

Committee for Risk Assessment
RAC

Annex 2
Response to comments document (RCOM)
to the Opinion proposing harmonised classification and
labelling at EU level of

hydrogen sulphide, hydrogen sulfide

EC Number: 231-977-3
CAS Number: 7783-06-4

CLH-O-0000007029-73-01/F

Adopted
16 September 2021

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON HYDROGEN SULPHIDE, HYDROGEN SULFIDE

COMMENTS AND RESPONSE TO COMMENTS ON CLH: PROPOSAL AND JUSTIFICATION

Comments provided during consultation are made available in the table below as submitted through the web form. Any attachments received are referred to in this table and listed underneath, or have been copied directly into the table.

All comments and attachments including confidential information received during the consultation have been provided in full to the dossier submitter (Member State Competent Authority), the Committees and to the European Commission. Non-confidential attachments that have not been copied into the table directly are published after the consultation and are also published together with the opinion (after adoption) on ECHA's website. Dossier submitters who are manufacturers, importers or downstream users, will only receive the comments and non-confidential attachments, and not the confidential information received from other parties. Journal articles are not confidential; however they are not published on the website due to Intellectual Property Rights.

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Substance name: hydrogen sulphide, hydrogen sulfide

EC number: 231-977-3

CAS number: 7783-06-4

Dossier submitter: Germany

GENERAL COMMENTS

Date	Country	Organisation	Type of Organisation	Comment number
17.12.2020	Germany	GHC Gerling, Holz & Co. Handels GmbH	Company-Manufacturer	1
Comment received				
<p>Hydrogen sulphide (CAS: 7783-06-4, EC: 231-977-3) is mainly used as an intermediate in the European Union. This is reflected by the active Reach-registrations: three registrations as transported isolated intermediate under 1000 t/a and only one full registration 10 - 100 t/a. When used as an intermediate, no danger to humans or the environment is to be expected, since the product is handled under strictly controlled conditions (pursuant to article 18 of Regulation (EC) No 1907/2006 – Reach). However, even when full registration is used, technical and organisational measures are in place to ensure that workers and the environment are not endangered. Very low occupational exposure limits are complied with (e.g., 5 ppmV), which are significantly below the discussed ATE for inhalative toxicity.</p> <p>Hydrogen sulphide is most dangerous as an unwanted (and sometimes unexpected) by-product, e.g., in sewers, biogas plants, manure. This is illustrated by the numerous cases of human injuries listed in the CLH report. It is questionable whether a stricter harmonised classification for acute toxicity inhalative will lead to a higher level of safety for the workers concerned.</p>				
Dossier Submitter's Response				
<p>The German CA appreciates the comments raised by the company. By using the converted Acute Toxicity point Estimate (cATpEs) value of 100 ppmV in the additivity formula for the purpose of mixture classification, a mixture containing 0.5 % H₂S would still be labelled as acutely toxic (Cat. 4), whereas otherwise a warning sign would not be</p>				

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applied. In the interest of human health, aiming for the highest possible level of protection is a priority.
RAC's response
<p>Thank you for your comment.</p> <p>Indeed, hydrogen sulfide poisoning typically occurs in settings such as sewers, manure handling, biogas plants or petroleum refineries, where classification and labelling of H₂S-containing atmospheres/mixtures can hardly be applied. Worker protection has to be achieved by other means, such as gas monitoring devices, safety rules, training of workers, availability of respiratory protection equipment.</p> <p>The classification threshold for mixtures is not part of the classification criteria for substances.</p>

OTHER HAZARDS AND ENDPOINTS – Acute Toxicity

Date	Country	Organisation	Type of Organisation	Comment number
17.12.2020	Germany	GHC Gerling, Holz & Co. Handels GmbH	Company-Manufacturer	2

Comment received
<p>The harmonised classification as Acute Tox 2 is sensible. However, the ATE 100 ppmV (gases) is questionable.</p> <p>An acute toxic estimate (ATE) of 100 ppmV results in a classification as Acute Tox 1 pursuant to table 3.1.2. of annex 1 of Regulation (EC) No 1272/2008 (CLP). Thus, an ATE of 100 ppmV would not be in line with a classification of Acute Tox 2.</p> <p>The ATE must be indicated in section 3 of the safety data sheet pursuant to Commission Regulation (EU) 2020/878. This way it is highlighted to downstream users. Downstream users are obligated to carry out a plausibility check. The contradicting classification as Acute Tox 2 in combination with an ATE of 100 ppmV would not pass the plausibility check. As result, each downstream user has to verify the classification, which results in an additional, unnecessary workload for the downstream user, the supply chain, manufacturers and helpdesks (ECHA and national).</p> <p>There are meaningful animal data studies in place to determine the inhalative toxicity of hydrogen sulphide. Relevant studies are provided in the CLH report. Even though most studies are already dated and not considered equivalent to current guideline studies such as OECD TG 403, this does not negate their validity. On the contrary, the results of all studies are in a narrow range of an ATE of 300 - 500 ppmV each (LC50 after corrections for 4 hours exposure time), which confirms the correctness of the studies. A new animal data study conducted according to current guidelines would not be justified. Reach sets high constraints on new animal testing. In particular, experiments on vertebrates must be avoided in order to protect animal welfare. Taking into account the already existing, reliable and meaningful study data, new animal experiments to confirm the ATE (once again) are not justifiable.</p> <p>Instead, the CLH report considers human data regarding hydrogen sulphide related acute inhalation toxicity. The most relevant and extensive information in the CLH report is provided by documented cases related to occupational accidents. Despite the large number of documented cases, the exact minimum concentration that causes lethality in humans is unknown. There is general consensus that instant severe acute toxicity can be</p>

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expected at ≥ 500 ppmV hydrogen sulphide. The CLH report argues, that the available evidence from human data indicates that the minimum concentration where mortality can be expected is in the range of 100 - 500 ppmV. This agrees with the animal data, which determined an ATE in the range of 300 - 500 ppmV.

Currently, an ATE of 444 ppmV is suggested by the Reach registration dossier based on the most relevant data study. While this agrees with both, the animal data and the human data, there are indications that a lower value would be more appropriate in terms of preventive protection. I.e., the ATE is used to determine the toxicity of mixtures. Using an ATE of 444 ppmV for calculation of mixture classification, a mixture of below 2.2 % hydrogen sulphide is not classified. However, this could lead to a false sense of security. In the event of release and after mixing with ambient air, local concentrations are likely still to be lethal. A lower ATE will result in stricter classifications of low concentration hydrogen sulphide mixtures and increase the awareness.

All scientific findings (animal data study, human data, CLH report) points to a classification as acute tox 2. Under no circumstances is a classification as acute tox 1 (which would be in line with an ATE of 100 ppmV) justified.

In conclusion, there is extensive and meaningful animal and human data for the inhalative acute toxicity of hydrogen sulphide available. The available data suggests an ATE of 300 – 500 ppmV (100 – 500 ppmV), which results in a classification as Acute Tox 2. There are indications that a conservative ATE might result in an increase of human safety, in particular, in the handling of mixtures. However, this ATE should be in the range of $> 100 - \leq 500$ ppmV to avoid confusion about the classification. An ATE of exactly 100 ppmV would suggest a classification as Acute Tox 1 pursuant to table 3.1.2. of Reach, while the available data clearly points to a classification of Acute Tox 2.

Dossier Submitter's Response

The German CA appreciates the comments raised by the company and acknowledges the confusion around an acute toxicity 2 classification and the proposed ATE of 100 ppmV. As explained in the CLH dossier, human data are considered more relevant for a number of reasons described on page 44. ECHAs guidance on the application of the CLP criteria (version 5.0, July 2017) states: *"Where human data are available, they should be used to estimate the ATE which can be used directly for classification [...] If there are no exact or quantitative lethal dose data the procedure described in CLP Annex I, 3.1.3.6.2.1(b) (see Section 3.1.3.3.5 of this Guidance) would have to be followed using Table 3.1.2 (see Section 3.1.3.3 of this Guidance) with an assessment of the available information on a semi-quantitative or qualitative basis. [...] The category should be justified by semi-quantitative or qualitative data and a subsequent derivation of a converted ATE (cATpE) according to CLP Annex I, Table 3.1.2 and subsequent use in the formulae"*. Given that acute toxicity effects observed in humans are consistent with Category 2 (100 – 500 ppmV) but no exact lethal concentration values could be determined, a converted Acute Toxicity point Estimate (cATpEs) value of 100 ppmV in accordance with table 3.1.2 was derived. The cATpEs of 100 ppmV is, thereby, primarily envisaged to be used as the appropriate ATE value to calculate the classification of a given mixture.

RAC's response

Thank you for your comment.
RAC considers the 4-hour rat LC₅₀ of 444 ppm from Tansy *et al.* (1981) sufficiently reliable for use as an ATE.

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Classification has to be based on the classification criteria. According to the references listed in the CLH report, there appears to be a consensus that potentially lethal pulmonary edema can occur in humans from prolonged exposure to ca. 250 ppm. However, RAC acknowledges the difficulty in determination of exposure concentration over a longer period in the human poisoning cases because of fluctuations and a steep dose-response. In addition, no well documented poisoning cases at exposure levels below the 4-hour mortality threshold in rats (i.e. 300-350 ppm) are presented in the CLH report. Consequently, it cannot be concluded with sufficient certainty that humans are more sensitive than rats.

A converted Acute Toxicity point Estimate should be used where no ATE is available (cf. CLP guidance, 3.1.3.3.4), which is not the case here given the availability of reliable animal data.

Consequently, RAC prefers an ATE of 440 ppm based on the rat study by Tansy *et al.* (1981). For a more detailed analysis please see the RAC opinion.

OTHER HAZARDS AND ENDPOINTS – Hazardous to the Aquatic Environment

Date	Country	Organisation	Type of Organisation	Comment number
17.12.2020	Germany	GHC Gerling, Holz & Co. Handels GmbH	Company-Manufacturer	3
Comment received				
<p>The harmonised classification as Aquatic Acute 1 is sensible.</p> <p>Hydrogen sulphide is currently classified as Aquatic Acute 1. This classification is supported by the reliable and meaningful studies of the Reach registration dossier. There is no new evidence on this classification. Also, the CLH report does not discuss this classification.</p> <p>Hence, hydrogen sulphide should be kept to be harmonised classified as Aquatic Acute 1.</p>				
Dossier Submitter's Response				
Noted.				
RAC's response				
Noted. The environmental classification of hydrogen sulfide has not been assessed by the DS.				

OTHER HAZARDS AND ENDPOINTS – Physical Hazards

Date	Country	Organisation	Type of Organisation	Comment number
17.12.2020	Germany	GHC Gerling, Holz & Co. Handels GmbH	Company-Manufacturer	4
Comment received				
<p>The harmonised classification as Flam. Gas 1A is sensible.</p> <p>Commission Regulation (EU) 2019/521 (12th ATP) introduced the hazard categories Flam. Gas 1A and Flam. Gas 1B, substituting the former category Flam. Gas 1.</p> <p>Hydrogen sulphide is harmonised classified as Flam. Gas 1. The amendment of the harmonised classification should take the changes made by the 12th ATP into account.</p> <p>Hydrogen sulphide has a lower explosion limit < 6 %. The auto ignition temperature is 270 °C (101.3 kPa). Relevant studies are provided in the CLH report. These physical properties suggest a classification as Flam. Gas 1A – H220 Extremely flammable gas.</p> <p>The harmonised classification as Press. Gas (Note U) is sensible.</p>				

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Hydrogen sulphide is a gas (boiling point -60 °C) and stored and transported in pressure receptacles.

The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR 2019) lists hydrogen sulphide (UN No 1053) in P200 table 2. This table includes all liquified and dissolved gases in contrast to table 1, which includes all compressed gases.

Dossier Submitter's Response

The German CA would like to thank the Company for supporting our proposed classification.

RAC's response

Thank you for your comments. RAC agrees with the proposed classifications for physical hazards.