

Committee of Experts on the Transport of Dangerous Goods  
and on the Globally Harmonized System of Classification  
and Labelling of Chemicals

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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

## Comments to the proposal to include pyrophoric gas in the GHS

### Transmitted by the European Industrial Gases Association (EIGA)

EIGA has the following comments to the proposal presented by the USA in documents ST/SG/AC.10/C.3/2013/69 – ST/SG/AC.10/C.4/2013/9

1. On pyrophoric gases to be as a separate hazard category and not as a sub-category within the flammable gas hazard class.

It would mean that all mixtures of pyrophoric gases that are not pyrophoric are not flammable. However binary mixtures with pyrophoric gases could be “flammable” (i.e. ignitable with a flame) without being “pyrophoric”. Pyrophoric gases have flammable characteristics (LEL, TCI) that are taken into account when deciding if a gas mixture containing flammable components (including pyrophoric) is flammable.

EIGA proposes to revise the chapter title as follows: **Chapter 2.2, Flammable gases (including chemically unstable gases and pyrophoric gases)**

2. On the auto-ignition temperature of 54.4°C as the criteria

The tests for pyrophoric liquids and solids are made at ambient temperature. If a higher temperature is requested, EIGA would take the rounded figure of 50°C that is a reference temperature in the definition of a gas in the GHS (...a substance which (i) at 50 °C has a vapour pressure .....).

EIGA proposes to use a similar wording as for the chemically unstable gases to introduce the criteria

**2.2.2.3** A flammable gas is additionally classified as pyrophoric if it meets the following criteria

Table 2.2.3 Criteria for pyrophoric gases

| Category       | Criteria   |
|----------------|--|
| Pyrophoric gas | A gas which ignites spontaneously in air at a temperature of 50 °C or below. |

3. On the absence of criteria for mixtures (item 10 of the proposal).

The absence of criteria infers that all mixture should be tested. Flammable gas mixtures are classified based on a calculation according to ISO 10156. Safe concentration limits have been defined for flammable mixtures containing “chemically unstable” components in section 35 of the Manual of Tests and Criteria. EIGA prefers to have a similar solution for flammable mixtures containing pyrophoric components and to define a safe concentration limit.

The limit of 1% that was selected in P200 of the Model Regulations is probably conservative for most pyrophoric gases (even for silane) but is currently used by the gases industry to classify mixtures both for transport and for the GHS.

Example: A 0.95% diborane mixture in nitrogen is shipped with a 2.1 flammable gas transport label but the phrase “May ignite spontaneously in contact with air” will only be mentioned in section 2.3 Other hazards of the SDS when the concentration is above 1% . EIGA prefers the wording using “May.....” that emphasizes that the reaction is not always taking place and that the explosive reaction of the mixture “pyrophoric gas-air” could be delayed as with any other flammable gas – air mixture.

EIGA proposes to introduce the criteria in a Note after the Table 2.2.3 as follows:

*“Note: In the absence of data on its auto-ignition temperature, a flammable mixture is classified as a pyrophoric gas if it contains more than 1% of pyrophoric component(s).”*

4. Hazard communication

A consequence to the above, Table 2.2.3 should be renumbered to Table 2.2.4 with a new column as follows:

**Table 2.2.4: Label elements for flammable gases (including chemically unstable and pyrophoric gases)**

|                         | Flammable gas           |                  | Chemically unstable gas                          |  | Pyrophoric Gas                                |
|-------------------------|-------------------------|------------------|--|--|---|
|                         | Category 1              | Category 2       | Category A                                       | Category B   | Pyrophoric Gas                                |
| <b>Symbol</b>           | Flame                   | <i>No symbol</i> | <i>No additional symbol</i>                      | <i>No additional symbol</i>  | <i>No additional symbol</i>                   |
| <b>Signal word</b>      | Danger                  | Warning          | <i>No additional signal word</i>                 | <i>No additional signal word</i>   | <i>No additional signal word</i>              |
| <b>Hazard statement</b> | Extremely flammable gas | Flammable gas    | May react explosively even in the absence of air | May react explosively even in the absence of air at elevated pressure and/or temperature | May ignite spontaneously in contact with air. |

5. Precautionary statements

As flammable gases, pyrophoric gases and gas mixtures will be assigned the relevant 4PS. EIGA agrees to add P222 *Do not allow contact with air* but is of the opinion that the proposed P233 *Keep container tightly closed* is aimed at solids and liquids. Due to their physical state, all gases should be kept in closed pressure receptacles.