Committee for Risk Assessment

RAC

Opinion

proposing harmonised classification and labelling
at Community level of

aluminium phosphide

ECHA/RAC/CLH-O-0000002201-92-01/F

Adopted

2 December 2011

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OPINION OF THE COMMITTEE FOR RISK ASSESSMENT ON A DOSSIER PROPOSING HARMONISED CLASSIFICATION AND LABELLING AT COMMUNITY LEVEL

In accordance with Article 37 (4) of the Regulation (EC) No 1272/2008 (CLP Regulation), the Committee for Risk Assessment (RAC) has adopted an opinion on the proposal for harmonised classification and labelling of

Substance Name: ***aluminium phosphide***

EC Number: ***244-088-0***

CAS Number: ***20859-73-8***

The proposal was submitted by ***Germany*** and received by RAC on ***25 March 2011***.

Harmonised classification proposed by the dossier submitter

	CLP Regulation (EC) No 1272/2008	Directive 67/548/EEC
Current entry in Annex VI CLP Regulation	Water-react. 1 H260 EUH029 EUH032 Acute Tox. 2* H300 Aquatic Acute 1 H400 M = 100	F; R15/29 T+; R28 R32 N; R50 C ≥ 0,25 % N; R50
Current proposal for consideration by RAC	Acute Tox. 2 H300 Acute Tox. 3 H311	Xn; R21
Resulting harmonised classification (future entry in Annex VI of CLP Regulation)	Water-react. 1 H260 EUH029 EUH032 Acute Tox. 2 H300 Acute Tox. 3 H311 Aquatic Acute 1 H400 M = 100	F; R15/29 T+; R28 Xn; R21 R32 N; R50 C ≥ 0,25 % N; R50

* Minimum classification

In addition, the dossier submitter proposes the following revisions to the labelling elements:
Deleting S28

Replacing S3/9/14 with S3/9/14/49
Adding S8, S22, S60

PROCESS FOR ADOPTION OF THE OPINION

Germany has submitted a CLH dossier containing a proposal together with the justification and background information documented in a CLH report. The CLH report was made publicly available in accordance with the requirements of the CLP Regulation at ***http://echa.europa.eu/consultations/harmonised_cl/harmon_cl_prev_cons_en.asp*** on ***25 March 2011***. Parties concerned and MSCAs were invited to submit comments and contributions by ***9 May 2011***.

ADOPTION OF THE OPINION OF RAC

Rapporteur, appointed by RAC: ***Teresa Borges***
Co-rapporteur, appointed by RAC: ***Karen van Malderen***

The opinion takes into account the comments of MSCAs and parties concerned provided in accordance with Article 37 (4) of the CLP Regulation.

The RAC opinion on the proposed harmonised classification and labelling has been reached on ***2 December 2011,*** in accordance with Article 37 (4) of the CLP Regulation, giving parties concerned the opportunity to comment.

The RAC Opinion was adopted by ***consensus***.

OPINION OF RAC

The RAC adopted the opinion that ***aluminium phosphide*** should be classified and labelled as follows:

Classification and labelling in accordance with the CLP Regulation (Regulation (EC) 1272/2008)

Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling[1]			Specific Conc. Limits, M-factors	Notes
				Hazard Class and Category Code(s)	Hazard state-ment Code(s)	Pictogram, Signal Word Code(s)	Hazard state ment Code(s)	Suppl. Hazard statement Code(s)		
015-004-00-8	Aluminium phosphide	244-088-0	20859-73-8	Water-react. 1 Acute Tox. 2 Acute Tox. 3 Acute Tox. 1 Aquatic Acute 1	H260 H300 H311 H330 H400	GHS02 GHS06 GHS09 Dgr.	H260 H300 H311 H330 H400	EUH029 EUH032	M = 100	-

Classification and labelling in accordance with the criteria of Directive 67/548/EEC

Index No	International Chemical Identification	EC No	CAS No	Classification	Labelling	Concentration Limits	Notes
015-004-00-8	Aluminium phosphide	244-088-0	20859-73-8	F; R15/29 T+; R26/28 Xn; R21 R32 N; R50	F; T+ ; N R:15/29-26/28-21-50 S:(1/2)-3/9/14/49-8-22-30-36/37-43-45-60-61	N; R50: C ≥ 0.25 %	

[1] RAC also recommends to add to the labelling, “P260 - Do not breath dust/fume/gas/mist/vapours/spray”

SCIENTIFIC GROUNDS FOR THE OPINION

The opinion relates only to those hazard classes that have been reviewed in the proposal for harmonised classification and labelling, as submitted by ***Germany***.

The classification proposal submitted by the German CA for aluminium phosphide deals with the revision of classification/labelling for acute oral and dermal toxicity. The current entry of aluminium phosphide in Annex VI of CLP Regulation covers its reactivity with water, release of toxic gases in contact with water and acids, minimum classification of oral acute toxicity and aquatic acute toxicity.

Aluminium phosphide belongs to a group of metal phosphides together with trimagnesium diphosphide, aluminium phosphide, trizinc diphosphide, tricalcium diphosphide which fulfil the criteria for grouping of substances and read across approach as defined in the section 1.5 of Annex XI of the Regulation 1907/2006/EC because they have the following common characteristics:

1) they have common functional group, which in this case is phosphorus atom, which during breakdown of metal phosphide release a phosphorus radical with trivalent binding capability;

2) all the metal phosphides have common breakdown products via physico-chemical process, particularly as a result of hydrolysis of phosphides in contact with water or biological fluids which is phosphine (PH_3). This substance is in fact responsible for most of the toxic activity of metal phosphides.

Thus, since the two criteria for grouping and read across-approach (common functional group and common breakdown product) are fulfilled it is highly probable that their physicochemical, toxicological and ecotoxicological properties are likely to be similar.

Therefore in the assessment of hazardous properties of aluminium phosphide the results of studies performed on other metal phosphides were also used as described in the Background Document (Annex 1). If a different metal phosphide was used as test material, dose levels were converted based on 100% release ratio of PH_3 by the respective compounds.

Acute Toxicity

Acute oral toxicity

Aluminium phosphide is highly toxic when administered orally to rats and mice. LD_{50} values of 8.7 and 14.8 mg/kg bw were obtained from two acute oral toxicity studies, in rat and mice respectively (Sterner *et al*. 1997 and Leuschner *et al*. 1992).

Based on the results of available studies the dossier submitter concluded that minimum classification as Acute Tox. 2, H300 of aluminium phosphide is justified.

The LD_{50} values (range from 8.7 to 14.8 mg/kg bw) obtained from these studies are within the range (5-50 mg/kg bw) for classification as Acute Tox. 2 H300 under Regulation (EC) 1272/2008 criteria and are below the value of 25 mg/kg bw established for the classification as T+; R28 “Very toxic if swallowed” according to Directive 67/548/EEC criteria.

Acute inhalation toxicity

From the acute inhalation studies presented in the Background Document, it can be concluded that the actual exposure was measured in relation to phosphine gas (PH_3). In the Roy, B.C. (1998) and Shimizu, Y. et al. (1982) studies, PH_3 was generated from AlP and Mg_3P_2 dust by using “dust/aerosol” generating chambers. By evaluating the study summaries, as they were presented in the CLH report, it was not possible to conclude on actual AlP and Mg_3P_2 concentration measurements.

Based on information concerning the hydrolysis kinetics of AlP (Schmitt, S. 2007), it appears that the liberation of PH_3 starts rapidly (up to 15 % PH_3 release in the first hour) and increases with the humidity (approx. 5 % release at 60 % and approx. 15 % at 90 % humidity after one hour). However, it takes some time (up to 200 hours, for AlP at 60 % humidity) to complete the liberation of PH_3 to 100 %.

However, in case of exposure to AlP dust particles in the workplace at several steps during the manufacture process, as illustrated by Schluter, Gutberlet and Holthenrich (2011), the metalphosphide particles will penetrate into the airways and alveoli and will be deposited in moist mucus and respiratory epithelium causing a very quick hydrolysis to phosphine.

Moreover, as referred in EHC 73 (1988), aluminium or magnesium phosphide powder, if inhaled, releases phosphine for absorption in contact with the moist respiratory epithelium. Studies by the inhalation route indicate that both the concentration and duration of exposure are important determinants of acute lethality and that different mammalian species are essentially similar in susceptibility.

Based on these considerations, LC_{50} for AlP dust have been calculated assuming 100 % of hydrolysis. Furthermore, RAC considers it to be relevant to classify aerosols of AlP for acute inhalation toxicity.

The classification criteria for acute inhalation toxicity for dusts for category 1 is ATE ≤ 0.05 mg/l, and for category 2 it is 0.05mg/l < ATE ≤ 0.5mg/l. The LC_{50} for AlP dust was calculated to be in the range of 0.02 – 0.12 mg/L. Due to deficiencies reported in Roy, B.C. (1998) and Shimizu, Y. et al. (1982) studies, it is proposed to take the LC_{50} value of 0.02 mg AlP/L obtained from the Waritz and Brown study (1975) in support to the classification criteria for acute inhalation toxicity category 1 (dust) - H330 “Fatal if inhaled” (ATE ≤ 0.05) within CLP criteria and to category T+; R26 “Very toxic for inhalation” (≤0.5mg/l/4h) according to DSD criteria.

Additional recommendations from RAC:

Phosphine is currently classified as T+; R26 “Very toxic by inhalation” according to Directive 67/548/EC and translated into a minimum classification as Acute Tox. 2* (inhalation) H330: “Fatal if inhaled” according to the CLP Regulation.

According to RAC, phosphine should be reclassified into acute inhalation toxicity category 1, having in mind that the LC_{50} values for phosphine from three studies are in a range between 11 – 51 ppm, well below the guidance values of 100 ppm for acute inhalation toxicity hazard category 1 for toxic gases. While the classification according to the DSD Directive, T+; R26, is appropriate since all LC_{50} values are in a range of 0.015 – 0.072mg/l which is well below the DSD guidance value ≤0.5mg/l/4h for this category.

Furthermore, it is recommended to add to the labelling, P260– “Do not breath dust/fume/gas/mist/vapours/spray” that translates from S22 – “Do not breath dust” according to Directive 67/548/EEC, as proposed by the dossier submitter.

Acute dermal toxicity

Aluminium phosphide displayed moderate acute dermal toxicity in a rat study compliant with OECD guideline 402. The LD_{50} (14days) was calculated as 900 mg/kg bw for both sexes.

During the public consultation some comments regarding this endpoint were received. Some Member States expressed that they were in support of this classification proposal. One Member State questioned whether it could be possible that the mortalities in this study were

due to phosphine being liberated since aluminium phosphide reacts with the moisture in the air and in sweat. If so, the observed mortalities could be secondary to phosphine gas toxicity.

RAC is of the opinion that it seems unlikely that the mortalities in the dermal toxicity study were due to inhaled phosphine (liberated from AlP) due to the occlusive conditions how the substance was applied to the skin of the animals. However, based on the submitted data it cannot be either confirmed or excluded that the occlusive dressing would have totally prevented phosphine gas from escaping the site of exposure.

Data about the potential of the gas to penetrate the skin are absent. The only information available is that the dermal absorption (based on expert judgement as no experimental data are available) of the metal phosphides is at a maximum 10%.
Assuming that: (i) the study of Dickhaus *et al*. (1987) followed the OECD guidelines where the occulation was tight and limited the evaporation of the gas, and (ii) without further information excluding ability of phosphine to penetrate the skin the results of this study is considered relevant for classification of AlP for acute dermal toxicity.

The LD_{50} value obtained from the acute dermal toxicity (LD_{50}: 900 mg/kg bw) is within the range (200-1000 mg/kg bw) for Acute Tox. 3; H311 under the Regulation (EC) 1272/2008 criteria and within the range (400-2000 mg/kg bw) for classification as Xn; R21 according to Directive 67/548/EEC criteria. The LD_{50} values of 461.2 mg/kg bw and 901 mg/kg bw obtained from two other studies (Stephen, F. 2000 and Joshi, M. 1998) performed with AIP, although non-compliant with guidelines, are in support of this hazard class classification.

According to RAC, the additional classification/labelling for acute dermal toxicity is justified.

Additional information

The Background Document, attached as Annex 1, gives the detailed scientific grounds for the Opinion.

ANNEXES:

Annex 1	Background Document (BD)[1]
Annex 2	Comments received on the CLH report, response to comments provided by the dossier submitter and RAC comments (excl. confidential information)

[1] The Background Document (BD) supporting the opinion contains scientific justifications for the CLH proposal. The BD is based on the CLH report prepared by a dossier submitter.