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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

Fifteenth session
Geneva, 9-11 July 2008
Item 2 (b) of the provisional agenda

UPDATING OF THE SECOND REVISED EDITION OF THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

Health hazards

Classification criteria for substances and mixtures, which in contact with water, release toxic gases

Transmitted by the expert from France [*/]

[*/] In accordance with the programme of work of the Sub-Committee for 2007-2008 approved by the Committee at its third session (refer to ST/SG/AC.10/C.4/24, Annex 2, item 2 (b) (i) and ST/SG/AC.10/34, para. 14).

Background

1. The Sub-Committee has decided to deal with the classification criteria for the above mentioned substances within the framework of a working group, led by France.

2. The working group met several times and had some email exchanges, from 2003 to 2006.

3. However, no much progress has been made since that time, in particular because some aspects of the issue depended on the outcome of the working group on toxic gas mixtures.

4. In addition to that, many experts who were initially involved in this work are no more members of the Sub-Committee while new experts, who might not be well aware of this work, have joined the Sub-Committee.

5. The expert from France would like to present the last document submitted by the working group to the Sub-Committee (see annex). Although it is drafted in a form of a proposal for new text it is not proposed for adoption, at this time. It is presented as such only because it gives a good picture and summary of the approach discussed in the working group. It should not be considered either as an agreed document from the working group.

7. Indeed many parts of this document need to be improved also taking care of the outcome of the toxic gas mixture working group. Comments concerning further work are underlined.

8. Noting that this issue has been included in the programme of work of the Sub-Committee for the current biennium, the Sub-Committee is invited:

(a) To comment and decide if this approach is still approved;

(b) To promote renewed participation for future work.

Annex

WORK OF THE WORKING GROUP ON SUBSTANCES WHICH IN CONTACT WITH WATER RELEASE TOXIC GASES

Inclusion of rate of evolution as classification criteria

1. As conclusion of the eighth session, the Sub-Committee of Experts decided not to adopt the proposal presented by the OECD in document ST/SG/AC.10/C.4/2003/9 on water activated toxicity. It was agreed that the inclusion of the criterion on the gas evolution rate would be considered over the biennial period 2005/2006. This involves a work along two axes:

- The definition of new classification criteria combining both properties: LC50 and the evolution rate;

- The development of methods for determining the evolution rate.

The Sub-Committee decided to continue the work on this question within the framework of a working group, led by France about the subject.

2. The estimate of the danger due to the production of toxic gas implies to consider two properties in an equal way: the acute toxicity of gas (LC50) and the gas evolution rate. The objective of this document is to explain the reasons why the parameter "evolution rate" must be introduced into the classification of the substances and mixtures which, in contact with water, release toxic gases, just like it was taken into account for the substances and mixtures which, in contact with water, release flammable gases:

(a) It is necessary to evaluate the intensity of toxicity (by the measurement of LC50), but also the concentration of toxic gas in the atmosphere, and so depending on the quantity of gas evolved in a given time frame for a given volume. In other words, the danger is coming from the ability to reach LC50 in a more or less short time;

(b) Generally speaking, it can be wondered, how it is possible to know that a substance emits gases (toxic or not) in contact with water, if the measurement of gas flow is not carried out;

(c) To determine the toxicity of gases, the measurement of the evolution rate must be accompanied by an analysis of produced gas. The measurement of produced gases is also included in method EC A.12 (quasi-identical to Test N.5 in sub-section 33.4.1.4 of the UN Manual of Tests and Criteria), described in Directive 92/69/EEC[1], used to determine if the reaction of a substance with water or the humid air involves the evolution of a dangerous quantity of a gas or several gases, likely to be very flammable;

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[1] *(Commission Directive 92/69/EEC of 31 July 1992 adapting to for the seventeenth time Council Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances).*

(d) The case of ferrosilicon may be considered as an example: ferrosilicon is an alloy of the FeSi type which in contact with water, emits toxic and/or flammable gases such as arsine, phosphine and/or dihydrogen (AsH_3, PH_3 and H_2). Currently, in the UN Recommendations, it is identified like a substance which, in contact with water, releases flammable gases (Division 4.3). Indeed, by chemical reaction with water, it produces dihydrogen. The accidentology indicates that the arsine and phosphine are also produced. However, from its chemical formula,it is not possible to predict the release of AsH_3 and PH_3, since these two elements (As and P) come in its manufacturing process in the form of impurities. Only the gas analysis would make it possible to detect them;

(e) Moreover, Test N.5 of the *UN Manual of Tests and Criteria*, must be supplemented to take into account the fact that the gas concentrations from which a danger of toxicity appears can be extremely low.

3. The expert from France proposes a modification of the draft proposal by OECD (ST/SG/AC.10/C.4/2003/9) on the substances and mixtures which, in contact with water, release toxic gases. The proposed modifications aim at including on the one hand, the evolution rate as a criterion of classification, and in the other hand, at removing from the document the parts concerning the classification of mixtures waiting for the conclusions of the work of the working group on toxic gas mixtures. The objective of this document is to start again the discussions within the above mentioned working group. Certain parts of this proposal need to be supplemented. The comments on this subject as well as the suggested items for future work appear in underlined text.

PROPOSAL FOR A NEW CHAPTER 3.X

"SUBSTANCES AND MIXTURES, WHICH IN CONTACT WITH WATER, RELEASE TOXIC GASES

3.x.1 Purpose, basis and applicability

3.x.1.1 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.

3.x.1.2 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 Test N.5 in sub-section 33.4.1.4 of the Manual of Tests and Criteria). 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.

3.x.1.3 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.

3.x.2 Definition

3.x.2.1 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.

3.x.3 Classification categories and criteria

3.x.3.1 Substances

1st Criterion for substances or mixtures which in contact with water emit toxic gases: Acute Toxicity Estimate of the emitted gas

3.x.3.1.1 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 Table 3.x.1 and its notes.

Table 3.x.1: 1st Criterion for substances or mixtures which in contact with water emit toxic gases

Category of toxic gas	1st Criterion
	Acute Toxicity Estimate of the emitted gas (see notes 1 and 2)
1	≤ 100 ppm
2	≤ 500 ppm
3	≤ 2500 ppm
4	≤ 5000 ppm
5	LC_{50} in the equivalent range of the oral and dermal LD_{50} 2000-5000 mg/kg/bodyweight (note 3)

NOTE 1: *See 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 1hour exposures should be calculated by dividing by a factor of 2 for gases.*

NOTE 3: *In 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.*

2nd Criterion for substances or mixtures which in contact with water emit toxic gases: Estimation on the gas evolution rate

3.x.3.1.2 A substance, which, in contact with water, emits toxic gases, is also classified according to the gas evolution rate, as determined by Test N.5 cited above, which must be taken into consideration for both substances and mixtures.

COMMENTS:

In Test N.5, intended for the measurement of the flammable gases evolution rate, the volume of produced gas is measured in any case suitable.

In the case of toxic gas, small quantities of gas can be released. It is then necessary to develop measurements *of very significant gas evolution rates* (allowing the measurement of a toxic gas concentration of 1 ppm, for example). These measurements could be done by using for example:

- an enclosure equipment (to measure the volume of gas from the determination of the pressure increase into equipment);
- a flowmeter (measurement of the volume of gas in real time).

In the case of a toxic gas, small quantities of gas can be released. The time of measurement of the rate of the gas evolution rate can also be extended to *X* days > 5 days (in Test N.5 concerning flammable gases, it is of 7 hours; If the evolution rate fluctuates or increases after 7 hours, the duration of measurement must be extended until a maximum of 5 days).

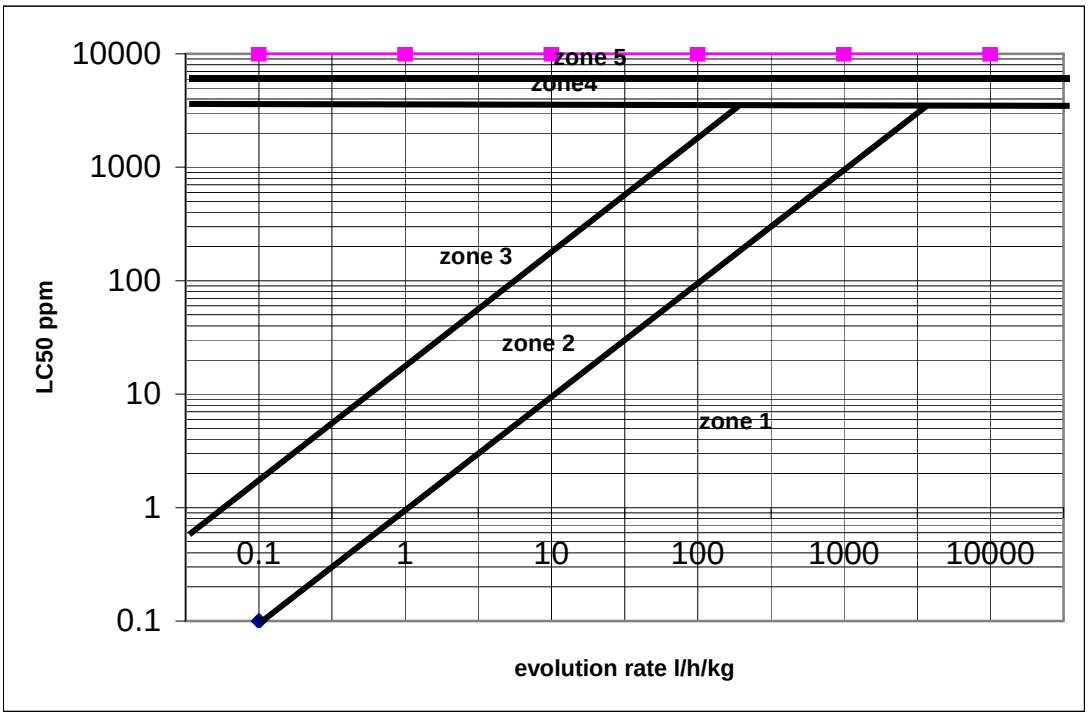
Combination of the Criteria applicable to the substances and mixtures which, in contact with water, emit toxic gases

3.x.3.1.3 A substance, which, in contact with water, emits toxic gases, is classified in one of the five categories according to the toxicity of produced gas and the gas evolution rate, as indicated in Figure 3.x.1 and its notes. Thus, the 5 categories of danger are determined according to the time necessary to reach the LC50 indicated in table 3.x.1 (notes 4 and 5).

3.x.3.1.4 Figure 3.x.1 defines the relation between gas evolution rate (in X-coordinate) and LC50 (in ordinate). The couple criteria-toxicity of produced gas (LC50) and evolution rate-relative to a given substance defines a point on the figure. The classification of the substance is given by the position of this point in one of the five zones of the figure.

Category	Zone
1	Zone 1
2	Zone 2
3	Zone 3
4	Zone 4
5	Zone5

Figure 3.x.1: Criteria applicable to the substances and mixtures which, in contact with water, emit toxic gases



***NOTE 4**: This diagram uses the evolution rate only inside the limits of toxicity, namely below a LC50 of 2500 ppm (category 3), such as defined in table 1. Thus, the evolution rate allows to take into account the dangers related to the substances which, produce toxic gases with a low flow and weakly toxic gases with a high flow. The introduction of the evolution rate like criterion of classification does not reduce the level of protection. This one is higher for the substances having an important evolution rate.*

***NOTE 5**: The evolution rates used in the case of the substances and mixtures which, in contact with water, release toxic gases, are not automatically identical to those used in the case of the substances and mixtures which, in contact with water, release flammable gases. It is necessary to propose cut-off values of gas flow.*

3.x.3.2 Classification of mixtures

COMMENTS: This part of the proposal will have to be supplemented according to the conclusions of the working group on mixture of toxic gases.

3.x.4 Hazard communication

3.x.4.1. General and specific considerations concerning labelling requirements are provided in Chapter 1.4. Annex 2 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. Table 3.x.2 below presents specific label elements for substances and mixtures that are classified as posing an inhalation toxicity hazard when in contact with water, Categories 1to 5 based on the criteria set forth in this chapter.

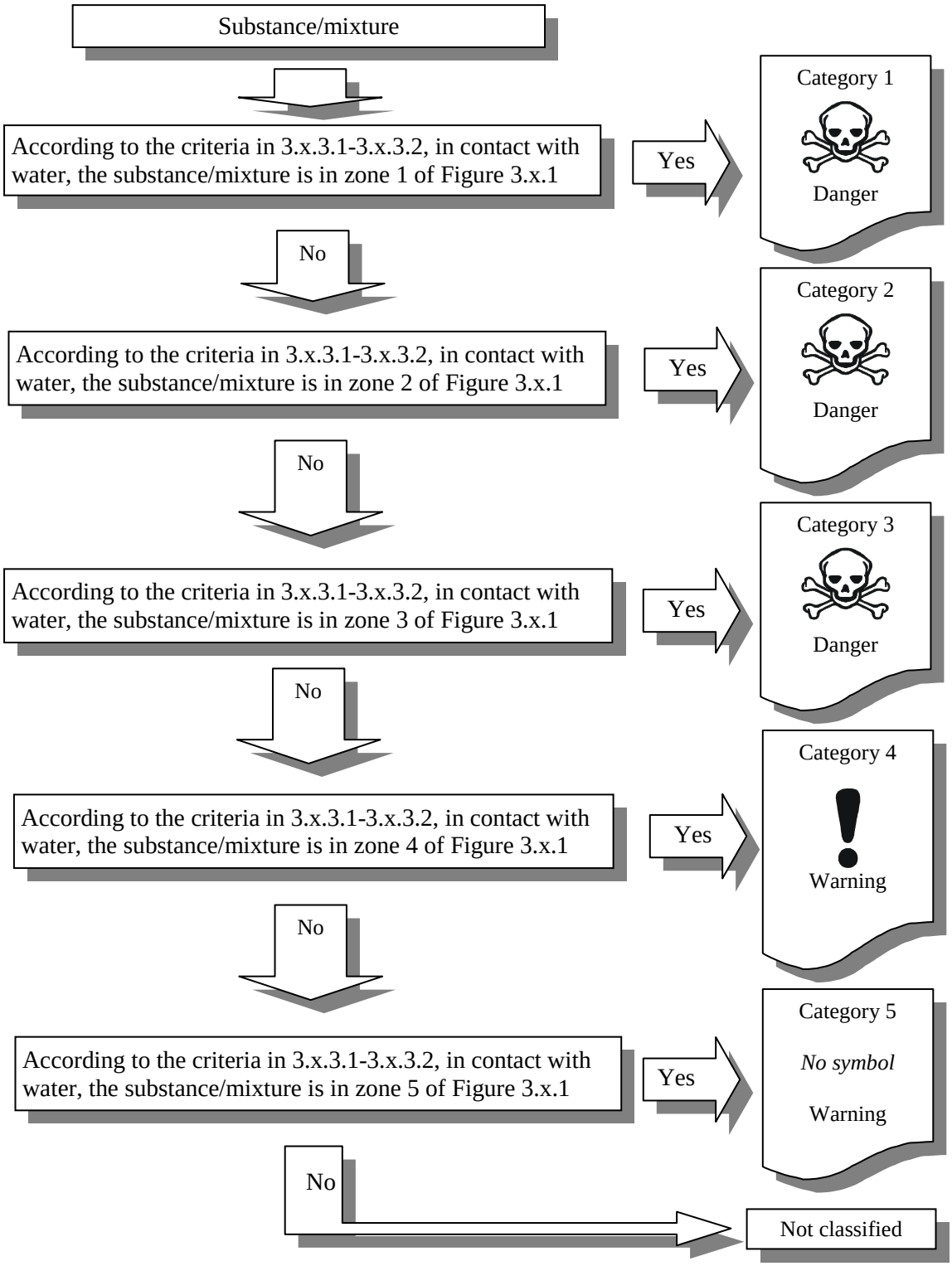
Table 3.x.2: Label elements for substances/mixtures, which in contact with water, release toxic gases

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

3.x.5 Decision logic

3.x.5.1 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.

3.x.5.1.1 *Decision logic for water activated toxicity*



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