Committee for Risk Assessment

RAC

Annex 1

Background document

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

trimagnesium diphosphide

ECHA/RAC/DOC CLH-O-0000002194-79-01/A1

EC number: 235-023-7
CAS number: 12057-74-8

Adopted

2 December 2011

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TABLES

PROPOSAL FOR HARMONISED CLASSIFICATION AND LABELLING

Substance Name: **Trimagnesium diphosphide**

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

CAS number: **12057-74-8**

Purity: Min. > 88 % w/w

Impurities/Additives: The confidential information can be found in the "Confidential Annex" or the technical dossier.

The current Annex VI entry and the proposed harmonised classification

	CLP Regulation (EC) No 1272/2008	**Directive 67/548/EEC (Dangerous Substances Directive; DSD)**
Current entry in Annex VI, CLP Regulation	Water-react. 1 H260 Acute Tox. 2* H300 Aquatic Acute 1 H400 EUH029 M = 100	F; R15 T+; R28 N; R50 R29 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, CLP Regulation)	Water-react. 1 H260 Acute Tox. 2 H300 Acute Tox. 3 H311 EUH029 EUH032 Aquatic Acute 1 H400 M = 100	F; R15 T+; R28 Xn; R21 R29 R32 N; R50 C ≥ 0,25 % N; R50

*Minimum classification

Proposed classification and labelling in accordance with the criteria of the CLP Regulation (Regulation (EC) 1272/2008):

Index No	International Chemical identification	EC No	CAS No	Classification		Labelling			Specific concentration 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	T

RAC supplement: P260 “Do not breathe dust/fume/gas/mist/vapours/spray”

Proposed 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≥0,25%	

JUSTIFICATION

*Please note that this Background Document supporting the RAC opinion has been prepared on the basis of the submitted CLH report. According to the "**RAC Working Procedure on Processing of Dossiers for Harmonised Classification and Labelling (May, 2010**)" the dossier submitter has integrated the comments received during the public consultation where relevant. For transparency, the information provided by the dossier submitter in the revised CHL report has not been modified*

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Chemical Name: Trimagnesium diphosphide

EC Name: Trimagnesium diphosphide

CAS Number: 12057-74-8

IUPAC Name: Trimagnesium diphosphide

1.2 Composition of the substance

The confidential information can be found in the "Confidential Annex" or the technical dossier.

Chemical Name: Trimagnesium diphosphide

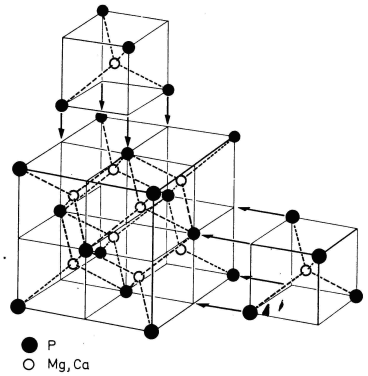
EC Number: 235-023-7

CAS Number: 12057-74-8

IUPAC Name: Trimagnesium diphosphide

Molecular Formula: Mg_3P_2

Structural Formula:



Molecular Weight: 134.86 g/mol

Typical concentration (% w/w): Min. > 88

1.3 Physico-chemical properties

Table 1: Summary of physico- chemical properties of trimagnesium diphosphide

REACH ref Annex, §	Property	IUCLID section	Value	[enter comment/reference or delete column]
VII, 7.1	Physical state at 20°C and 101.3 kPa	4.1	grey powder with a foul fishy, garlic-like odour	EC Safety Data Sheet (2004), Detia Freyberg GmbH
VII, 7.2	Melting/freezing point	4.2	no melting point was observed under test conditions up to 500 °C	Smeykal, H. (2002); report no. 20020428.01
VII, 7.3	Boiling point	4.3	no boiling point was observed under test conditions up to 500 °C at 1013.3 hPa	Smeykal, H. (2002); report no. 20020428.01
VII, 7.4	Relative density	4.4	1.47 at 23.8 °C	Smeykal, H. (2002); report no. 20020428.02
VII, 7.5	Vapour pressure	4.6	<< 10-5 Pa at 25 °C	Smeykal, H. (2002); report no. 20020428.01
VII, 7.6	Surface tension	4.10	not determined (hydrolysis)	
VII, 7.7	Water solubility	4.8	not determined (hydrolysis)	
VII, 7.8	Partition coefficient n-octanol/water (log value)	4.7	not determined (hydrolysis)	
VII, 7.9	Flash point	4.11	only required for liquids	
VII, 7.10	Flammability	4.13	Flammable solids: The test substance could not be ignited with a flame. The substance is not a highly flammable solid in the sense of Guideline 92/69/EEC, A.10. Flammability in contact with water: In contact with water the test substance evolves highly flammable gases in dangerous quantities. The gas ignites spontaneously. The substance is highly flammable in the sense of Guideline 92/69/EEC, A.12 Pyrophoric properties: The classification procedure need not to be applied because the inorganic substance is known to be stable into contact with air at room temperature for prolonged periods of time (days).	Smeykal, H. (2002); report no. 20020428.03 Smeykal, H. (2002); report no. 20020428.03 BAM, II.2 (2010)
VII, 7.11	Explosive properties	4.14	Trimagnesium diphosphide	Smeykal, H. (2002); report no. 20020428.04

			has no explosive properties in the sense of Guideline 92/69/EEC, A.14.	
VII, 7.12	Relative Self-ignition temperature for solids	4.12	Guideline 92/69/EEC, A.16: No self ignition was registered until the maximum temperature of 405 °C.	Smeykal, H. (2002); report no. 20020428.04
VII, 7.13	Oxidising properties	4.15	The classification procedure need not be applied because the inorganic substance does not contain oxygen or halogen atoms.	BAM, II.2 (2010)
	Thermal stability	4.19	OECD Test No.113 (DSC): Neither an endothermic nor an exothermal effect until 500°C (No self-reactive substance)	Smeykal, H. (2002); report no. 20020428.01

Table 2: Summary of physico- chemical properties of phosphine

REACH ref Annex, §	Property	IUCLID section	Purity/Specification	Value	[enter comment/reference or delete column]
VII, 7.1	Physical state at 20°C and 101.3 kPa	4.1	Phosphine, technical purity unknown	Gaseous with a fouly, fishy or garlic -like odour	Römpp, 2006: Version 2.10. Georg Thieme Verlag 2006
VII, 7.2	Melting/freezing point	4.2	Phosphine, technical purity unknown	-133°C	Römpp, 2006: Version 2.10. Georg Thieme Verlag 2006
VII, 7.3	Boiling point	4.3	Phosphine, technical purity unknown	-87°C	Römpp, 2006: Version 2.10. Georg Thieme Verlag 2006
VII, 7.4	Relative density	4.4	Phosphine, technical purity unknown	1.53 at 20 °C A density of 1.41 g/L was calculated on the basis of an ideal gas.	Römpp, 2006: Version 2.10. Georg Thieme Verlag 2006
VII, 7.5	Vapour pressure	4.6	Phosphine, technical purity unknown	3295 kPa at 22 °C	CRC Handbook of Chemistry and Physics 1991: 82nd Edition 1991-1992, page 6-91
VII, 7.6	Surface tension	4.10		The test has not be conducted as a surface tension of > 60mN/m at 20°C is expected to due the chemical structure of the substance.	
VII, 7.7	Water solubility	4.8	Phosphine, purity unknown	24 ml / 100 ml water at 24 °C	Phosphine and Selected Metal Phosphides, WHO, Geneva, 1988, p. 17–19
VII, 7.8	Partition coefficient n-octanol/water (log value)	4.7	Phosphine, technical purity unknown	Log Pow 0.9 at 21 °C	W. Schlösser, 1989: Untersuchungsbericht Octanol-Wasser-Verteilungskoeffizient von PH3, Labor für Geoanalytik, Hildesheim, Germany, Auftrags-Nr. 05011, 29.09.1989
VII, 7.9	Flash point	4.11		The submission of data or the performance of a test on the flash-point of Phosphine is not considered to be required since it is no liquid whose	Justification, Detia, 2004

				vapours can be ignited.	
VII, 7.10	Flammability	4.13	Phosphine pure grade	auto ignition temperature of 38°C Extremely flammable and pyrophoric	Phosphine and Selected Metal Phosphides, WHO, Geneva, 1988, p. 17 – 19
VII, 7.11	Explosive properties	4.14	Phosphine, purity unknown	Phosphine forms explosive mixtures with air concentrations greater than 1.8%	Phosphine and Selected Metal Phospides, WHO, Geneva, 1988, p. 17 – 19
VII, 7.12	Relative Self-ignition temperature for solids	4.12		Test item is no solid.	
VII, 7.13	Oxidising properties	4.15		Only for solids (EC method A. 17)	
	Thermal stability	4.19		Thermal decomposition at 550°C	Application for registration of "Detia Gas-Ex-B forte", Detia Freyberg GmbH, Laudenbach, B/7, 16.12.94

2 MANUFACTURE AND USES

2.1 Manufacture

Not relevant for this type of dossier.

2.2 Identified uses

Trimagnesium diphosphide is used as insecticide, rodenticide, talpicide and leporicide.

2.3 Uses advised against

Not relevant for this type of dossier.

3 CLASSIFICATION AND LABELLING

3.1 Classification in Annex I of Directive 67/548/EEC

F; R15/29
T+; R28
N; R50
(Index number: 015-005-00-3)

3.2 Classification in Annex I of Regulation (EC) No. 790/2009 (1st ATP to Regulation (EC) No. 1272/2008)

Water-react. 1, H260
Acute Tox. 2*, H300 (* Minimum classification)
Aquatic Acute 1, H400
(Index number: 015-005-00-3)

3.3 Self classification(s)

4 ENVIRONMENTAL FATE PROPERTIES

No modifications of existing environmental classification is proposed.

5 HUMAN HEALTH HAZARD ASSESSMENT

The metal phosphides such as trimagnesium diphosphide, aluminium phosphide, trizinc diphosphide, tricalcium diphosphide fulfil the criteria for grouping and read across as defined in the section1.5 of Annex XI of the Regulation 1907/2006/EC beacuse 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 (Holleman, A. F., 2001; Knight, M. W. 2006)

2) All the metal phosphides have of common breakdown products via physical-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 toxic activity of metal phosphides (Dikshith T. S. S., Prakash V. Diwan 2003;
http://www.fao.org/docrep/X5042E/x5042E0a.htm)
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 the assessment presented in the following subsections is based on the notion that the toxicity of metal phosphides is primarily characterised by the effects caused by liberation of hydrogen phosphide (PH_3) gas. For this reason, studies performed with other metal phosphides or PH_3 itself were considered adequate for assessing Mg_3P_2 toxicity. If a different metal phosphide than trimagnesium diphosphide was used as test material, dose levels were converted based on the respective maximum amount of PH_3 liberable by the respective compounds. Unless otherwise noted, studies were conducted under GLP conditions.

5.1 Toxicokinetics (absorption, metabolism, distribution and elimination)

Table 3: Summary of toxicokinetic studies

Method/ Guideline	**Route**	**Species, Strain, Sex, No/group**	**Dose levels, Duration of exposure**	**Results**	**Reference**
No guideline, Non-GLP	Oral	Rats, number, bw and sex not stated	Zinc ^{32}P-phosphide, suspension in milk 40 mg/kg bw (> LD_{50}) and lower dose (not specified), single application	Mortality↑ at high dose, PH_3 detectable in liver	Curry, A.S. et al. (1959); Nature 184, 642 – 643
		Rats, sex not stated, 6 animals	Zinc ^{32}P-phosphide, suspension in milk 10 mg/rat, single application	Mortality↑, phosphide and PH_3 detectable in liver	
		Rats and guinea pigs, no further information given	No information given	Urinary excretion: main product is hypophosphite	

Method/ Guideline	**Route**	**Species, Strain, Sex, No/group**	**Dose levels, Duration of exposure**	**Results**	**Reference**
No guideline, Non-GLP	Oral, subcutan-eous, per rectum	Rattus norvegicus Berk, number, bw and sex not stated	Zinc ^{32}P-phosphide, suspended in water 40 mg/kg bw	Oral application: After 6-8 h, ^{32}P was detectable in all organs and tissues with temporarily higher levels in liver and medulla oblongata. Application per rectum: After 24 h ^{32}P was detectable in large intestine, arterial blood, liver and kidneys. Subcutaneous injection: After 24 h ^{32}P was detectable only around the point of injection	Andreev, S.B. et al. (1959): 2nd Int. Conf. Peaceful Uses Atomic Energy 1958 (27), 85 – 92
	Oral		Zinc phosphide, ^{32}P- and ^{65}Zn- labelled, pure compound Sublethal, lethal, 2-, 3- and 4-fold lethal doses	The distribution of ^{32}P was similar to that in the above experiment. ^{65}Zn was found in all organs. The ratio of ^{32}P to ^{65}Zn was different in different tissues.	
Not applicable	Inhalation			Inhaled PH_3 is considered to be readily absorbed through the lungs, excretion with urine as hypophosphite and phosphite and via lungs as PH_3	WHO (1988), Environmental Health Criteria 73, pp 48-51 (1)

(1) This refers to a section on the toxicokinetics and metabolism in mammals within a WHO monograph on phosphine and metal phosphides. Although not a study report in itself, it represents an opinion peer-reviewed by a round of international experts and should be used to complement the submitted data base in the absence of other experimental data.

The available studies for this endpoint are of low reliability. However, in light of the chemical nature of trimagnesium phosphide as well as for reasons of animal welfare, it was decided that further testing would not provide essential new information and that the available studies could be used for risk assessment.

Following oral administration of zinc phosphide, ^{32}P was rapidly absorbed from the gastrointestinal tract. Inhaled PH_3 is considered to be rapidly and quantitatively absorbed through the lungs. ^{32}P was detectable in all organs and tissues, with temporarily higher levels in liver and medulla oblongata. PH_3 is excreted as such with the expired air or, after metabolic oxidation, with the urine in the form of hypophosphite and phosphite.

In the absence of experimental data, for dermal absorption of both trimagnesium diphosphide and PH_3 a default value of a maximum of 10 % was assumed based on expert judgement in consideration of the following reasoning:

- Due to the nature of the formulated product (pellets or tablets), only a minor part of the a.s., if any, is expected to come into contact with the skin.
- Contact with the (humid) skin surface would be expected to initiate liberation of PH_3 gas making systemic absorption highly unlikely.
- In previous evaluations by both the WHO (Environmental Health Criteria 73 of 1988) and the German 'MAK Commission' for trimagnesium diphosphide/PH_3 dermal absorption was stated to be ‘negligible’. However, under special occlusive conditions of dermal exposure aluminium phosphide, and most probably other phosphides can be absorbed through skin causing skin irritation and death of animals (Dickhaus, S. and Heisler, E. 1987).

- In decades of approved use, no casualties or serious intoxications have been reported for operators dermally exposed to trimagnesium diphosphide.

5.2 Acute toxicity

5.2.1 Acute toxicity: oral

Table 4: Summary of acute toxicity studies

Method/ Guideline	Route	Species, Strain, Sex, No/group	Dose levels (mg/kg bw)	Value LD_{50}/ (mg/kg bw)	Remarks	Reference
Similar to OECD 401, Non-GLP	Oral	Rat, Wistar albino 5M+5F	Trimagnesium diphosphide, 1 % in vaseline (petrolatum) 8.97-10-11.3-12.6 (calculated as pure a.s.)	11.2 for M+F:	**R 28**	Sterner, W. and Chibanguza, G. (1980), report no. 1-4-666-79
OECD 401	Oral	Mouse, NMRI/HAN Bö 5M+5F	Aluminium phosphide, suspended in sesame oil 6.81-10.0-14.7-21.5	AlP - 14.8 for M+F: (17.2 calculated for Mg_3P_2:)	**R 28**	Leuschner, J. (1992), report no. 7129/92
Similar to OECD 401, Non-GLP	Oral	Rat, Wistar albino 5M+5F	Aluminium phosphide, 1 % in vaseline (petrolatum) 7.94-8.92-10.0-11.2	AlP - 8.7 for M+F: 10.1 calculated for Mg_3P_2	**R 28**	Sterner, W. and Stiglic, A. (1977), report no. 0-0-51-77

Trimagnesium diphosphide is of high toxicity when administered orally to rats. In mice, only a study performed with aluminium phosphide is available, demonstrating comparable acute toxicity. The minimum classification as "Acute Tox. 2", H300 is confirmed.

Comparison with classification criteria

The oral LD_{50} for rats of trimagnesium diphosphide is equal 11,2 mg/kg bw (Sterner, W. and Chibanguza, G. 1980) and for mice after recalculation from aluminium phosphide to Mg_3P_2 in read across approach the oral LD_{50} is equal 17,2 mg/kg (Leuschner, J. 1992). Both oral LD_{50} of Mg_3P_2 are below 25 mg/kg bw thus substance toxicity meets the criteria specified in the Directive 67/548/EEC for category of acute toxicity: T+, R 28 - Very toxic if swallowed. Both oral LD_{50} of trimagnesium diphosphide are within criteria for acute toxicity Category 2 Regulation 1272/2008/EC being in a range of 5 to 50 mg/kg bw thus trimagnesium diphosphide should be classified - Acute Tox.2, H300 - Fatal if swallowed.

5.2.2 Acute toxicity: inhalation

This endpoint was not covered in the DS proposal.

Harmonised classification for acute inhalation toxicity is proposed by RAC

During the public consultation one Member State proposed an additional classification for aluminium phosphide as Acute Tox. 1, H330 according to Regulation (EC) 1272/2008 and as T+, R26 according to Directive 67/548/EC based on the LC_{50}=0,048 mg/l of phosphine liberated from aluminium phoshide in study Roy, B.C. (1998). Therefore that possibility has been explored below. In table 5 data on LC50 for phosphine from three studies are summarized and recalculated to LC50 of Mg3P2 assuming 100% hydrolysis of dust to phosphine and magnesium hydroxide.

Table 5: Summary of acute toxicity studies of phosphine

Method / Guideline	**Route**	**Species, Strain, Sex, No/group**	**Dose levels**	**PH_3 LC_{50} Value (mg/L air /4h) (ppm)**	**Calculated LC_{50} /4h of trimagnesium diphosphide aerosol which would provide the median lethal concentration of phosphine (assuming 100% hydrolysis reaction to PH_3) to**	**Reference**
No guideline, non GLP	Inhalation, head only exposure chamber Exposure most probably to gaseous phosphine and aerosol of AlP	Rat Wistar, 5M+5 F	PH_3, developed from aluminium phosphide 0-15.4-26-47 ppm	0.048 mg/L (34.6 ppm) for male and femals rats 34.6 ppm for males and females	0.0952 mgMg_3P_2/L	Roy, B.C. (1998) TOX2006-215
Similar to OECD 403, Non-GLP	Inhalation, whole body, 1 hour exposure to gaseous phosphine generated by reaction of magnesium phosphide and distilled water	Rat, Slc:SD 10M+ 10F	Different amounts of trimagnesium diphosphide put into exposure chamber and then a water was added to produce calculated concentrations of phosphine : 150-165-182-200-220-242 ppm, results of direct concentration measurement not provided	calculated for 4 hour exposure 0.072mg PH_3/l for male SD rats or 51 ppm calculated for 4 hour exposure 0.063mgPH_3/l for female SD rats or 44 ppm 0.29mg/PH_3/l (204ppm) for male rats for 1 hour exposure 0.25mgPH_3/l (179ppm) for SD female rats for 1 hour exposure	0.14mg Mg_3P_2/l for males 0.13mg Mg_3P_2/l for females	Shimizu, Y. et al. (1982), report no. NRI 82-7489
Not mentioned, Non-GLP	Inhalation, whole body, 4 hours exposure to gaseous phosphine from container	Rat, ChR-CD 6M+0 F	PH_3 Dose levels not reported	0.015 mg /L air (11 ppm) for male rats	0,030 mgMg_3P_2/L	Waritz, R.S. and Brown R.M. (1975); Amer. Ind. Hyg. Assoc. J., p 452

(1) PH_3 was included into Annex I to Directive 67/548/EEC with R 26, whereas the different phosphides were not classified for inhalation toxicity.

(2) 1 ppm PH_3 is equivalent to 1.41 µg/L air, density of pure PH_3 (20 °C): (34 g/mol)/(24.1 L/mol) = 1.41 g/L

(3) Assuming an hourly respiratory volume (rat) of 45 L/(h kg bw)

It should be noted that in all these studies the animals were not exposed to aerosol of trimagnesium diphosphide or aluminium phosphide (which could hydrolyse in the airways or alveoli to produced phosphine), but the animals were exclusively or mostly exposed to phosphine gas from a gas container or a gas generated already in container of metal phosphide being a part of "dust' generating system. It is not possible to determine a proportion of phospine gas and metal phosphide aerosol in the inhalation air (Roy at al. 1998; Shimizu 1982) due to a way phosphine or phosphide aerosol were generated and measured. The efficiency of hydrolysis of powdered aluminium phosphide by water present as humidity in the air was probably rather low as can judged by the data provided by Dr Stefan Schmidt, Detia Freyburg GmbH. These results (Detia Freyburg GmbH) indicate that degassing (hydrolysis of metal phosphides to phosphine in air) of various formulations of magnesium or aluminium phosphide such a pellets, tablets, Degesch plates, magnesium and

aluminium phosphide bags is rather low and is highly dependent on air humidity. In case of magnesium phosphide pellets a 100% of degassing in air with 90% humidity is observed after ca.48 hours, in air with 60 humidity after 100 hours (Detia Freyburg GmbH). Less than 20% of the Mg_3P_2 tablets is degassed within first 4 hours in air with 35% humidity, less than 40% or 60% is degassed within first 4 hours in air with 60% and 90% humidity, respectively.

Acute toxicity hazard class of Mg_3P_2 is a subject of revision and read across approach is used for trimagnesium diphosphide from aluminium phosphide, rapporteurs are of the opinion that the revision of the classification for acute inhalation toxicity of trimagnesium diphosphide should proceed in the same way as for aluminium phosphide draft proposal. As presented in table 5 we have calculated LC_{50} for Mg_3P_2 dust assuming 100% of hydrolysis. We consider two situations in which phosphine might be released from Mg_3P_2 as result of hydrolysis: 1) due to water in air humidity with rather low efficiency 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 Dr Stefan Schmidt, Detia Freyburg GmbH. So it is rather not probable that Mg_3P_2 dust will quickly hydrolyze in air to produce phosphine, only a small part ca. 10%-20% will hydrolyze in 1-4 hours depending also upon level of humidity. However, when dust particle will penetrate to airways and alveoli and will be deposited in mucus containing water the hydrolysis will be very quick with conversion of Mg_3P_2 to phosphine and magnesium hydroxide. Based on these considerations it is proposed to classify acute inhalation toxicity of aerosol of Mg_3P_2 because it was shown in the analysis of Schlueter et al. (2011) that Mg_3P_2 aerosol may occur in air of workplaces.

Conclusion:

LC_{50} for trimagnesium disphosphide dust was calculated to be in a range of 0.030 – 0.14 mg/l (Table5). The classification criteria for acute inhalation toxicity for dusts for category 1 is ATE ≤ 0.05 mg/l, thus taking into account the lowest value of LC_{50} for Mg_3P_2 – 0.03 mg/l the substance is proposed to be classified to Acute Tox. 1. The other calculated LC_{50} values 0.095 mg/l and 0.14 are very close to this borderline value. The highest values 0.13-0. 14 mg/l were obtained in the study (Shimizu,1982) where exposure lasted only for 1 hour and concentration was not measured but calculated based on amount Mg_3P_2 added to a chamber with water. The LC_{50} value of 0.095mg/kg was obtained based on the study of Roy, in which the method of measurement was not very well documented. Thus the lowest value based on the result of study of Waritz and Brown (1975) should be used for classification purpose.

This would support classification within acute toxicity Category 1 for dust (ATE ≤ 0.05) - H330 Fatal if inhaled within CLP criteria and to category T^+ R26 Very toxic for inhalation according to DSD criteria.

To the same category of acute inhalation toxicity within CLP should be reclassified phosphine which is currently classified Acute Tox. 2* (and T+, R26) , what seem to be inappropriate having in mind LC50 of phosphine from three studies in a range 11 – 51 ppm which are all well below the guidance values of 100 ppm for acute inhalation toxicity hazard category 1 for toxic gases. While the phosphine classification T+, R26 is appropriate since its LC50 values are in a range of 0.015 – 0.072mg/l which is well below a DSD guidance value ≤0.5mg/l/4h for this category.

5.2.3 Acute toxicity: dermal

Table 6: Summary of acute toxicity studies

Method/ Guideline	**Route**	**Species, Strain, Sex, No/group**	**Dose levels (mg/kg bw)**	**Value LD_{50}/LC_{50} (mg/kg bw)**	**Reference**
OECD 402	Dermal	Rat, Wistar albino 5M+5F	Aluminium phosphide (without further vehicle) 500-1000-2000	LD_{50} M+F (d 14): 900 Expressed as Mg_3P_2: 1047 **R21**	Dickhaus, S. and Heisler, E. (1987), report no. 1-4-142-87

Only a dermal study performed with aluminium phosphide is available, demonstrating moderate acute dermal toxicity. Since both metal phosphides react with moisture to produce phosphine gas, the substance responsible for the toxicity of the product, tests with aluminium phosphide, can be used to assess the toxicity of trimagnesium phosphide. Assuming that aluminium phosphide has been applied to the skin as crystalline granules and not moistened, the contact to the skin would have been less intimate than when a fluid had been present so that higher doses would be needed to yield the same effects as with a fluid. However, moistening would have led to an immediate liberation of phosphine gas and thus to a lower dermal dose of the toxic principle which would have been lost to the environment before the application site was covered. In both cases the amount of substance in contact with the skin cannot be determined accurately and, therefore, it is unlikely that the difference in skin contact properties would lead to a different classification. The dermal LD_{50} of aluminium phosphide was 1520 mg/kg bw (24 hours) or 900 mg/kg bw (day 14) for both sexes. A comparable amount of phosphine gas is expected to be liberated from a dose of 1047 mg/kg bw of trimagnesium phosphide. Based on the read-across between aluminium and trimagnesium phosphide, additional classification/labelling for acute dermal toxicity (R21 according to Annex VI of Council Directive 67/548/EEC; Acute Tox 3 H311 according to Annex I of Regulation (EC) No. 1272/2008) is proposed for trimagnesium phosphide.

As noticed during the public consultation, metal phosphides have been evaluated as active substances in Plant Protection and Biocidal products and during the evaluation process also other studies have been made available, such as acute dermal toxicity studies for aluminium phosphide and zinc phosphide. In the CLH report only one dermal study performed with aluminium phosphide is presented for classification proposal without any additional justification.

Data on the acute dermal toxicity of metal phosphides (as mentioned in relevant parts of DAR for magnesium phosphide (November 2007)), are summarised in the Table below.

As given in the DAR for magnesium phosphide (November 2007), the acceptability of the available dermal toxicity studies for metal phoshides, (including study Dickhaus, S. and Heisler, E. (1987)), are considered to be supplementary. However, the obtained LD_{50} -values of above mentioned dermal toxicity studies are in the same range and indicate moderate toxicity for aluminium phosphide (ca. 460-900 mg/kg bw) and for zinc phosphide (1000 mg/kg bw) as well.

Based on the submitted data it is not clear whether occlusive dressing would have prevented phosphine gas from escaping the site of exposure (nasal irritation was observed in one study (Joshi. M. (1998)).

Table 7: Summary of acute dermal toxicity studies

Method/ Guideline	Species, strain, Sex, No/ group	Dose levels (mg/kg bw)	Value LD_{50}	Remarks/deviations	Results	Reference
OECD 402	Rat, Wistar albino 5M+5F	Aluminium phosphide, 500-1000-2000 (occlusive conditions, 24 hours)	LD_{50} M+F (d 14): 900 mg/kg bw Expressed as Mg_3P_2: 1047 mg/kg bw	Purity/batch number of test material not stated Vehicle not stated – not clear whether the test substance had been applied moistened or applied as a powder. The size of the exposed skin area is not reported. The method of calculation LD_{50} is not mentioned but performed with combination with Gauss´ integral method	No death occurred at 500 mg/kg bw AlP/kg bw, while at dose of 1000 mg/kg bw 3/5 M and 3/5 F died (days 1 -7) and all animals died at 2000 mg/kg bw (days 1-4). Body weight gain was gradually reduced at increasing AlP dose levels. Animals showed sedation, apathy, coma prior to death. In all dose groups light oedema and haemorrhagic infiltration were observed at treated skin area. No information is given concerning recovery of survivors.	Dickhaus, S. and Heisler, E. (1987) report no. 1-4-142-87, 09/1987
OPPTS 870.1200	Rat Wistar, 5M/each level + 5 F/highest level	Aluminium phosphide 0-280-420-630 Moistened with peanut oil. (occlusive conditions, 24 hours)	LD_{50} M+F: 461.2 mg/kg bw Expressed as Mg_3P_2: 535 mg/kg bw	Temperature of experimental animal room was higher during the study (27-28°C instead of recommended 20±3°C) This study should be disregarded since temperature of animal room was much higher than recommended, which most probably make animals much more sensitive to toxic action of aluminium phosphide.	No death occurred at 280 mg/kg bw. All early deaths occurred within 48 hours after dermal application. At dose of 420 mg/kg bw 2/5M died (day 1 – 5 hours 30 min) and at dose of 630 mg/kg bw 4/5 M and 4/5F died (day 1 – 5 hours 30 min – 2x, 48 hours – 2x) . Clinical signs in treated animals on the day of dosing and the day after - lethargy, tremors, abdominal breathing and piloerection. No signs were observed on the subsequent days up to the end of observation period. All surviving animals showed normal body weight gain following dosing. At necropsy no external abnormalities were detected. Vascular/inflammatory alteration in lungs, mottling of liver and haemorragic contents in stomach and small intestinal	Stephen F. (2000), JRF report study No. 2566
No guideline, Non-GLP	Rat Wistar 5M + 5F	Aluminium phosphide 0-637.7-1275-2550 Moistened	LD_{50} M+F: 901 mg/kg bw Expressed	Temperature of experimental animal room was higher during the study (27-28°C instead of recommended 20±3°C) Observation period limited to 7 days This study should be disregarded since	At dose of 637.7 mg/kg bw 1/5M and 1/5F died (day 1 – 1-3 hours), while at dose of 1275 mg/kg bw 4/5M and 4/5 F died (day 1 -24 hour) and all animals died at 2550 mg/kg bw (F: 2x 1-3 hour (day 1), 3x24 hour (day1); M: 1x 1-3 hour (day 1), 4x24 hour (day1). Clinical signs in treated animals on the day of dosing	Joshi M. (1998), JRF report study No. 363,27.10

Method/ Guideline	Species, strain, Sex, No/ group	Dose levels (mg/kg bw)	Value LD_{50}	Remarks/deviations	Results	Reference
		with peanut oil (occlusive conditions, 24 hours)	as Mg_3P_2: 1045 mg/kg bw	temperature of animal room was much higher than recommended, which most probably make animals much more sensitive to toxic action of aluminium phosphide.	and the day after dosing were lethargy, abdominal breathing, nasal irritation, polyurea and diarrhoea. No signs were observed on the subsequent days up to the end of observation period. All surviving animals showed normal body weight gain following dosing.	
Comparable to 92/69/EEC, B3 (Intact skin)	Rat, Wistar albino 5M + 5F	Zinc phosphide 1000-2000-4000 (occlusive conditions, 24 hours)	LD_{50} M+F (d 14): 1000 mg/kg/bw Expressed as Mg_3P_2: 520 mg/kg bw	Zinc phoshide (80%) -purity/batch number of test material not mentioned. No identification if active substance or a product has been tested. Different information regarding the observation period for mortality were given in study protocol (7 days) and summary and results (14 days).	No death occurred at 1000 mg/kg bw. At dose of 2000 mg/kg bw 2/5M and 4/5F died (24 hours) and 4/5 M and 4/5F died (7days) and all animals died at 4000 mg/kg bw (4/5M and 4/5F in 24 hours, 5/5M and 5/5F in 7 days). Animals showed sedation, apathy, and tremor. Back posture apathy and coma were seen in animals which died. At necropsy no remarkable compound related macroscopic changes in main tissue and organs were observed. Haemorrhagic infiltrations were seen at the application sites. Dose related decrease of weight gain with increasing dose levels was observed.	Dickhaus, S. and Heisler, E. (1980) report no. 1-4-258-80

Note:

From studies with aluminium or magnesium phosphide the corresponding phosphine value can be obtained by multiplying the dose with a factor of 0,586 based on the molecular weights of phosphine (PH_3: 33.998g/mol) and aluminium phosphide (AlP: 57,96 g/mol), as well as by a factor 0,504 based on the molecular weights of phosphine and magnesium phosphide (Mg_3P_2: 134.86 g/mol) and the molecular ratio (2 moles of phosphine are released from one mole of magnesium phoshide).

Based on this calculation, factor of 1.16 (0.586/0,504) was used to deduce LD_{50} values for magnesium phosphide from values obtained for aluminium phoshide

From studies with zinc phosphide the corresponding phoshine value can be obtained by multiplying the dose with a factor of 0,26 based on the molecular weights of phosphine and zinc phoshide (Zn_3P_2 : 258,17) and the molecular ratio (2 moles of phosphine are released from one mole of zinc phoshide). To deduce LD_{50} values for magnesium phosphide from values obtained for zinc phophide a factor 0,52 (0.263/0,504 = 0,52) was used.

Comparison with classification criteria

The dermal LD_{50} for rats of trimagnesium diphosphide, after recalculation from aluminium phosphide in read across approach to Mg_3P_2 is equal 1047 mg/kg bw (Dickhaus, S. and Heisler, E., 1987)). Such a value of LD_{50} meets the classification criteria specified in the Directive 67/548/EEC for harmful substance by dermal route ($400< LD_{50} \leq 2000$ mg/kg bw). Thus classification Mg_3P_2 to category Xn, R 21, harmful in contact with skin is warranted.

Based on the acute dermal studies on aluminium phoshide and zinc phosphide presented in DAR for magnesium phosphide (November 2007), the LD_{50} 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.

According to Annex I of Regulation (EC) No. 1272/2008) guidance values for acute dermal toxicity are different than in Directive 67/548/EEC. They are for Category 3 ($200 <LD_{50} \leq 1000$ mg/kg bw) and for category 4 ($1000 <LD_{50} \leq 2000$ mg/kg bw. Based on the acute dermal studies on aluminium phoshide and zinc phosphide the dermal LD_{50} values for trimagnesium diphosphide are in the range of 520 to 1047 mg/kg bw which falls into category 3; ($200 <LD_{50} \leq 1000$ mg/kg bw)

Conclusions:

Although all of the studies of dermal acute toxicity of aluminium and zinc phosphide have limitations with regard to determination/calculation of the exact LD_{50} values, they are, after applying read-across and recalculation to trimagnesium diphosphide in the range of 520 to 1047 mg/kg bw, therefore trimagnesium diphoshide could be classified according Annex I of Regulation (EC) No. 1272/2008) as Acute Tox 3, H311 Toxic in contact with the skin and according to according Directive 67/548/EEC) as Xn, R 21, harmful in contact with skin. .

5.2.4 Acute toxicity: other routes

No data are available

5.2.5 Summary and discussion of acute toxicity

The toxicity of trimagnesium phosphide is related to the liberation of phosphine gas upon contact with moisture.

It is considered to display moderate acute dermal toxicity based on a read-across from data on aluminium phosphide. Therefore, additional classification/labelling for acute dermal toxicity (R21 according to Annex VI of Council Directive 67/548/EEC; Acute Tox 3 H311 according to Annex I of Regulation (EC) No. 1272/2008) is proposed.

The oral LD_{50} for rats of trimagnesium diphosphide is equal 11,2 mg/kg bw (Sterner, W. and Chibanguza, G. 1980) and for mice after recalculation from aluminium phosphide to Mg_3P_2 in read across approach the oral LD_{50} is equal 17,2 mg/kg (Leuschner, J. 1992). Both oral LD_{50} of Mg_3P_2 are below 25 mg/kg bw thus substance toxicity meets the criteria specified in the Directive 67/548/EEC for category of acute toxicity: T+, R 28 - Very toxic if swallowed. Both oral LD_{50} of trimagnesium diphosphide are within criteria for acute toxicity Category 2 Regulation 1272/2008/EC being in a range of 5 to 50 mg/kg bw thus trimagnesium diphosphide should be classified - Acute Tox.2, H300 - Fatal if swallowed.

Although all of the studies of dermal acute toxicity of aluminium and zinc phosphide have limitations with regard to determination/calculation of the exact LD_{50} values, they are, after applying read-across and recalculation to trimagnesium diphosphide in the range of 520 to 1047 mg/kg bw, therefore trimagnesium diphoshide could be classified according Annex I of Regulation (EC) No. 1272/2008) as Acute Tox 3, H311 Toxic in contact with the skin and according to according Directive 67/548/EEC) as Xn, R 21, harmful in contact with skin.

Based on the information from three acute inhalation toxicity studies presented in this Background Document, it appeared that actual exposure of phosphine gas was measured. The LC_{50} for trimagnesium diphosphide dust was calculated from LC_{50} of phosphine by applying a factor of 1.98 (MW Mg_3P_2/MW PH_3 x 2) assuming 100% hydrolysis. LC_{50} for trimagnesium diphosphide dust is to be in a range of 0.030 – 0.14 mg/l (table 5). RAC is of the opinion that the lowest LC_{50} value of 0.03 mg/l for Mg_3P_2 obtained from the Waritz and Brown study (1975) is the most convenient to be used for classification. This value supports classification for Mg_3P_2 dust as acute toxicity Category 1 - H330 Fatal if inhaled according to criteria of Regulation (EC) No. 1272/2008 (ATE$\leq$ 0.05 mg/l) and to category T^+ R26 Very toxic for inhalation according to criteria of Directive 67/548/EEC (LC_{50} < 0.25 mg/l/4hr). The other calculated LC_{50} values 0.095 mg/l and 0.14 mg/l for Mg_3P_2 are very close to this borderline value and are considered to give additional support for classification.

As it is believed that PH_3 is liberated from metal phosphides rather more readily by acids than by water, this appears to be accidental. It is proposed to harmonise C & L in this regard, i.e. label Mg_3P_2 also with R32.

5.3 Irritation

5.3.1 Skin

This endpoint is not covered in this proposal.

5.3.2 Eye

This endpoint is not covered in this proposal.

5.3.3 Respiratory tract

No experimental data available.

5.3.4 Summary and discussion of irritation

No modification of the existing classification is proposed.

5.4 Corrosivity

This endpoint is not covered in this proposal.

5.5 Sensitisation

5.5.1 Skin

This endpoint is not covered in this proposal.

5.5.2 Respiratory system

No experimental data are available.

5.5.3 Summary and discussion of sensitisation

No modification of the existing classification is proposed.

5.6 Repeated dose toxicity

This endpoint is not covered in this proposal.

5.7 Mutagenicity

This endpoint is not covered in this proposal.

5.8 Carcinogenicity

This endpoint is not covered in this proposal.

5.9 Toxicity for reproduction

This endpoint is not covered in this proposal.

5.10 Other effects

This endpoint is not covered in this proposal.

5.11 Derivation of DNEL(s) or other quantitative or qualitative measure for dose response

Not relevant for this type of dossier.

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO-CHEMICAL PROPERTIES

6.1 Explosivity

In a standard study (Smeykal, H. (2002); report no. 20020428.04), Trimagnesium diphosphide was found not to exhibit any explosive properties.
No classification for explosivity is proposed.

6.2 Flammability

Solid substance

In standard study (Smeykal, H. (2002); report no. 20020428.03) Trimagnesium diphosphide was classified as highly flammable in the sense of Guideline 92/69/EEC, A.12.

In standard study (Smeykal, H. (2002); report no. 20020428.03) Trimagnesium diphosphide could not be ignited with a flame. The substance is not a highly flammable solid in the sense of Guideline 92/69/EEC, A.10, and did not exhibit any pyrophoric properties. In standard study (Smeykal, H. (2002); report no. 20020428.04) no self ignition according to Guideline 92/69/EEC, A.16 was registered until the maximum temperature of 405 °C.

Flammability in contact with water

In contact with water the test substance evolves highly flammable gases in dangerous quantities. The gas ignites spontaneously. The substance is highly flammable in the sense of Guideline 92/69/EEC, A.12 (Smeykal, H. (2002); report no. 20020428.03)

Existing classification and labelling based on Directive 67/548/EEC:

F Highly flammable; R15/R29 Contact with water liberates extremely flammable, toxic gases

R15 Contact with water liberates extremely flammable gases

R29 Contact with water liberates toxic gas

Proposed classification and labelling based on Regulation (EC) No 1272/2008:

Water-react. 1, H260; EUH029, GHS02, Danger

According to the Regulation (EC) 1272/2008, supplemental hazard information EU032 – Contact with acids liberates toxic gas shall be assigned to a substances and mixtures which react with acids to evolve gases classified for acute toxicity in category 1 or 2 in dangerous amounts, such as salts of hydrogen cyanide, sodium azide.

Additional risk phrase R32 “Contact with acids liberates very toxic gas” shall be assigned in accordance with classification criteria specified in the Directive 67/548/EEC for substances which react with acids to evolve very toxic gases in dangerous amounts.

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 diphosphide should be classified with risk phrase R32 and EUH032 – “Contact with acids liberates very toxic gas “.

6.3 Oxidising potential

No experimental data on oxidising properties:

Testing can be waived based on a consideration of the chemical structure in accordance with REACH Column 2 of Annex VII, section 7.13: The classification procedure need not be applied because the inorganic substance does not contain oxygen or halogen atoms,
No classification for oxidising properties is proposed.

7 ENVIRONMENTAL HAZARD ASSESSMENT

No modifications of existing environmental classification is proposed.

JUSTIFICATION THAT ACTION IS REQUIRED ON A COMMUNITY-WIDE BASIS

There was agreement on Community Level that for active ingredients in biocidal and plant protection products harmonised C & L should be sought for all phys.-chem., toxicological, and ecotoxicological endpoints addressed by the corresponding legislations.

OTHER INFORMATION

The data and conclusions presented here have already undergone a peer review by experts from the company applying for annex I inclusion, the European Member States, and the European Commission (ECB/EFSA) in the context of the inclusion procedure for trimagnesium diphosphide into annex I of Dir. 98/8/EC and annex I of Dir. 91/414/EEC, respectively.

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