division 4.2 if, in tests performed in accordance with the test method given in 2.2.2.1 (a), the gas ignites spontaneously in air at a temperature of 54 °C or below.”

## Proposal 4

15. In 3.2, Dangerous Goods Lists, insert the following new entries to identify disilane and unlisted pyrophoric gases and pyrophoric gas mixtures (it is noted that some pyrophoric gases, e.g. phosphine, are toxic and the combination toxic and flammable should be used):

UN No.	Name and description	Class or division	Subsidiary hazard	UN packing group	Special provisions	Limited and excepted quantities		Packagings and IBCs		Portable tanks and bulk containers	
						(7a)	(7b)	Packing instruction	Special packing provisions	Instructions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
-	3.1.2	2.0	2.0	2.0.1.3	3.3	3.4	3.5	4.1.4	4.1.4	4.2.5 / 4.3.2	4.2.5
xxxx	DISILANE	2.1	4.2			0	E0	P200			
xxxx	COMPRESSED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2			0	E0	P200			
xxxx	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2			0	E0	P200			
xxxx	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8			0	E0	P200			
xxxx	LIQUEFIED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2			0	E0	P200			
xxxx	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2			0	E0	P200			
xxxx	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8			0	E0	P200			

## Proposal 5

16. In 4.1.4.1, packing instruction P200, insert the following new entries (based on former proposal 3 which has been amended to include LC<sub>50</sub> toxic gases):

P200 PACKING INSTRUCTION (cont'd) P200													
Table 1: COMPRESSED GASES													
UN No.	Name and description	Class or Division	Subsidiary hazard	LC <sub>50</sub> ml/m <sup>3</sup>	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar <sup>a</sup>	Maximum working pressure, bar <sup>a</sup>	Special packing provisions
xxxx	COMPRESSED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2		X	X	X	X	X	10			q, z
xxxx	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2	≤ 5000	X	X	X	X	X	5			q, z
xxxx	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8	≤ 5000	X	X	X	X	X	5			q, z

P200 PACKING INSTRUCTION (cont'd) P200													
Table 2: LIQUEFIED GASES AND DISSOLVED GASES													
UN No.	Name and description	Class or Division	Subsidiary hazard	LC <sub>50</sub> ml/m <sup>3</sup>	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar	Filling ratio	Special packing provisions
xxxx	DISILANE	2.1	4.2		X	X	X	X		10	225	0.39	q
xxxx	LIQUEFIED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2		X	X	X	X		10			q, z
xxxx	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2	≤ 5000	X			X		5			q, z
xxxx	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8	≤ 5000	X			X		5			q, z

17. Annex 1 includes a datasheet for disilane.

18. The filling ratio of disilane has been developed from P200 3 (c) as there is no published data available (see Annex 2).

## Proposal 6

19. In 3.2, Dangerous Goods Lists, and in 4.1.4.1 for packing instruction P200 add the subsidiary hazard of Division 4.2, Substances liable to spontaneous combustion, in column (4) of UN 1911, DIBORANE, UN 2199, PHOSPHINE and UN 2203, SILANE as follows (new entry is underlined):

UN No.	Name and description	Class or division	Subsidiary hazard	UN packing group	Special provisions	Limited and excepted quantities		Packagings and IBCs		Portable tanks and bulk containers	
						(7a)	(7b)	Packing instruction	Special packing provisions	Instructions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
-	3.1.2	2.0	2.0	2.0.1.3	3.3	3.4	3.5	4.1.4	4.1.4	4.2.5 / 4.3.2	4.2.5
1911	DIBORANE	2.3	2.1 <u>4.2</u>			0	E0	P200			
2199	PHOSPHINE	2.3	2.1 <u>4.2</u>			0	E0	P200			
2203	SILANE	2.1	<u>4.2</u>			0	E0	P200			

P200 PACKING INSTRUCTION (cont'd)													
Table 2: LIQUEFIED GASES AND DISSOLVED GASES													
UN No.	Name and description	Class or Division	Subsidiary hazard	LC <sub>50</sub> ml/m <sup>3</sup>	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar	Filling ratio	Special packing provisions
1911	DIBORANE	2.3	2.1, <u>4.2</u>	80	X			X		5	250	0.07	d, k, o
2203	SILANE	2.1	<u>4.2</u>		X	X	X	X	X	10	225 250	0.32 0.36	q q
2199	PHOSPHINE	2.3	2.1, <u>4.2</u>	20	X			X		5	225 250	0.30 0.45	d, k, q

## Safety implications

20. No safety implications are foreseen, and CGA and EIGA are of the opinion that safety in the transport of the above pyrophoric gases will be enhanced.

## Annex I

### Data sheet to be submitted to the United Nations for new or amended classification or substances

Submitted by CGA and EIGA

Date: 5 February 2021

Supply all relevant information including sources of basic classification data. Data should relate to the production the form to be transported. State test methods. Answer all questions - if necessary state "not known" or "not applicable" - If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

#### Section 1. SUBSTANCE IDENTITY

1.1 Chemical name: **DISILANE**

1.2 Chemical formula: **Si<sub>2</sub>H<sub>6</sub>**

1.3 Other names/synonyms: **Disilicon hydride**

1.4.1 UN number: **3161 Liquefied Gas, Flammable, N.O.S. (Disilane). Current number used for transport)**

1.4.2 CAS number: **1590-87-0**

1.5 Proposed classification for the Recommendations

1.5.1 proper shipping name: **DISILANE**

1.5.2 class/division: **2.1** subsidiary risk(s): **pyrophoric** Packing group: **not applicable**

1.5.3 proposed special provisions, if any: **Forbidden for air transport**

1.5.4 proposed packing instruction(s): **P200**

#### Section 2. PHYSICAL PROPERTIES

2.1 Melting point or range: **-133 °C**

2.2 Boiling point or range: **-14.3 °C**

2.3 Relative density at:

2.3.1 15 °C: **0.675 (no data available on temperature)**

2.3.2 20 °C: **no data available**

2.3.3 50 °C: **no data available**

2.4 Vapour pressure at:

2.4.1 50 °C: **7.4 bar(a) or 740 kPa**

2.4.2 65 °C: **no data available**

2.5 Viscosity at 20 °C: **not applicable**

2.6 Solubility in water at 20 °C: **completely soluble**

2.7 Physical state at 20 °C: **gas**

2.8 Appearance at normal transport temperatures, including colour and odour: **colourless, mouldy odour**

2.9 Other relevant physical properties

#### Section 3. FLAMMABILITY

3.1 Flammable vapour

3.1.1 Flash point (2.3.3'): **not applicable for gases and gas mixtures**

3.1.2 Is combustion sustained? (2.3.1.3") **not applicable for gases and gas mixtures**

3.2 Autoignition temperature: **-50 °C**

3.3 Flammability range (LEL/UEL): **(Pyrophoric)**

3.4 Is the substance a flammable solid? (2.4.2<sup>1</sup>): **no**

#### **Section 4. CHEMICAL PROPERTIES**

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity? **no**

4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1<sup>1</sup>): **no**

4.3 Is the substance a desensitized explosive? (2.4.2.4<sup>1</sup>): **no**

4.4 Is the substance a self-reactive substance? (2.4.1<sup>1</sup>): **no**

4.5 Is the substance pyrophoric? (2.4.3<sup>1</sup>): **yes**

4.5.1 If yes, give details: **this substance is not a liquid or solid. The substance ignites spontaneously in air as silane (UN 2203)**

4.6 Is the substance liable to self-heating? (2.4.3<sup>1</sup>): **no**

4.7 Is the substance an organic peroxide? (2.5.1<sup>1</sup>): **no**

4.8 Does the substance in contact with water emit flammable gases? (2.4.4<sup>1</sup>): **no**

4.9 Does the substance have oxidizing properties? (2.5.1<sup>1</sup>): **no**

4.10 Corrosivity (2.8<sup>1</sup>): **this substance is not known to be corrosive**

4.11 Other relevant chemical properties: **no data available**

#### **Section 5. HARMFUL BIOLOGICAL EFFECTS**

5.1 LD50, oral (2.6.2.1.1<sup>1</sup>): **this substance is not known to be toxic by ingestion**

5.2 LD50, dermal (2.6.2.1.2<sup>1</sup>): **this substance is not known to be toxic by contact with the skin**

5.3 LC50, inhalation (2.6.2.1.3<sup>1</sup>): **this substance is not known to be toxic by inhalation**

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3): **this substance is completely gaseous at 20°C**

5.5 Skin exposure (2.8<sup>1</sup>) results: **this substance is not known to be toxic by contact with the skin**

5.6 Other data: **no data available**

5.7 Human experience: **no data available**

#### **Section 6. SUPPLEMENTARY INFORMATION**

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents) **Shutting off the source of the gas is the preferred method of control. If this is not possible, do not extinguish; cool point of release with a water spray or fog being careful not to extinguish flame.**

6.1.2 Spillage: **Keep area evacuated and free from ignition sources until any spilled liquid has evaporated (ground free from frost). Dust deposited can be vacuum cleaned or the area hosed down with water.**

6.2 Is it proposed to transport the substance in:

6.2.1 Bulk Containers (6.8<sup>1</sup>): **no**

6.2.2 Intermediate Bulk Containers (6.5<sup>1</sup>): **no**

6.2.3 Portable tanks (6.7<sup>1</sup>): **no**

If yes, give details in Sections 7, 8 and/or 9.

**Section 7. BULK CONTAINERS (only complete if yes in 6.2.1)**

7.1 Proposed type(s): **Not applicable**

**Section 8. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.2)**

8.1 Proposed type(s): **Not applicable**

**Section 9. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.3)**

9.1 Description of proposed tank (including IMO tank type if known): **Not applicable**

9.2 Minimum test pressure: **Not applicable**

9.3 Minimum shell thickness: **Not applicable**

9.4 Details of bottom openings, if any: **Not applicable**

9.5 Pressure relief arrangements: **Not applicable**

9.6 Degree of filling: **Not applicable**

9.7 Unsuitable construction materials: **Not applicable**



## Annex II

### Filling Ratio of Disilane

As there is no data available for the filling ratio of disilane it has been developed from P200 3 (c) for low pressure liquefied gases and gas mixtures for which relevant data are not available, the maximum filling ratio shall be determined as follows:

$$FR = (0.0032 \times BP) - 0.24 \times d_1$$

Where FR= maximum filling ratio,  
BP= Boiling Point (in Kelvin),  
d<sub>1</sub>= density of the liquid at boiling point (in kg/l).

For disilane

Boiling point in Kelvin =  $(273.15 + (-14.3)) = 258.85 \text{ K}$

Density (d<sub>1</sub>) = 0.675

$$FR = ((0.0032 \times 258.85) - 0.24) \times 0.675$$

This gives a filling ratio of 0.397, which has been rounded down to 0.39.