

manganese dioxide

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier:

Product name	: manganese dioxide
Synonyms	: slimes and sludges, zinc sulfate electrolytic; MnO ₂ rich material, cell mud, anode mud, MnO ₂ sludge, Pb Mn cell mud, manganese sludge, anode cleaning sludge
Registration number REACH	: 01-2119467168-30-0000 (Nyrstar Belgium NV/SA) 01-2119467168-30-0003 (Nyrstar Budel BV) 01-2119467168-30-0006 (Nyrstar France SAS)
Product type REACH	: Substance/UVCB : Transported isolated intermediate : On-site isolated intermediate
CAS number	: 69012-43-7
EC number	: 273-742-8

1.2 Relevant identified uses of the substance or mixture and uses advised against:

1.2.1 Relevant identified uses

Under Regulation (EC) No 1907/2006 the substance is defined as an on-site and transported isolated intermediate and must be used in correspondence to that status, including the application of strictly controlled conditions

Industrial use: manufacturing of chemicals

For further details concerning the management measures: see the attached annex

1.2.2 Uses advised against

No uses advised against known

1.3 Details of the supplier of the safety data sheet:

Supplier of the safety data sheet

Nyrstar Belgium N.V. on behalf of Nyrstar Sales & Marketing A.G.
Zinkstraat 1
B-2490 Balen
☎ +32 14 44 95 00
☎ +32 14 81 05 31
infoSDS@nyrstar.com

Nyrstar Budel B.V. on behalf of Nyrstar Sales & Marketing A.G.
Hoofdstraat 1
6024 AA Budel-Dorplein
☎ +32 14 44 96 80
☎ +32 14 44 95 52
infoSDS@nyrstar.com

Nyrstar France S.A.S. on behalf of Nyrstar Sales & Marketing A.G.
Rue Jean Jacques Rousseau
F-59950 Aubry
☎ +32 14 44 96 80
☎ +33 3 27 88 39 48
infoSDS@nyrstar.com

Manufacturer of the product

NYRSTAR Sales & Marketing AG
Tessinerplatz 7
CH-8002 Zürich
☎ +41 44 745 81 00
☎ +41 44 745 81 10
infoSDS@nyrstar.com

1.4 Emergency telephone number:

24h/24h (Telephone advice: English, French, German, Dutch):
+32 14 58 45 45 (BIG)

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture:

manganese dioxide

2.1.1 Classification according to Regulation EC No 1272/2008

Classified as dangerous according to the criteria of Regulation (EC) No 1272/2008

Class	Category	Hazard statements
Carc.	category 2	H351: Suspected of causing cancer.
Repr.	category 1A	H360Df: May damage the unborn child. Suspected of damaging fertility.
STOT RE	category 1	H372: Causes damage to organs through prolonged or repeated exposure if swallowed and if inhaled.
Acute Tox.	category 4	H332: Harmful if inhaled.
Acute Tox.	category 4	H302: Harmful if swallowed.
Aquatic Acute	category 1	H400: Very toxic to aquatic life.
Aquatic Chronic	category 1	H410: Very toxic to aquatic life with long lasting effects.

2.1.2 Classification according to Directive 67/548/EEC-1999/45/EC

Classified as dangerous in accordance with the criteria of Directives 67/548/EEC and 1999/45/EC

Repr. Cat. 1; R61 - May cause harm to the unborn child.

Repr. Cat. 3; R62 - Possible risk of impaired fertility.

Carc. Cat. 3; R40 - Limited evidence of a carcinogenic effect

Xn; R20/22 - 48/20/22 - Harmful by inhalation and if swallowed. Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.

N; R50-53 - Very toxic to aquatic organisms. May cause long-term adverse effects in the aquatic environment.

2.2 Label elements:

Labelling according to Regulation EC No 1272/2008 (CLP)



Contains manganese dioxide; lead(II)sulfate.

Signal word

Danger

H-statements

H351	Suspected of causing cancer.
H360Df	May damage the unborn child. Suspected of damaging fertility.
H372	Causes damage to organs through prolonged or repeated exposure if swallowed and if inhaled.
H302 + H332	Harmful if swallowed or if inhaled.
H410	Very toxic to aquatic life with long lasting effects.

P-statements

P202	Do not handle until all safety precautions have been read and understood.
P281	Use personal protective equipment as required.
P260	Do not breathe dust.
P309 + P311	IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician.
P304 + P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P301 + P312	IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell.

2.3 Other hazards:

CLP

Slightly irritant to respiratory organs

Slightly irritant to eyes

SECTION 3: Composition/information on ingredients

3.1 Substances:

Name (REACH Registration No)	CAS No EC No	Conc. (C)	Classification according to DSD/DPD	Classification according to CLP	Note	Remark
zinc oxide (-)	1314-13-2 215-222-5	0%<C<1%	N; R50-53	Aquatic Acute 1; H400 Aquatic Chronic 1; H410	(1)(2)	Component
lead(II)sulfate (-)	7446-14-2 231-198-9	2.93% <C<29.27 %	Repr. Cat. 1; R61 Repr. Cat. 3; R62 Xn; R20/22 R33 N; R50-53	Repr. 1A; H360Df Acute Tox. 4; H332 Acute Tox. 4; H302 STOT RE 2; H373 Aquatic Acute 1; H400 Aquatic Chronic 1; H410	(1)(2)(10)	Component

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

2 / 17

manganese dioxide

manganese dioxide (-)	1313-13-9 215-202-6	55.36% <C<94.91 %	Xn; R20/22	Acute Tox. 4; H332 Acute Tox. 4; H302	(1)(2)	Component
calcium sulfate (-)	7778-18-9 231-900-3	0% <C<4.85%			(2)	Component
strontium sulphate (-)	7759-02-6 231-850-2	0% <C<5.24%				Component

(1) For R-phrases and H-statements in full: see heading 16

(2) Substance with a Community workplace exposure limit

(10) Subject to restrictions of Annex XVII of Regulation (EC) No. 1907/2006

3.2 Mixtures:

Not applicable

SECTION 4: First aid measures

4.1 Description of first aid measures:

General:

Check the vital functions. Unconscious: maintain adequate airway and respiration. Respiratory arrest: artificial respiration or oxygen. Cardiac arrest: perform resuscitation. Victim conscious with laboured breathing: half-seated. Victim in shock: on his back with legs slightly raised. Vomiting: prevent asphyxia/aspiration pneumonia. Prevent cooling by covering the victim (no warming up). Keep watching the victim. Give psychological aid. Keep the victim calm, avoid physical strain. Depending on the victim's condition: doctor/hospital.

After inhalation:

Remove the victim into fresh air. Respiratory problems: consult a doctor/medical service.

After skin contact:

Rinse with water. Soap may be used. Take victim to a doctor if irritation persists.

After eye contact:

Rinse with water. Do not apply neutralizing agents. Take victim to an ophthalmologist if irritation persists.

After ingestion:

Rinse mouth with water. Immediately after ingestion: give lots of water to drink. Do not induce vomiting. Consult a doctor/medical service if you feel unwell.

4.2 Most important symptoms and effects, both acute and delayed:

4.2.1 Acute symptoms

After inhalation:

No effects known.

After skin contact:

No effects known.

After eye contact:

No effects known.

After ingestion:

Vomiting. Abdominal pain. Diarrhoea. Irritation of the gastric/intestinal mucosa.

4.2.2 Delayed symptoms

No effects known.

4.3 Indication of any immediate medical attention and special treatment needed:

If applicable and available it will be listed below.

SECTION 5: Firefighting measures

The information in this section is a general description. If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

5.1 Extinguishing media:

5.1.1 Suitable extinguishing media:

Adapt extinguishing media to the environment.

5.1.2 Unsuitable extinguishing media:

No unsuitable extinguishing media known.

5.2 Special hazards arising from the substance or mixture:

On burning: release of harmful/irritant gases/vapours.

5.3 Advice for firefighters:

5.3.1 Instructions:

Take account of environmentally hazardous firefighting water. Use water moderately and if possible collect or contain it.

5.3.2 Special protective equipment for fire-fighters:

Gloves. Safety glasses. Protective clothing. Reactivity hazard: compressed air/oxygen apparatus. Reactivity hazard: gas-tight suit. Large spills/in enclosed spaces: compressed air apparatus. Heat/fire exposure: compressed air/oxygen apparatus.

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

3 / 17

manganese dioxide

SECTION 6: Accidental release measures

The information in this section is a general description. If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

6.1 Personal precautions, protective equipment and emergency procedures:

Prevent dust cloud formation. No naked flames.

6.1.1 Protective equipment for non-emergency personnel

See heading 8.2

6.1.2 Protective equipment for emergency responders

Gloves. Safety glasses. Protective clothing. Reactivity hazard: compressed air/oxygen apparatus. Reactivity hazard: gas-tight suit. Large spills/in enclosed spaces: compressed air apparatus.

Suitable protective clothing

See heading 8.2

6.2 Environmental precautions:

Contain released substance, pump into suitable containers. Plug the leak, cut off the supply. Dam up the solid spill. Take account of toxic/corrosive precipitation water. Prevent soil and water pollution. Prevent spreading in sewers.

6.3 Methods and material for containment and cleaning up:

Prevent dust cloud formation. Scoop solid spill into closing containers. Carefully collect the spill/leftovers. Clean contaminated surfaces with an excess of water. Wash clothing and equipment after handling. Take collected spill to manufacturer/competent authority.

6.4 Reference to other sections:

See heading 13.

SECTION 7: Handling and storage

The information in this section is a general description. If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

7.1 Precautions for safe handling:

Avoid raising dust. Keep away from naked flames/heat. Observe very strict hygiene - avoid contact. Keep container tightly closed. Remove contaminated clothing immediately. Do not discharge the waste into the drain.

7.2 Conditions for safe storage, including any incompatibilities:

7.2.1 Safe storage requirements:

Store in a dry area. Keep only in the original container. Store at ambient temperature. Meet the legal requirements.

7.2.2 Keep away from:

Heat sources, combustible materials, oxidizing agents, reducing agents, (strong) acids, organic materials.

7.2.3 Suitable packaging material:

No data available

7.2.4 Non suitable packaging material:

No data available

7.3 Specific end use(s):

If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

SECTION 8: Exposure controls/personal protection

8.1 Control parameters:

8.1.1 Occupational exposure

a) Occupational exposure limit values

If limit values are applicable and available these will be listed below.

The Netherlands

Calciumsulfaat	Time-weighted average exposure limit 8 h	0.5 mg/m ³	Private occupational exposure limit value
Lood en anorg. verbindingen (rook en stof) (als Pb)	Time-weighted average exposure limit 8 h	0.15 mg/m ³ (a.31)	Private occupational exposure limit value; a.31: as Pb; fume/dust
Mangaanverbindingen (als Mn)	Short time value	3 mg/m ³ (a.27)	Private occupational exposure limit value; a.27: as Mn
	Time-weighted average exposure limit 8 h	1 mg/m ³ (a.27)	Private occupational exposure limit value; a.27: as Mn
Zinkoxide (rook)	Time-weighted average exposure limit 8 h	5 mg/m ³ (a.53)	Private occupational exposure limit value; a.53: fume

EU

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

4 / 17

manganese dioxide

Inorganic lead and its compounds	Time-weighted average exposure limit 8 h	0,15 mg/m ³	Binding occupational exposure limit value
----------------------------------	------------------------------------------	------------------------	-------------------------------------------

Belgium

Calcium (sulfate de) (anhydrate, hemihydrate, dihydrate, gypse)	Time-weighted average exposure limit 8 h	10 mg/m ³	
Manganèse et ses composés (en Mn)	Time-weighted average exposure limit 8 h	0.2 mg/m ³	
Plomb inorg. (poussières et fumées) (en Pb)	Time-weighted average exposure limit 8 h	0.15 mg/m ³	
Zinc (oxyde de) (fumées)	Short time value	10 mg/m ³	
	Time-weighted average exposure limit 8 h	5 mg/m ³	

USA (TLV-ACGIH)

Lead, inorganic compounds, as Pb	Time-weighted average exposure limit 8 h	0.05 mg/m ³	TLV - Adopted Value
Zinc oxide	Short time value	10 mg/m ³ (R)	TLV - Adopted Value; (R): Respirable fraction
	Time-weighted average exposure limit 8 h	2 mg/m ³ (R)	TLV - Adopted Value; (R): Respirable fraction
Calcium sulfate	Time-weighted average exposure limit 8 h	10 mg/m ³ (E)	TLV - Adopted Value; (E): The value is for particulate matter containing no asbestos and < 1% crystalline silica
Manganese, inorganic compounds, as Mn	Time-weighted average exposure limit 8 h	0.1 mg/m ³ (I)	TLV - Adopted Value; (I): Inhalable fraction

Germany

Calciumsulfat	Time-weighted average exposure limit 8 h	6 mg/m ³	TRGS 900
anorganischen Manganverbindungen	Time-weighted average exposure limit 8 h	0.5 mg/m ³	TRGS 900
Blei und anorganischen Bleiverbindungen	Time-weighted average exposure limit 8 h	0.1 mg/m ³	TRGS 505

France

Calcium (sulfate de)	Time-weighted average exposure limit 8 h	10 mg/m ³	VL: Valeur non réglementaire indicative
Zinc (oxyde de, fumées)	Time-weighted average exposure limit 8 h	5 mg/m ³	VL: Valeur non réglementaire indicative
Zinc (oxyde de, poussières)	Time-weighted average exposure limit 8 h	10 mg/m ³	VL: Valeur non réglementaire indicative
Plomb métallique et composés, en Pb	Time-weighted average exposure limit 8 h	0.1 mg/m ³	VRC: Valeur réglementaire contraignante

UK

Manganese inorganic compounds (as Mn)	Time-weighted average exposure limit 8 h	0.5 mg/m ³	Workplace exposure limit (EH40/2005)
Gypsum inhalable dust	Time-weighted average exposure limit 8 h	10 mg/m ³	Workplace exposure limit (EH40/2005)
Gypsum respirable dust	Time-weighted average exposure limit 8 h	4 mg/m ³	Workplace exposure limit (EH40/2005)
Lead other than lead alkyls	Time-weighted average exposure limit 8 h	0,15 mg/cm ³	Occupational exposure limit (Control of lead at work)

b) National biological limit values

If limit values are applicable and available these will be listed below.

8.1.2 Sampling methods

Product name	Test	Number
Lead	OSHA	ID 121
Lead	OSHA	ID 125G
Lead, Inorganic surface dusts (as Pb)	OSHA	ID 121
Manganese	OSHA	ID 121
Manganese	OSHA	ID 125
Manganese	OSHA	ID 125G
Sulfites, & Sulfates	NIOSH	6004
Zinc (Elements)	NIOSH	7300
Zinc Oxide	NIOSH	7502
Zinc Oxide	OSHA	ID 121
Zinc Oxide	NIOSH	7030
Zinc Oxide Fume	OSHA	ID 125

8.1.3 Applicable limit values when using the substance or mixture as intended

If limit values are applicable and available these will be listed below.

8.1.4 DNEL/PNEC values

DNEL - Workers

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

5 / 17

manganese dioxide

zinc oxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects dermal	83 mg/kg bw/day	
	Long-term systemic effects inhalation	5 mg/m ³	

manganese dioxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	0.2 mg/m ³	
	Long-term systemic effects dermal	0.00414 mg/kg bw/day	

calcium sulfate

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Acute systemic effects inhalation	5082 mg/m ³	
	Long-term systemic effects inhalation	21.17 mg/m ³	

DNEL - General population

zinc oxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects dermal	83 mg/kg bw/day	
	Long-term systemic effects inhalation	2.5 mg/m ³	
	Long-term systemic effects oral	0.83 mg/kg bw/day	

manganese dioxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	0.043 mg/m ³	
	Long-term systemic effects dermal	0.0021 mg/kg bw/day	

calcium sulfate

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Acute systemic effects inhalation	3811 mg/m ³	
	Acute -systemic effects oral	11.4 mg/kg bw/day	
	Long-term systemic effects inhalation	5.29 mg/m ³	
	Long-term systemic effects oral	1.52 mg/kg bw/day	

PNEC

zinc oxide

Compartments	Value	Remark
Fresh water	20.6 µg/l	
Marine water	6.1 µg/l	
STP	52 µg/l	
Fresh water sediment	117.8 mg/kg sediment dw	
Marine water sediment	56.5 mg/kg sediment dw	
Soil	35.6 mg/kg soil dw	

8.1.5 Control banding

If applicable and available it will be listed below.

8.2 Exposure controls:

The information in this section is a general description. If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

8.2.1 Appropriate engineering controls

Avoid raising dust. Keep away from naked flames/heat. Measure the concentration in the air regularly. Carry operations in the open/under local exhaust/ventilation or with respiratory protection.

8.2.2 Individual protection measures, such as personal protective equipment

Observe very strict hygiene - avoid contact. Keep container tightly closed. Do not eat, drink or smoke during work.

a) Respiratory protection:

Dust production: dust mask with filter type P3. High dust production: self-contained breathing apparatus.

b) Hand protection:

Gloves.

- materials (good resistance)

Butyl rubber, chlorinated polyethylene, nitrile rubber, neoprene, PVC, chlorinated polyethylene.

c) Eye protection:

Safety glasses. In case of dust production: protective goggles.

d) Skin protection:

Protective clothing. Dustproof clothing.

8.2.3 Environmental exposure controls:

See headings 6.2, 6.3 and 13

SECTION 9: Physical and chemical properties

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

6 / 17

manganese dioxide

9.1 Information on basic physical and chemical properties:

Physical form	Solid
Odour	Odourless
Odour threshold	Not applicable
Colour	Grey to brown-black
Particle size	D50 = 929 mm D80 = 2083 mm
Explosion limits	No data available
Flammability	Non combustible
Log Kow	Not applicable
Dynamic viscosity	No data available
Kinematic viscosity	No data available
Melting point	193 °C ; 1013 hPa
Boiling point	No data available
Flash point	Not applicable
Evaporation rate	No data available
Vapour pressure	No data available
Relative vapour density	Not applicable
Solubility	water ; insoluble
Relative density	4.09 ; 20 °C
Decomposition temperature	No data available
Auto-ignition temperature	No data available
Explosive properties	No chemical group associated with explosive properties
Oxidising properties	No chemical group associated with oxidising properties
pH	No data available

Physical hazards

No physical hazard class

9.2 Other information:

No data available

SECTION 10: Stability and reactivity

10.1 Reactivity:

No data available.

10.2 Chemical stability:

Stable under normal conditions.

10.3 Possibility of hazardous reactions:

Reacts with many compounds: (increased) risk of fire/explosion. Reacts with (some) acids: release of toxic and corrosive gases/vapours.

10.4 Conditions to avoid:

Avoid raising dust. Keep away from naked flames/heat.

10.5 Incompatible materials:

Combustible materials, oxidizing agents, reducing agents, (strong) acids, organic materials.

10.6 Hazardous decomposition products:

No data available.

SECTION 11: Toxicological information

11.1 Information on toxicological effects:

11.1.1 Test results

Acute toxicity

manganese dioxide

No (test)data available

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

7 / 17

manganese dioxide

zinc oxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Gender	Value determination
Oral	LD50	Equivalent to OECD 401	> 5000 mg/kg		Rat		Experimental value
Dermal	LD50		> 7940 mg/kg		Rabbit		Literature study
Inhalation (dust)	LC50	Equivalent to OECD 403	>5.7 mg/l	4 h	Rat		Experimental value

lead(II)sulfate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Gender	Value determination
Oral			category 4				Annex VI
Inhalation			category 4				Annex VI

manganese dioxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Gender	Value determination
Oral			category 2				Literature study
Inhalation			category 2				Literature study

calcium sulfate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Gender	Value determination
Oral	LD50	OECD 420	>1584 mg/kg bw		Rat	Female	Experimental value
Inhalation (dust)	LC50	OECD 403	>2.61 mg/l air	4 h	Rat	Male/female	Experimental value

Conclusion

Harmful if swallowed.
Harmful if inhaled.
Low acute toxicity by the dermal route

Corrosion/irritation

manganese dioxide

No (test)data available

zinc oxide

Route of exposure	Result	Method	Exposure time	Time point	Species	Value determination
Eye	Not irritating	OECD 405	24 h	24; 72 hours	Rabbit	Experimental value
Skin	Not irritating	OECD 404	24 h	24 hours	Rabbit	Experimental value

calcium sulfate

Route of exposure	Result	Method	Exposure time	Time point	Species	Value determination
Eye	Not irritating	OECD 405		72 hours	Rabbit	Experimental value
Skin	Not irritating	OECD 404	4 h	72 hours	Rabbit	Experimental value

Conclusion

Not classified as irritating to the skin
Not classified as irritating to the eyes

Respiratory or skin sensitisation

manganese dioxide

No (test)data available

zinc oxide

Route of exposure	Result	Method	Exposure time	Observation time point	Species	Gender	Value determination
Skin	Not sensitizing	Human observation	2 days (continuous)	72 hours	Human		Experimental value

calcium sulfate

Route of exposure	Result	Method	Exposure time	Observation time point	Species	Gender	Value determination
Skin	Not sensitizing	OECD 406	6 h	24; 48 hours	Guinea pig	Male	Experimental value

Conclusion

Not classified as sensitizing for skin

Specific target organ toxicity

manganese dioxide

No (test)data available

manganese dioxide

zinc oxide

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Gender	Value determination
Oral	NOEL	OECD 408	3000 ppm		No effect	13 weeks (daily)	Rat	Male/female	Read-across
Inhalation (aerosol)	NOAEL		2.7 mg/m ³ air		No effect	5 days (3h/day)	Guinea pig	Male	Experimental value

lead(II)sulfate

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Gender	Value determination
Oral			STOT RE cat.2						Annex VI
Dermal			STOT RE cat.2						Annex VI
Inhalation			STOT RE cat.2						Annex VI

calcium sulfate

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Gender	Value determination
Oral	NOAEL	OECD 422	79 mg/kg bw/day	Blood	No effect	35 day(s)	Rat	Male	Experimental value
Oral	LOAEL	OECD 422	237 mg/kg bw/day	Blood	Change in the haemogramme /blood composition	35 day(s)	Rat	Male	Experimental value

Conclusion

Causes damage to organs through prolonged or repeated exposure if swallowed.

Causes damage to organs through prolonged or repeated exposure if inhaled.

Mutagenicity (in vitro)

manganese dioxide

No (test)data available

zinc oxide

Result	Method	Test substrate	Effect	Value determination
Negative	Equivalent to OECD 471	Bacteria (S.typhimurium)	No effect	Experimental value

lead(II)sulfate

Result	Method	Test substrate	Effect	Value determination
Negative	Ames test			Experimental value
Ambiguous				Experimental value

calcium sulfate

Result	Method	Test substrate	Effect	Value determination
Negative with metabolic activation, negative without metabolic activation	OECD 471	Bacteria (S.typhimurium)	No effect	Experimental value
Negative with metabolic activation, negative without metabolic activation	OECD 471	Escherichia coli	No effect	Experimental value
Negative with metabolic activation, negative without metabolic activation	OECD 476	Mouse (lymphoma L5178Y cells)	No effect	Experimental value

Mutagenicity (in vivo)

manganese dioxide

No (test)data available

zinc oxide

Result	Method	Exposure time	Test substrate	Gender	Organ	Value determination
Negative	OECD 474		Mouse	Male		Experimental value

calcium sulfate

Result	Method	Exposure time	Test substrate	Gender	Organ	Value determination
Negative	OECD 474		Mouse	Male	Blood	Experimental value

Carcinogenicity

manganese dioxide

No (test)data available

manganese dioxide

calcium sulfate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Gender	Value determination	Organ	Effect
Oral	NOAEL	Other	256 mg/kg bw/day	104 weeks (daily)	Rat	Male	Experimental value		No effect
Oral	NOAEL	Other	284 mg/kg bw/day	104 weeks (daily)	Rat	Female	Experimental value		No effect

Reproductive toxicity

manganese dioxide

No (test)data available

zinc oxide

	Parameter	Method	Value	Exposure time	Species	Gender	Effect	Organ	Value determination
Developmental toxicity	NOAEL		88 mg/kg bw/day	5 days (gestation, daily)	Guinea pig		No effect		Read-across
Effects on fertility	NOAEL (F1)	Equivalent to OECD 416	7.5 mg/kg bw/day	22 weeks (daily)	Rat	Male/female	No effect		Read-across

lead(II)sulfate

	Parameter	Method	Value	Exposure time	Species	Gender	Effect	Organ	Value determination
Developmental toxicity			category 1A						Annex VI
Effects on fertility			category 2						Annex VI

calcium sulfate

	Parameter	Method	Value	Exposure time	Species	Gender	Effect	Organ	Value determination
Developmental toxicity	NOAEL	Equivalent to OECD 414	1600 mg/kg bw/day	10 day(s)	Mouse		No effect	General	Experimental value
	NOAEL	Equivalent to OECD 414	1600 mg/kg bw/day	10 day(s)	Rat		No effect	General	Experimental value
	NOAEL	Equivalent to OECD 414	1600 mg/kg bw/day	13 day(s)	Rabbit		No effect	General	Experimental value
Effects on fertility	NOAEL	OECD 422	790 mg/kg bw/day	2 week(s)	Rat	Male/female	No effect		Experimental value

Conclusion CMR

Suspected of causing cancer.

May damage the unborn child. Suspected of damaging fertility.

Toxicity other effects

manganese dioxide

No (test)data available

Chronic effects from short and long-term exposure

manganese dioxide

ON CONTINUOUS/REPEATED EXPOSURE/CONTACT: Feeling of weakness. Loss of appetite. Loss of weight. Sleeplessness. Brain affection. Behavioural disturbances. Delusions. Disturbed tactile sensibility. Movement disturbances. Coordination disorders. Disturbed motor response. Tremor. Coughing. Respiratory difficulties. Risk of pneumonia. Change in the haemogramme/blood composition. Impairment of the blood forming system. Possible premature birth. Discolouration of the gums.

SECTION 12: Ecological information

12.1 Toxicity:

manganese dioxide

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity invertebrates	LC50	US EPA	73.56 µg/l	48 h	Ceriodaphnia dubia	Semi-static	Fresh water	Read-across
Long-term toxicity fish	EC10		17.8 µg/l	7 day(s)	Cyprinus carpio	Flow-through system	Fresh water	Read-across

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

10 / 17

manganese dioxide

zinc oxide

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	LC50	ASTM E729-88	0.169 mg/l	96 h	Oncorhynchus mykiss	Static system	Fresh water	Read-across; Zinc ion
Acute toxicity invertebrates	LC50	OECD 202	0.33 - 0.66 mg/l	48 h	Daphnia magna	Static system	Fresh water	Read-across; Zinc ion
Toxicity algae and other aquatic plants	IC50	OECD 201	0.136 mg/l	72 h	Pseudokirchneriella subcapitata	Static system	Fresh water	Experimental value; Zinc ion
Long-term toxicity fish	NOEC	OECD 215	0.199 mg/l	30 day(s)	Oncorhynchus mykiss	Flow-through system	Fresh water	Read-across; Zinc ion
Long-term toxicity aquatic invertebrates	NOEC		0.31 mg/l	21 day(s)	Daphnia magna	Semi-static	Fresh water	Read-across; Zinc ion
Toxicity aquatic micro-organisms	EC50	Equivalent to OECD 209	5.2 mg/l	3 h	Activated sludge	Static system	Fresh water	Read-across; Inhibitory

lead(II)sulfate

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	TLm		7.48 mg/l	96 h	Pimephales promelas			Literature study; Lead ion
Acute toxicity invertebrates	LC50		0.3 mg/l	48 h	Daphnia magna			Literature study; Lead ion
Toxicity algae and other aquatic plants	EC50		0.14 mg/l		Selenastrum capricornutum			Literature study; Lead ion

calcium sulfate

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	LC50		2980 mg/l	96 h	Lepomis macrochirus			

Conclusion

Very toxic to aquatic life with long lasting effects.

12.2 Persistence and degradability:

Biodegradability: not applicable

12.3 Bioaccumulative potential:

manganese dioxide

Log Kow

Method	Remark	Value	Temperature	Value determination
	Not applicable			

zinc oxide

Log Kow

Method	Remark	Value	Temperature	Value determination
		1.53		Estimated value

lead(II)sulfate

Log Kow

Method	Remark	Value	Temperature	Value determination
		1.13		Estimated value

manganese dioxide

Log Kow

Method	Remark	Value	Temperature	Value determination
	No data available			

calcium sulfate

Log Kow

Method	Remark	Value	Temperature	Value determination
	No data available			

strontium sulphate

Log Kow

Method	Remark	Value	Temperature	Value determination
	No data available			

Conclusion

No straightforward conclusion can be drawn based upon the available numerical values

manganese dioxide

12.4 Mobility in soil:

zinc oxide

(log) K_{oc}

Parameter	Method	Value	Value determination
log K _{oc}		2.2	Literature study

Conclusion

No straightforward conclusion can be drawn based upon the available numerical values

12.5 Results of PBT and vPvB assessment:

The criteria of PBT and vPvB as listed in Annex XIII of Regulation (EC) No 1907/2006 do not apply to inorganic substances.

12.6 Other adverse effects:

manganese dioxide

Global warming potential (GWP)

None of the known components is included in the list of substances which may contribute to the greenhouse effect (Regulation (EC) No 842/2006)

Ozone-depleting potential (ODP)

Not classified as dangerous for the ozone layer (Regulation (EC) No 1005/2009)

zinc oxide

Ground water

Ground water pollutant

SECTION 13: Disposal considerations

The information in this section is a general description. If available, the documentation for on-site isolated intermediates will be attached in annex to support safe handling arrangements.

13.1 Waste treatment methods:

13.1.1 Provisions relating to waste

Waste material code (Directive 2008/98/EC, Decision 2000/0532/EC).

06 03 13* (solid salts and solutions containing heavy metals). Depending on branch of industry and production process, also other waste codes may be applicable. Hazardous waste according to Directive 2008/98/EC.

13.1.2 Disposal methods

Recycle/reuse. Remove waste in accordance with local and/or national regulations. Hazardous waste shall not be mixed together with other waste.

Different types of hazardous waste shall not be mixed together if this may entail a risk of pollution or create problems for the further management of the waste. Hazardous waste shall be managed responsibly. All entities that store, transport or handle hazardous waste shall take the necessary measures to prevent risks of pollution or damage to people or animals. Do not discharge into surface water (Directive 2000/60/EC, Council decision 2455/2001/EC).

Treat using the best available techniques before discharge into drains or the aquatic environment.

13.1.3 Packaging/Container

Waste material code packaging (Directive 2008/98/EC).

15 01 10* (packaging containing residues of or contaminated by dangerous substances).

SECTION 14: Transport information

Road (ADR)

14.1 UN number:

UN number	3077
-----------	------

14.2 UN proper shipping name:

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.
Techn./chem. name ADR	lead(II)sulfate

14.3 Transport hazard class(es):

Hazard identification number	90
Class	9
Classification code	M7

14.4 Packing group:

Packing group	III
Labels	9

14.5 Environmental hazards:

Environmentally hazardous substance mark	yes
------------------------------------------	-----

14.6 Special precautions for user:

Special provisions	274
Special provisions	335
Special provisions	601

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

12 / 17

manganese dioxide

Limited quantities

Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

Rail (RID)

14.1 UN number:

UN number	3077
-----------	------

14.2 UN proper shipping name:

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.
Techn./chem. name RID	lead(II)sulfate

14.3 Transport hazard class(es):

Hazard identification number	90
Class	9
Classification code	M7

14.4 Packing group:

Packing group	III
Labels	9

14.5 Environmental hazards:

Environmentally hazardous substance mark	yes
------------------------------------------	-----

14.6 Special precautions for user:

Special provisions	274
Special provisions	335
Special provisions	601
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

Inland waterways (ADN)

14.1 UN number:

UN number	3077
-----------	------

14.2 UN proper shipping name:

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.
Techn./chem. name ADN	lead(II)sulfate

14.3 Transport hazard class(es):

Class	9
Classification code	M7

14.4 Packing group:

Packing group	III
Labels	9

14.5 Environmental hazards:

Environmentally hazardous substance mark	yes
------------------------------------------	-----

14.6 Special precautions for user:

Special provisions	274
Special provisions	335
Special provisions	601
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

Sea (IMDG/IMSBC)

14.1 UN number:

UN number	3077
-----------	------

14.2 UN proper shipping name:

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.
Techn./chem. name IMO	lead(II)sulfate

14.3 Transport hazard class(es):

Class	9
-------	---

14.4 Packing group:

Packing group	III
Labels	9

14.5 Environmental hazards:

Marine pollutant	P
Environmentally hazardous substance mark	yes

14.6 Special precautions for user:

Special provisions	274
Special provisions	335

manganese dioxide

Special provisions	966
Special provisions	967
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code:

Annex II of MARPOL 73/78	Not applicable
--------------------------	----------------

Air (ICAO-TI/IATA-DGR)

14.1 UN number:

UN number	3077
-----------	------

14.2 UN proper shipping name:

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.
Techn./chem. name ICAO	lead(II)sulfate

14.3 Transport hazard class(es):

Class	9
-------	---

14.4 Packing group:

Packing group	III
Labels	9

14.5 Environmental hazards:

Environmentally hazardous substance mark	yes
------------------------------------------	-----

14.6 Special precautions for user:

Special provisions	A97
Special provisions	A158
Special provisions	A179
Passenger and cargo transport: limited quantities: maximum net quantity per packaging	30 kg G

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

European legislation:

REACH registration

This substance is handled under Strictly Controlled Conditions in accordance with Reach regulation Article 17(3) for on-site isolated intermediates and, in case the substance is transported to other sites for further processing, the substance should be handled at these sites under Strictly Controlled Conditions as specified in Reach regulation Article 18(4). Site documentation to support safe handling arrangements including the selection of engineering, administrative and personal protective equipment controls in accordance with risk based management systems is available at each manufacturing site. Written confirmation of application of Strictly Controlled Conditions should be available at the premises of every affected Distributor and Downstream Processor/User of the Registrants' intermediate.

Information exposure scenarios

This safety data sheet does not contain an exposure scenario; exempted as (isolated) intermediate

REACH Annex XVII - Restriction

Contains component(s) subject to restrictions of Annex XVII of Regulation (EC) No 1907/2006: restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles.

	Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
lead(II)sulfate	Lead sulphates; PbSO 4	Shall not be placed on the market, or used, as substances or in mixtures, where the substance or mixture is intended for use as paint. However, Member States may, in accordance with the provisions of International Labour Organization (ILO) Convention 13, permit the use on their territory of the substance or mixture for the restoration and maintenance of works of art and historic buildings and their interiors, as well as the placing on the market for such use. Where a Member State makes use of this derogation, it shall inform the Commission thereof.
lead(II)sulfate	Substances which appear in Part 3 of Annex VI to Regulation (EC) No 1272/2008 classified as toxic to reproduction category 1A or 1B (Table 3.1) or toxic to reproduction category 1 or 2 (Table 3.2) and listed as follows: - Reproductive toxicant category 1A adverse effects on sexual function and fertility or on development (Table 3.1) or reproductive toxicant category 1 with R60 (May impair fertility) or R61 (May cause harm to the unborn child) (Table 3.2) listed in Appendix 5 - Reproductive toxicant category 1B adverse effects on sexual function and fertility or on development (Table 3.1) or reproductive toxicant category 2 with R60 (May impair fertility) or R61 (May cause harm to the unborn child) (Table 3.2) listed in Appendix 6	Without prejudice to the other parts of this Annex the following shall apply to entries 28 to 30:1. Shall not be placed on the market, or used, — as substances, — as constituents of other substances, or, — in mixtures, for supply to the general public when the individual concentration in the substance or mixture is equal to or greater than: — either the relevant specific concentration limit specified in Part 3 of Annex VI to Regulation (EC) No 1272/2008, or, — the relevant concentration specified in Directive 1999/45/EC where no specific concentration limit is set out in Part 3 of Annex VI to Regulation (EC) No 1272/2008. Without prejudice to the implementation of other Community provisions relating to the classification, packaging and labelling of substances and mixtures, suppliers shall ensure before the placing on the market that the packaging of such substances and mixtures is marked visibly, legibly and indelibly as follows: "Restricted to professional users".2. By way of derogation, paragraph 1 shall not apply to: (a) medicinal or veterinary products as defined by Directive 2001/82/EC and Directive 2001/83/EC; (b) cosmetic products as defined by Directive 76/768/EEC;

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

14 / 17

manganese dioxide

		<p>(c) the following fuels and oil products:</p> <ul style="list-style-type: none"> — motor fuels which are covered by Directive 98/70/EC, — mineral oil products intended for use as fuel in mobile or fixed combustion plants, — fuels sold in closed systems (e.g. liquid gas bottles); <p>(d) artists' paints covered by Directive 1999/45/EC;</p> <p>(e) the substances listed in Appendix 11, column 1, for the applications or uses listed in Appendix 11, column 2. Where a date is specified in column 2 of Appendix 11, the derogation shall apply until the said date.</p>
lead(II)sulfate	Lead and its compounds	<p>1. Shall not be placed on the market or used in any individual part of jewellery articles if the concentration of lead (expressed as metal) in such a part is equal to or greater than 0,05 % by weight.2. For the purposes of paragraph 1:</p> <p>(i) "jewellery articles" shall include jewellery and imitation jewellery articles and hair accessories, including:</p> <ul style="list-style-type: none"> (a) bracelets, necklaces and rings; (b) piercing jewellery; (c) wrist watches and wrist-wear; (d) brooches and cufflinks; <p>(ii) "any individual part" shall include the materials from which the jewellery is made, as well as the individual components of the jewellery articles.3. Paragraph 1 shall also apply to individual parts when placed on the market or used for jewellery-making.4. By way of derogation, paragraph 1 shall not apply to:</p> <p>(a) crystal glass as defined in Annex I (categories 1, 2, 3 and 4) to Council Directive 69/493/EEC (*);</p> <p>(b) internal components of watch timepieces inaccessible to consumers;</p> <p>(c) non-synthetic or reconstructed precious and semiprecious stones (CN code 7103, as established by Regulation (EEC) No 2658/87), unless they have been treated with lead or its compounds or mixtures containing these substances;</p> <p>(d) enamels, defined as vitrifiable mixtures resulting from the fusion, vitrification or sintering of minerals melted at a temperature of at least 500 °C. (*) OJ L 326, 29.12.1969, p. 36.5. By way of derogation, paragraph 1 shall not apply to jewellery articles placed on the market for the first time before 9 October 2013 and jewellery articles produced before 10 December 1961.6. By 9 October 2017, the Commission shall re-evaluate this entry in the light of new scientific information, including the availability of alternatives and the migration of lead from the articles referred to in paragraph 1 and, if appropriate, modify this entry accordingly.</p>

National legislation The Netherlands

manganese dioxide

Waste identification (the Netherlands)	LWCA (the Netherlands): KGA category 05
Waterbezwaarlijkheid	1

lead(II)sulfate

SZW - List of reprotoxic substances (fertility)	Possible risk of impaired fertility
SZW - List of reprotoxic substances (development)	Hazardous to the foetus

manganese dioxide

SZW - List of reprotoxic substances (fertility)	Possible risk of impaired fertility
SZW - List of reprotoxic substances (development)	Possibly hazardous to the foetus

National legislation Germany

manganese dioxide

WGK	3; Classification water polluting based on the components in compliance with Verwaltungsvorschrift wassergefährdender Stoffe (VwVwS) of 27 July 2005 (Anhang 4)
-----	-----------------------------------------------------------------------------------------------------------------------------------------------------------------

zinc oxide

TA-Luft	TA-Luft Klasse 5.2.5/I
Schwangerschaft Gruppe	C
Schwangerschaft Gruppe	C
MAK 8-Stunden-Mittelwert mg/m ³	<p>Zink und seine anorganischen Verbindungen (alveolengängige Fraktion); 0,1 mg/m³; gemessen als alveolengängige Fraktion (vgl. Abschn. Vd) S. 191)</p> <p>Zink und seine anorganischen Verbindungen (einatembare Fraktion); 2 mg/m³; gemessen als einatembare Fraktion (vgl. Abschn. Vd) S. 191)</p>

lead(II)sulfate

MAK - Krebserzeugend Kategorie	2
MAK - Keimzellmutagen Kategorie	3A
TA-Luft	TA-Luft Klasse 5.2.2/II

manganese dioxide

TA-Luft	TA-Luft Klasse 5.2.2/III
Schwangerschaft Gruppe	C
MAK 8-Stunden-Mittelwert mg/m ³	Mangan und seine anorganischen Verbindungen (einatembare Fraktion); 0,2 mg/m ³ ; gemessen als einatembare Fraktion (vgl. Abschn. Vd) S. 191)

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

15 / 17

manganese dioxide

calcium sulfate

TA-Luft	TA-Luft Klasse 5.2.1
Schwangerschaft Gruppe	C
Schwangerschaft Gruppe	C
Schwangerschaft Gruppe	C
Schwangerschaft Gruppe	C
MAK 8-Stunden-Mittelwert mg/m ³	Calciumsulfat (alveolengängige Fraktion); 1.5 mg/m ³ ; gemessen als alveolengängige Fraktion (vgl. Abschn. Vd) S. 191)
	Calciumsulfat (eintembare Fraktion); 4 mg/m ³ ; gemessen als eintembare Fraktion (vgl. Abschn. Vd) S. 191)
	Calciumsulfat (alveolengängige Fraktion); 1.5 mg/m ³ ; gemessen als alveolengängige Fraktion (vgl. Abschn. Vd) S. 191)
	Calciumsulfat (eintembare Fraktion); 4 mg/m ³ ; gemessen als eintembare Fraktion (vgl. Abschn. Vd) S. 191)

National legislation France

manganese dioxide

No data available

lead(II)sulfate

Catégorie cancérogène	(C1A,C1B,C2)
-----------------------	--------------

National legislation Belgium

manganese dioxide

No data available

Other relevant data

manganese dioxide

No data available

lead(II)sulfate

TLV - Carcinogen	Lead, inorganic compounds, as Pb; A3
------------------	--------------------------------------

manganese dioxide

TLV - Carcinogen	Manganese, inorganic compounds, as Mn; A4
------------------	-------------------------------------------

15.2 Chemical safety assessment:

No chemical safety assessment is required; registered as an isolated intermediate.

SECTION 16: Other information

Information based on classification according to CLP

Labelling according to Directive 67/548/EEC-1999/45/EC (DSD/DPD)

Not listed in Annex I of Directive 67/548/EEC et sequens. Labelling established on the basis of the available data.

Labels



Toxic



Dangerous for the environment

Contains: manganese dioxide; lead(II)sulfate.

R-phrases

- 61 May cause harm to the unborn child
- 20/22 Also harmful by inhalation and if swallowed
- 40 Limited evidence of a carcinogenic effect
- 48/20/22 Also harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
- 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
- 62 Possible risk of impaired fertility

S-phrases

- 53 Avoid exposure - obtain special instructions before use
- 20 When using do not eat or drink
- 36 Wear suitable protective clothing
- 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)
- 57 Use appropriate container to avoid environmental contamination

Full text of any R-phrases referred to under headings 2 and 3:

- R20/22 Harmful by inhalation and if swallowed
- R33 Danger of cumulative effects
- R40 Limited evidence of a carcinogenic effect

Reason for revision: 1.2;8.1;8.2;15.1

Publication date: 2013-05-07

Date of revision: 2013-12-10

Revision number: 0001

Product number: 28902

16 / 17

manganese dioxide

R48/20/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R50 Very toxic to aquatic organisms
R53 May cause long-term adverse effects in the aquatic environment
R61 May cause harm to the unborn child
R62 Possible risk of impaired fertility

Full text of any H-statements referred to under headings 2 and 3:

H302 Harmful if swallowed.
H332 Harmful if inhaled.
H351 Suspected of causing cancer.
H360Df May damage the unborn child. Suspected of damaging fertility.
H372 Causes damage to organs through prolonged or repeated exposure if swallowed and if inhaled.
H373 May cause damage to organs through prolonged or repeated exposure.
H400 Very toxic to aquatic life.
H410 Very toxic to aquatic life with long lasting effects.

(*) = INTERNAL CLASSIFICATION BY BIG

PBT-substances = persistent, bioaccumulative and toxic substances

DSD Dangerous Substance Directive

DPD Dangerous Preparation Directive

CLP (EU-GHS) Classification, labelling and packaging (Globally Harmonised System in Europe)

Specific concentration limits CLP

lead(II)sulfate	C ≥ 2.5 %	Repr. 2 ;H361f	CLP Annex VI (ATP 0)
	C ≥ 0.5 %	STOT RE 2 ;H373	CLP Annex VI (ATP 0)

Specific concentration limits DSD

lead(II)sulfate	C ≥ 2,5 %	Repr. Cat. 3; R62	Annex VI
	C ≥ 1 %	Xn; R20/22	Annex VI
	C ≥ 0,5 %	R33	Annex VI

The information in this safety data sheet is based on data and samples provided to BIG. The sheet was written to the best of our ability and according to the state of knowledge at that time. The safety data sheet only constitutes a guideline for the safe handling, use, consumption, storage, transport and disposal of the substances/preparations/mixtures mentioned under point 1. New safety data sheets are written from time to time. Only the most recent versions may be used. Old versions must be destroyed. Unless indicated otherwise word for word on the safety data sheet, the information does not apply to substances/preparations/mixtures in purer form, mixed with other substances or in processes. The safety data sheet offers no quality specification for the substances/preparations/mixtures in question. Compliance with the instructions in this safety data sheet does not release the user from the obligation to take all measures dictated by common sense, regulations and recommendations or which are necessary and/or useful based on the real applicable circumstances. BIG does not guarantee the accuracy or exhaustiveness of the information provided and cannot be held liable for any changes by third parties. This safety data sheet is only to be used within the European Union, Switzerland, Iceland, Norway and Liechtenstein. Any use outside of this area is at your own risk. Use of this safety data sheet is subject to the licence and liability limiting conditions as stated in your BIG licence agreement or when this is failing the general conditions of BIG. All intellectual property rights to this sheet are the property of BIG and its distribution and reproduction are limited. Consult the mentioned agreement/conditions for details.

This annex contains information on risk management measures as specified in appendix 3 of the registration dossier for isolated on-site and transported intermediates

1. Brief description of technological process applied in manufacture of the intermediate EC 273-742-8

- During the Zinc electrolysis, insoluble oxy-sulphates, (i.e. Lead- & calcium-sulphate and Manganese di-oxide) can be formed at the Lead-anode surface ; part of it falls down in the cells another part sticks to the Lead-anode surface and is separated during the anode-cleaning steps
- The Pb-Mn cellmud is regularly collected from the bottom of the cells and from the anode-cleaning devices. It is settled, washed and filtered.
- Transfer of the Pb-Mn cellmud occurs in big-bags or containers or covered bulk load trucks, according to applicable regulation
- The 'Pb Mn cellmud' is a lumpy wet filtercake with an average Lead-content of 20-30% w/w and is typically used in production units of Lead metal (EC 231-100-4) or Lead compounds and recovery of precious metals
- Waste of the process:
 - None

2. Brief description of technological processes applied in use of the intermediate EC 273-742-8

- The 'Pb Mn cellmud' is unloaded from transport trucks, ADR-big-bags or containers, ...and transferred to storage silo's through especially designed transfer units,
- The 'Pb Mn cellmud' is optionally blended with other Lead-containing primary or secondary materials
- The mixture is continuously fed to smelting furnaces (i.e. ISA, Blast furnace, ISF ...) or similar for further smelting extraction of lead and lead compounds, and precious metals
- Waste treatment:
 - None
 - During pyrometallurgical treatment: slag. The slag is dumped if not re-used in road filling.

3. Means of rigorous containment and minimisation technologies applied by the registrant during the manufacturing and /or use process

⇒ Description of the technical means to rigorously contain the substance

- Process enclosures and closed circuits where relevant and possible
- Containment of liquid volumes in sumps to collect/prevent accidental spillage, acid solutions are treated adequately
- Potential dryers are operated under strong aspiration (negative pressure towards atmospheric pressure)
- All processes are performed in a confined area
- The process is managed and controlled from a separate control-room.

⇒ Identification of residual emissions to workplace & environment

Residual exposures at the workplace and the environment are assessed from regular measurements of dust/metals and represent usually a global exposure to several steps in a process. Dust control: dust and metals in dust needs to be measured in the workplace air (static or individual) according to national regulations.

- Workplaces: dust, metal concentrations?

Annex to the Safety Data Sheet

Slimes and Sludges, zinc sulfate electrolytic (273-742-8)

- Workers: biomonitoring – blood for Pb, twice a year if appropriate or according to regulation
 - Environment air: stack point source measurement (dust, metal concentrations)
 - Environment water: typically measured prior to discharge, if emissions to surface waters are relevant
- Some non-process waters can be generated containing Mn/Pb (e.g. from cleaning)

⇒ Description of the procedural and control technologies to minimise emission and resulting exposure

- The Pb Mn cellmud residue is kept moist, so dust formation/emission is by definition limited
- In the use phase, where it is dried, air emissions are controlled by use of air emission abatement devices e.g. filters, wet scrubbers. This may create a general negative pressure at the system openings (loading, sampling, production exit).
- regular sampling, cleaning, maintenance
- On-site waste water treatment techniques are applied to prevent releases to water (if applicable) e.g.: chemical precipitation, sedimentation and filtration.
- Local exhaust ventilation systems
- Special care for the general establishment and maintenance of a clean working environment by e.g.:
 - Cleaning of process equipment and workshop
 - Contained storage of leach residue in covered areas
- All residues formed during the leaching process (and gas-cleaning system at use site), are recovered and either recycled in the system or handled further according to waste legislation
- Wearing of gloves and protective clothing is compulsory
- With normal handling of the moist residue, no respiratory personal protection (breathing apparatus) is necessary.
- Eyes: safety glasses are recommended or compulsory

⇒ Specification of management means and training that particularly contribute to the functioning of the technical means described above

- integrated management system is implemented on the workplace e.g. ISO 9000, ISO ICS13100 series, ISO 1400X series, EMAS, or alike and, as usually applicable, by being IPPC-compliant (cf. NFM-BREF)
- housekeeping and hygiene procedures in place
- training provided for internal and external cleaning teams or technicians
- Follow up HS by medical unit: biomonitoring if required (e.g.. Pb, ...)

4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate

- Means of containment and minimisation technologies are same as above
- Blending, and optionally pelletizing, and furnaces are operated under strong aspiration (negative pressure towards atmospheric pressure)
- The zinc leach residue is unloaded from [pneumatic] transport trucks, train, ADR-big-bags or containers, ...and transferred to storage zones or silo's through especially designed transfer units
- Material composition, handling, storage procedures and general guidance on safe use are communicated to the personnel or downstream (external) user by means of Safety Data Sheet

5. Special procedures applied before cleaning and maintenance

- Procedures are in place to ensure safe cleaning and maintenance operations
 - Stopping (part of) the process
 - Cooling down and proper ventilation of equipment
 - Switch off power supply & lock out procedure
 - Special PPE mandatory for cleaning personnel or maintenance technicians
 - Planning and training for internal and external personnel
- general guidance on safe use is communicated to the personnel or downstream (external) user by means of Safety Data Sheet

6. Describe activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities

Accident release measures:

- **Workers:** Immediately contact emergency personnel. Keep unnecessary personnel away.
- Use suitable protective equipment.
- **Environment:** Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers.
- **Cleaning:** If emergency personnel are unavailable, vacuum or carefully scoop up spilled material and place in an appropriate container for disposal by incineration. Avoid creating dusty conditions and prevent wind dispersal.

Fire: Use an extinguishing agent suitable for the surrounding fire. No specific hazard. Fire water contaminated with this material must be contained and prevented from being discharged to any waterway, sewer or drain. Thermal decomposition products are sulfur oxides (SO₂, SO₃ etc.) and some metallic oxides. Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Periodic maintenance: (Furnace and associated equipment if applicable, Off-gas treatment system, Repair operations, Observational tasks and control activities), the following measures are taken:

- General protective and hygiene measures: Eating, drinking and smoking should be prohibited in areas where this material is handled, stored and processed. Workers should wash hands and face before eating, drinking and smoking. Separate storing of protective / work clothing is necessary. Avoid contact of spilled material and runoff with soil and surface waterways. Use process enclosures, local exhaust ventilation or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fumes or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.
- Respiratory protection: Use a properly fitted, particulate filter respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
- Hand protection: Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Eye protection : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists, gases or dusts.
- Body protection: Usual chemical work clothing.
- Cleaning activity : (Process equipment, workshop): same applies

7. Waste information

- The intermediate is a product for the production of zinc as a metal. If the normal processing route cannot be adhered to, returning it to the producer is recommended. Disposal should be in accordance with the official regulations (hazardous waste)
- PPE equipment is collected and disposed of
- Packaging?

Annex to the Safety Data Sheet

Slimes and Sludges, zinc sulfate electrolytic (273-742-8)

Slimes and Sludges, zinc sulfate electrolytic (273-742-8) process scheme

Lifecycle of slimes and sludges is illustrated by the colored forms

