Committee for Risk Assessment

RAC

Annex 1
Background document
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

The background document is a compilation of information considered relevant by the dossier submitter or by RAC for the proposed classification. It includes the proposal of the dossier submitter and the conclusion of RAC. It is based on the official CLH report submitted to consultation. RAC has not changed the text of this CLH report but inserted text which is specifically marked as 'RAC evaluation'. Only the RAC text reflects the view of RAC.

Adopted

16 March 2023

CLH report

Proposal for Harmonised Classification and Labelling

Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2

International Chemical Identification: tetraphosphorus trisulphide; phosphorus sesquisulphid

EC Number: **215-245-0**

CAS Number: **1314-85-8**

Index Number: **015-012-00-1**

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ANNEX 1 - BACKGROUND DOCUMENT TO RAC OPINION ON TETRAPHOSPHORUS TRISULPHIDE; PHOSPHORUS SESQUISULPHIDE

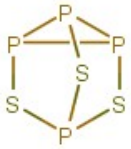
CONTENTS

ANNEX 1 - BACKGROUND DOCUMENT TO RAC OPINION ON TETRAPHOSPHORUS TRISULPHIDE; PHOSPHORUS SESQUISULPHIDE

1 IDENTITY OF THE SUBSTANCE

1.1 Name and other identifiers of the substance

Table 1: Substance identity and information related to molecular and structural formula of the substance

Name(s) in the IUPAC nomenclature or other international chemical name(s)	Tetraphosphorus trisulphide; phosphorus sesquisulphid
Other names (usual name, trade name, abbreviation)	Phosphorus sesquisulfide
ISO common name (if available and appropriate)	-
EC number (if available and appropriate)	215-245-0
EC name (if available and appropriate)	Tetraphosphorus trisulphide
CAS number (if available)	1314-85-8
Other identity code (if available)	015-012-00-1 (Index Number)
Molecular formula	P4S3
Structural formula	
SMILES notation (if available)	S1P2P3P2SP1S3
Molecular weight or molecular weight range	220.09
Information on optical activity and typical ratio of (stereo) isomers (if applicable and appropriate)	-
Description of the manufacturing process and identity of the source (for UVCB substances only)	-
Degree of purity (%) (if relevant for the entry in Annex VI)	> 98.5%

1.2 Composition of the substance

Table 2: Constituents (non-confidential information)

Constituent (Name and numerical identifier)	**Concentration range (% w/w minimum and maximum in multi-constituent substances)**	**Current CLH in Annex VI Table 3.1 (CLP)**	**Current self-classification and labelling (CLP)**
Tetraphosphorus trisulphide; phosphorus sesquisulphid Index No 1314-85-8 EC No 215-245-0 CAS No1314-85-8	> 98.5%	Flam. Sol. 2 (H228) Water-react. 1 (H260) Acute Tox. 4* (H302) Aquatic Acute 1 (H400)	Flam. Solid 1 (H228) Water-react. 1 (H260) Acute Tox. 3 (H301) Aquatic Acute 1 (H400) STOT Rep. Exp. 2 (H373) Skin Sens. 1 (H317) Eye Damage 1 (H318)

Current classification considers the new studies that were performed to fulfil the provisions of REACH Annex VIII. The minimum classification proposed in Annex VI of CLP is maintained.

Table 3: Impurities (non-confidential information) if relevant for the classification of the substance

Impurity (Name and numerical identifier)	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3.1 (CLP)	Current self-classification and labelling (CLP)	The impurity contributes to the classification and labelling
Water	< 0.4%	-	-	-
Unknown impurities of tetraphosphorus trisulphide; phosphorus sesquisulphid	< 1.5%	-	-	-

None contribute to the classification of the substance.

Table 4: Additives (non-confidential information) if relevant for the classification of the substance

Additive (Name and numerical identifier)	Function	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3.1 (CLP)	Current self-classification and labelling (CLP)	The additive contributes to the classification and labelling
-	-	-	-	-	-

None are present.

Table 5: Test substances (non-confidential information)

Identification of test substance	Purity	Impurities and additives (identity, %, classification if available)	Other information	The study(ies) in which the test substance is used
Tetraphosphorus trisulphide; phosphorus sesquisulphid	99.1%	-	batch 040017 and batch CS9-6287	As detailed under the Annex I to the CLH report

The test items were sampled from representative batches of the production process (batch 040017 and batch **CS9-6287)** and are, therefore, equivalent to the substance for which a modified CLH is proposed.

2 PROPOSED HARMONISED CLASSIFICATION AND LABELLING

2.1 Proposed harmonised classification and labelling according to the CLP criteria

Table 6:

	Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors	Notes
					Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	Suppl. Hazard statement Code(s)		
Current Annex VI entry	015-012-00-1	tetraphosphorus trisulphide; phosphorus sesquisulphid	215-245-0	1314-85-8	Flam. Sol. 2 Water-react. 1 Acute Tox. 4 * Aquatic Acute 1	H228 H260 H302 H400	GHS02 GHS07 GHS09 Dgr	H228 H260 H302 H400			T
Dossier submitters proposal	015-012-00-1	tetraphosphorus trisulphide; phosphorus sesquisulphid	215-245-0	1314-85-8	**Modify** Flam. Sol. 1 **Add** Self-heating Solid 1 **Remove** Water-react. 1 Aquatic Acute 1	**Retain** H228 **Add** H251 **Remove** H260 H400	**Retain** GHS02 GHS07 Dgr **Remove** GHS09	**Retain** H228 **Add** H251 **Remove** H260 H400			**Retain** T
Resulting Annex VI entry if agreed by RAC and COM	015-012-00-1	tetraphosphorus trisulphide; phosphorus sesquisulphid	215-245-0	1314-85-8	Flam. Sol. 1 Self-heating Solid 1 Acute Tox. 4 *	H228 H251 H302	GHS02 GHS07 Dgr	H228 H251 H302			T

Note T:

This substance may be marketed in a form which does not have the physical hazards as indicated by the classification in the entry in Part 3. If the results of the relevant method or methods in accordance with Part 2 of Annex I of this Regulation show that the specific form of substance marketed does not exhibit this physical property or these physical hazards, the substance shall be classified in accordance with the result or results of this test or these tests. Relevant information, including reference to the relevant test method(s) shall be included in the safety data sheet.

Table 7: Reason for not proposing harmonised classification and status under public consultation

Hazard class	Reason for no classification	Within the scope of consultation
Explosives	**data conclusive but not sufficient for classification**	**Yes**
Flammable gases (including chemically unstable gases)	hazard class not applicable	No
Oxidising gases	hazard class not applicable	No
Gases under pressure	hazard class not applicable	No
Flammable liquids	hazard class not applicable	No
Flammable solids	**harmonised classification proposed**	**Yes**
Self-reactive substances	**data conclusive but not sufficient for classification**	**Yes**
Pyrophoric liquids	hazard class not applicable	No
Pyrophoric solids	**data conclusive but not sufficient for classification**	**Yes**
Self-heating substances	**harmonised classification proposed**	**Yes**
Substances which in contact with water emit flammable gases	**data conclusive but not sufficient for classification**	**Yes**
Oxidising liquids	hazard class not applicable	No
Oxidising solids	**data conclusive but not sufficient for classification**	**Yes**
Organic peroxides	hazard class not applicable	No
Corrosive to metals	**data conclusive but not sufficient for classification**	**Yes**
Acute toxicity via oral route	not evaluated in this dossier	No
Acute toxicity via dermal route	not evaluated in this dossier	No
Acute toxicity via inhalation route	not evaluated in this dossier	No
Skin corrosion/irritation	not evaluated in this dossier	No
Serious eye damage/eye irritation	not evaluated in this dossier	No
Respiratory sensitisation	not evaluated in this dossier	No
Skin sensitisation	not evaluated in this dossier	No
Germ cell mutagenicity	not evaluated in this dossier	No
Carcinogenicity	not evaluated in this dossier	No
Reproductive toxicity	not evaluated in this dossier	No
Specific target organ toxicity-single exposure	not evaluated in this dossier	No
Specific target organ toxicity-repeated exposure	not evaluated in this dossier	No
Aspiration hazard	not evaluated in this dossier	No
Hazardous to the aquatic environment	**data conclusive but not sufficient for classification**	**Yes**
Hazardous to the ozone layer	not evaluated in this dossier	No

3 HISTORY OF THE PREVIOUS CLASSIFICATION AND LABELLING

Tetraphosphorus trisulphide; phosphorus sesquisulphid was originally classified under Dangerous Substance Directive (67/548/EEC) as F; R11, Xn; R22. The classification was updated for environmental effects in 25th ATP (Dir. 98/98/EC).

The DSD classification was agreed by the TC Environmental Effects C&L in 1997 (Dir. 67/548/EEC) [ECBI/29/97 - Rev. 2]:

F; R11

Xn; R22

N; R50

The current CLP classification is a translation thereof and is included in Annex VI (CLP00):

Flam. Sol. 2;

Water-react. 1;

Acute Tox. 4 *;

Aquatic Acute 1

Classification as N; R50 was based on analogy with hydrogen sulphide. For tetraphosphorus trisulphide no LC_{50} 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.

RAC general comment

Tetraphosphorus trisulphide is currently classified as H228 Flam. Sol. 2, H260 Water-react. 1, H302 Acute Tox. 4 and H400 Aquatic Acute 1. 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 itself. The aim of this CLH dossier is the re-evaluation of the existing harmonised classification based on new data. The dossier proposes to **modify** H228 Flam Sol. 2 into H228 Flam. Sol. 1, to add H251 Self-heating Solid 1 and to **remove** H260 Water-react. 1, as well as H400 Aquatic Acute 1.

Tetraphosphorus trisulphide or phosphorus sesquisulphid or P_4S_3 is an inorganic compound, is unaffected by exposure to the atmosphere and does not react noticeably with water. The final products of the reaction of tetraphosphorus trisulphide with boiling water, in which decomposition proceeds very gradually, is a mixture of hypophosphorus and phosphorus acid.

Table: *Physicochemical properties of tetraphosphorus trisulphide*

Property	**Value**
Physical state @ 20 ºC, 101.3 kPa	Solid
Melting point	174 ºC

Boiling point	409 ºC
Relative density	2.026 @23 ºC
Vapour pressure (estimated)	1.3 * 10^{-7} Pa
Solubility in water @ 20 ºC, pH=3.6	29.3 mg/L
K_{oc} calculated	0.82 L/kg
log K_{ow} calculated	-0.23

Use and application

Tetraphosphorus trisulphide has been used extensively in the manufacture of 'strike-anywhere' matches. The substance is registered under REACH at 10-100 t per year. The starting materials for the manufacturing process are yellow phosphorus and sulphur.

4 JUSTIFICATION THAT ACTION IS NEEDED AT COMMUNITY LEVEL

[B.] Justification that action is needed at Community level is required.

Reason for a need for action at Community level:

- *Change in existing entries due to new data*

Further detail on need of action at Community level
According to new data, modification of the existing entries is appropriate. Additional studies have been recently carried out, which allow further assessment of the classification of the substance.

The requested change of harmonised classification removes this substance from the scope of the Seveso Directive (Directive 2012/18/EU of the European Parliament and of the Council of 4 July 2012 on the control of major-accident hazards involving dangerous substances), with appreciable socio-economic advantages similar to those mentioned above as well as for safety and awareness of the general population that lives nearby the Company Plant. The CLH report, initially drafted by Italmatch Chemicals S.p.A, was submitted by the Italian Istituto Superiore di Sanità (ISS) in accordance with article 37(6) of CLP.

5 IDENTIFIED USES

Tetraphosphorus trisulphide; phosphorus sesquisulphid is an inorganic compound whose main and only application is in the industry of "strike anywhere" matches, where it totally replaced white and yellow phosphorus that were formerly used in the 19th century. The toxicity of white and yellow phosphorus, responsible of the "Fossy jaw" disease that caused osteonecrosis of the jaw to many workers, as well as their high reactivity made tetraphosphorus trisulphide the perfect alternative for matches industry.

The substance is registered under REACH at 10 – 100 tonnes per year.

The identified uses, as reported in the REACH registration dossier, are:

- Manufacturing
- Formulation
- Matches production
- Use of the match

The manufacturing process takes place in a very controlled area, due to the high flammability of the final product and the toxicity of the starting material yellow phosphorous. The total manufactured quantity is

limited, never exceeding the quantity of 30 t/y, with an average of 15-20 t/y. However, as Italmatch Chemicals SpA is probably the only manufacturer, this substance maintains a strategic role. Description of the relevant manufacturing steps:

Starting materials:
Sulphur (CAS 7704-34-9; EC 231-722-6)
Yellow phosphorus (CAS 7723-14-0, 12185-10-3; EC 231-768-7)

Molten yellow phosphorus and sulphur react immediately at controlled temperature. The tetraphosphorus trisulphide formed is distilled, condensed in a water condenser and transferred to the subsequent crushing, milling and sieving steps.
Tetraphosphorus trisulphide is distributed among different sites in the EU and outside the EU. Tetraphosphorus trisulphide is usually packaged and handled at room temperature in contact with air. Yellow phosphorous spontaneously ignites in contact with air when present at concentrations down to 0.04%. No residual yellow phosphorous is therefore present in tetraphosphorus trisulphide at such concentration levels, since tetraphosphorus trisulphide is routinely handled in contact with air, but no spontaneous ignition occurs.

Next step in the life cycle is the formulation with a proper resin and other substances, like potassium chlorate ($KClO_3$) which is a highly reactive oxidising agent that is necessary to promote combustion. The final product, containing about 15% tetraphosphorus trisulphide, is placed on the top of wood or plastic sticks and dried to make the final matches ready to use.

6 DATA SOURCES

Tetraphosphorus trisulphide; phosphorus sesquisulphid is a chemical substance registered under REACH Regulation (EC) No 1907/2006. The present evaluation exclusively relies on data submitted in the registration dossier. Some details of the summaries were not included when considered not relevant for a decision on the classification and labelling of this substance. For more details the reader is referred to the registration dossier.

7 PHYSICOCHEMICAL PROPERTIES (AS IN THE IUCLID REGISTRATION DOSSIER)

Table 8: Summary of physicochemical properties

Property	Value	Reference	Comment (e.g. measured or estimated)
Physical state at 20°C and 101.3 kPa	Solid	-	Visual
Melting/freezing point	174 °C		Measured
Boiling point	409 °C		Measured
Relative density	2.026 at 23 °C		Measured
Vapour pressure	1.3 * 10^-7 Pa		Estimated QSAR
Surface tension	Not applicable	-	-
Water solubility	29.3 mg/L at T= 20 °C pH= 3.6.		Measured
Partition coefficient n-octanol/water	-	-	-
Flash point	-	-	-
Flammability	Flammable solid	-	Measured

Property	Value	Reference	Comment (e.g. measured or estimated)
Explosive properties	Non explosive		According to the REACH Regulation according to the structural formula
Self-ignition temperature	84 °C		Measured
Oxidising properties	Non oxidising		According to the REACH Regulation, the study does not need to be conducted when the substance is highly flammable. Furthermore, the substance does not show oxidising properties based on its structural formula (it contains no oxygen or halogen atom).
Granulometry	d90 = 268 µm d50 = 83.0 µm d10 = 15.1 µm		Measured
Stability in organic solvents and identity of relevant degradation products	-	-	-
Dissociation constant	Not applicable	-	-
Viscosity	-	-	-

8 EVALUATION OF PHYSICAL HAZARDS

The physical hazards of tetraphosphorus trisulphide; phosphorus sesquisulphid were evaluated by considering:

- the available experimental data on flammability, self-heating and ability of the substances 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.5 and Test N.4, respectively). Those data formed the basis for the proposed revision of the classification as a Flammable solid Category 1 instead of 2, for the proposed addition of the classification as a Self-heating substance Category 1, as well as for the proposed removal of the classification as a Water-reactive substance Category 1;
- the molecule structure, to check for structural alerts that would trigger the need to further investigate the explosive, self-reactive and oxidising properties;
- the experience of the applicant in the manufacturing and handling of the substance, to address spontaneous ignition when in contact with air at normal temperatures;
- the physical state of the substance.

More details are presented as follows.

8.1 EXPLOSIVES

8.1.1 Short summary and overall relevance of the information provided on explosive properties

There are no chemical groups associated with explosive properties present in the molecule. In addition, no exothermic decomposition was observed during Differential Thermal Analysis (study reference: M. Leonardi and U. Zucchelli, Internal test report: Relative density, melting point, boiling point and flammability of P_4S_3, 2017). Since there are no indications from the screening procedure that tetraphosphorus trisulphide may possess explosive properties, no further testing is deemed necessary.

8.1.2 Comparison with the CLP criteria

According to the CLP Regulation (EC n.1272/2008, Annex I, Part 2, paragraphs 2.1.4.2 and 2.1.4.3):

A substance or mixture shall not be classified as explosive:

(a) When there are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are:

- C-C unsaturation (e.g. acetylenes, acetylides, 1, 2-dienes),
- C-Metal, N-Metal (e.g. Grignard reagents, organo-lithium compounds),
- Contiguous nitrogen atoms (e.g. azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides)
- Contiguous oxygen atoms (e.g. peroxides, ozonides)
- N-O (e.g. hydroxyl amines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles)
- N-halogen (e.g. chloramines, fluoroamines)
- O-halogen (e.g. chlorates, perchlorates, iodosyl compounds)

or

(b) When the substance or mixture contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

or

(c) When the organic substance or a homogenous mixture of organic substances contains chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C (the temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g). The exothermic decomposition energy may be determined using a suitable calorimetric technique.

or

(d) For mixtures of inorganic oxidizing substances with organic material(s), the concentration of the inorganic oxidising substance is:

- less than 15 % by mass, if the oxidizing substance is assigned to Categories 1 or 2;
- less than 30 % by mass, if the oxidizing substance is assigned to Category 3.

As regards tetraphosphorus trisulphide, there are no chemical groups associated with explosive properties in the molecule. As a result, condition (a) is satisfied, whereas condition (b) is not applicable. Condition (c) is not applicable, because tetraphosphorus trisulphide is not an organic substance and does not contain chemical groups associated with explosive properties; in addition, no exothermic decomposition was observed during Differential Thermal Analysis (study reference: M. Leonardi and U. Zucchelli, Internal test report: Relative density, melting point, boiling point and flammability of P_4S_3, 2017). Condition (d) is not applicable, either, being tetraphosphorus trisulphide a substance, not a mixture.
Since there are no indications from the screening procedure that the substance may possess explosive properties, no further testing is deemed necessary.

8.1.3 Conclusion on classification and labelling for explosive properties

Tetraphosphorus trisulphide fulfils criterion (a) of the screening procedure provided for explosive properties (no chemical groups associated with explosive properties). It can be concluded that tetraphosphorus trisulphide is not to be classified as explosive, according to the CLP Regulation (EC n.1272/2008).

8.2 FLAMMABLE GASES (INCLUDING CHEMICALLY UNSTABLE GASES)

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.3 OXIDISING GASES

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.4 GASES UNDER PRESSURE

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.5 FLAMMABLE LIQUIDS

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.6 FLAMMABLE SOLIDS

Table 9: Summary table of studies on flammable solids

Method	Results	Remarks	Reference
UN Recommendations on the Transport of Dangerous Good (RTDG), Manual of Tests and Criteria: Test N.1 (Test method for readily combustible solids)	The screening test was positive (burning time: 39 s) and the full burning rate test was performed. Burning times: 30, 25, 27, 26, 31, and 29 s. The wet zone did not stop the propagation of the flame	Batch number: 040017 No GLP compliance	Leonardi M and Zucchelli U, 2017

8.6.1 Short summary and overall relevance of the provided information on flammable solids

The flammability of the substance was tested according to the UN Recommendations on the Transport of Dangerous Good (RTDG), Manual of Tests and Criteria: Test N.1 (Test method for readily combustible solids). The screening test was positive (the burning of a 200 mm length of the powder train occurred in 39 s) and, therefore, the full burning rate test was performed. The burning times of the test item were less than 45 s: 30, 25, 27, 26, 31, and 29 s. In each and any of the six test runs, the wet zone did not stop the propagation of the flame.

8.6.2 Comparison with the CLP criteria

According to the CLP Annex I, Part 2, table 2.7.1. a solid is considered flammable in Category 1 if in the burning rate of the test substance: (a) wetted zone does not stop fire and (b) burning time <45 seconds or burning rate >2.2 mm/s. For Category 2 it is required that (a) wetted zone stops the fire for at least 4 minutes and (b) burning time <45 seconds or burning rate >2.2 mm/s.

8.6.3 Conclusion on classification and labelling for flammable solids

Under the experimental conditions of the UN RTDG, Manual of Tests and Criteria: Test N.1, the burning times of the test item were less than 45 s. In each and any of the six test runs, the wet zone did not stop the propagation of the flame. It can be concluded that tetraphosphorus trisulphide should be classified as Flammable solid Category 1 with hazard statement H228 (Flammable solid), retaining the pictogram “GHS02: Flame” with the signal word “Danger”, according to the CLP Regulation (EC n.1272/2008).

8.7 SELF-REACTIVE SUBSTANCES

8.7.1 Short summary and overall relevance of the provided information on self-reactive substances

Tetraphosphorus trisulphide does not contain any functional group that might trigger the classification as a self-reactive substance. In addition, no exothermic decomposition was observed during Differential Thermal

Analysis (study reference: M. Leonardi and U. Zucchelli, Internal test report: Relative density, melting point, boiling point and flammability of P_4S_3, 2017). No further testing is, therefore, deemed as necessary.

8.7.2 Comparison with the CLP criteria

According to the CLP Regulation (EC n.1272/2008, Annex I, Part 2, paragraph 2.8.4.2):

Substances and mixtures must be considered for classification in this hazard class as a self-reactive substance or mixture unless:

(a) There are no chemical groups present in the molecule associated with explosive or self-reactive properties; examples of such groups are given in Tables A6.1 and A6.2 in Appendix 6 of the UN RTDG, Manual of Tests and Criteria.

8.7.3 Conclusion on classification and labelling for self-reactive substances

There are no chemical groups or any other indications associated with explosives or self-reactive properties in the molecule. It can be concluded that tetraphosphorus trisulphide is not to be classified as a self-reactive substance, according to the CLP Regulation (EC n.1272/2008).

8.8 PYROPHORIC LIQUIDS

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.9 PYROPHORIC SOLIDS

8.9.1 Short summary and overall relevance of the provided information on pyrophoric solids

Experience in manufacturing and handling of tetraphosphorus trisulphide demonstrates the stability of the substance in air at room temperature for prolonged periods of time. No further testing is, therefore, deemed as necessary.

8.9.2 Comparison with the CLP criteria

According to the CLP Regulation (EC n.1272/2008, Annex I, Part 2, paragraph 2.10.1):

Pyrophoric solid means a solid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

8.9.3 Conclusion on classification and labelling for pyrophoric solids

Based on the applicant's experience in the manufacturing and handling of the substance, it can be concluded that tetraphosphorus trisulphide is not to be classified as a pyrophoric solid, according to the CLP Regulation (EC n.1272/2008).

8.10 SELF-HEATING SUBSTANCES

Table 10: Summary table of studies on self-heating substances

Method	Results	Remarks	Ref.
UN Recommendations on the Transport of Dangerous Good (RTDG), Manual of Tests and Criteria: Test N. 4 (Test method for self-heating solids)	Exothermic activity and ignition were observed in a 25 mm sample cube at 140°C, with a temperature rise of ca. 340°C. On completion of the test, no sample remained.	Batch number: CS9-6287 GLP study No deviations	Younis S, 2020

8.10.1 Short summary and overall relevance of the provided information on self-heating substances

The self-heating properties of the substance were tested according to the UN Recommendations on the Transport of Dangerous Goods (RTDG), Manual of Tests and Criteria: Test N.4 (Test method for self-heating solids). The substance was tested in a 25 mm sample cube at 140°C. A positive test result (i.e. dangerous self-heating) was observed, i.e. spontaneous ignition occurred, with the sample temperature exceeding the oven temperature by more than 60°C during the 24-hr period.

8.10.2 Comparison with the CLP criteria

According to the CLP Annex I, Part 2, table 2.11.1. the classification criteria for self-heating substances or mixtures are:

Category 1: A positive result is obtained in a test using a 25 mm sample cube at 140°C

Category 2: (a) a positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and the substance or mixture is to be packed in packages with a volume of more than 3 m^3; or (b) a positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a positive result is obtained in a test using a 100 mm cube sample at 120°C and the substance or mixture is to be packed in packages with a volume of more than 450 litres; or (c) a positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and a positive result is obtained in a test using a 100 mm cube sample at 100°C.

8.10.3 Conclusion on classification and labelling for self-heating substances

Under the experimental conditions of the UN RTDG, Manual of Tests and Criteria: Test N.4, a positive test result (i.e. dangerous self-heating) was observed in a 25 mm sample cube at 140°C, where spontaneous ignition occurred, with the sample temperature exceeding the oven temperature by more than 60°C during the 24-hr period. It can be concluded that tetraphosphorus trisulphide should be classified as a Self-heating substance Category 1 with hazard statement H251 (Self-heating: may catch fire), with the pictogram "GHS02: Flame" and with the signal word "Danger", according to the CLP Regulation (EC n.1272/2008).

8.11 SUBSTANCES WHICH IN CONTACT WITH WATER EMIT FLAMMABLE GASES

Table 11: Summary table of studies on substances which in contact with water emit flammable gases

Method	Results	Remarks	Reference
UN Recommendations on the Transport of Dangerous Good (RTDG), Manual of Tests and Criteria: Test N. (Test method for substances which in contact with water emit flammable gases)	Preliminary steps (1 to 3): no gas generation or spontaneous ignition. Final step: no spontaneous ignition after 5 days for test number 1 and after 7 hours for test number 2-3. The generated gas was flammable during test number 1, with a maximum rate of gas generation of 0.7 L kg^{-1} h^{-1}	Batch number: CS9-628 GLP study No deviations	Younis S, 2020

8.11.1 Short summary and overall relevance of the provided information on substances which in contact with water emit flammable gases

The ability of the substance to emit flammable gases on contact with water was tested according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Test N.5. (Test method for substances which in contact with water emit flammable gases).

Three preliminary steps and a final step were conducted. The test item was not sieved prior to testing, due to concerns about potential reaction during the sieving process. No stirring was performed at any stage of the analysis.

No gas generation or spontaneous ignition was observed in the preliminary steps (1 to 3). During the final step, no spontaneous ignition was observed after 5 days for test number 1 and after 7 hours for test number 2-3. The generated gas was, however, flammable during test number 1, with a maximum rate of gas generation of 0.7 L $kg^{-1}h^{-1}$.

After Step 4, test 1 the evolved gas was analysed using a mass spectrometer and an increased response was found on mass numbers 12, 14, 16, 17, 28, 32, 34, 40 and 44. The increase in mass numbers 32 and 34 is suspected to be due to hydrogen sulphide H_2S, which is classified as Flammable gas Category 1 with hazard statement H220 (Extremely flammable gas).

The maximum rate of gas generated for step 4 test 1 was observed between 99 and 100 hours.

8.11.2 Comparison with the CLP criteria

According to the CLP Annex I, Part 2, table 2.12.1. the classification criteria for substances or mixtures which in contact with water emit flammable gas are:

Category 1: any substance or mixture which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.

Category 2: any substance or mixture which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Category 1.

Category 3: any substance or mixture which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Categories 1 and 2.

8.11.3 Conclusion on classification and labelling for substances which in contact with water emit flammable gases

Under the experimental conditions of the UN RTDG, Manual of Tests and Criteria: Test N.5, no gas generation or spontaneous ignitions was observed in the preliminary steps. During the final step, no spontaneous ignition was observed after 5 days for test number 1 and after 7 hours for test numbers 2-3. The generated gas was, however, flammable during test number 1, with a maximum rate of gas generation of 0.7 L kg^{-1} h^{-1}. It can be concluded that no classification as per CLP Regulation (EC) No. 1272/2008 should be given for tetraphosphorus trisulphide.

8.12 OXIDISING LIQUIDS

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

8.13 OXIDISING SOLIDS

8.13.1 Short summary and overall relevance of the provided information on oxidising solids

Tetraphosphorus trisulphide satisfies the screening criteria reported in the CLP Regulation, equivalent in principle to Section 6 of Appendix 6 to the UN RTDG, Manual of Tests and Criteria, since it is an inorganic substance which does not contain any oxygen or halogen atom. In addition, testing is not applicable to flammable solids.

8.13.2 Comparison with the CLP criteria

According to the CLP Regulation (EC n. 1272/2008), 2.14.4.1 section, for organic substances or mixtures the classification procedure for the oxidising substance class shall not apply if:

- the substance or mixture does not contain oxygen, fluorine or chlorine; or

- the substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bound only to carbon or hydrogen.

For inorganic substances or mixtures, the classification procedure shall not apply if they do not contain oxygen or halogen atoms.

8.13.3 Conclusion on classification and labelling for oxidising solids

Tetraphosphorus trisulphide does not contain any oxygen or halogen atoms. According to the screening procedure provided for the identification of oxidizing solids, it can be concluded from its structure that tetraphosphorus trisulphide is not to be classified as an oxidizing solid, according to the CLP Regulation (EC n.1272/2008).

8.14 ORGANIC PEROXIDES

Hazard class not applicable, the substance evaluated in this dossier is not an organic peroxide.

8.15 CORROSIVE TO METALS

Hazard class not applicable, due to the physical state of the substance evaluated in this dossier (solid).

There is no reference in the definition of corrosive to metals (as in the CLP regulation, Annex I, 2.16.1 section) to the physical state of the substances or mixtures that need consideration for potential classification in this hazard class. However, according to the classification criteria, only substances and mixtures for which the application of the UN Test C.1 (described in part III, Section 37.4.1.1 of the UN RTDG, Manual of Tests and Criteria) is relevant need to be considered.
Application of classification criteria in the UN RTDG, Manual of Tests and Criteria, Section 37.4 excludes solids, while ‘liquids and solids that may become liquids (during transport)’, should be considered for such a classification. It can be concluded that, based on its physical state (solid) and melting point (174°C / Study reference: M. Leonardi and U. Zucchelli, Internal test report: Relative density, melting point, boiling point and flammability of P4S3, 2017), this hazard class does not apply to tetraphosphorus trisulphide.

RAC evaluation of physical hazards

Summary of the Dossier Submitter’s proposal

The Dossier Submitter (DS) proposed to change the harmonised classification of tetraphosphorus trisulphide – from Flammable solid Category 2 to Flammable solid Category 1, to add Self-heating Solid 1 and to remove Water-react. 1

Tetraphosphorus trisulphide is solid and therefore hazard classes for gases and liquids are not applicable. Tetraphosphorus trisulphide does not contain the bivalent O-O group and is thus not an organic peroxide.

Explosives

The DS proposed no classification, based on the lack of indications from the screening procedure according to CLP Annex I, 2.1.4.:
- absence of functional groups potentially associated with explosive properties
- tetraphosphorus trisulphide is not an organic substance
- no exothermic decomposition was observed during Differential Thermal Analysis according to test report by Leonardi M., 2017.

Flammable solids

DS proposed to revise the current harmonised classification as Flammable solid Category 2 and classify tetraphosphorus trisulphide as Flammable solid Category 1 with the hazard statement H228 (Flammable solid), based on the results of Test N.1 performed by Leonardi M. and Zucchelli U, 2017, according to UN RTDG, Manual of Tests and Criteria. The CLP criteria are met since the burning time of the test item was less than 45 s. e.g. 30, 25, 27, 26, 31, 29 s, and in each and any of the six test runs the wet zone did not stop the propagation of the flame.

Self-reactive substance

The DS proposed no classification based on the absence of functional groups potentially associated with explosive and self-reactive properties. In addition, no exothermic decomposition was observed during a Differential Thermal Analysis (study reference: M. Leonardi and U. Zucchelli, Internal test report: Relative density, melting point, boiling point and flammability of P_4S_3, 2017).

Pyrophoric solids

The DS proposed no classification based on experience in handling. Experience in manufacturing and handling of tetraphosphorus trisulphide demonstrates the stability of the substance in air at room temperature for prolonged periods of time.

Self-heating substances

The DS proposed classification of tetraphosphorus trisulphide as Self-heating substance Category 1 based on the positive result (i.e., dangerous self-heating) of a UN Test N.4 (Younis S, Final report: Flammability Testing on a Sample of Phosphorus Sesquisulphide P_4S_3, 2020). Exothermic activity and spontaneous ignition were observed in a 25 mm sample cube at 140 °C, with a temperature rise of ca. 340 °C. On completion of the test, no sample remained.

Substance or mixture which in contact with water emits flammable gas

The DS proposed no classification based on that the criteria of CLP regulation (Annex I, Part 2, table 2.12.1) for this hazard class are not applicable to tetraphosphorus trisulphide.

The ability of the substance to emit flammable gases in contact with water was tested according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Test N.5. (Younis S, 2020).

Three preliminary steps and a final step were conducted. The test item was not sieved prior to testing, due to concerns about potential reaction during the sieving process. No stirring was performed at any stage of the analysis.

No gas generation or spontaneous ignition was observed in the preliminary steps (1 to 3). During the final step, no spontaneous ignition was observed after 5 days for test number 1 and after 7 hours for test number 2-3. The generated gas was, however, flammable during test number 1, with a maximum rate of gas generation of 0.7 L $kg^{-1}h^{-1}$.

After Step 4 in test 1 the evolved gas was analysed using a mass spectrometer and an increased response was found on mass numbers 12, 14, 16, 17, 28, 32, 34, 40 and 44. The increase in mass numbers 32 and 34 is suspected to be due to hydrogen sulphide H_2S, which is classified as Flammable gas Category 1A with hazard statement H220 (Extremely flammable gas).

The maximum rate of gas generated for step 4 in test 1 was observed between 99 and 100 hours.

Oxidising solids

The DS proposed no classification as an oxidising solid based on the absence of oxygen or halogen atoms in the molecule of tetraphosphorus trisulphide. For inorganic substances or mixtures, the classification procedure according to CLP regulation (Annex I, Part 2, section 2.14.4.1) shall not apply if they do not contain oxygen or halogen atoms.

Corrosive to metals

The DS proposed no classification because this hazard class does not apply to tetraphosphorus trisulphide taking into account physical state of the substance evaluated in this dossier (solid) and melting point (174 °C; Study reference: M. Leonardi and U. Zucchelli, 2017). Application of classification criteria in the UN RTDG, Manual of Tests and Criteria, Section 37.4 excludes solids, while 'liquids and solids that may become liquids (during transport)', should be considered to determine the corrosion hazard with the UN Test C.1 (described in part III, Section 37.4.1.1 of the UN RTDG, Manual of Tests and Criteria).

Note T

Note T: "This substance may be marketed in a form which does not have the physical hazards as indicated by the classification in the entry in Part 3. If the results of the relevant method or methods in accordance with Part 2 of Annex I of this Regulation show that the specific form of substance marketed does not exhibit this physical property or these physical hazards, the substance shall be classified in accordance with the result or results of this test or these tests. Relevant information, including reference to the relevant test method(s) shall be included in the safety data sheet."

DS proposed to retain note T as included to the current harmonised classification.

Comments received during consultation

One Member State Competent Authority (MSCA) comment was received and agreed with the proposed classification by DS as Flam. Sol. 1 and Self-heat. 1, however they questioned the removal of the Water-react. 1 classification and suggested that 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.

The MSCA provided information reported in PubChem with reference to the Kirk-Othmer Encyclopedia of Chemical Technology, under the section on Phosphorus Compounds (2006) and a book titled "Phosphorus and its Compounds" by Van Wazer (1959), indicating that phosphorus sesquisulphide decomposes (hydrolyses) in water with the hydrolysis reaction relatively slow in cold water but becoming faster upon heating and producing mainly hydrogen sulphide and orthophosphoric acid, H3PO4; in neutral solutions, the hydrolysis products include PH3 (3 %), H3PO2 (38 %), H3PO3 (49 %) and H3PO4 (6 %); while in alkaline solutions, the hydrolysis products include PH3 (5 %), H3PO2 (15 %), H3PO3 (75 %). However, the DS provided more information on the above process: hydrolysis products were obtained in the reaction of phosphorus sesquisulfide with boiling water, in which the decomposition proceeds very gradually whereas "under ordinary conditions, phosphorus sesquisulfide is unaffected by exposure to the atmosphere; it also does not react noticeably with water at ordinary temperatures". In support of that, according to a publication by D. E. C. Corbridge, 'Phosphorus, an Outline of its Chemistry, Biochemistry and Technology' (1990), P_4S_3 is the most stable amongst phosphorus sulphides It is very stable in cold or hot water and is only slowly attacked in acid solution, while its alkaline hydrolysis can produce only traces of PH_3 and H_2S. Also, in the DS's opinion there are no grounds to invalidate the results from the study conducted under GLP according to the UN RTDG Test N.5. Thus, the DS did not agree that "adequate and reliable information" proving that in practice the substance emits flammable gases when in contact with water is available.This is also supported by experience in the manufacture of P_4S_3 (the substance is washed with water in the purification step). Also, in the criteria for classification of 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 the procedure of this test (section 33.5.3.1), it is stated that 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.

In addition, the MSCA is of the opinion that the supplementary hazard statement code EUH029 'Contact with water liberates toxic gas' would be justified as H_2S is classified as Acute Tox. 2; H330 according to the RAC opinion (CLH-O-0000007029-73-01/F). The DS replied that based on Annex II section 1.2.1 of the CLP regulation, EUH029 should be assigned for substances and mixtures which in contact with water or damp air, evolve gases (classified for acute toxicity in category 1, 2 or 3) in potentially dangerous amounts. However, there is no data on the ability of a tetraphosphorus trisulphide to emit gases in potentially dangerous amounts at normal conditions of uses.

Assessment and comparison with the classification criteria

Explosives

The evaluation of explosivity was performed on a Weight of Evidence basis:

- **Structural considerations** – no explosive properties are expected based on the structure of the compound (the list of organic moieties in table A6.1 associated with explosivity is only an example list and does not preclude application of expert judgement based on structure for inorganics and organics not included in the list) and no double bonds are present in the molecule of P_4S_3 (containing trivalent phosphorus) which proves the lower reactivity of this sulfide compared to other

sulfides (e.g. tetraphosphorus decasulfide (CAS no: 1314-80-3) P_4S_{10}) containing double bonds (with pentavalent phosphorus);

- A **Differential Scanning Calorimetry** shows that the only thermal events are the melting and boiling points.

For these reasons RAC agrees with the DS conclusion **not to classify the substance as an explosive** based on conclusive data.

Flammable solids

RAC agrees with the DS to **classify tetraphosphorus trisulphide as Flam. Sol. 1, H228 (Flammable solid)**, based on the observed burning behaviour. The melting point of the substance is 174 °C. The test method N.1 required in the CLP Criteria for solid substance (CLP 2.7.2.1, UN RTDG, Manual of Tests and Criteria, Part III, sub-section 33.2.1) was performed. The results of this test met classification criteria for Flam. Sol., Category 1 in accordance with Table 2.7.1 of CLP regulation: (a) wetted zone does not stop fire and (b) burning time is less than 45 seconds.

Self-reactive substances

Based on the same reasoning reported in the explosives section, RAC agrees with the DS conclusion **not to classify the compound as self-reactive substance** based on conclusive data.

Pyrophoric solids

According to the CLP Regulation (Annex I, 2.10.1): pyrophoric solid means a solid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air.

RAC agrees with the DS conclusion **not to classify tetraphosphorus trisulphide as pyrophoric solid**. Experience in manufacture and handling shows that the substance does not ignite spontaneously on coming into contact with air at normal temperatures in accordance with paragraph 2.10.4.1. of CLP regulation.

Self-heating substances

RAC agrees with the DS to **classify tetraphosphorus trisulphide as Self-heat. 1, H251 (Self-heating; may catch fire)** based on the positive result obtained in UN Test N.4 (UN RTDG, Manual of Tests and Criteria, Part III, sub-section 33.3.1.6) using a 25 mm and 100 mm sample cube at 140 °C. Therefore, tetraphosphorus trisulphide met the criteria of category 1 for self-heating substances in table 2.11.1 and figure 2.11.1 of CLP regulation.

Substances which in contact with water emit flammable gases

RAC agrees with the DS conclusion that **the classification criteria (in accordance with CLP regulation, Annex I, Part 2, table 2.12.1) for any of the three categories for this class are not met for tetraphosphorus trisulphide**. In all samples of tetraphosphorus trisulphide tested using test N.5 (Part III, sub-section 33.4.1.4 of the UN RTDG, Manual of Tests and Criteria), no spontaneous ignition was observed in tested samples after 5 days and after 7 hours. The generated gas was however flammable during the test in one sample for which the measuring time was extended to a maximum time of 5 days, with a maximum rate of gas generation of 0.7 L kg^{-1} h^{-1} (observed between 99 and 100 hours of the test). Since the maximum rate of evolution of flammable gas was not

greater than 1 litre per kilogram of substance per hour, tetraphosphorus trisulphide should not be classified as a substance which in contact with water, emit flammable gases.

The following information is considered supplementary to support no-classification for tetraphosphorus trisulphide as 'a substance which in contact with water emit flammable gases':

- In the test performed according to OECD Guideline 111 - Hydrolysis as a Function of pH (Nebuloni M., 2017), no remarkable hydrolysis to H_2S in buffered solutions (at 25°C) was observed for 5 days. In conclusion, tetraphosphorus trisulfide is stable to hydrolysis at room temperature in acid, neutral and basic conditions;
- P_4S_3 is the most stable amongst phosphorus sulphides and is very stable in cold or hot water and is only slowly attacked in acid solution; its alkaline hydrolysis can produce only traces of PH_3 and H_2S (according to: D. E. C. Corbridge. Phosphorus, an Outline of its Chemistry, Biochemistry and Technology, 1990);
- the manufacturing process of P_4S_3 is carried out largely in water (the substance is washed with water in the purification step) and experience in the manufacture confirmed its stability (as provided by DS in reply to MSCA comment during public consultations).

Additional labelling for water-reactive substances and mixtures with EUH029 - 'Contact with water liberates toxic gas'

The statement EUH029 should be assigned for substances and mixtures which in contact with water or damp air, evolve gases classified for acute toxicity in category 1, 2 or 3 in potentially dangerous amounts. Based on data and information provided for the assessment of tetraphosphorus trisulfide as 'Substances which in contact with water emit flammable gases' **this additional labelling with EUH029 is considered by RAC as not required**.

Oxidising solids

RAC agrees with the DS conclusion on **no classification of tetraphosphorus trisulphide as an oxidising solid** based on classification consideration in paragraph 2.14.4.2. of CLP regulation: *for inorganic substances or mixtures the classification procedure for this class shall not apply if they do not contain oxygen or halogen atoms*.

Corrosive to metals

RAC agrees with the DS **not to classify tetraphosphorus trisulphide as corrosive to metals** considering that this hazard class is applicable only for 'liquids and solids that may become liquids (during transport)' according to classification procedure in the section 37.4.1.1. A measured melting point of tetraphosphorus trisulphide is greater than the test temperature used in the UN Test C.1 test (55 °C).

Note T

RAC agrees to **retain note T** in entry to Annex VI of CLP Regulation for tetraphosphorus trisulphide.

9 TOXICOKINETICS (ABSORPTION, METABOLISM, DISTRIBUTION AND ELIMINATION)

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

9.1 Short summary and overall relevance of the provided toxicokinetic information on the proposed classification(s)

The provided toxicokinetic information are not relevant for the proposed classification.

10 EVALUATION OF HEALTH HAZARDS

10.1 ACUTE TOXICITY-ORAL ROUTE

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.2 ACUTE TOXICITY-DERMAL ROUTE

Not evaluated in this dossier.

10.3 ACUTE TOXICITY-INHALATION ROUTE

Not evaluated in this dossier.

10.4 SKIN CORROSION/IRRITATION

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.5 SERIOUS EYE DAMAGE/EYE IRRITATION

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.6 RESPIRATORY SENSITISATION

Not evaluated in this dossier.

10.7 SKIN SENSITISATION

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.8 GERM CELL MUTAGENICITY

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.9 CARCINOGENICITY

Not evaluated in this dossier.

10.10 REPRODUCTIVE TOXICITY

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.11 SPECIFIC TARGET ORGAN TOXICITY-SINGLE EXPOSURE

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.12 SPECIFIC TARGET ORGAN TOXICITY-REPEATED EXPOSURE

Not evaluated in this dossier. For further details refer to the REACH Registration Dossier.

10.13 ASPRIRATION HAZARD

Not evaluated in this dossier.

11 EVALUATION OF ENVIRONMENTAL HAZARDS

11.1 RAPID DEGRADABILITY OF ORGANIC SUBSTANCES

11.1.1 Ready biodegradability

The study was not conducted since tetraphosphorus trisulphide; phosphorus sesquisulphid is inorganic. According to section 4.1.2.10.1 of the CLP "For inorganic compounds and metals, the concept of degradability as applied to organic compounds has limited or no meaning".

11.1.2 BOD_5/COD

Not available.

11.1.3 Hydrolysis

Table 12: Summary table of studies on hydrolysis

Method	Test material	Results	Remarks	Reference
OECD TG 111	Tetraphosphorus trisulphide; phosphorus sesquisulphid Purity: 99.1%	No gas evolution (H_2S) at pH 4, 7 and 8	No GLP	Nebuloni M, 2017

The stability of the tetraphosphorus trisulphide to hydrolysis was investigated according to OECD TG 111.

The experiment was performed to determine:

(i) the rate of hydrolysis of the test substance as a function of pH and
(ii) the identity or nature and rates of formation of hydrolysis products

This investigation was carried out by monitoring the hydrogen sulphide (H_2S) evolution in different buffer pH solutions (pH= 4, 7 and 8) for 5 days. The gaseous product (H_2S) was collected and measured by a device connected to the container according to the Dietrich-Fruhling method. From the volume of the produced gas (H_2S) in relation to the sample amount and from the volume evolution on the time, it was possible to assess abiotic hydrolytic transformations of P_4S_3 in aquatic systems at pH values normally found in the environment. For the assessment, the solubility at room temperature of H_2S in water was also considered. From the information available in literature, the solubility of H_2S in water is indicated as 0.385 g/100 g H_2O.

No gas evolution was noted in any of the pHs tests (4, 7 and 8) therefore it is assumed that the hydrolysis rate of the substance under the tested conditions is close to 0 %. There was however a minor decrease of the pH of the solutions (from pH 7 to 6.5 and from pH 8 to 7.3) that could be ascribed to a low amount of phosphates and to the H_2S developed during the 5-day test. If any H2S was formed it could be below the limit of detection of the analytical method used and therefore this is only an assumption based on the decrease of pH.

In conclusion, tetraphosphorus trisulphide is stable to hydrolysis at room temperature in acid, neutral and basic conditions.

The reliability of the study as per its Registration dossier is 2 (reliable with restrictions) according to the Klimisch criteria. The study was conducted as per the OECD Guideline 111 and was sufficiently described and it meets the acceptable scientific criteria. However, a reliability of 2 was given as the study was not conducted under GLP conditions. Also some deviations from the OECD Guideline 111 were noted, such as the pHs used were 4, 7 and 8 instead of 4, 7 and 9 and the temperature of the preliminary study was at 20°C instead of 50°C. Nevertheless these deviations are not considered to impact the reliability of the study.

11.1.4 Other convincing scientific evidence

No other scientific evidence is available.

11.2 ENVIRONMENTAL TRANSFORMATION OF METALS OR INORGANIC METAL COMPOUNDS

Not applicable.

11.3 ENVIRONMENTAL FATE AND OTHER RELEVANT INFORMATION

The substance is an inorganic compound that is not hydrolysed. Some of the properties such as ready biodegradation and logKow are not available since the studies were not conducted due to the inorganic nature of the substance. However, a calculated LogKow (EpiSuite v.4.11) suggests that the substance has a low potential for bioaccumulation. Furthermore, a predicted value for partition coefficient organic carbon-water was calculated by EUSES 2.1.2 as Koc = 0.82 L/kg. Considering this predicted value, a low adsorption potential is expected.

To sum up, the hydrolysis and biodegradation are not expected to be the principal degradation route in the environment and the substance should have a low bioaccumulation potential.

11.4 BIOACCUMULATION

Not evaluated in this dossier as these data are not available. The Partition coefficient of the substance is not available as the substance is an inorganic compound. However, EPI Suite v.4.11 calculated the value of -0.23, even though inorganic salts are out of the applicability domain. A logKow lower than 4 suggests a low potential for bioaccumulation.

11.5 ACUTE AQUATIC HAZARD

Table 13: Summary of relevant information on acute aquatic toxicity

Method	Species	Test material	Results[1]	Remarks	Reference
OECD TG 203	*Danio Rerio*	Tetraphosphorus trisulphide; phosphorus sesquisulphid Purity: 99.1%	LC_{50} 96 h >100 mg/L (loading rate) > 5.82 mg/L (geometric mean 0-96 h) pH 6.7-8.1 (0h; 96h)	Batch number: 040017 GLP compliance	Anonymous (2017)
OECD TG 202	*Daphnia Magna*	Tetraphosphorus trisulphide; phosphorus sesquisulphid Purity: 99.1%	EC_{50} 48 h >100 mg/L (loading rate) >2.8 mg/L (geometric mean 0-48 h) pH 6.7-7.1 (0h; 48h)	Batch number: 040017 GLP compliance	Anonymous (2017)

Method	Species	Test material	Results[1]	Remarks	Reference
OECD TG 201	*Desmodesmus subspicatus*	Tetraphosphorus trisulphide; phosphorus sesquisulphid Purity: 99.1%	E_rC_{50} 72 h >100 mg/L (loading rate) >2.5 mg/L (geometric mean 0-72 h) pH 7.4-8.2 (0h; 72h)	Batch number: 040017 GLP compliance	Anonymous (2017)
OECD TG 209	Micro-organisms in an activated sludge	Tetraphosphorus trisulphide; phosphorus sesquisulphid Purity: 99.1%	EC_{50} 3h = 471 mg/L (nominal concentration) and NOEC = 31.6 mg/L	Batch number: 040017 GLP compliance	Anonymous (2017)

11.5.1 Acute (short-term) toxicity to fish

The acute lethal toxicity of tetraphosphorus trisulphide to the Zebrafish *Danio rerio* was investigated according to test guideline OECD TG 203 and EU Mehod C.1., under static exposure conditions over a period of 96 h.

The only applied loading rate was 100 mg/L. Therefore, this study represents a limit test. This test concentration was chosen based on preceding acute toxicity tests carried out with *Algae* and *Daphnia*, where a 72h E_rC_{50} of >100 mg/L and a 48 h EC_{50} of >100 mg/L, based on loading rates, were determined, respectively.

The test item is solid, poorly soluble (29.3 mg/L at a pH 3.6 and ca. 20 °C), with a purity of 99.1%. Therefore, the test medium consisted of a saturated stock solution, prepared by addition of the test item to natural water, 96-h stirring and filtration. The concentration of the substance was determined by phosphorus-analytics at the beginning and at the end of the exposure phase. These analyses confirmed the low solubility of the test item. The effective concentrations were assessed based on the geometric mean of the measured concentrations of the test item, as well as on the loading rates. The substance in the fish medium presents a solubility between 5.8-5.9 mg/L that corresponds to the measured concentration at 0 and 96 h. The pH of the test solution at 0h is 6.7 and at 96 h is 8.1.

At the loading rate of 100 mg/L of tetraphosphorus trisulphide, none of a total of seven fish died after 96 h of exposure. No mortality was observed in the blank control.

Toxic effects other than mortality, such as loss of coordination, hypo- or hyperactivity and swimming on the back, were not observed.

The no-observed-effect concentration (NOEC) was 5.82 mg/L mean measured concentration (based on phosphorus-analytics) or 100 mg/L loading rate.

Based on the binominal theory, the absence of mortality in such a test design provides at least 99% confidence that the median lethal concentration (LC_{50}) of the test item to *Danio rerio* (Zebrafish) is greater than the measured concentration of 5.82 mg/L or 100 mg/L loading rate.

The study was conducted as per the OECD 203 guideline and under GLP conditions. As per the Guidance on CLP criteria (version 5, July 2017), tests consistent with OECD Test Guideline 203 (Fish 96-hour LC_{50}) or equivalent should be used for classification. No deviations from the guideline were reported. The study is considered to have a reliability of 1 (reliable without restriction) as per Klimisch criteria and it is considered as reliable to be used for the CLP classification.

11.5.2 Acute (short-term) toxicity to aquatic invertebrates

The median effect concentration (EC_{50}) and the no-effect concentration (NOEC) of tetraphosphorus trisulphide to *Daphnia magna* were investigated under static exposure conditions over a period of 48 h, following guideline OECD TG 202 and EU Method C.2.

The test item tetraphosphorus trisulphide is solid, poorly soluble (29.3 mg/L at a pH 3.6 and ca. 20 °C), with a purity of 99.1%. The test solutions were prepared by directly adding the test item to *Daphnia* medium in a glass vessel, stirring this mixture for 96 h and filtering it. The single investigated loading rate was 100 mg/L. Forty individual *Daphnia* divided into 2 test vessels were exposed to the test item, and 60 *Daphnia* divided into 3 test vessels were used as blank controls. The determination of the test item concentrations was based on phosphorus-analytics (photometry after a chemical extraction step). Total phosphorus (total P) was measured at the beginning and at the end of the test. These analyses revealed that the concentrations of test item were stable over the whole 48 h period and corresponded to 2.8% and 2.7% of the nominal loading rate at the beginning and end of the test, respectively. The substance in *Daphnia* medium presents a solubility around 3 mg/l that corresponds to the measured concentration at 0 (2.76 mg/L) and 48 h (2.74 mg/L). The pH of the test solution at 0h is 6.7 and at 48 h is 7.1.

The effective concentrations EC_x were assessed based on the loading rates of the test item as well as on the measured concentration.

No significant effects (≤10% immobilization) were observed at 100 mg/L loading rate or in the blank controls, neither after 24 h of exposure nor after 48 h. Therefore, the median effect concentrations (EC_{50}) of tetraphosphorus trisulphide on *Daphnia magna* after 24 h as well as after 48 h of exposure were estimated to be >100 mg/L loading rate or >2.8 mg/L measured concentration.

The NOEC values after 24 h and after 48 h of exposure were 100 mg/L loading rate or 2.8 mg/L measured concentration. All validity criteria were fulfilled.

The study was conducted as per the OECD 202 guideline and under GLP conditions. As per the Guidance on CLP criteria (version 5, July 2017), tests consistent with Guideline 202 Part 1 (Daphnia acute) or USA-EPA OPPTS 850.1035 (Mysid acute toxicity) or equivalent should be used for classification. No deviations from the guideline were reported. The study is considered to have a reliability of 1 (reliable without restriction) as per Klimisch criteria and it is considered as reliable to be used for the CLP classification.

11.5.3 Acute (short-term) toxicity to algae or other aquatic plants

The growth inhibitory effects of tetraphosphorus trisulphide to the green alga *Desmodesmus subspicatus* were investigated according to test guideline OECD TG 201, over a period of 72 h.

The test item is solid, poorly soluble (29.3 mg/L at a pH 3.6 and ca. 20 °C), with a purity of 99.1%. The test solutions were prepared by directly adding the test item to algal medium in a glass vessel, stirring this mixture for 96 h and filtering it. The only loading rate was 100 mg/L. Six parallel test vessels were used for the test item and six for the blank controls. The determination of the test item concentrations was based on phosphorus-analytics (photometry after a chemical extraction step). Total phosphorus (total P) was measured at the beginning and at the end of the test. These analyses revealed that the concentrations of test item were stable over the whole 48 h period and corresponded to 2.8% and 2.2% of the nominal loading rate at the beginning and end of the test, respectively. The substance in the algae medium presents a solubility between 2-3 that corresponds to the measured concentration at 0 (2.8 mg/L) and 72 h (2.21 mg/L). The pH of the test solution at 0h is 7.4 and at 72 h is 8.2.

The effective concentrations EC_x were assessed based on the loading rates of the test item as well as on the measured concentration. With respect to both endpoints growth rate and yield (algal biomass), no significant effects were observed at 100 mg/L loading rate, as compared to the blank controls.

Therefore, 72h E_rC_{50} and E_yC_r values of the test item on the green alga *Desmodesmus subspicatus* were estimated to be >100 mg/L loading rate or >2.5 mg/L measured concentration. The NOE_rC and NOE_yC values were both 100 mg/L loading rate or 2.5 mg/L measured concentration. All validity criteria were fulfilled.

The study was conducted as per the OECD 201 guideline and under GLP conditions. As per the Guidance on CLP criteria (version 5, July 2017) tests consistent with OECD Test Guideline 201 (Algal growth inhibition) should be used. No deviations from the guideline were reported. The study is considered to have a reliability of 1 (reliable without restriction) as per Klimisch criteria and it is considered as reliable to be used for the CLP classification.

11.5.4 Acute (short-term) toxicity to other aquatic organisms

The respiration inhibitory effects of tetraphosphorus trisulphide to the microorganisms of activated sludge of a municipal sewage treatment plant were investigated according to test guideline OECD TG 209, under aerobic static conditions over an exposure time of 3 hours.

The loading rates of the test item were 1000, 316, 100, 31.6 and 10.0 mg/L.

Three parallel test vessels were used for each concentration of the test item and six vessels for the blank controls.

No chemical analysis of test concentrations was conducted. For the calculation of the effective concentrations, the loading rates of the test item were used, assuming the test item to be stable in water over 3 h.

After 3 hours of exposure, the following inhibition of the activated sludge respiration was observed, as compared to the blank controls: 61 % at 1000 mg/L, 47 % at 316 mg/L and 22 % at 100 mg/L. No significant inhibition was observed at 31.6 and 10.0 mg/L.

The EC_{50} 3h value of tetraphosphorus trisulphide to activated sludge is 471 mg/L (95% confidence limit: 372 – 619 mg/L).

The no observed concentration (NOEC) was 31.6 mg/L, as determined by Dunnett's test.

11.6 LONG-TERM AQUATIC HAZARD

No long-term studies on fish or aquatic invertebrates are available. The NOEC value determined in the study on aquatic plants can be used for the long-term aquatic hazard evaluation (refer to section 11.5.3).

11.7 COMPARISON WITH THE CLP CRITERIA

11.7.1 Acute aquatic hazard

The acute aquatic toxicity was evaluated on the three aquatic trophic levels: fish, aquatic invertebrates and algae. The following results were obtained in the experimental studies conducted according to the relevant OECD Guidelines:

- LC_{50} 96h *Danio Rerio* >100 mg/L loading rate; > 5.82 mg/L (measured concentration): experimental data obtained testing the substance according to OECD TG 203.

- EC_{50} 48h *Daphnia Magna* >100 mg/L loading rate; > 2.8 mg/L (measured concentration): experimental data obtained testing the substance according to OECD TG 202.

- ErC_{50} 72h *Desmodesmus subspicatus* >100 mg/L (loading rate); > 2.5 mg/L (measured concentration): experimental data obtained testing the substance according to OECD TG 201.

The substance does not present any toxic effects on the three organisms and therefore no sensitive species has been identified. More specifically no fish were found dead, no daphnids were immobilised and the algal growth inhibition was 0.2% at the highest concentrations tested at each study (100 mg/L loading rate). The LC_{50} and the EC_{50} for daphnia and algae were found to be above the minimum CLP criteria of 1 mg/l so Aquatic Acute classification is not warranted.

11.7.2 Long-term aquatic hazard (including bioaccumulation potential and degradation)

The substance is considered ‘not rapidly degradable’. The stability of the Tetraphosphorus trisulphide to hydrolysis was investigated according to OECD TG 111 (Nebuloni M, 2017) concluding that the substance is stable to hydrolysis at room temperature in acid, neutral and basic conditions. Furthermore, the only available data, indicating a low potential for bioaccumulation,is a calculated LogKow of -0.23, even though inorganic salts are out of the applicability domain.

For the substance only unbounded LC50 and EC50 values are present, therefore the surrogate approach cannot be used to derive fish and invertebrate chronic classification from acute data. Only algae NOEC value of 2.5 mg/L is thus used for classification purposes.

In conclusion, considering that the substance is not readily biodegradable and the LogKow is ≤ 4 and the NOEC is 2.5 mg/L, no classification for Aquatic toxicity is suggested.

11.8 CONCLUSION ON CLASSIFICATION AND LABELLING FOR ENVIRONMENTAL HAZARDS

The acute toxicity data suggest that the substance should not be classified in Aquatic Acute 1 as the LC_{50} for fish and the EC_{50} for crustacea and algae is above 1 mg/L. The substance does not fulfil the criteria for environmental hazards according to CLP Regulation. Aquatic Acute 1, should be removed.

Regarding chronic aquatic hazard, tetraphosphorus trisulphide is considered not rapidly degradable with a low potential for bioaccumulation in the aquatic environment. Chronic toxicity data is available for algae only and the surrogate approach cannot be applied because of unbounded L/EC50 values; the long-term toxicity NOEC is > 2.5 mg/L, therefore no chronic aquatic classification is proposed.

Based on the above results, it is suggested that tetraphosphorus trisulphide should not be assigned any classification for environment. Thus, it is suggested that the substance is declassified in relation to the current environmental classification.

RAC evaluation of aquatic hazards (acute and chronic)

Summary of the Dossier Submitter's proposal

The Dossier Submitter proposed no classification for tetraphosphorus trisulphide regarding aquatic hazard, based on all available data, noting that studies on degradation and aquatic toxicity were available. The DS noted the following when concluding on the classification:

- Based on a study performed by Nebuloni (2017) showing that tetraphosphorus trisulphide is stable to hydrolysis at 20 °C in acidic, neutral, and basic conditions, this substance should be considered not rapidly degradable;
- Based on the acute aquatic toxicity studies performed on fish, aquatic invertebrates and algae, no toxic effects were observed for tetraphosphorus trisulphide and, consequently, Aquatic Acute classification is not warranted;
- Based on the available chronic endpoint for algae, this substance not being rapidly degradable and the impossibility to apply the surrogate approach on unbounded acute endpoints, Aquatic Chronic classification is not warranted.

Degradation

A ready biodegradability test was not available since tetraphosphorus trisulphide is an inorganic substance.

The hydrolysis study by Nebuloni (2017) was performed according to the OECD TG 111, but not under GLP. During this study, hydrolysis of tetraphosphorus trisulphide as a function of pH was monitored and hydrogen sulphide evolution was measured in buffer solutions pH = 4,7, and 8 for 5 days. No remarkable hydrolysis to H_2S for 5 days was observed in any of the

pH value tested at 20 ºC. Decrease of the pH of the solution from pH 7 to pH 6.5 and from pH 8 to pH 7.3 was observed. This could be due to the development of a small amounts of phosphates and H_2S during the 5-day test. As a limitation of the study, it must be noted that it is a non-GLP study and according to OECD TG 111 with deviation in pH and temperature.

***Table**: Comparison of study by Nebuloni (2017) and OECD TG 111*

OECD TG 111	**Nebuloni (2017)**	**Reliability**
	Non GLP	Klimisch criteria 2 "reliable with restrictions"
pH 4, 7 and 9	pH 4,7 and 8	
Temperature 50 ºC	Temperature 20 ºC	
Duration 5 days	Duration 5 days	

Based on the obtained results, it could be concluded by the DS that tetraphosphorus trisulphide is stable to hydrolysis at 20 ºC and acidic, neutral and basic conditions.

The DS considered tetraphosphorus trisulphide to be not rapidly degradable, for classification and labelling purposes.

Bioaccumulation

Measured or estimated BCF test data are not available. The EPI Suite v.4.11 calculated $LogK_{ow}$ value of -0.23. A log K_{ow} below 4 suggests a low potential for bioaccumulation, according to the CLP Regulation.

***Table:** Summary of the available data on the tetraphosphorus trisulphide environmental hazard studies on aquatic toxicity*

Method, Guideline, GLP status, Reliability, reference	**Species, No/ group**	**Test substance, Concentration levels, Duration of exposure**	**Results**
OECD TG 203 GLP Klimisch 1 Anonymous, 2017	*Danio Rerio* 7 fish in exposure group	LC_{50} >100 mg/L (loading rate); 96 h LC_{50} > 5.82 mg/L (measured concentration); 96 h	None of a total of seven fish died after 96 h of exposure; no mortality in control group No other toxic effects were observed (loss of coordination, hypo- or hyperactivity and swimming on the back)
OECD TG 202 GLP Klimisch 1 Anonymous, 2017	*Daphnia Magna* 40 *Daphnia* in exposure group 60 *Daphnia* in blank control group	EC_{50} > 100 mg/L (loading rate); 48 h EC_{50} > 2.8 mg/L (measured concentration); 48 h	No significant effects (<10 % immobilisation) were observed
OECD TG 201 GLP Klimisch 1 Anonymous, 2017	*Desmodesmus subspicatus* 6 vessels to test 6 vessels for blank control	E_rC_{50} > 100 mg/L (loading rate); 72 h E_rC_{50} > 2.5 mg/L (measured concentration); 72 h NOE_rC = 100 mg/L (loading rate); 72h NOE_rC = 2.5 mg/L (loading rate); 72h	No significant effect on growth rate and yield

Aquatic acute toxicity

The acute toxicity of tetraphosphorus trisulphide to Zebrafish *Danio rerio* was tested according to OECD TG 203. The test was performed under GLP and no deviations from the guideline were reported. All the values of the pH, temperature and oxygen concentration during the test were within the acceptable range. The study has a reliability of 1 rated as Klimisch criteria. The test was carried out on 7 fish under static exposure conditions over a period of 96 h. The only applied loading rate was 100 mg/L of tetraphosphorus trisulphide, therefore this study represents a limit test.

None of the 7 fish died after 96 h of exposure. There were no other toxic effects observed, such as e.g., loss of coordination, hypo- or hyperactivity and swimming on the back. No mortality was observed in the control. Geometric mean of the measured concentration in test solution was 5.82 mg/L. Based on the binominal theory and the lack of toxic effects in the test, it could be stated that for *Danio rerio* (Zebrafish) the median lethal concentration (LC_{50}) is greater than the measured value of 5.82 mg/L at 100 mg/L loading rate.

The median effect concentration (EC_{50}) of tetraphosphorus trisulphide to *Daphnia magna* were investigated under static exposure condition over a period of 48 h. The test was performed following OECD TG 202 and EU method C.2. under GLP conditions. No deviations from the

guideline were reported therefore the study is considered to have reliability of 1 rated as Klimisch criteria.
The investigated loading rate was 100 mg/L which corresponded to the measured concentration of 2.8 mg/L. Test was carried out on 40 Daphnia magna. No effects were observed neither after 24 h nor after 48 h of exposure. No effects were observed in the control. Therefore, the median effect concentration (EC_{50}) of tetraphosphorus trisulphide on Daphnia magna was estimated to be >100 mg/L loading rate or >2.8 mg/L measured concentration.

The growth inhibitory effects of tetraphosphorus trisulphide to the green alga *Desmodesmus subspicatus* were investigated over a period of 72 h. The test was performed according to the OECD TG 201 and under GLP conditions, without reported deviations from the guideline. The study is considered to have a reliability of 1 rated as Klimisch criteria.
The only loading rate of tetraphosphorus trisulphide was 100 mg/L. Six parallel test vessels and six control vessels were used. The concentration of the test item was stable during the 48-h test and corresponds to the measured concentration 2.8 mg/L at 0 h and 2.21 mg/L at 72 h.
With respect to both endpoints growth and yield, no effects were observed at 100 mg/L loading rate. Therefore, 72 h E_rC_{50} and E_yC_r values of the tetraphosphorus trisulphide on the green alga *Desmodesmus subspicatus* were estimated to be above 100 mg/L loading rate or above 2.5 mg/L measured concentration.

The DS concluded that the acute toxicity data suggest that the substance should not be classified as Aquatic Acute 1 since the LC50 for fish and the EC50 for crustacea and algae is above 1 mg/L; no sensitive species was identified due to the lack of presence of toxic effects on all the tested organisms at the highest concentration tested (100 mg/L loading rate). The substance does not fulfil the criteria for environmental hazards according to CLP Regulation therefore Aquatic Acute 1 should be removed.

Aquatic chronic toxicity

Long-term studies on fish and aquatic invertebrates are not available. Only a NOEC value of 2.5 mg/L over a period of 72 hours for green alga *Desmodesmus subspicatus* is available and, thus, used for the purpose of aquatic chronic classification. The test was performed according to the OECD TG 201 and under GLP conditions, without reported deviations from the guideline. The study is considered to have a reliability of 1 rated as Klimisch criteria.

Since only unbounded acute toxicity effect values (LC_{50} and EC_{50}) are present for all three trophic levels, the surrogate approach, as described in Table 4.1.0 (b)(iii) of Annex I in CLP regulation, cannot be used to derive chronic classification from the acute dataset.

Based on Table 4.1.0 (b)(i), considering that the substance is not rapidly degradable and the log Kow is ≤ 4 and the NOEC for Desmodesmus subspicatus is 2.5 mg/L, no aquatic chronic classification is suggested.

Comments received during consultation

Two comments regarding environmental hazard classification were received during the consultation. One from a member state which agrees with the proposal to remove the classification Aquatic Acute 1, H400.

The second comment is from a National Authority (NA) in which concern regarding hydrolysis study was raised. The NA did not indicate preference regarding Aquatic Acute classification. However, the NA raised a question about further information regarding formation of hydrogen sulphide as a transformation product of tetraphosphorus sulphide under environmental relevant conditions. The NA suggested that read-across of the chronic toxicity data for hydrogen sulphide should be considered for classification of tetraphosphorus sulphide.

In response to the comments, DS pointed out that the applicant is willing to perform an additional test according to the OECD TG 111, Hydrolysis as a function of pH, which is measuring the possible hydrolysis product at pH 4, 7 and 9, at 50 °C for 5 days.

RAC agrees with the DS proposal. No gas evolution was reported by Nebuloni in the hydrolysis study. Also, according to literature data, tetraphosphorus trisulphide is unaffected by exposure to the atmosphere and does not react with water at ordinary temperatures and the main hydrolysis products of tetraphosphorus trisulphide are H_3PO_3 and H_3PO_2 (D. E. C. Corbridge, Phosphorus: An Outline of Its Chemistry, Biochemistry and Technology, Fifth Edition, Studies in Inorganic Chemistry. Elsevier: Amsterdam. 1995.).

Assessment and comparison with the classification criteria

Degradation

RAC agrees with the DS that for the purpose of classification and labelling, tetraphosphorus trisulphide is considered as not rapidly degradable. The basis for this conclusion is that tetraphosphorus trisulphide is stable to hydrolysis at room temperature in acid, basic and neutral conditions in the absence of other available information for an inorganic substance.

Bioaccumulation

RAC agrees with the DS that for the purpose of classification, tetraphosphorus trisulphide has a low potential to bioaccumulate in aquatic organisms. The basis for this conclusion is the calculated log Kow value of -0.23, which is below the CLP Regulation threshold of 4.

Aquatic toxicity

Conclusion on aquatic classification

Reliable acute aquatic toxicity data are available for fish, aquatic invertebrates, algae. The lowest estimated mean measured 72 h E_rC_{50} value is above 2.5 mg/L for *Desmodesmus subspicatus* which is above the minimum CLP criteria of 1 mg/L. Consequently, RAC concludes in line with the proposal by the DS **to remove the current Aquatic Acute classification**.

No long-term studies on fish and aquatic invertebrates are available and the surrogate approach cannot be used to derive a chronic classification based on acute test data due to unbounded values. Only algae NOEC value of 2.5 mg/L for *Desmodesmus subspicatu*s is available for the purpose of classification. Tetraphosphorus trisulphide is considered not rapidly degradable with a low potential for bioaccumulation in the aquatic environment. Consequently, RAC concludes in line with the proposal by the DS that **no chronic aquatic classification is warranted.**

12 EVALUATION OF ADDITIONAL HAZARDS

12.1 Hazardous to the ozone layer

No additional hazards were evaluated in this dossier.

13 ADDITIONAL LABELLING

None.

14 REFERENCES

Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances.

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Younis S, Final report: Flammability Testing on a Sample of Phosphorus Sesquisulphide P_4S_3, 2020.

Nebuloni M., Study report: Degradation of P_4S_3 (phosphorus sesquisulphide): Hydrolysis in function to the pH (OECD/OCDE 111 directives). Testing laboratory: Redox S.r.l. Report number: 779/17, Owner company: Italmatch Chemicals SpA, Report date: Nov 30, 2017.

Phosphorus sesquisulphide 96-hour Acute Toxicity to *Danio rerio* (Zebrafish) OECD 203 Commission Regulation (EC) No 440/2008. C.1. (study report), Report no: A17-01588. Owner company; Italmatch Chemicals SpA, Report date: Nov 9, 2017.

Phosphorus sesquisulphide - 48-hour Acute Toxicity to *Daphnia magna* OECD 202, Commission Regulation (EC) No 440/2008. C.2. (study report), Report no: A17-01062. Owner company; Italmatch Chemicals SpA, Report date: Nov 3, 2017.

Phosphorus sesquisulphide - Fresh water algal growth inhibition test with *Desmodesmus subspicatus* OECD 201, Commission Regulation (EC) No 761/2009. C.3. (study report), Report no: A17-01061. Owner company; Italmatch Chemicals SpA, Report date: Nov 3, 2017.

Tetraphosphorus Trisulfide - Test for inhibition of oxygen consumption by activated sludge: Respiration Inhibition Test, Arcadis Schweiz LTD, Ifangstrasse 11, CH-8952 Schlieren.

15 ANNEXES

The study summaries of the original study reports mentioned in the sections above, including details and results, are available in the Annex I to the CLH report.