

**Committee for Risk Assessment**  
**RAC**

**Opinion**  
proposing harmonised classification and labelling  
at Community level of  
**trimagnesium diphosphide**  
**ECHA/RAC/DOC CLH-O-0000002194-79-01/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:** *trimagnesium diphosphide*

**EC Number:** *235-023-7*

**CAS Number:** *12057-74-8*

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

**Harmonised classification proposed by the dossier submitter**

	<b>CLP Regulation (EC) 1272/2008</b>	<b>Directive 67/548/EEC</b>
Current entry in Annex VI CLP Regulation	Water-react. 1 H260 EUH029 Acute Tox. 2* H300 Aquatic Acute 1 H400 M = 100	F; R15/29 T+; R28 N; R50 C ≥ 0,25 % N; R50
Current proposal for consideration by RAC	Acute Tox. 2 H300 Acute Tox. 3 H311 EUH032	T+; R28 Xn; R21 R32
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 R32 T+; R28 Xn; R21 N; R50 C ≥ 0,25 % N; R50

\* Minimum classification

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

Deleting S28

Adding S8, S30, S36/37, S60, S3/9/14/49

## **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](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: *Boguslaw Baranski*

Co-rapporteur, appointed by RAC: *Helena Polakovicova*

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 *trimagnesium diphosphide* should be classified and labelled as follows <sup>1</sup>:

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<sup>1</sup> Note that not all hazard classes have been evaluated

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

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)		
015-005-00-3	magnesium phosphide; trimagnesium diphosphide	235-023-7	12057-74-8	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
015-005-00-3	magnesium phosphide; trimagnesium diphosphide	235-023-7	12057-74-8	F; R15/29 T+; R26 T+; R28 Xn; R21 R32 N; R50	F; R15/29 T+; R26 T+; R28 Xn; R21 R32 N; R50 S : (1/2)-3/9/14/49-8-22-30-36/37-43-45-60-61	N; R50: C <sub>≥</sub> 0,25%	

## 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 Competent Authority for trimagnesium diphosphide deals with the revision of classification/labelling for acute oral and dermal toxicity and for liberation of very toxic gas in contact with acids. The current entry of trimagnesium diphosphide in Annex VI of the CLP Regulation covers its reactivity with water, minimum classification of oral acute toxicity and aquatic acute toxicity.

The phosphine (PH<sub>3</sub>), which develops after contact of trimagnesium diphosphide with water by spontaneous hydrolysis of the phosphide, is very toxic gas. PH<sub>3</sub> is liberated from metal phosphides rather more readily by acids than by water. Therefore, it is proposed to harmonise classification/labelling in this regard, i.e. to label trimagnesium diphosphide also with R32 - Contact with acids liberates toxic gas - according to Directive 67/548/EEC and according to CLP classification with supplemental hazard information: EUH032 - Contact with acids liberates toxic gas.

Trimagnesium diphosphide belongs to a group of metal phosphides together with aluminium phosphide, trizinc diphosphide, tricalcium diphosphide which fulfil the criteria for grouping and read across 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<sub>3</sub>). This substance is in fact responsible for most of 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 trimagnesium phosphide the results of studies performed on other metal phosphides were also used as described in the Background Document.

### **Acute Toxicity**

#### Acute oral toxicity

Based on the results of available studies the dossier submitter concluded that minimum classification as “Acute Tox. 2, H300” of trimagnesium diphosphide is justified.

The LD<sub>50</sub> for rats of trimagnesium diphosphide is equal to 11,2 mg/kg bw which is below 25 mg/kg bw thus it meets the criteria specified in the Directive 67/548/EEC for very toxic substance by oral route which warrants classification: T+, R 28. The LD<sub>50</sub> of trimagnesium diphosphide by oral route is within criteria for Category 2 acute toxicity according to Annex I of Regulation 1272/2008/EC being in a range of 5 to 50 mg/kg bw. Thus trimagnesium diphosphide should be classified as Acute Tox. 2, H300.

#### Acute dermal toxicity

The dermal LD<sub>50</sub> for rats of trimagnesium diphosphide, after recalculation from aluminium phosphide in read across approach to Mg<sub>3</sub>P<sub>2</sub> is equal to 1047 mg/kg bw (Dickhaus, S. and Heisler, E., 1987)). Such a value of LD<sub>50</sub> meets the classification criteria specified in the Directive 67/548/EEC for harmful substance by dermal route (400 < LD<sub>50</sub> ≤ 2000 mg/kg bw). Thus classification of Mg<sub>3</sub>P<sub>2</sub> to category Xn, R 21, harmful in contact with skin is warranted.

Based on other acute dermal studies on aluminium phosphide and zinc phosphide for magnesium phosphide, the LD<sub>50</sub> values for rats expressed as trimagnesium diphosphide are in the range of 520 to 1047 mg/kg bw that support proposed classification as Xn, R 21, harmful in contact with skin according to Directive 67/548/EEC.

All the studies on dermal acute toxicity of aluminium and zinc phosphide have limitations with regard to determination/calculation of the exact LD<sub>50</sub> values as outlined in the Background Document. LD<sub>50</sub> values are, after applying read-across and recalculation to trimagnesium diphosphide, in the range of 520 to 1047 mg/kg bw. Therefore trimagnesium diphosphide should be classified according to Annex I of the CLP Regulation as Acute Tox 3, H311, “Toxic in contact with skin” and according to Directive 67/548/EEC as Xn, R 21, “Harmful in contact with skin”.

#### Acute inhalation toxicity

There are three experimental studies on animals which allow estimation of acute inhalation toxicity of Mg<sub>3</sub>P<sub>2</sub> dust (see the Background Document). However, in none of these studies the animals were exposed to aerosol of trimagnesium diphosphide or aluminium phosphide. The animals were exposed to phosphine gas from a gas container or a gas generated by hydrolysis of metal phosphides by water. However, phosphine may be generated by hydrolysis of Mg<sub>3</sub>P<sub>2</sub> aerosol present in the air of the working zone. There are two situations when phosphine might be released from Mg<sub>3</sub>P<sub>2</sub> as result of hydrolysis:

- 1) due to water in air humidity with rather low efficiency (as discussed in the Background Document);

or

- 2) Due to water in mucus covering membranes lining airways and alveoli when dust particles are deposited on them with rather high efficiency.

The hydrolysis in air due to water present as humidity is rather slow as demonstrated by data provided by, Detia Freyburg GmbH.. So it is not probable that Mg<sub>3</sub>P<sub>2</sub> dust will quickly hydrolyze in air to produce phosphine, only a small part (ca. 10%-20%) will hydrolyze in 1-4 hours depending upon level of humidity. However, when dust particle penetrates to airways and alveoli and is deposited in mucus containing water the hydrolysis is very quick with conversion of Mg<sub>3</sub>P<sub>2</sub> to water. Taking this into account, it is proposed to classify acute inhalation toxicity of Mg<sub>3</sub>P<sub>2</sub> aerosol based on inhalation toxicity of phosphine.

LC<sub>50</sub> for phosphine from three studies are in a range 0.015 – 0.072 mg/l (table 5 in the Background Document).

LC<sub>50</sub> for trimagnesium diphosphide dust calculated based on the values of LC<sub>50</sub> from three studies on rats is in a range of 0.030 – 0.14 mg/l as presented in table 5 of the background document.

The classification criteria for acute inhalation toxicity for dust for category 1 is ATE (acute toxicity estimate) ≤ 0.05 mg/l, and for category 2 (0.05 mg/l < ATE ≤ 0.5 mg/l). Thus taking into account the lowest value of LC<sub>50</sub> for Mg<sub>3</sub>P<sub>2</sub> i. e. 0.03 mg/l the substance is proposed to be classified to category 1. The other calculated LC<sub>50</sub> values 0.095 mg/l and 0.14 are very close

to this value. The highest values 0.13-0.14 mg/l were obtained from the study (Shimizu, 1982) where exposure lasted only for 1 hour and concentration was not measured but calculated based on amount of  $Mg_3P_2$  added to a chamber with water. The  $LC_{50}$  value of 0.095 mg/kg was obtained based on the study of Roy (1998), where the method of measurement is not very well documented. Due to deficiencies reported in Roy, (1998), it is proposed to take the  $LC_{50}$  value 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 ( $ATE \leq 0.05$ ) within CLP criteria and to category T+ R26 Very toxic for inhalation ( $\leq 0.5\text{mg/l/4h}$ ) according to DSD criteria.

In the opinion of RAC the existing data warrant classification of  $Mg_3P_2$  dust for acute toxicity Category 1, H330, "Fatal if inhaled" because its estimated  $LC_{50}$  value is below CLP guidance value( i.e.  $\leq 0.05$  mg/l) and to category T+ R26, "Very toxic for inhalation" because its  $LC_{50}$  values is below 0.25 mg/l according to DSD criteria.

Phosphine, which is currently classified as Acute Tox. 2\* (and T+, R26), should be reclassified to the same category of acute inhalation toxicity according to the CLP Regulation. The current classification seems to be inappropriate having in mind  $LC_{50}$  of phosphine from three studies in a range of 11 – 51 ppm which is well below the guidance values of 100 ppm for acute inhalation toxicity hazard category 1 for toxic gases. Nevertheless, the phosphine classification T+, R26 is appropriate since its  $LC_{50}$  values are in a range of 0.015 – 0.072 mg/l which are well below DSD guidance value  $\leq 0.5$  mg/l/4h for this category.

### **Other hazards**

Since phosphine ( $PH_3$ ), which has high acute inhalation toxicity (Acute Tox.2; H330 – Fatal if inhaled), is released from  $Mg_3P_2$  in contact with acids in potential dangerous amounts, the trimagnesium diphosphie should also be classified with risk phrase R32 and EUH032 – "Contact with acids liberates very toxic gas "

### **Additional information**

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

### **ANNEXES:**

- |         |   |
|---------|---|
| Annex 1 | Background Document (BD) <sup>1</sup>   |
| Annex 2 | Comments received on the CLH report, response to comments provided by the dossier submitter and RAC comments (excl. confidential information) |

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<sup>1</sup> 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.