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 Globally Harmonized System of Classification and Labelling of Chemicals

28 November 2016

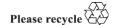
Thirty-second session
Geneva, 7-9 December 2016
Item 2 (g) of the provisional agenda
Classification criteria and related hazard communication:
miscellaneous

Proposal for a new chapter for chemicals under pressure

Submitted by the European Chemical Industry Council (CEFIC) and the European Industrial Gases Association (EIGA)

Introduction

- 1. Some years ago the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG Sub-committee) implemented new UN numbers for chemicals under pressure (UN3500 UN3505). These products function similarly to aerosol dispensers (UN 1950), but are packed in pressure receptacles (refillable and non-refillable) up to 450 litres. These UN-numbers are also used by the EIGA members to transport liquids that are packed under a head of pressure for inerting the product or to facilitate its transfer in the process lines (e.g. benzene under hydrogen pressure). With the implementation of GHS in more and more countries, the question came up, how these products need to be classified and labelled according to GHS.
- 2. Current GHS chapters do not appropriately cover the hazards associated with this product type, leading to confusion and possibly resulting in over- or under-classification of products. An assignment to existing chapters on flammable gases, liquids, or solids would potentially miss to communicate important hazards. For example, Chapter 2.3 does not recognize pressure receptacles like gas cylinder, it only describes aerosol cans.
- 3. Therefore CEFIC and EIGA proposed to introduce a new chapter into GHS to cover these type of products (document UN/SCEGHS/31/INF.11). During the Sub-Committee meeting in July 2016 the document was discussed and some questions were made, in particular about the possibility to include the classification of these products in existing chapters and to justify the cut-off values.
- 4. Chemicals under pressure used for spray applications present the same hazards as the uses of aerosol cans that could be considered as one of the packaging possibilities for chemicals under pressure. This approach has been taken in the proposal outlined in Annex I.
- 5. However, *chemicals under pressure* and *aerosols* are treated separately and differently in the TDG and in order to keep the consistency with the provisions in TDG requirements and the different test procedures for aerosols, a complete merge of the requirements is not possible and the proposed revised chapter 2.3 in Annex I looks lengthy and complicated. As an alternative a separate new chapter "chemicals under pressure" is proposed in Annex II.



- 6. The attached proposal contains 3 categories, 2 for extremely flammable and flammable chemicals under pressure and 1 for non-flammable chemicals under pressure with new related labelling requirements. With that it follows the structure, which is available for aerosols. The same applies for the labelling requirements, although new hazard statements need to be implemented as well.
- 7. In order to differentiate "chemical under pressure" from "gas mixtures" that may also contain liquid components, and to differentiate "liquids" under a low gas pressure head for inerting with the "chemical under (high) pressure, it is necessary to introduce some cut-off values.
 - (a) The components of "chemical under pressure" are "predominantly liquids or solids", while the components of gas mixtures are "predominantly gaseous".
 50% of liquids or solids is proposed as a cut-off value to differentiate chemical under pressure from gas mixtures.
 - (b) 2 bar (gage) is the minimum pressure used in chapter 2.5 Gases under pressure and is proposed as the cut-off value to differentiate Chemicals under pressure from liquids packed under a low pressure head of gas.
- 8. Subsequent changes to the annexes or other chapters of the GHS have not been taken into consideration at this point in time. They will be included in further proposals, when the way forward is clearer.

Annex I

Combined chapter "Aerosols and chemicals under pressure"

"CHAPTER 2.3

AEROSOLS AND CHEMICALS UNDER PRESSURE

"2.3.1 Definitions

- 2.3.1.1 Aerosols, this means aerosol dispensers, are any non-refillable receptacles made of metal, glass or plastics and containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in a gas, as a foam, paste or powder or in a liquid state or in a gaseous state.
- 2.3.1.2 Chemicals under pressure are substances or mixtures, containing 50% or more by mass of liquids, pastes or powders, pressurized with a propellant in a receptacle at a pressure of 200 kPa (gauge) or more at 20°C. The propellant (gas) can be a compressed, liquefied or dissolved gas under pressure.
- 2.3.1.3 Mixtures, containing less than 50% by mass of liquids, pastes or powders, shall be classified as gas mixtures or liquids depending on the pressure in the receptacles (see flowchart in 2.3.X).
- 2.3.1.4 Chemicals under pressure are typically used for spray applications. The receptacle needs to be connected to spray application equipment such as a hose and a wand assembly to allow the contents to be ejected as solid or liquid particles in suspension in a gas; as a foam, paste, or powder; or in a liquid state.

2.3.2 Classification criteria

- 2.3.2.1 Aerosols <u>and chemicals under pressure</u> shall be considered for classification as flammable in accordance with section 2.3.2.2 if they contain any component which is classified as flammable according to the following criteria set out in this section:
 - Liquids with a flash point ≤ 93 °C, which includes flammable liquids according to Chapter 2.6;
 - Flammable gases (see Chapter 2.2);
 - Flammable solids (see Chapter 2.7).
- **NOTE 1:** Flammable components do not cover pyrophoric, self-heating or water-reactive substances and mixtures because such components are never used as aerosol contents or as constituents in chemicals under pressure.
- NOTE 2: Aerosols <u>and chemicals under pressure</u> do not fall additionally within the scope of chapters 2.2 (flammable gases), 2.5 (gases under pressure), 2.6 (flammable liquids) and 2.7 (flammable solids). Depending on their contents, aerosols <u>and chemicals under pressure</u> may however fall within the scope of other hazard classes, including their labelling elements.
- 2.3.2.2 An aerosol is classified in one of the three categories for this class on the basis of its components, of its chemical heat of combustion and, if applicable, of the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test

(for spray aerosols) in accordance with decision logics 2.3.1 (a) to 2.3.1(c) in 2.3.4.1 and sub-sections 31.4, 31.5 and 31.6 of Part III of the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*. Aerosols which do not meet the criteria for inclusion in Category 1 or Category 2 shall be classified in Category 3.

NOTE: Aerosols containing more than 1% flammable components or with a heat of combustion of at least 20 kJ/g, which are not submitted to the flammability classification procedure in this chapter should be classified as aerosols, Category 1.

2.3.2.2.2 The category of the chemical under pressure is determined by the composition, the flammability of the components and the heat of combustion of the whole mixture (see decision logic 2.3.5.1).

2.3.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4.). Annex 1 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

	Aerosol			Chemical under pressure		
	Category 1	Category 2	Category 3	Category 1	Category 2	Category 3
Symbol	Flame	Flame	No symbol	Flame	Flame	Gas cylinder
Signal word	Danger	Warning	Warning	Danger	Warning	Warning
Hazard statement	Extremely flammable aerosol. Pressurized container: May burst if heated	Flammable aerosol. Pressurized container: May burst if heated	Pressurized container: May burst if heated	Extremely flammable. Chemical under pressure	Flammable. Chemical under pressure	Chemical under pressure

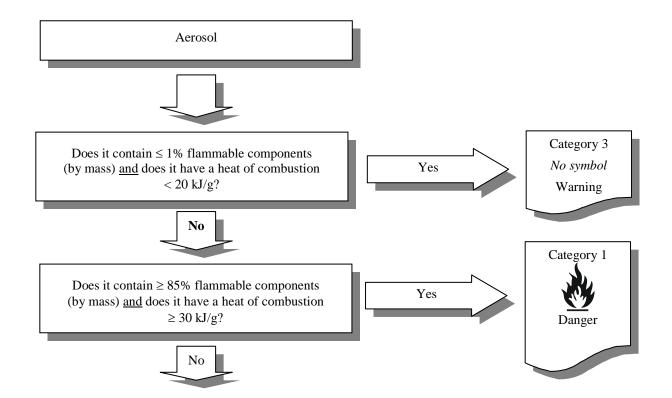
Table 2.3.1: Label elements for aerosols and chemicals under pressure

2.3.4 Decision logic and guidance for aerosols

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

2.3.4.1 Decision logic

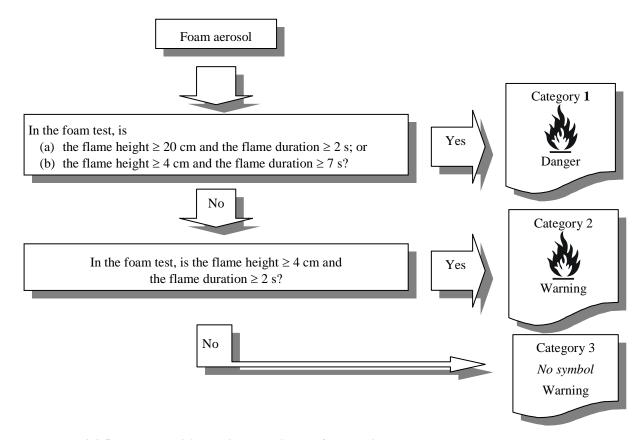
To classify an aerosol data on its flammable components, on its chemical heat of combustion and, if applicable, the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols) are required. Classification should be made according to the decision logic 2.3 (a) to 2.3 (c).



For spray aerosols, go to decision logic 2.3 (b); For foam aerosols, go to decision logic 2.3 (c);

Decision logic 2.3 (b) for spray aerosols Spray aerosol Category 1 In the ignition distance test, does ignition occur at a Yes distance ≥ 75 cm? Danger No Category 2 Does it have a heat of combustion < 20 kJ/g? No Warning Yes Category 2 In the ignition distance test, does ignition occur at a Yes distance ≥ 15 cm? Warning No Category 2 In the enclosed space ignition test, is: (a) the time equivalent $\leq 300 \text{ s/m}^3$; or Yes (b) the deflagration density $\leq 300 \text{ g/m}^3$? Warning No Category 3 No symbol Warning

Decision logic 2.3 (c) for foam aerosols



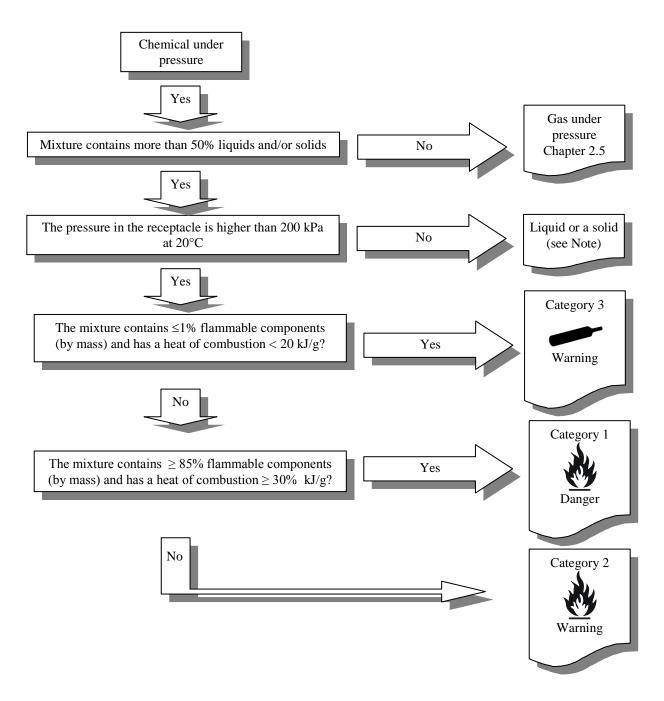
2.3.5 Decision logic and guidance for chemical under pressure

Mixture of liquids, pastes or powders under pressure may potentially be classified ascChemical under pressure, gas mixtures or liquids

For "Chemicals under pressure" their classification for flammability shall be based on the concentration in mass of the flammable components (gaseous, liquids or solids) and/or on the heat of combustion.

2.3.5.1 Decision logic

Decision logic 2.3.5.1 for mixtures made of one or more solids and/or liquids and one or more compressed or liquefied gases



NOTE: Liquid mixtures containing components, which are all classified as flammable liquids and flammable gases, should be classified as flammable liquid, Category I, if the content of liquefied flammable gases is \geq 5%.

2.3.5 Guidance

The chemical heat of combustion (ΔHc), in kilojoules per gram (kJ/g) is the product of the theoretical heat of combustion ($\Delta hcomb$) and the combustion efficiency, usually less than 1.0 (a typical efficiency is 0.95 or 95%).

For a composite formulation, the chemical heat of combustion is the summation of the weighted heats of combustion for the individual components, as follows:

$$\Delta Hc(product) = \sum_{i}^{n} [wi\% \times \Delta Hc(i)]$$

Where:

 Δ Hc = chemical heat of combustion (kJ/g);

wi% = mass fraction of component I in the product;

 Δ Hc(i)= specific heat of combustion (kJ/g) of component I in the product

The chemical heat of combustion can be found in the literature, calculated or determined by tests (see ASTM D 240, ISO/FDIS 13943:1999 (E/F) 86.1 to 86.3 and NFPA 30B."

Annex II

New chapter for chemicals under pressure

"Chapter 2.XX

CHEMICALS UNDER PRESSURE

2.XX.1 Definitions

Chemicals under pressure are substances or mixtures, containing 50% or more by mass of liquids, pastes or powders, pressurized with a propellant in a receptacle at a pressure of 200 kPa (gauge) or more at 20°C. The propellant (gas) can be a compressed, liquefied or dissolved gas under pressure.

Mixtures, containing less than 50% by mass of liquids, pastes or powders, shall be classified as gas mixtures or liquids depending on the pressure in the receptacles – see flowchart in 2.XX.4.

Chemicals under pressure are typically used for spray applications. The receptacle needs to be connected to spray application equipment such as a hose and a wand assembly to allow the contents to be ejected as solid or liquid particles in suspension in a gas; as a foam, paste, or powder; or in a liquid state.

A chemical under pressure in an aerosol dispenser shall be covered under Chapter 2.3 (Aerosols).

Flammable component means flammable solid, liquid or gas.

2.XX.2 Classification criteria

The chemical under pressure shall be classified based on the hazard characteristics of the components in the receptacle:

- · Propellant;
- · Liquid; and/or
- · Solid.

Flammable components are flammable liquids and liquid mixtures, flammable solids and solid mixtures, or flammable gases or gas mixtures meeting the following criteria:

- (i) A flammable gas is a gas which meets the criteria in 2.2 of these Regulations.
- (ii) A flammable solid is a solid which meets the criteria of 2.7 of these Regulations.
- (iii) A flammable liquid is a liquid which meets the criteria of 2.6 of these Regulations

The category of the chemical under pressure is determined by the flammability of the components and the heat of combustion of the whole mixture.

NOTE: Chemicals under pressure do not fall additionally within the scope of chapters 2.2 (flammable gases), 2.5 (gases under pressure), 2.6 (flammable liquids) and 2.7 (flammable solids). Depending on their contents, chemicals under pressure may however fall within the scope of other hazard classes, including their labelling elements.

2.XX.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in Hazard Communication: Labelling (Chapter 1.4). Annex 1 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authorities.

Table 2.XX: Label elements for chemical under pressure

	Chemical under Pressure				
	Category 1	Category 2	Category 3		
Symbol	Flame	Flame	Gas cylinder		
	Gas cylinder	Gas cylinder			
Signal word	Danger	Warning	Warning		
Hazard statement	Extremely flammable. Chemical under pressure	Flammable. Chemical under pressure	Chemical under pressure		

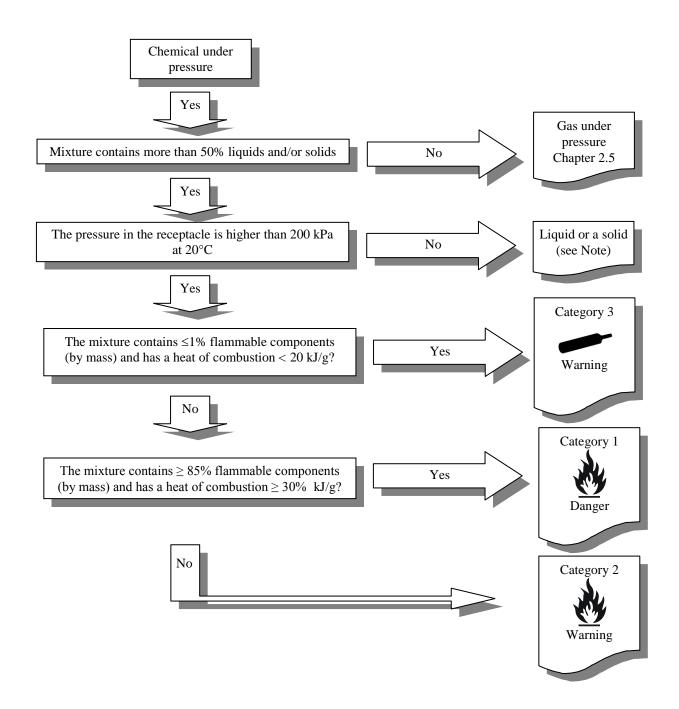
2.XX.4 Decision logic and guidance

Mixture of liquids, pastes or powders under pressure may potentially be classified as Chemical under pressure, gas mixtures or liquids

For "Chemicals under pressure" their classification for flammability shall be based on the concentration in mass of the flammable components (gaseous, liquids or solids) and/or on the heat of combustion.

2.XX.4.1 Decision logic

Decision logic 2.XX for mixture made of one or more solids and/or liquids and one or more compressed or liquefied gases



NOTE: Liquid mixtures containing components, which are all classified as flammable liquids and flammable gases, should be classified as flammable liquid, Category 1, if the content of liquefied flammable gases is $\geq 5\%$.

2.XX.4.2 Guidance

The chemical heat of combustion (Δ Hc), in kilojoules per gram (kJ/g) is the product of the theoretical heat of combustion (Δ Hcomb) and the combustion efficiency, usually less than 1.0 (a typical efficiency is 0.95 or 95%).

For a composite formulation, the chemical heat of combustion is the summation of the weighted heats of combustion for the individual components, as follows:

$$\Delta Hc(product) = \sum_{i}^{n} [wi\% \times \Delta Hc(i)]$$

Where:

 Δ Hc = chemical heat of combustion (kJ/g);

wi% = mass fraction of component I in the product;

 Δ Hc(i)= specific heat of combustion (kJ/g) of component I in the product

The chemical heat of combustion can be found in the literature, calculated or determined by tests (see ASTM D 240, ISO/FDIS 13943:1999 (E/F) 86.1 to 86.3 and NFPA 30B."