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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

Twelfth session
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Item 2(b) of the provisional agenda

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

Health hazards

Toxic gas mixtures

Transmitted by the expert from the United States of America on behalf of the informal intersessional working group on toxic gas mixtures

Introduction

1. After adoption of the GHS in December of 2002, concerns were raised regarding the adequacy of the criteria for classification of gas mixtures for acute toxicity. At the fifth session of the Sub-Committee of Experts (July of 2003), the European Industrial Gases Association (EIGA) presented a document that proposed changes to the criteria (ST/SG/AC.10/C.4/2003/1). EIGA provided further information regarding the proposed changes in a second document (ST/SG/AC.10/C.4/2003/7). In response to these concerns, the Sub-Committee established a correspondence group to reconsider the classification criteria for toxic gas mixtures. The work of the correspondence group was reported to the Sub-Committee at its seventh session (July 2004) (ST/SG/AC.10/C.4/2004/7). The Sub-Committee recognized that this was a complex issue, and

determined that a working group would more efficiently continue the work. The Sub-Committee requested that OECD establish a working group to review the criteria for classification and labelling of gas mixtures and agreed on a mandate for that group (ST/SG/AC.10/C.4/14, Annex 1).

2. At its eleventh session in July of 2006, the Sub-Committee of Experts indicated that, after consideration by the OECD working group, a majority of experts were of the opinion that the current GHS classification approach for toxic gas mixtures was not satisfactory and that there was a need for further work. The Sub-Committee agreed on terms of reference for an informal intersessional working group on toxic gas mixtures and assigned the working group with the task of developing draft text for toxic gas mixtures, and if necessary, for pure gases (ST/SG/AC.10/C.4/22, Annex 2). Members of the working group included Canada, the Compressed Gas Association (CGA), EIGA, France, Germany, and the United States of America.

3. The fundamental concern with the current GHS criteria for classification of gas mixtures for acute toxicity is that certain gas mixtures would not be classified as posing an acute inhalation hazard even though such mixtures are currently classified as hazardous in North America and Europe and have caused intoxication, including deaths, in humans (see ST/SG/AC.10/C.4/2006/14). The current GHS criteria therefore reduce the level of protection with regard to these gas mixtures, and do not provide adequate protection to exposed persons.

4. The discrepancy between the current GHS criteria and the US, Canadian, and EU requirements, as well as the impact of the proposed change, is presented in Table 1 with regard to 53 gases considered economically significant.

5. The proposed change is the consensus of all experts in the intersessional working group, with the understanding that this does not represent countries' positions. It is the result of several years of discussion and consideration of a wide variety of alternatives for addressing this issue by other working groups. No other mutually acceptable alternative was found during this time.

6. One expert in the working group believes that, in addition to the proposed change, the upper cut-off value for Category 3 for gases should be increased in order to trigger the more stringent labelling requirements that would be, in his view, appropriate for the hazard presented. This opinion is not shared by other experts in this working group.

7. The proposal includes the following changes:

(a) for classification of gases for acute toxicity, the upper cut-off value for Category 4 is changed from 5000 ppm to 20000 ppm;

(b) to maintain consistency with the practice of setting Converted Acute Toxicity point estimates for Categories 3 – 5 at a point approximately $1/10^{th}$ from the lower end of the range (Table 3.1.2, Note 2), the Converted Acute Toxicity point estimate for gases for Category 4 is changed from 3000 to 4500; and

(c) the decision logic for acute toxicity is revised to reflect the change in the classification criteria.

8. The proposed upper cut-off value of 20000 ppm for Category 4 was chosen because it approaches the mixture classification thresholds used in the existing systems of the EU, USA and Canada (as can be seen from Table 1). The proposed change thus represents a practical approach that will effectively remedy the loss of protection under the current GHS classification criteria.

Table 1. Classification of gas mixtures for acute toxicity

Gas	LC_{50} (ppm)	Threshold Above Which Gas Mixture Would Be Classified (in %)			
		GHS (Cat. 4)	USA and Canada	EU (Xn)	Proposed change (Cat. 4)
Hydrogen Selenide	1	0.02	1	0.02	0.005
Hydrogen Telluride	1	0.02	1	0.02	0.005
Phosgene	2.5	0.05	1	0.02	0.013
Phosphine	10	0.2	1	0.02	0.050
Arsenic Pentafluoride	10	0.2	1	0.1	0.050
Arsine	10	0.2	1	0.02	0.050
Stibine	10	0.2	1	0.02	0.050
Nitrosyl Chloride	17.5	0.35	1	0.02	0.088
Sulphur Tetrafluoride	20	0.4	1	0.02	0.10
Selenium Hexafluoride	25	0.5	1	0.02	0.13
Cyanogen Chloride, Stabilised	40	0.8	1	0.02	0.20
Diborane	40	0.8	1	0.02	0.20
Nitric oxide	57.5	1.15	1	0.1	0.29
Chlorine Pentafluoride	61	1.22	1	0.02	0.31
Tungsten Hexafluoride	80	1.6	1	0.02	0.40
Fluorine	92.5	1.85	1	0.02	0.46
Phosphorus Pentafluoride	95	1.9	1	0.02	0.48
Chlorine	146.5	2.93	1	0.5	0.73
Chlorine Trifluoride	149.5	2.99	1	0.5	0.75
Dichlorosilane	157	3.14	1	0.5	0.79
Cyanogen	175	3.5	1	0.5	0.88
Carbonyl Fluoride	180	3.6	1	0.5	0.90
Boron Trifluoride	193.5	3.87	1	0.02	0.97
Phosphorus Trifluoride	210	4.2	1	0.5	1.05
Silicon Tetrafluoride	225	4.5	1	0.5	1.13
Hexafluoroacetone	235	4.7	1	0.5	1.18
Germane	310	6.2	1	0.02	1.55
Hydrogen Sulphide	356	7.12	1	0.02	1.78
Bromomethane	425	8.5	1	0.5	2.13
Hydrogen Fluoride	483	9.66	1	0.02	2.42

Gas	LC_{50} (ppm)	Threshold Above Which Gas Mixture Would Be Classified (in %)			
		GHS (Cat. 4)	USA and Canada	EU (Xn)	Proposed change (Cat. 4)
Hexafluoro-1,3-Butadiene	650	13	1	5	3.25
Methyl Mercaptan	675	13.5	1	5	3.38
Carbonyl Sulphide	850	17	1	0.5	4.25
Bromotrifluoroethylene	1000	20	1	5	5.00
Chlorotrifluoroethylene	1000	20	1	0.5	5.00
Sulphur Dioxide	1260	25.2		5	6.30
Boron Trichloride	1270.5	25.41		0.02	6.35
Hexafluoroisobutene	1325	26.5		0.5	6.63
Hydrogen Chloride	1405	28.1		0.5	7.03
Hydrogen Bromide	1430	28.6		0.5	7.15
Hydrogen Iodide	1430	28.6		0.5	7.15
Ethylene Oxide	1450	29		0.5	7.25
Sulphuryl Fluoride	1510	30.2		0.5	7.55
Carbon Monoxide	1880	37.6		0.5	9.40
Ammonia	2000	40		0.5	10.00
Hexafluoropropylene	2800	56		5	14.00
Nitrogen Trifluoride	3350	67		5	16.75
Methylamine	3500	70		5	17.50
Trimethylamine	3500	70		5	17.50
Chloromethane	4150	83		5	20.75
Dimethylamine[1]	5500			5	27.50
Octafluorobutene[1]	6100			5	30.50
Silane[1]	9500				47.50

[1] *These gases would not be classified under the existing GHS as their 4-h LC_{50} value is higher than 5000 ppm.*

Proposal

Table 3.1.1 In the fifth column ("Category 4") in the fourth row ("Gases") replace "5000" with "20000".

Table 3.1.2 In the second column ("Classification category or experimentally obtained acute toxicity range estimate") in the fourth row ("Gases") replace "5000" with "20000".

In the third column ("Converted Acute Toxicity point estimate") in the fourth row ("Gases") replace "3000" with "4500".

3.1.5 Decision logic

In Decision logic 3.1.1, the text box that follows "No" from Category 3 that reads as follows:

"According to the criteria in 3.1.2 to 3.1.3.4, does it have an:

- Oral LD_{50} >300 but ≤2000 mg/kg bodyweight, **or**
- Dermal LD_{50} >1000 but ≤2000 mg/kg bodyweight, **or**
- Inhalation (gas) LC_{50} >2500 but ≤5000 ppm, **or**
- Inhalation (vapour) LC_{50} >10 but ≤20 mg/l, **or**
- Inhalation (dust/mist) LC_{50} >1 but ≤5 mg/l?"

replace "5000 ppm" for gas Inhalation with "20000 ppm".
