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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

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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals : Miscellaneous

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

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Item 2 (g) of the provisional agenda

Classification criteria and hazard communication: Miscellaneous

Pyrophoric gas: proposal to include pyrophoric gas as a new hazard in the GHS

Transmitted by the expert from the United States of America

Introduction

1. Pyrophoric gases are a workplace hazard that have caused loss of life, injuries and significant damage to workplaces. Although pyrophoric gases generally fall into the flammable gas category and are subject to the corresponding components of the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals (GHS), a distinction between a flammable gas and a pyrophoric gas is not currently made within the GHS.

2. All pyrophoric gases are covered under the flammable gas hazard class, but the hazard statement is considered not to be sufficient to communicate the hazard posed by pyrophoric gases.

3. 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 are packaged in such way so that they are not exposed to air. However, since the Sub-Committee of Experts on the TDG (TDG Sub-Committee) is the focal point for the physical hazards, the expert from the United States of America is also requesting the Sub-committee's views on this proposal.

4. This paper presents some background on the topic, discusses the issues, and presents a proposal for including the hazard in the GHS.

Accident history

5. Silane is the most commonly used pyrophoric gas, resulting in a number of industrial accidents. A 2010 article in Scientific American1 identified several incidents involving silane, including those listed below.

(a) On November 23, 2005 in Taiwan, a silane release in a gas cabinet, exploded and killed a worker. The release ruptured the gas cabinet, igniting a blaze that ripped through the factory, releasing other silane and ammonia cylinders.

(b) In 2007, in Bangalore, India, a silane explosion decapitated a worker and threw his body through a brick wall.

6. The article in *Scientific American* also quoted Eugene Ngai, a retired chemical engineer and well-known silane expert: "Of all the toxic or reactive molecules that [solar] industry uses, silane has been involved in 10 fatalities in the last 20 years. All the others put together, it's been zero."

7. In other incidents, silane was released into a gas cabinet without immediate ignition and exploded after a delay. These incidents include one fatality in Germany (1976), and three separate incidents in Japan (1989, 1990, and 1996), which resulted in a total of three fatalities, and four injuries.

Background

8. The U.S. Occupational Safety and Health Administration's (OSHA's) Hazard Communication Standard has covered pyrophoric gases in the workplace since the 1980s. It is defined as "a substance or mixture in a gaseous state that will ignite spontaneously in air at a temperature of 54.4 ºC (130 ºF) or below." Pyrophoric gases are common in the semiconductor/electronics industries. Examples of these gases and their associated industries include:

- Arsine – semiconductors
- Diborane – electronics
- Dicobalt octacarbonyl - oxo synthesis catalyst (aldehydes to alkenes)
- Diphosphane – lab chemical synthesis
- Nickel carbonyl – by-product of nickel purification
- Phosphine – metal catalyst, insecticide
- Silane - semiconductors, medical adhesive component (bio to inert surfaces; i.e., titanium to bone implants)

9. In the United States of America, the most commonly used gases (arsine, diborane, and silane) are used in closed systems in the workplace, in limited or small qualities, and are handled as a highly hazardous substance.

[1] http://www.scientificamerican.com/article.cfm?id=explosive-gas-silane-used-to-make-photovoltaics

Communication in other countries

10. Pyrophoric gases are most often transported as flammable gases in the United States of America, Canada and Germany, since all pyrophoric gases fulfil the criteria for classification as flammable gas. The gases are labelled with the flame pictogram. Several, such as arsine, may also be transported as flammable liquids.

11. In the German Technical Rules, clarifying text points out that in addition to being classified as flammable, some gases are also pyrophoric and that gases should be considered as pyrophoric when their auto-ignition temperature is below 100 °C. The German Technical Rules also state that mixtures containing a pyrophoric gas should be considered as pyrophoric if they contain 1 mole-percent or more of a pyrophoric component.

Issues

12. The workplace does not have a consistent means of identifying and communicating the hazards of pyrophoric gas. Specifically, the GHS does not include it as a hazard, nor does it identify appropriate label elements, including a signal word, pictogram, and hazard and precautionary statements for pyrophoric gases. However, the GHS does provide classification and label elements for the pyrophoric liquid and solid hazard classes.

13. OSHA recently updated its Hazard Communication Standard and included pyrophoric gas as an additional physical hazard. The Hazard Communication Standard requires that hazards associated with these gases be communicated to users, and includes a definition and label elements for pyrophoric gases.

14. It is anticipated that a consistent approach to communicating this hazard would be beneficial for safety. For example, currently some safety data sheets (SDSs) provide incomplete hazard information and do not inform the chemical user that the substance self-ignites when exposed to air.

15. To facilitate harmonization and ensure that these highly dangerous chemicals contain the appropriate hazard warnings, it is suggested that pyrophoric gases be addressed within the GHS to ensure information about this hazard is communicated in a consistent and harmonized fashion.

Proposal to include pyrophoric gases in the GHS

16. To facilitate harmonization of labelling and communication of the hazards associated with pyrophoric gases, the Sub-Committee is invited to consider in principle including pyrophoric gases as a new category in the flammable gas hazard class.

17. The draft proposed amendments to the GHS provided for discussion include revisions to Chapter 2.2, Flammable gases (including chemically unstable gases). The revisions include a change to the title of the chapter, a new definition, new classification criteria, and updated label elements for pyrophoric gases. The proposed amendments are presented below.

- **Revised chapter title**: Chapter 2.2, Flammable gases (including chemically unstable gases and pyrophoric gases)
- **Definition**: A *pyrophoric gas* is a substance or mixture in a gaseous state that will ignite spontaneously in air at a temperature of 54.4 ºC (130 ºF) or below.

- **Classification criteria**:

Criteria for pyrophoric gases

Category	Criteria
Pyrophoric Gas	A gas which ignites spontaneously in air at a temperature of 54.4 ºC (130 ºF) or below.

- **Label elements**: Current Table 2.2.3 would be revised to read as follows:

Table 2.2.3: 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**
Symbol	Flame	*No symbol*	*No additional symbol*	*No additional symbol*	Flame
Signal word	Danger	Warning	*No additional signal word*	*No additional signal word*	Danger
Hazard statement	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	Catches fire spontaneously if exposed to air

18. The Sub-committee is invited to provide feedback on the proposal. The feedback will be used to convert this informal proposal into a working document including all necessary editorial changes for approval at the next Sub-Committee session.