Committee for Risk Assessment

RAC

Annex 2

Response to comments document (RCOM)

to the Opinion proposing harmonised classification and labelling at EU level of

Tetraphosphorus trisulphide; phosphorus sesquisulphide

EC Number: 215-245-0
CAS Number: 1314-85-8

CLH-O-0000007262-79-01/F

Adopted

16 March 2023

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON TETRAPHOSPHORUS TRISULPHIDE; PHOSPHORUS SESQUISULPHID

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: tetraphosphorus trisulphide; phosphorus sesquisulphid
EC number: 215-245-0
CAS number: 1314-85-8
Dossier submitter: Italy

OTHER HAZARDS AND ENDPOINTS – Hazardous to the Aquatic Environment

Date	Country	Organisation	Type of Organisation	Comment number
08.07.2022	France		MemberState	1
Comment received				
FR agrees with the proposal to remove the classification Aquatic Acute 1, H400. In the history of the previous classification and labelling part (p 6), it is indicated : "Classification as N; R50 was based on analogy with hydrogen sulphide. For tetraphosphorus trisulphide no LC50 data were available, but tetraphosphorus trisulphide reacts with water to form hydrogen sulphide which is classified N; R50, then the TC agreed that by analogy tetraphosphorus trisulphide should be classified with N; R50" We think that it would be useful to add information on the test that showed that tetraphosphorus trisulphide reacts with water to form H2S. If H2S was previously reported as a degradation product of tetraphosphorus trisulphide, it is not clear why the recent hydrolysis test OECD TG 111 (Nebuloni M, 2017) did not show the formation of H2S.				
Dossier Submitter's Response				
As detailed below, the applicant is willing to perform an additional test according to OECD TG 111 (Hydrolysis as a function of pH).				
RAC's response				
Thank you for comment.				

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON TETRAPHOSPHORUS TRISULPHIDE; PHOSPHORUS SESQUISULPHID

Date	Country	Organisation	Type of Organisation	Comment number
15.07.2022	United Kingdom	Health and Safety Executive	National Authority	2

Comment received

Tetraphosphorus trisulphide; phosphorus sesquisulphid, (EC: 215-245-0; CAS: 1314-85-8)

The harmonised classification for tetraphosphorus trisulphide was agreed under the Dangerous Substances Directive (DSD) as R50 based on read-across ecotoxicity data from hydrogen sulphide because tetraphosphorus trisulphide reacts with water to form hydrogen sulphide and no data were available for tetraphosphorus trisulphide. Hydrogen sulphide has a harmonised classification (Index # 016-001-00-4) of Aquatic Acute 1, seemingly also agreed under DSD as R50.

The more recent non-GLP hydrolysis study (mainly following OECD TG 111) with tetraphosphorus trisulphide (Nebuloni, 2007) included in the current CLH report showed no formation of hydrogen sulphide under the study conditions. However, this study has some deviations/limitations – principally, i) it ran for only 5 days at room temperature/20°C, and ii) only covered pH 4, 7 and 8 not pH 9 and an increase in hydrolysis may occur with higher pH. This means the levels of hydrogen sulphide formed in the environment over a relevant time period are unclear. Is there further information to consider the anticipated formation of hydrogen sulphide as a transformation product of tetraphosphorus trisulphide under environmentally relevant conditions? This is key to determining if hydrogen sulphide should be considered a relevant transformation product for acute / chronic hazard classification of tetraphosphorus trisulphide.

If hydrogen sulphide is considered a relevant transformation product for hazard classification over chronic time scales, read-across of the chronic toxicity data for hydrogen sulphide should also be considered for the aquatic chronic hazard classification of tetraphosphorus sulphide. For example, the EU REACH registration for hydrogen sulphide (ECHA, 2020) includes long-term ecotoxicity data indicating that an Aquatic Chronic 1 classification may be applicable.

References:
ECHA (2020) EU REACH registration dossier for hydrogen sulphide [online]. Available from: https://echa.europa.eu/en/registration-dossier/-/registered-dossier/14463/1/2 (Accessed 13 July 2022)

Dossier Submitter's Response

The Dossier Submitter agrees with the arguments raised by DE and as reported below the applicant propose to perform an additional test according to OECD TG 111, Hydrolysis as a function of pH, which is measuring the possible hydrolysis products at pH 4, 7 and 9, at 50°C for 5 days.

RAC's response

Thank you for comment.

OTHER HAZARDS AND ENDPOINTS – Physical Hazards

Date	Country	Organisation	Type of Organisation	Comment number
11.07.2022	Germany		MemberState	3

Comment received

Physical hazards:
Unfortunately, the information in the CLH report is not sufficient to be able to assess the individual physical hazard classes.
We would appreciate it if the test reports in the IUCLID dossier were also available in addition to the references given in the CLH report with regard to the physico-chemical properties.
The test results regarding the classification as flammable solid and self-heating substance seem to be justified and therefore we agree with the proposed classifications by the dossier submitter.

Substances which in contact with water emit flammable gases:
DE CA does not support the proposal removing the classification as a Water-reactive substance Category 1, H260. The experimental data and the conclusion about the change in classification are not plausible in our opinion.
Phosphorus sesquisulfide decomposes (hydrolyzes) in water with the hydrolysis reaction relatively slow in cold water but becoming faster upon heating producing mainly hydrogen sulfide and orthophosphoric acid, H_3PO_4; in neutral solutions, the hydrolysis products include PH_3 (3%), H_3PO_2 (38%), H_3PO_3 (49%) and H_3PO_4 (6)(1); in alkaline solutions, the hydrolysis products include PH_3 (5%), H_3PO_2 (15%), H_3PO_3 (75%), see Reference: https://pubchem.ncbi.nlm.nih.gov/compound/Phosphorus-sesquisulfide#section=Other-Experimental-Properties

Calculation of expected quantity of H_2S is based on following reaction stoichiometry:
$P_4S_3 + 9H_2O \rightarrow 3H_2S + H_3PO_3 + 3H_3PO_2$
10,7 g = 0,0486 mol of P_4S_3
220.09 g/mol
Molar volume for ideal gas: 24.055 l/mol at 20 °C and 101.325 kPa
When 10.7 g of P_4S_3 decompose in water, a quantity of 3.507 l (0.0486 mol*3*24.055 l/mol) of H_2S is produced.

The experimental data found a maximum rate of gas generation of 0.7 L kg-1 h-1 in a single test.
The difference between experimental result and expected quantity of H_2S by calculation was not considered and should taken into account when this leads in changing of the harmonized classification. Hydrogen sulfide has to be classified as "Flam. Gas 1A, H220". H220: Extremely flammable gas.
The evolved gas was analysed using a mass spectrometer. However, the mass number 34 determined by using the mass spectrometer can be assigned to both H_2S and PH_3. Phosphine is highly flammable and spontaneously flammable in air (pyrophoric); auto-ignition temperature is reported to be 38 °C at 101.3 kPa.
The experimental apparatus and the evaluation procedure should be examined for sources of errors.

For the purposes of classification, specific cases require further evaluation in accordance with CLP Art. 12 (a): adequate and reliable information demonstrates that in practice the physical hazards of a substance or a mixture differ from those shown by tests.
In addition, the Definition as given in Section 2.12 in Annex I to CLP is: Substances or

mixtures which, in contact with water, emit flammable gases means solid or liquid substances or mixtures which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

Therefore, the conclusion that tetraphosphorus trisulphide does not meet the classification criteria for substances that evolve flammable gases in contact with water, based on a single test report, should be considered critically.

In addition to the proposed classification, the supplementary hazard statement code EUH029 'Contact with water liberates toxic gas' would be justified as H2S is classified as Acute Tox. 2; H330 according to the RAC opinion (https://echa.europa.eu/documents/10162/1876203a-6568-f408-ab80-4759f36f97e9).

Dossier Submitter's Response

Thank you DE for your extensive comment. Since different critical issues have been raised by DE, please find as follows the Dossier Submitter's responses, point by point:

- "**Unfortunately, the information in the CLH report is not sufficient to be able to assess the individual physical hazard classes.**"
All the available tests carried out on P4S3 to address physical hazards (flammability, self-heating and ability of the substance to emit flammable gases when in contact with water, obtained according to the UN RTDG, Manual of Tests and Criteria: Test N.1, Test N.4 and Test N.5, respectively) have been summarized in the CLH report. On the other hand, as explained under Sec. 8 of the CLH report, any other physical hazards classes have been addressed based on considerations on the physical state, the molecule structure and the experience of the applicant in the manufacturing and handling of the substance. In addition, Annex I to the CLH report has been drafted, displaying more detailed information, to support the Dossier Submitter's proposal for harmonized classification and labelling.
All in all, the Dossier Submitter is of the opinion that each and any physical hazard class has been adequately covered by data or a justification for the non-submission of the data. The conclusions drawn by the Dossier Submitter's on physical hazards are transparent and traceable.

- "**We would appreciate it if the test reports in the IUCLID dossier were also available in addition to the references given in the CLH report with regard to the physico-chemical properties.**"
Sorry, but since the evaluation of the physico-chemical properties referenced in the CLH report under Section 7 is out-of-the-scope of the current exercise, the Dossier Submitter is of the opinion that the corresponding test reports do not actually need to be made available.

- "**The test results regarding the classification as flammable solid and self-heating substance seem to be justified and therefore we agree with the proposed classifications by the dossier submitter.**"
Thank you DE for supporting the Dossier Submitter's view.

- i. "**Substances which in contact with water emit flammable gases: DE CA does not support the proposal removing the classification as a Water-reactive substance Category 1, H260. The experimental data and the conclusion about the change in classification are not plausible in our opinion.**
[…]
https://pubchem.ncbi.nlm.nih.gov/compound/Phosphorus-sesquisulfide#section=Other-Experimental-Properties"
The possibility of P4S3 to hydrolyze and evolve H2S is reported in PubChem with reference to the Kirk-Othmer Encyclopedia of Chemical Technology, under the section on Phosphorus Compounds. This section describes the different compounds that Phosphorus may form

with Sulfur. In spite of the similarities of the structures, nevertheless those compounds display a different chemical behaviour. The table on the hydrolysis products is taken from a book titled "Phosphorus and its Compounds" and edited by Van Wazer, in 1959. This publication explains the hydrolysis of P4S10 in water, but – as far as P4S3 is concerned – it states that "*Under ordinary conditions, phosphorus sesquisulfide is unaffected by exposure to the atmosphere. It also does not react noticeably with water at ordinary temperatures.*" After describing the possible oxidation when exposed to oxygen, it adds: "*The final products of the reaction of phosphorus sesquisulfide with boiling water, in which the decomposition proceeds very gradually, are listed in Table 6-2. It should be noted that this sulfide is believed to hydrolyze primarily to a mixture of hypophosphorous and phosphorous acids.*" In fact, Table 6-2, which is also reported in the Kirk-Othmer Encyclopedia of Chemical Technology, is listing H3PO3 and H3PO2 as the main hydrolysis products of P4S3. In support of that, there is a relatively more recent publication (embedded below) with a section dedicated to the stability of Phosphorus Sulphide, stressing the concept that P4S3 is the most stable amongst the Phosphorus Sulphides and its alkaline hydrolysis can produce only traces of PH3 and H2S:

corbridge_stability_
phosphorous sulph

Most important, the applicant has lately clarified that the manufacturing process of P4S3 is carried out largely in water and is willing to provide additional details on that, in order to further support – by means of their experience in the manufacture of the substance – the actual stability of P4S3 in water. According to the applicant, impurities such as P4S10 are removed by hydrolysis in the purification step, while leaving P4S3 at a high purity level. Should the P4S3 degrade in water (i.e. hydrolyze) as readily as other phosphorous compounds do, it would not be possible to wash the substance in water at manufacture.

ii. "**Calculation of expected quantity of H2S is based on following reaction stoichiometry:**

P4S3 + 9H2O→3H2S + H3PO3 + 3H3PO2
10,7 g = 0,0486 mol of P4S3
220.09 g/mol
Molar volume for ideal gas: 24.055 l/mol at 20 °C and 101.325 kPa

When 10.7 g of P4S3 decompose in water, a quantity of 3.507 l (0.0486 mol*3*24.055 l/mol) of H2S is produced.
The experimental data found a maximum rate of gas generation of 0.7 L kg-1 h-1 in a single test.
The difference between experimental result and expected quantity of H2S by calculation was not considered and should taken into account when this leads in changing of the harmonized classification."

We can follow the reasoning behind the above calculation. Theoretically, 3.507 L of H2S can be stoichiometrically evolved from 10.7 g of P4S3 (equivalent to 327.8 L kg-1), according to the above reaction scheme. However, we do not agree with DE's conclusion that such a theoretical calculation should be regarded in contrast with the experimental results from the UN RTDG Test N. 5. Considering the above reaction as "complete" and the evolved gas as "ideal" bring on the safe side, but we wonder whether both assumptions can be considered that realistic. Most important, without any data/information on the kinetics of the reaction, it is unclear why any of the three criteria for classification as substances which in contact with water emit flammable gases should be considered as met. The trigger values for classification are expressed as litres per kilogram of substance over any one minute (category 1) or litres per kilogram of substance over one hour (category 2 or 3). Whereas, the above calculation does not provide any indication regarding the time

span over which 3.507 L of H2S would be evolved - in theory and under overly-conservative assumptions - from 10.7 g (1 hr? 1 d? 1 week?). In our view, the outcome from the above calculation and the maximum rate of gas measured under UN RTDG Test N. 5 conditions are not even comparable (L kg-1 *vs.* L kg-1 h-1).

iii. "**Hydrogen sulfide has to be classified as "Flam. Gas 1A, H220". H220: Extremely flammable gas.**
In both the CLH report and Annex I, the classification of H2S will be revised as indicated by DE, in compliance with the RAC opinion adopted on 16 September 2021. Thank you very much for noticing.

iv. **"The evolved gas was analysed using a mass spectrometer. However, the mass number 34 determined by using the mass spectrometer can be assigned to both H2S and PH3. Phosphine is highly flammable and spontaneously flammable in air (pyrophoric); auto-ignition temperature is reported to be 38°C at 101.3 kPa. The experimental apparatus and the evaluation procedure should be examined for sources of errors.**"
P4S3 was tested under GLP according to the UN RTDG Test N. 5. At evaluation stage, the Dossier Submitter found no evident reasons to invalidate the study. We do not share DE's doubts on the reliability of the conducting laboratory and/or of the experimental procedure followed to obtain the results submitted to remove the classification of P4S3 as a Water-reactive substance Category 1, H260.

v. "**For the purposes of classification, specific cases require further evaluation in accordance with CLP Art. 12 (a): adequate and reliable information demonstrates that in practice the physical hazards of a substance or a mixture differ from those shown by tests.**
[…]
Therefore, the conclusion that tetraphosphorus trisulphide does not meet the classification criteria for substances that evolve flammable gases in contact with water, based on a single test report, should be considered critically."
In the Dossier Submitter's opinion, there are no grounds to invalidate the results/conclusions from the study conducted under GLP according to the UN RTDG Test N. 5. We do not agree that "adequate and reliable information" (proving that in practise the substance emits flammable gases when in contact with water) is available that should overrule the available experimental results, which are also supported by the applicant's experience in the manufacture of P4S3 (the substance is washed with water in the purification step).
On the other hand, we understand DE's concerns and fully agree on the need to address those concerns in the CLH report. If DE agrees, we propose to improve the proposal to remove the classification of P4S3 as a Water-reactive substance Category 1, H260 by adding the reasoning/considerations given in response to items i. and ii. above.
Moreover, it is the Dossier Submitter's understanding that the applicant is willing to perform an additional test according to OECD TG 111 (Hydrolysis as a function of pH), in order to measure any hydrolysis products at pH 4, 7 and 9, at 50°C for 5 days. If DE agrees on the proposal, the new data would remove any residual doubt regarding the stability of P4S3 in water, while smoothing any concern related to the possible formation of either H2S or PH3.

vi. "**In addition to the proposed classification, the supplementary hazard statement code EUH029 `Contact with water liberates toxic gas' would be justified as H2S is classified as Acute Tox. 2; H330 according to the RAC opinion (https://echa.europa.eu/documents/10162/1876203a-6568-f408-ab80-4759f36f97e9)."**
In light of the above responses to items i., ii., iii., iv. and v. and in consideration of the

applicant's proposal to test according to OECD TG 111, in the Dossier Submitter's view no further action is deemed necessary.
RAC's response
Thank you for your comments and in-depth analysis. However RAC agrees with DS's response. In support to the DS's opinion it should be mentioned that criteria for classification a substance which, in contact with water, emits flammable gases based on results of reliable test N.5 (Part III, sub-section 33.5 of the UN RTDG, Manual of Tests and Criteria) and according to procedure of this test (section 33.5.3.1) the substance should be tested in its commercial form at ambient temperate (20°C). Therefore, consideration of the products of hydrolysis reaction at 100°C and with 100% yield is not appropriate for this classification.