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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-second session Geneva, 27 November-6 December 2017 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 Gas Association (CGA) and the European Industrial Gases Association (EIGA)*

Background

1. The packing instruction P200 in section 4.1.4 outlines in (5) q Gas Specific Provisions for "pyrophoric gases and mixtures containing more than 1% of pyrophoric compounds". Pyrophoric gases are not identified as such in the Dangerous Goods List of the Model Regulations.

2. Pyrophoric gases are not defined in Chapter 2.2 *Class 2-Gases* and were only recently defined in Chapter 2.2 *Flammable Gases* of the GHS.

3. 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 already listed in the Dangerous Goods List.

4. CGA and EIGA members have become concerned that the pyrophoric hazard for pyrophoric gas mixtures and disilane are not identified.

^{*} In accordance with the programme of work of the Sub-Committee for 2017-2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, paragraph 98 and ST/SG/AC.10/44, paragraph 14)

5. Disilane (CAS RN 1590-87-0) is a pyrophoric liquefied gas under pressure. At atmospheric pressure, it boils at 14°C and its vapour pressure at 20°C is 2.3 bar. Furthermore, it is spontaneously flammable in air.

6. A generic number is used for its transport (UN 3161) and its 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 aircrafts. All other pyrophoric materials in UN Model Regulations are forbidden for transport by air freight, in cargo and passenger aircrafts.

7. As there is no identification for pyrophoric gases (or disilane) at 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.

8. 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.

9. There are four proposals:

(i) To add into the UN Model Regulations Chapter 2.2 the criteria for pyrophoric gases as adopted in the GHS;

(ii) To add into the Dangerous Goods List new entries for disilane and N.O.S. entries that are pyrophoric which are not currently listed;

(iii) To add into the Packing Instruction P200 new entries for disilane and N.O.S. entries that are pyrophoric which are not currently listed;

(iv) To add a subsidiary hazard of Division 4.2, Substances liable to spontaneous combustion to UN 1911, Diborane, UN 2199, Phosphine and UN 2203, Silane.

Proposals

Proposal 1

10. To add after the existing text in 2.2.2.1 (a) 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. 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

11. To create new entries in the Dangerous Goods list to identify disilane and unlisted pyrophoric gases and pyrophoric gas mixtures. It should be noted that some pyrophoric gases, for example, phosphine are toxic and the combination toxic and flammable should be used.

UN		Class	Subsi-	UN	Special	Limit	ed and	Packagings	and IBCs	Portable tanks and bulk containers		
No.	Name and description	or division	diary hazard	packing group	provi- sions		epted ntities	Packing instruction	Special packing provisions	Instruc- tions	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				
	COMPRESSED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2			0	E0	P200				
	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2			0	E0	P200				
	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8			0	E0	P200				
	LIQUEFIED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2			0	E0	P200				
	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2			0	E0	P200				
	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8			0	E0	P200				

Proposal 3

12. To add into the list of Packing Instruction under 4.1.4.1 P200, the following new entries

P200			PACE	KING INST	FRUC	TION (cont'd)						P200
			Table	e 1: COMP	RESSE	ED GAS	SES						
UN No.	Name and description	Class or Division	Subsidiary hazard	LCs0 ml/m ³	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar ^a	Maximum working pressure, bar ^a	Special packing provisions
XXXX	COMPRESSED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2		Х	Х	Х	X	Х	10			q, z
XXXX	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2		Х			X		5			q, z
XXXX	COMPRESSED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8		X			Х		5			q, z

P200		P	ACKI	NG INST	RUC	FION	(cont	t'd)					P200
	Table 2	: LIQU	EFIEI) GASES	AND	DISS	OLV	ED G	ASES	5			
UN No.	Name and description	Class or Division	Subsidiary hazard	LC ₅₀ ml/m ³	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		Х	Х	Х	Х		10	225 250	0.32 0.36	q
XXXX	LIQUEFIED GAS, FLAMMABLE, PYROPHORIC, N.O.S.	2.1	4.2		Х	Х	Х	Х		10			q, z
XXXX	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, N.O.S.	2.3	2.1, 4.2		Х			Х		5			q, z
XXXX	LIQUEFIED GAS, TOXIC, FLAMMABLE, PYROPHORIC, CORROSIVE, N.O.S.	2.3	2.1, 4.2, 8		Х			Х		5			q, z

13. Appendix 1 includes a datasheet for disilane.

Proposal 4

14. In the Dangerous Goods List and the Packing Instruction, add the subsidiary hazard of Division 4.2, Substances liable to spontaneous combustion, to UN 1911, DIBORANE, UN 2199, PHOSPHINE and UN 2203, SILANE to align with the new entry for disilane.

P200			PACE	KING INST	RUCI	TION (cont'd)						P200
			Table	e 1: COMP	RESSE	ED GAS	SES						
UN No.	Name and description	Class or Division	Subsidiary hazard	LC ₅₀ ml/m ³	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar ^a	Maximum working pressure, bar ^a	Special packing provisions
XXXX	DISILANE	2.1	4.2		Х	Х	Х	Х		10	225 250	0.32 0.36	q
2203	SILANE	2.1	4.2		Х	Х	Х	Х		10			q
1911	DIBORANE	2.3	2.1, 4.2	80	Х			Х		5	250	0.07	d, k, o
2199	PHOSPHINE	2.3	2.1, 4.2	20	Х			Х		5	225 250	0.30 0.45	d, k, q

P200		P	ACKI	NG INST	RUC	ΓΙΟΝ	(con	t'd)					P200
	Table 2	2: LIQU	EFIEI) GASES	AND	DISS	OLV	ED G	ASES	5			
UN No.	Name and description	Class or Division	Subsidiary hazard	LC ₅₀ ml/m ³	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	Х	Х	Х		10	225 250	0.32 0.36	q
2203	SILANE	2.1	4.2		X	X	X	Х		10			q
1911	DIBORANE	2.3	2.1, 4.2	80	X			X		5	250	0.07	d, k, o
2199	PHOSPHINE	2.3	2.1, 4.2	20	X			X		5	225 250	0.30 0.45	d, k, q

Safety implications

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

Annex

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

Submitted by: CGA and EIGA

Date: 31 August 2017

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: Si2H6
- 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): none 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: 2.2 (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): 1.37 - 96 vol % (Pyrophoric)

3.4 Is the substance a flammable solid? $(2.4.2^1)$: 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^{1}) : no

4.3 Is the substance a desensitized explosive? $(2.4.2.4^{1})$: no

4.4 Is the substance a self-reactive substance? $(2.4.1^1)$: no

4.5 Is the substance pyrophoric? $(2.4.3^{1})$: 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? $(2.4.3^1)$: no

4.7 Is the substance an organic peroxide? $(2.5.1^{1})$: no

4.8 Does the substance in contact with water emit flammable gases? $(2.4.4^{1})$: no

4.9 Does the substance have oxidizing properties? $(2.5.1^{1})$: no

4.10 Corrosivity (2.8¹): 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 (2.6.2.1.1¹): this substance is not known to be toxic by ingestion

5.2 LD50, dermal (2.6.2.12¹): this substance is not known to be toxic by contact with the skin

5.3 LC50, inhalation (2.6.2.1.3¹): 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 (2.8^1) 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 (6.8^1) : **no**

6.2.2 Intermediate Bulk Containers (6.5¹): **no**

6.2.3 Portable tanks (6.7¹): **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 filing: Not applicable

9.7 Unsuitable construction materials: Not applicable