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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 Globally  
Harmonized System of Classification  
and Labelling of Chemicals  
(Sixth session, 10-12 December 2003,  
agenda item 2)

**PROPOSALS OF AMENDMENTS TO THE GLOBALLY HARMONIZED SYSTEM OF  
CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)**

Substances / Mixtures, which in contact with Water, release Toxic Gases

Transmitted by the Organization for Economic Co-operation and Development (OECD)

**Discussion of Rate of Evolution**

1. During the fifth Session of the UNSCEGHS, some concern was expressed regarding the draft proposal on substances and mixtures, which, in contact with water, release toxic gases. The objective of this document is to explain the reasons why OECD agreed on an optional evolution rate, leaving the cut-off values to transport authorities.
2. As part of the OECD Task Force deliberations concerning substances / mixtures, which, in contact with water, release toxic gases, the Task Force considered the “rate of evolution” parameter that is considered in the Substances / Mixtures, which in contact with water release flammable gases.
3. The OECD Task Force considered:
  - a) The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is based on existing systems. Among the systems that have existing criteria for this hazard class (workplace chemicals in Canada, the EU system for substances and preparations, US DOT), no system includes a cut-off value for the rate of evolution (See OECD document ENV/JM/MONO(2003)3);
  - b) No Task Force member provided scientific data to support whether the rates of evolution used for substances / mixtures, which in contact with water release flammable gases are the appropriate rates of evolution for substances/mixtures, which in contact with water release toxic gases;

- c) A survey of 67 substances, which in contact with water release toxic gases, was done. The survey compared the proposed criteria both using and setting aside the rate of evolution. The survey showed that 19/67 substances (28%) moved to the next lower hazard class. Therefore, all systems which would use a rate of evolution would reduce the level of protection;
- d) The proposal agreed by the Task Force (Note 4 to Table 1 of the Annex to this document) will not prevent transport authorities:
  - considering an evolution rate cut-off value for classification;
  - setting evolution rate cut-off values for packing group assignment.

**ANNEX****PROPOSAL FOR CHAPTER 3.X:****Substances and mixtures, which in contact with water, release toxic gases****Purpose, basis and applicability**

A1. This hazard class provides for the classification of substances or mixtures, which in contact with water release toxic gases. These substances or mixtures, when dry, will not emit gases with dangerous toxic properties. However, these substances or mixtures have the potential to come into contact with water and pose hazards in transport, storage, supply and use.

A2. The classification is based on the acute toxicity estimate (ATE) of the emitted gases and may include consideration of the quantity of the emitted gas as it evolves in a given time frame (i.e., the rate of gas evolution, for both substances and mixtures, as determined by UN Method 33.4.1.4 Test N.5). The toxicity of a gas is a measure of the health hazard associated with the gas. The gas evolution rate is a measure of the reactivity of the substance with water and indirectly is a measure of the quantity of toxic gas that may be present in a given time frame.

A3. In addition to their toxic effects, some of the emitted gases may also be corrosive. Guidance for labelling toxic gases that are also corrosive is found in paragraphs 3.1.2.6.5, and 3.1.4 of Chapter 3.1.

**Definition**

A4. A substance or mixture that in contact with water at ambient temperature, emits toxic gas(es) that poses a health hazard to humans. These substances or mixtures may be solid or liquid.

**Classification categories and criteria***Substances*

A5. A substance, which, in contact with water, emits toxic gases, is classified in one of five categories, based on the toxicity of the emitted gas, according to the Table 1 and its notes.

**Table 1: Criteria for Substances or Mixtures which in Contact with Water Emit Toxic Gases**

Category	Criteria (note 4)
	Acute Toxicity Estimate of the emitted gas (note 1, note 2)
1	≤100 ppm
2	≤500 ppm
3	≤2500 ppm
4	≤5000 ppm
5	LC <sub>50</sub> in the equivalent range of the oral and dermal LD <sub>50</sub> 2000-5000 mg/kg/bodyweight (note 3)

**NOTE 1:** See subsection 3.1.3.3(b) for explanation of Acute Toxicity Estimate (ATE).

**NOTE 2:** Inhalation cut-off values in the table are based on 4 hour testing exposures. Conversion of existing inhalation toxicity data which has been generated according to 1 hour exposures should be calculated by dividing by a factor of 2 for gases.

**NOTE 3:** In the Globally Harmonized System for the Classification and Labelling of Chemicals, Chapter 3.1, numerical values for acute inhalation toxicity in Category 5 were not included but instead specified as doses “equivalent” to the range of 2000-5000 mg/kg/bodyweight by the oral or dermal route. The following value is provided as guidance in determining the equivalent dose for gases: 5000 ppm to 12500 ppm.

**NOTE 4:** The gas evolution rate, as determined by UN Method 5 cited above, may be taken into consideration by certain authorities for both substances and mixtures.

A6. If a substance in contact with water emits a mixture of toxic gases, classification is based on the mixture of toxic gases (see paragraph A8).

#### **Classification of Mixtures**

A7. If a mixture when in contact with water emits a single toxic gas, classification is based on the toxicity of the gas, according to Table 1 and its notes.

A8. If a mixture or substance when in contact with water emits a mixture of toxic gases, two options are available for classification. A weighted averages calculation can be performed on the gaseous mixture based on the composition of the gaseous phase and the toxicities of the individual gases (See *The Globally Harmonized System for the Classification and Labelling of Chemicals*, Chapter 3.1). Alternatively, classification can be based on the classification of the most toxic gaseous component as outlined in Table 1 and its notes.

**Table 2: Classification Summary**

<b>Substance or a mixture which in contact with water releases:</b>	<b>Classify based on:</b>
A single toxic gas	The ATE of the toxic gas (See Table 1)
A mixture of toxic gases	The ATE of the gaseous mixture based on the composition of the gaseous phase and the toxicities of the individual gases, calculated as a weighted average; or
	The ATE of the most toxic gaseous component.

## Hazard communication

A9. General and specific considerations concerning labelling requirements are provided in Hazard Communication: Labelling (The Globally Harmonized System for the Classification and Labelling of Chemicals, Chapter 1.4). The Globally Harmonized System for the Classification and Labelling of Chemicals, Annex 2 contains summary tables about classification and labelling. The Globally Harmonized System for the Classification and Labelling of Chemicals, Annex 3 contains examples of precautionary statements and pictograms, which can be used where allowed by the competent authority. The table below presents specific label elements for substances and mixtures that are classified as posing an inhalation toxicity hazard when in contact with water, Categories 1-5 based on the criteria set forth in this chapter.

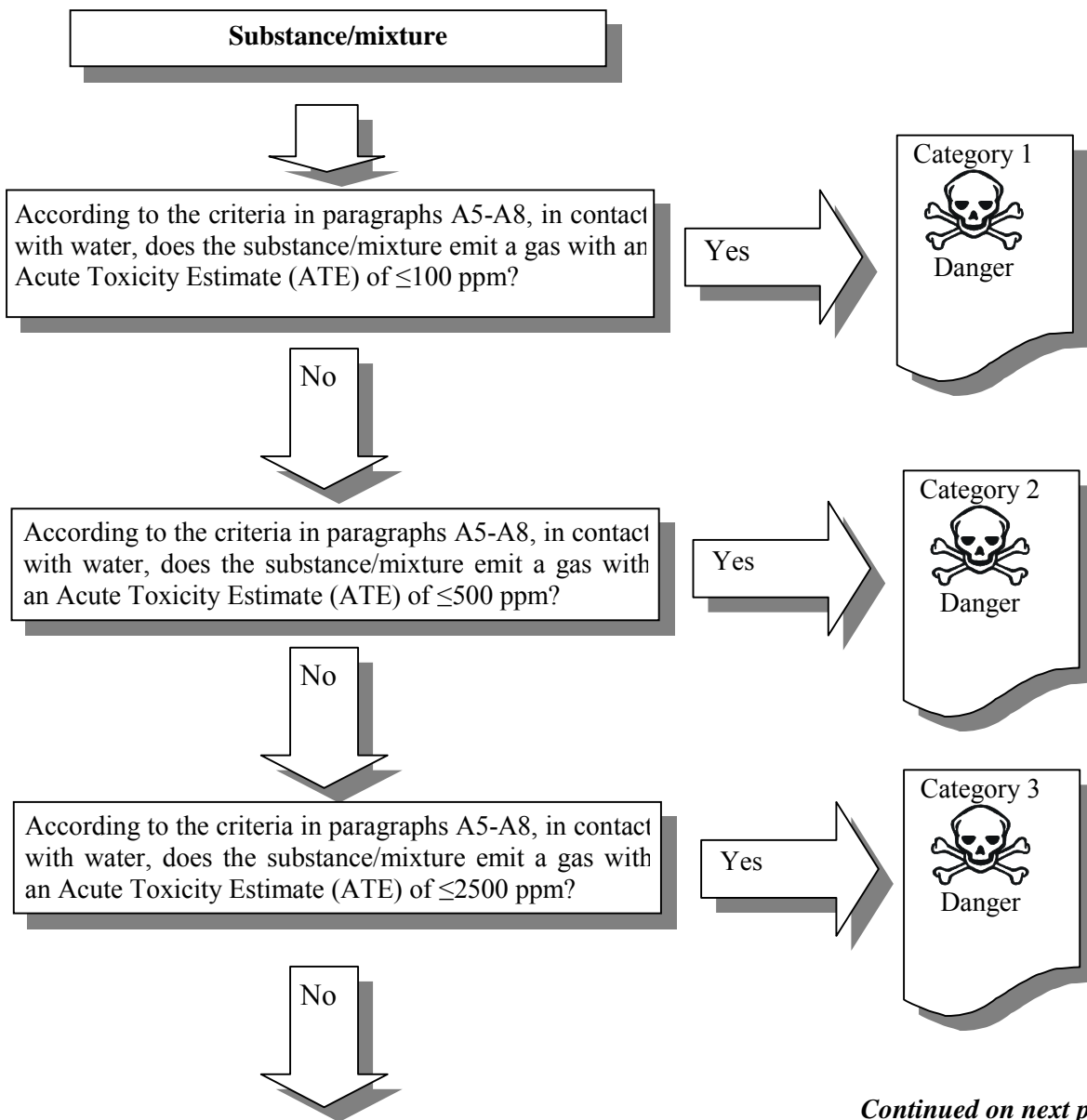
**Table 3: Label elements for substances/mixtures, which in contact with water, release toxic gases**

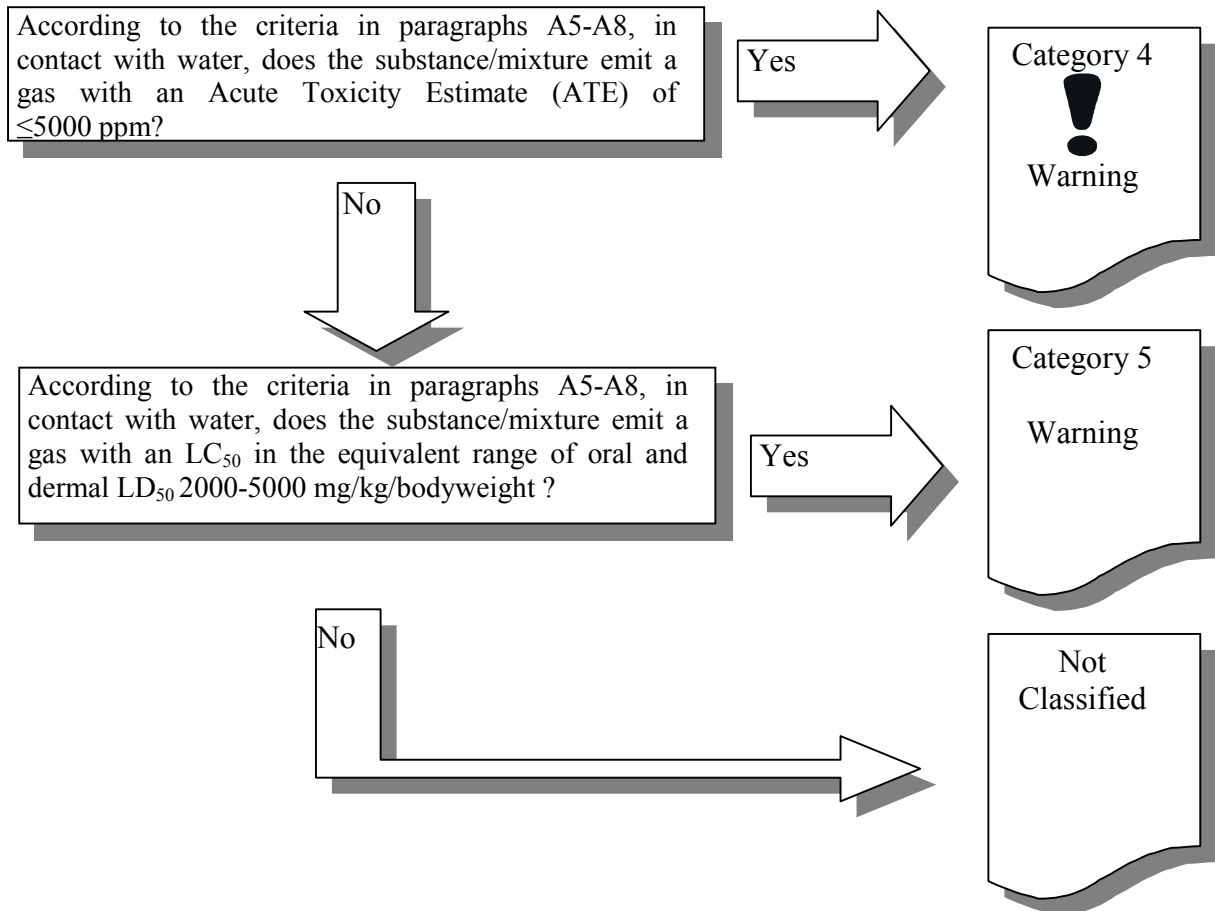
Category	Symbol	Signal Word	Hazard Statement
1	Skull and Crossbones	Danger	In contact with water releases gases which are fatal if inhaled
2	Skull and Crossbones	Danger	In contact with water releases gases which are fatal if inhaled
3	Skull and Crossbones	Danger	In contact with water releases gases which are toxic if inhaled
4	Exclamation mark	Warning	In contact with water releases gases which are harmful if inhaled
5	No symbol	Warning	In contact with water releases gases which may be harmful if inhaled

## Decision logic

A10. The decision logic which follows is not part of the harmonized classification system but is provided here as additional guidance. It is strongly recommended that the person responsible for classification study the criteria before and during use of the decision logic.

**Decision Logic for Water Activated Toxicity**





**NOTE:** Annex 1 (Allocation of label elements) and Annex 2 (Classification and labelling summary tables) of the GHS should further be completed accordingly.

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