Committee for Risk Assessment

RAC

Annex 2

Response to comments document (RCOM)

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

tricalcium diphosphide

EC number: 215-142-0

CAS number: 1305-99-3

ECHA/RAC/CLH-O-0000003602-81-01/A2

Adopted
7 March 2013

ANNEX 1 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON TRICALCIUM DIPHOSPHIDE

COMMENTS AND RESPONSE TO COMMENTS ON CLH: PROPOSAL AND JUSTIFICATION

ECHA has compiled the comments received via the internet that refer to several hazard classes and entered them under each of the relevant categories/headings as comprehensively as possible. Please note that some of the comments might occur under several headings, when splitting the information provided is not reasonable.

Substance name: Tricalcium diphosphide
EC number: 215-142-0
CAS number: 1305-99-3

Dossier submitter: Germany

GENERAL COMMENTS

Date	Country	Organisation	Type of Organisation	Comment number
08/07/2012	Germany	Chemische Fanrik Wülfel GmbH & Co.KG	Company-Manufacturer	1

Comment received

The published CLH report was performed on basis of the DAR Calcium phosphide (Tricalcium diphosphide) 2007 without reference to the Reporting and Evaluation table, EFSA Scientific Report(2008) 183, 1-59, and Directive 2008/125/EC of 19 December 2008, respectively.
As Notifier and manufacturer of the active substance Calcium phosphide we have made many corrections in the report (see uploaded pdf file).
Following pages are involved: Part A: 1,7,8,10-16,18
Part B: 19,20,22,25-33,37-44

ECHA comment: The document "Revision of CLH report_ Tricalcium Diphosphide_rev_04_07_Redacted.pdf" was submitted as a separate attachment. Attachment no. 1.

Dossier Submitter's response

Noted.

RAC's response

OK

Date	Country	Organisation	Type of Organisation	Comment number
19/07/2012	Spain		MSCA	2

Comment received

p.5 Proposal for harmonised classification and labelling
The Spanish CA agrees with the German proposal to classify calcium phosphide as:
- Water-react. 1, H260: In contact with water releases flammable gases which may ignite spontaneously and EUH029 Contact with water liberates toxic gas according to Regulation EC 1272/2008 and as F; R15/29 Contact with water liberates toxic extremely flammable gases according to Directive 67/548/EC
- Acute Tox. 2 (oral,) H300: Fatal if swallowed according to Regulation EC 1272/2008 and as T+; R28 Very toxic if swallowed according to Directive 67/548/EC.
- Acute Tox. 3 (dermal,) H311: Fatal if swallowed according to Regulation EC 1272/2008 and as Xn; R21 Harmful in contact with the skin according to Directive 67/548/EC.
Besides, the following additional classification is proposed:
- Acute Tox. 1 (inhalation,) H330: Fatal if inhaled according to Regulation EC 1272/2008 and as T+; R26 Very toxic by inhalation according to Directive 67/548/EC.
- EUH032 according to CLP Regulation and as R32 according to Dir. 67/548/CE.
With regard to the irritant/corrosive properties, Germany proposes to classify calcium phoshide as Skin Corr. 1A, H314: Causes severe skin burns and eye damage according to Regulation EC

1272/2008 and as C; R35: Causes severe burns according to Directive 67/548/EC. However, it could be considered a less severe classification of calcium phosphide as: Skin Irrit. 2, H315, Eye Irrit. 1, H318 and STOT-SE 3, H335 according to CLP Regulation and as R37/38-41, according to Dir. 67/548/CE.

Dossier Submitter's response

Please refer to comment number 5 and 9.

RAC's response

RAC agrees on remarks made by Spain with exception to issues regarding skin and eye irritation. Please refer to comment number 8. Furthermore, with respect to STOT-SE 3, H335 according to CLP Regulation and R37/38-41, according to Dir. 67/548/CE, RAC has the following considerations: having in mind that, there are no human or animal data which could be compared with criteria for respiratory tract irritation set in section 3.8.2.2.1 of annex I of CLP regulation, the proposal for classification of tricalcium diphosphide to STOT SE 3, H335 is not justified. The irritant properties of this substance or its decomposition products are sufficiently covered in other hazard classes. In addition, a danger linked with single acute inhalation exposure seem to adequately communicated by classification with Acute Tox. 1, H330 and EUH029 contact with water liberates very toxic gases.

Date	Country	Organisation	Type of Organisation	Comment number
26/07/2012	France		MSCA	3

Comment received

FR proposes a classification in Acute Toxicity Category 1, H330.

Instead of classification for Skin Corr. 1A, H314; FR proposes a classification in Skin Irrit.2, H315, Eye dam. 1, H318 and STOT SE 3, H335.

Dossier Submitter's response

Please refer to comment number 5 and 7.

RAC's response

RAC agrees for Eye Dam. 1 – H318 but with respect to skin irrit. 2 – H315 and STOT SE 3, H335 please refer to comment number 8.

OTHER HAZARDS AND ENDPOINTS

Acute Toxicity

Date	Country	Organisation	Type of Organisation	Comment number
08/07/2012	Germany	Chemische Fanrik Wülfel GmbH & Co.KG	Company-Manufacturer	4

Comment received

Two acute toxicity studies we have attached.
1. Acute oral toxicity study on Calcium phosphide (OECD, GLP), p. 25 and pp. 27-29
2. Acute inhalation toxicity study of Calcium phosphide (4h , OECD 403, GLP), p.26, and pp. 31-33 (see also Part A, Table 2, and sub-sections 4.2.3, 4.2.4, and 4.2.5 on pages 37-38 in Part B).

ECHA comment: The document "Revision of CLH report_ Tricalcium Diphosphide_rev_04_07_Redacted.pdf" was submitted as a separate attachment. Attachment no. 1.

Dossier Submitter's response

These two attached acute toxicity studies were already presented in the DAR (B.6.11 Acute toxicity studies of preparations). Due to the fact, that these studies were conducted with the preparation 'Polytanol' (purity 17.6 %), they were not described in the CLH-Dossier on the active substance tricalcium diphosphide.

RAC's response

Agrees with DS

Date	Country	Organisation	Type of Organisation	Comment number
19/07/2012	Spain		MSCA	5

Comment received

p. 21. Summary and discussion of acute toxicity
Acute oral toxicity
The Spanish CA supports the proposed classification of calcium phosphide as Acute Tox. 2 (oral, H300: Fatal if swallowed (limits LD50 = 5-50 mg/kg bw) according to Regulation EC 1272/2008 and as T+; R28: Very toxic if swallowed (limits LD50 ≤ 25 mg/kg bw) according to Directive 67/548/EC. This classification is due to the LD50 values obtained in one oral toxicity study in rats with aluminium phosphide LD50 = 8.7 mg/kg bw (Sterner, 1977) equivalent to 13.8 mg/kg bw of calcium phosphide.
Acute dermal toxicity
The Spanish CA supports the proposed classification of calcium phosphide as Acute Tox. 3 (dermal), H311: Toxic in contact with skin (limits LD50 = 200-1000 mg/kg bw) according to Regulation EC 1272/2008 and as Xn; R21 Harmful in contact with skin (limits LD50 = 400-2000 mg/kg bw) according to Directive 67/548/EC. This classification is due to the LD50 values obtained in three acute dermal toxicity studies in rats with aluminium phosphide: LD50 = 461.2 mg/kg bw (Stephen, 2000) equivalent to 733.3 mg/kg bw of calcium phosphide, LD50= 900 mg/kg bw (Dickhaus, 1987) equivalent to 1431 mg/kg bw of calcium phoshide and LD50= 901 mg/kg bw (Joshi, 1998) equivalent to 1432.6 mg/kg bw of calcium phosphide.
Acute inhalation toxicity
The acute inhalation toxicity is not covered by the German Proposal. However, the Spanish CA proposes a classification for calcium phosphide as Acute Tox. 1 (inhalation,) H330: Fatal if inhaled according to Regulation EC 1272/2008 and as T+; R26 Very toxic by inhalation according to Directive 67/548/EC. This classification is due to the obtained value (Roy, 1998) LC50 = 0,048 mg/l (phosphine levels liberated from aluminium phosphide dust). Moreover, it is reported that phospine gas is released from inhaled aluminium phosphide dust (analogous to calcium phoshide) in the moist air sacs of the lung (see references 1 and 2). Phosphine is classified as T+; R26 Very toxic by inhalation according to Directive 67/548/EC and as Acute Tox. 2* (minimum classification), H330: Fatal if inhaled according to CLP Regulation.
The draft EFSA Scientific Report (2008) proposed, as well, to classify calcium phosphide with T+; R26.
This is in line with the RAC opinion to classify aluminium phosphide (December 2011) as Acute Tox. 1, H330 and T+; R26. Taking into account the toxicity mechanism of calcium phosphide with regard to aluminium phosphide (both of them release phosphine gas and the same inhalation studies were considered for their evaluation) the Spanish CA considers the convenience of applying the same acute inhalation toxicity classification. It was also referred in the RAC meeting the quick hydrolysis of metal phosphides powders, if inhaled, to phosphine gas in contact with the moisture of respiratory epithelium.

References
1. Gehring, P.J., Nolan, R.J., Watanabe, P.G. and Schumann, A.M. 1991. Chapter 14: Solvent, Fumigants and Related Compounds, In Hayes, W.J. and Laws, E.R., Jr. (Eds.) Handbook of Pesticide Toxicology, Academic Press, New York, NY.
2. U.S. Department of Health and Human Services. 1994. File: Aluminum Phosphide Hazardous Substance Data Base (HSDB). HHS. Washington, DC.

Dossier Submitter's response

Acute Inhalation: Metal phosphides were not classified with regard to inhalation toxicity so far, only phosphine which is developed by spontaneous hydrolysis. However, while preparing the CLH-Dossier on tricalcium diphosphide the RAC Opinion to classify aluminium phosphide as Acute Tox. 1; H330 and T+; R26 was not published. In any case, classification of tricalcium diphopshide as Acute Tox. 1; H330 and T+; R26 is supported.

RAC's response

OK

Date	Country	Organisation	Type of Organisation	Comment

				number
26/07/2012	France		MSCA	6

Comment received

• Acute toxicity: inhalation (p.22 and p.27)
There are two experimental studies on animals which allow estimation of acute inhalation toxicity of Ca3P2 in the report. The available non protected data (Waritz,, 1975), is also relevant to support classification. In these studies the animals were exposed to phosphine gas. Phosphine gas may be generated by hydrolysis of Ca3P2. Assuming 100% hydrolysis reaction to PH3, LC50 on rats range from 0.04 mg Ca3P2/L to 0.19 mg Ca3P2/L.
Taking into account the lowest value, the substance need to be classified for acute toxicity Category 1, H330, "Fatal if inhaled" because its estimated LC50 value is below CLP guidance value (i.e. ≤ 0.05 mg/l) and to category T+ R26, "Very toxic for inhalation" because its LC50 values is below 0.25 mg/l according to DSD criteria.

Dossier Submitter's response

Metal phosphides were not classified with regard to inhalation toxicity so far, only phosphine which is developed by spontaneous hydrolysis. However, while preparing the CLH-Dossier on tricalcium diphosphide the RAC Opinion to classify further metal phosphides as Acute Tox. 1; H330 and T+; R26 was not published. In any case, classification of tricalcium diphopshide as Acute Tox. 1; H330 and T+; R26 is supported.

RAC's response

OK

Skin hazardous

Date	Country	Organisation	Type of Organisation	Comment number
08/07/2012	Germany	Chemische Fanrik Wülfel GmbH & Co.KG	Company-Manufacturer	7

Comment received

Correction C&L proposal (Part A: p. 7, 10, Part B: pp. 39-41)
Basis: read-across principle, reference substance: calcium dihydroxide;
Reports: Determination of alkaline reserve of calcium dihydroxide by method of Young et al. (see uploaded file, this is confidential) and the animal tests published on ECHA Web site (Registration dossier of calcium dihydroxide)
See also EFSA Scientific Report(2008)183, p. 2, p.8 and p.31).

*ECHA comment: The **confidential** attachment document "Study report" [CSL-11-0330-Wülfel_Köhler_Bericht_Mö[1].pdf] was submitted as a separate attachment. Attachment no. 2.*

Dossier Submitter's response

First of all, the test item in the study report mentioned above was 'Prontox Wühlmausgas' which contains calciumcarbid (purity 76.6 – 80.0%) but not calcium dihydroxide and therefore the read-across has to be confirmed by physico-chemical experts.

The provided study revealed that the test item 'Prontox-Wühlmausgas' has an alkali reserve of 14.1 and the classification of the test item can be estimated to be irritant but not corrosive according to Young et al.. 1988. However, according to the 'Guidance to Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of substances and mixtures' (Annex I: 3.2.2.2., page 220) '*…pH extremes like ≤ 2 and ≥ 11.5 may indicate the potential to cause skin effects. …..If consideration of alkali/acid reserve suggests the substance may not be corrosive despite the low or high pH value, then further testing shall be carried out to confirm this, preferably by use of an appropriate validated in vitro test'*. Up to now, no in vitro test is available.

Furthermore, the animal studies published on ECHA Web site for registration of calcium hydroxide are

not available, when preparing the CLH-Dossier.

RAC's response

Registration dossier of calcium dihydroxide published on ECHA website is taken into account for RAC final assessment

Date	Country	Organisation	Type of Organisation	Comment number
19/07/2012	Spain		MSCA	8

Comment received

p. 29. Summary and discussion of corrosion/irritation
Germany proposes a classification for calcium phosphide as Skin Corr. 1A, H314: Causes severe skin burns and eye damage according to Regulation EC 1272/2008 and as C; R35: Causes severe burns according to Directive 67/548/EC. There are no available irritation studies with calcium phosphide. This proposed classification is based on the extreme pH of calcium hydroxide (hydrolysis product of calcium phosphide), about 12-13, considered extreme pH according to both Regulation EC 1272/2008 and Dir. 67/548/EC (extreme pH: ≤ 2 and ≥ 11.5).
However, in the Chemical Safety Report (under REACH) of calcium hydroxide several submitted irritation studies seemed to discard corrosion and confirmed irritation to the eye and the skin (proposed classification in Chemical Safety Report as Xi; R37-38-41).
A more in depth and detailed evaluation on the irritation/corrosion properties of calcium phosphide could be conducted by RAC.

Dossier Submitter's response

Agreed. Please refer to comment number 7.

RAC's response

Registration dossier of calcium dihydroxide published on ECHA website is taken into account for RAC final assessment applying read-across principle. Detailed evaluation shows that tricalcium diphosphide has potential to damage eye and should be classified as skin irritant according to the DSD. The information is not sufficient to come to a conclusion on irritation according to the CLP criteria. .

Date	Country	Organisation	Type of Organisation	Comment number
26/07/2012	France		MSCA	9

Comment received

• Irritation (4.4, p.29-31)
The classification of tricalcium diphosphide C R35 (causes severe burns) seems conservative as only water solution of calcium hydroxide would lead to a pH > 11.5. Classification Xi R41 R37/38 may be appropriate according to DSD criteria or skin irrit.2, H315, Eye dam. 1, H318 and STOT SE 3, H335 according to CLP criteria.

Dossier Submitter's response

Please refer to comment number 7.
Classification for STOT-SE 3, H335 should be discussed at the RAC meeting.

RAC's response

Please refer to comments number 2 and 8.

Eye hazard

Date	Country	Organisation	Type of Organisation	Comment number
08/07/2012	Germany	Chemische Fanrik Wülfel GmbH & Co.KG	Company-Manufacturer	10

Comment received

Correction C&L proposal (Part A: p.7, 11, Part B: pp. 41-43)

Basis: read-across principle, reference substance: calcium dihydroxide, Reports: animal tests published on ECHA Web site (Registration dossier of calcium dihydroxide, and EFSA Scientific Report (2008)183, p. 2, p. 8, and p.31).
Dossier Submitter's response
Noted.
RAC's response
Registration dossier of calcium dihydroxide published on ECHA website is taken into account for RAC final assessment

Specific target organ toxicity – single exposure

Date	Country	Organisation	Type of Organisation	Comment number
08/07/2012	Germany	Chemische Fanrik Wülfel GmbH & Co.KG	Company-Manufacturer	11
Comment received				
New C&L proposal (Part A: p.7,11, Part B: pp. 38-39) Basis: read-across principle, reference substance: calcium dihydroxide Data: recommendation from SCOEL for data to exposure related observations on humans for calcium oxide and calcium dihydroxide (SCOEL/SUM/137, February 2008,health surveillance data) See also the registration dossier of calcium dihydroxide published on ECHA Web site.				
Dossier Submitter's response				
Noted.				
RAC's response				
OK				

Physical hazard

Date	Country	Organisation	Type of Organisation	Comment number
19/07/2012	Spain		MSCA	12
Comment received				
p. 18. Summary of discussion of Physico-chemical properties Flammability The Spanish CA supports the proposed classification of calcium phosphide as Water-react. 1, H260: In contact with water releases flammable gases which may ignite spontaneously and EUH029 Contact with water liberates toxic gas according to Regulation EC 1272/2008 and as F; R15/29 Contact with water liberates toxic extremely flammable gases according to Directive 67/548/EC. The classification is based on the well known chemical properties of calcium phosphide to generate toxic gas phosphine in contact with water and the results obtained in flammability studies (Karl, 1983). Contact with acids liberates very toxic gases The Spanish CA considers that calcium phosphide requires the supplementary hazard statement code EUH032 Contact with acids liberates very toxic gas according to Regulation EC 1272/2008 and a classification as R32 Contact with acids liberates very toxic gases according to Directive 67/548/EC. The classification is based on the well known chemical properties of calcium phosphide to generate toxic gas phosphine in contact with acids.				
Dossier Submitter's response				
Germany supports this statement				
RAC's response				
OK				

REFERENCES: none

ATTACHMENTS RECEIVED:

1. **Revision of CLH report_ Tricalcium Diphosphide_rev_04_07_Redacted.pdf.** Submitted by Germany / Chemische Fanrik Wülfel GmbH & Co.KG/ Company-Manufacturer. Comment is attached separately.

2. **CSL-11-0330-Wülfel_Köhler_Bericht_Mö[1].pdf [Study report].** Submitted by Germany / Chemische Fanrik Wülfel GmbH & Co.KG/ Company-Manufacturer. **Confidential document**.