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)\footnote{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)}

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.
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.
<table>
<thead>
<tr>
<th>UN No.</th>
<th>Name and description</th>
<th>Class or division</th>
<th>Subsidiary hazard</th>
<th>UN packing group</th>
<th>Special provisions</th>
<th>Limited and excepted quantities</th>
<th>Packagings and IBCs</th>
<th>Portable tanks and bulk containers</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.2</td>
<td>DISILANE</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0.1.3</td>
<td>3.3</td>
<td>3.4</td>
<td>3.5</td>
<td>4.1.4</td>
</tr>
<tr>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
<tr>
<td>3.1.2</td>
<td>COMPRESSED GAS, TOXIC,</td>
<td>2.1</td>
<td>2.1, 4.2</td>
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<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
<tr>
<td>2.3</td>
<td>COMPRESSED GAS, TOXIC,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
<tr>
<td>2.3</td>
<td>COMPRESSED GAS, TOXIC,</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
<tr>
<td>2.1</td>
<td>LIQUEFIED GAS, TOXIC,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
<tr>
<td>2.3</td>
<td>LIQUEFIED GAS, TOXIC,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E0</td>
<td>P200</td>
</tr>
</tbody>
</table>

**Proposal 3**

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

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<table>
<thead>
<tr>
<th>UN No.</th>
<th>Name and description</th>
<th>Class or Division</th>
<th>Subsidiary hazard</th>
<th>L.C. m³</th>
<th>Cylinders</th>
<th>Tubes</th>
<th>Pressure drums</th>
<th>Bundles of cylinders</th>
<th>MECs</th>
<th>Test period, years</th>
<th>Test pressure, bar</th>
<th>Maximum working pressure, bar</th>
<th>Special packing provisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>xxxx</td>
<td>COMPRESSED GAS, FLAMMABLE, PYROPHORIC,</td>
<td>2.1</td>
<td>4.2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>10</td>
<td>q, z</td>
<td></td>
<td>q, z</td>
</tr>
<tr>
<td>xxxx</td>
<td>N.O.S.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>xxxx</td>
<td>COMPRESSED GAS, TOXIC, FLAMMABLE,</td>
<td>2.1</td>
<td>4.2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>q, z</td>
<td></td>
<td>q, z</td>
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<tr>
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<td>PYROPHORIC, N.O.S.</td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>4.2, 8</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>q, z</td>
<td></td>
<td>q, z</td>
</tr>
<tr>
<td>xxxx</td>
<td>CORROSIVE, N.O.S.</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>
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.
Table 2: LIQUEFIED GASES AND DISSOLVED GASES

<table>
<thead>
<tr>
<th>UN No.</th>
<th>Name and description</th>
<th>Class or Division</th>
<th>Subsidiary hazard</th>
<th>L_C₅₀ m³</th>
<th>Cylinders</th>
<th>Tubes</th>
<th>Pressure drums</th>
<th>Bundles of Cylinders</th>
<th>MECCs</th>
<th>Test period, years</th>
<th>Test pressure, bar</th>
<th>Filling ratio</th>
<th>Special packing provisions</th>
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</thead>
<tbody>
<tr>
<td>xxxx</td>
<td>DISILANE</td>
<td>2.1</td>
<td>4.2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>10</td>
<td>225</td>
<td>250</td>
<td>0.32</td>
<td>q</td>
</tr>
<tr>
<td>2203</td>
<td>SILANE</td>
<td>2.1</td>
<td>4.2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>10</td>
<td></td>
<td></td>
<td>q</td>
<td></td>
</tr>
<tr>
<td>1911</td>
<td>DIBORANE</td>
<td>2.3</td>
<td>2.1, 4.2</td>
<td>80</td>
<td>X</td>
<td></td>
<td>X</td>
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<td>0.07</td>
<td></td>
<td>d, k, o</td>
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<tr>
<td>2199</td>
<td>PHOSPHINE</td>
<td>2.3</td>
<td>2.1, 4.2</td>
<td>20</td>
<td>X</td>
<td></td>
<td>X</td>
<td>5</td>
<td>225</td>
<td>250</td>
<td>0.30</td>
<td>0.45</td>
<td>d, k, q</td>
</tr>
</tbody>
</table>

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 (2.8.1): **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): **this substance is not known to be toxic by ingestion**

5.2 LD50, dermal (2.6.2.12): **this substance is not known to be toxic by contact with the skin**

5.3 LC50, inhalation (2.6.2.1.3): **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 (6.8¹): 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