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Sub-Committee of Experts
on the Globally Harmonized System of Classification
and Labelling of Chemical
(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 expert from France

1. In document ST/SG/AC.10/C.4/2003/9, the OECD proposes to introduce a new chapter concerning substances and mixtures, which in contact with water, release toxic gases (also called WAT substances). We welcome in principle the inclusion of this new hazard class in the GHS.

2. However, in our view, the proposed text (i) contains internal contradictions and (ii)does not properly cover all the hazard properties of these substances.

3. The text in para.A2 of the Annex to ST/SG/AC.10/C.4/2003/9 states that the classification is based on the ATE of the emitted gases and on the quantity of emitted gases.

4. But in the actual criteria (para.A5), there is no mention of the gas evolution rate and the classification is based on the ATE of the gas only, which is in contradiction with para.A2.

5. Further on in the text, Note 4 to table 1 provides that "certain competent authorities may take the evolution rate into consideration" in the classification criteria.The way it is drafted, this may include any national or modal competent authority and thus makes criteria in A5 useless.

6. In the introductory text justifying the proposal it is said that taking into account the evolution rate systematically results in downgrading the level of danger. This conclusion would be based on a survey of 67 substances, but no actual data are presented. It is regretable that the Sub-Committee is asked to make a decision with such poor supporting information.

7. The ATE of the emitted gases is not an intrinsic hazard property of the WAT substances themselves; it is an intrinsic hazard property of the emitted gas. In our understanding, the hazard property of the WAT substances is a combination of the ATE of the gas and of the evolution rate of this emitted gas (quantity of gas), because the danger comes from the concentration of the gas in the atmosphere. This is not a problem only encountered in the transport sector, but also in storage and other working places.

8. According to table 1 of the Annex to ST/SG/AC.10/C.4/2003/9, the limits of ATE considered for the gas toxicity vary with a factor of 25 (from 100 to 2500ppm).In some cases, this factor may be bigger, when comparing highly toxic gases with less toxic gases (several thousand). On the other hand, the evolution rate limits set in the UN N5 Test vary with a factor of 600 (from 1 l/h/kg to 10 l/mn/kg), although in reality, in some cases, the variation factor may be of several thousand too. That proves that the evolution rate is a factor as important as the ATE, given the fact that the danger comes from the actual concentration of toxic gas in the atmosphere.

9. It is not true that including the gas evolution rate systematically leads to a classification in a lower hazard category. This is clearly illustrated through the examples given in the annex to this document. Based on these examples, the ATE-based criteria proposed by OECD overestimate the hazard of substances with a low emission rate and underestimate the hazard of substances with a high emission rate, leading to misjudgement that may have dramatical consequences.

10. Considering the above-mentioned points it is proposed:

    (a) Not to adopt the proposal as in annex of ST/SG/AC.10/C.4/2003/9;

    (b) To invite the OECD to transmit to the secretariat the detailed survey mentioned in para. 3(c) of ST/SG/AC.10/C.4/2003/9. These data should then be made available to all the experts of the Sub-Committee possibly on the SCE GHS website, as soon as possible;

11. France will draft modifications to the proposal annexed to ST/SG/AC.10/C.4/2003/9, taking account of the gas evolution rate in the way it enhances safety. The measurement of evolution rate shall be based on UN N5 test but the evolution rate cut-off values to consider in the criteria for WAT does not have to follow the same limits than for substances emitting flammable gases. A proposal from France will be submitted at the next session of the Sub-Committee.

ANNEX

Some nitrides emit ammonia in presence of water. One example is Lithium Nitride (NLi_3) . According to the UN model Regulations, it is a Class 4.3 Packing Group I substance (UN 2806): substance which in contact with water emits flammable gases (ammonia is both flammable and toxic). This means that the emission rate is superior to 10 l/mn/kg mesured in the UN N5 Test. The data concerning the toxicity of ammonia are as follows:

- CL50(4h) = 2000 ppm
- IDLH = 500 ppmV

According to the current GHS criteria and the OECD proposal, this substance is classified:

- "Substance which in contact with water emits toxic gases" **CAT 3**
- "Substance which in contact with water emits flammable gases" **CAT 1**

Comparison of the flammability hazard and the toxicity hazard

To make this comparison easy, let's consider a total hydrolysis of 10kg of Lithium Nitride in a room of 3 meter height:

- At a distance of 2 meters an ignition source will provoke the fire of a volume of approximately 40m3 of ammonia;
- Under a distance of 37 meters a person will be exposed to an atmosphere where the concentration will be over the IDLH value. The CL50 will be reached at a distance of 18m.

Therefore, this substance is by far more dangerous because of its toxic effect than because of its flammability.

- Toxicity is always manifest and does not need an external factor such as ignition;
- The distance where the danger is significant is respectively 18 (IDHL) or 9 times (CL50) bigger in the case of toxicity.

However, the hazard category for flammability is 1 and according to the OECD proposed criteria in ST/SG/AC.10/C.4/2003/9 for WAT, the category for toxicity would be 3, which is certainly irrelevant and create internal contradiction within the GHS.

Comparison with other WAT substances

Ferrosilicon (UN 1408, Class 4.3, PG III) produces very low quantities of arsine and phosphine together with hydrogen.The CL50 (4h) of arsine and phosphorine is 10 ppm. The evolution rate is around 1 l/h/kg, all gases included. Let's consider that the evolution rate of the toxic gas is 1 l/h/kg which is a maximizng hypothesis.

Comparing this with the previous example, the evolution rate of lithium nitride is more than 600 times bigger than the evolution rate of ferrosilicon ; the CL50 (4h) of ammonia (2000ppm) is only 200 times bigger than the CL50 (4h) of ferrosilicon.

Comparing lithium nitride and ferrosilicon, the time when lethal concentration will be reached for the same amount of substance is 3 times less in the case of lithium nitride. So, it would be logical to consider that lithium nitride is more dangerous than ferrosilicon with respect to the WAT.

But, using the OECD criteria leads to a classification of lithium nitride in Category 3 and ferrosilicon in category 1, which again is irrelevant.

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