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# SAFETY DATA SHEET MINERAL FERTILIZERS WITH COPPER AND MANGANESE

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

# 1.1. Product identifier

Product name:

POLISH NAME	ENGLISH NAME
LUBOFOSKA 3,5-14-16 Z MIEDZIĄ I MANGANEM	LUBOFOSKA 3,5-14-16 WITH COPPER AND MANGANESE
LUBOFOSKA POD ZBOŻE	LUBOFOSKA FOR CROPS

Mineral fertilizer is a mixture containing inorganic substances such as ammonium sulphate, ammonium phosphate, potassium chloride, magnesite, superphosphate, copper and manganese sulphate

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

Sector: Agriculture

<u>Identified use:</u> fertilizer formulation - preparation of fertilizer mixtures, professional use of fertilizers, consumer use of fertilizers

Use advised against: None

# 1.3. Details of the supplier of the safety data sheet

LUVENA S.A.

ul. Romana Maya 1

62-030 Luboń

+48 509 809 109

e-mail of the person responsible for preparation of this safety sheet danuta.rybarczyk@luvena.pl

# 1.4. Emergency telephone number

Emergency telephone number: 112

POLAND Chemical Substances Office +48 42 2538 400/401 Open on working days from 08:00 to 16:00

#### **SECTION 2: Hazards identification**

# 2.1. Classification of the substance or mixture

Eye Dam. 1 Serious eye damage, cat.1

H318 Causes serious eye damage

Aquatic Chronic 3 Hazardous to the aquatic environment — Chronic Hazard cat.3

H412 Harmful to aquatic life with long lasting effects

# 2.2. Label elements

# Pictogram:



Signal Word: DANGER

Identifier: contains superphosphate

**Hazard Statement** 

H318 Causes serious eye damage

H412 Harmful to aquatic life with long lasting effects

# **Precautionary Statement:**

P280 Wear protective gloves/ protective clothing/ eye protection/ face protection

P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do.

Continue rinsing.

P 310 Immediately call a POISON CENTER or doctor/a physician

P 501 Dispose of contents to the container intended for recycling or waste treatment in line with the applicable regulations

# 2.3. Other risks

Mixtures of inorganic compounds, therefore it is not assessed as PBT and vPvB.

The ingredients are not endocrine disrupting substances.

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# **SECTION 3: Composition / information on components**

### 3.1. Substances

Not applicable - mixture safety data sheet

### 3.2. Mixtures

The mixture contains the following dangerous components:

### Superphosphate

Concentration: <50 %

Type of substance: multi constituent substance

Identification numbers:

CAS No	EC No.	Index No.
8011-76-5	232-379-5	-

IUPAC name: Superphosphate Chemical formula: not determined Registration No.: 01-2119488967-11-xxxx

Classification according to the Regulation CE No. 1272/2008 (CLP) refers to 100% of the substance:

Eye Dam. 1 Serious eye damage, cat. 1 H318 Causes serious eye damage

ATE oral> 2000 mg/kg ATE skin > 5000 mg/kg ATE inhalation > 5 mg/l Manganese sulphate

Manganese sulphate
Concentration: < 0.7%
Identification numbers:

CAS No	EC No.	Index No.
7785-87-7	232-089-9	025-003-00-4

Registration No.: 05-2117368475-33-xxxx

Classification according to the Regulation CE No. 1272/2008 (CLP) refers to 100% of the substance:

STOT RE 2 Specific target organ toxicity — Repeated exposure, cat. 2

H 373 May cause damage to organs through through prolonged or repeated exposure through respiratory tract and after swallowing

Aquatic Chronic 2 Hazardous to the aquatic environment — Chronic Hazard cat. 2

H411 Toxic to aquatic life with long lasting effects.

Risk factor M: 1

# Copper sulphate

Concentration: < 0.5% Identification numbers:

CAS No	EC No.	Index No.
7758-99-8	616-477-9	029-004-00-0

Chemical name: hydrated copper(II) sulphate Registration No.: 01-2119520566-40-xxxx

Classification according to the Regulation CE No. 1272/2008 (CLP) refers to 100% of the substance:

Acute Tox. 4 Acute toxicity (oral) cat. 4

H302 Harmful if swallowed Eye Irrit. 2 Eye irritation cat. 2 H 319 Causes serious eye irritation. Skin Irrit. 2 Skin irritation cat. 2 H 315 Causes skin irritation.

Aquatic Acute 1 Hazardous to the aquatic environment — Acute Hazard cat. 1

H400 Very toxic to aquatic life

Risk factor M: 10

Aquatic Chronic 1 Hazardous to the aquatic environment — Chronic Hazard cat. 1

H410 Very toxic to aquatic life with long lasting effects

Risk factor M: 1

ATE in accordance with annex VI part 3 of Regulation EC No. 1272/2008: oral = 481 mg/kg

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### **SECTION 4: First aid measures**

#### **Description of first aid measures** 4.1.

### 4.1.1. Inhalation.

If undesirable symptoms occur (e.g. dizziness, sleepiness and irritation of respiratory system) take the injured person out of the contaminated environment to fresh air. If the person does not breathe, apply artificial respiration and in case of breathing difficulties, supply oxygen and consult a physician. Immediately consult a physician in case of intensive inhalation of the dust.

4.1.2. Skin contact Wash the contaminated skin with copious amount of water with soap for at least 15 minutes, removing thoroughly the contaminated clothes and shoes. Consult a physician in case the irritation lasts.

#### 4.1.3. Eye contact

Immediately rinse eyes with copious amount of running water for at least 15 minutes, lifting the upper and lower eyelid from time to time. Remove contact lenses, if any, and are easy to remove. Continue rinsing. Immediately consult POISONING TREATMENT CENTER or a physician

#### 4.1.4 Digestion

If the injured person feels unwell, consult a physician. Wash the mouth out with copious amount of water and give plenty of water to drink. Do not induce vomiting. Do not administer anything orally, if the injured person is unconscious. If the symptoms do not abate, provide medical assistance.

# Most important symptoms and effects, both acute and delayed

Acute effect: irritating to the eyes

Long term effects: not known

#### Indications of any immediate medical attention and special treatment needed 4.3.

Inhalation of gases produced during fire and thermal decomposition, containing phosphorus and sulphur oxides, may have irritating and caustic effect on respiratory system. Effect on lungs may be delayed.

# **SECTION 5: Fire-fighting measures**

# **Extinguishing media**

Fire in the environment should be extinguished with the use of extinguishing measures as appropriate for the burning materials.

#### Special hazards arising from the substance or mixture

During fire there may be produced hazardous gases or vapours: phosphorus and sulphur oxides

#### 5.3. Advice for firefighters

fire clothing. No special measures necessary. In case of wear personal breathing apparatus protective Avoid inhalation of vapours, stand on the leeward side. Ensure maximum ventilation - open windows and doors.

# **SECTION 6: Accidental release measures**

#### Personal precautions, protective equipment and emergency procedures 6.1.

Avoid dust formation conditions and prevent wind dispersal. Provide adequate ventilation. Avoid contact with eyes, skin and clothing. Wear appropriate personal protective equipment - protective clothing, protective gloves, eye protection.

For emergency responders:

Wear appropriate personal protective equipment - protective clothing, protective gloves, eye protection.

# **Environmental precautions**

Avoid contamination of water, water intakes or sewers. In case of accidental pollution, notify appropriate authorities.

#### 6.3. Methods and materials for containment and cleaning up

Collect the spilled material and place it with appropriate containers marked with the labels: for recycling or neutralisation. Wash off with copious amounts of water. Avoid dust clouds and spreading by the wind.

# Reference to other sections

Personal protective measures - see section 8

Handling of waste - see section 13.

# **SECTION 7: Handling and storage**

#### 7.1. Precautions for safe handling

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Avoid contact with eyes, skin and clothes. Avoid excessive generation of dust. Protect from moisture. Avoid contamination with flammable materials (e.g. diesel fuel, grease, etc.) and/or other incompatible materials - see 10.5. Carefully clean all equipment prior to maintenance and repair.

Do not eat, drink or smoke during handling the mixture. Wash yourself thoroughly after work.

### 7.2. Conditions for safe storage, including any incompatilities

This fertilizer should be stored in unit packages or in bulk, provided it is secured against direct exposure to atmospheric conditions. Fertilizer in bulk may be stored in heaps formed on hardened, impermeable ground, after prior covering with water tight material or in roofed, permeable to air facilities.

Store the product away from alkalies, ammonium nitrate.

#### 7.3. Specific end use(s)

Recommendations on constituent substances relating to identified uses have been identified in the following exposure scenarios annexed to this safety data sheet:

Exposure scenario	Use
ES3 Superphosphate	Use at industrial site
ES4 Superphosphate	Consumer use of Superphosphates as granular fertilizer
ES5 Superphosphate	Use by professional worker - Professional use of Superphosphates as granular fertilizer

# **SECTION 8: Exposure control / personal protection**

The operational conditions and risk management measures as well as the risk assessment related to the component have been determined in the exposure scenarios.

# 8.1. Control parameters

Total dust TLV 10 mg/m<sup>3</sup>

# **Copper sulphate**

Oxides dusts and soluble salts converted into Cu

TLV: 0.1 mg/m<sup>3</sup>
TLV-STEL: 0.3 mg/m<sup>3</sup>

Manganese sulphate

Manganese and its inorganic compounds converted into Mn

TLV:  $0.3 \text{ mg/m}^3$ 

Methods of exposure assessment:

PN-Z-04008-7:2002 PN-Z-04008-7:2002/AZ1:2004 Sampling: dust and chemical air pollution. Dosimetric and stationary method PN-91/Z-04030.05 Concentration of total dust Range: (0.15 - 25.0) mg/m³ Filtration and weighing method

PN-91/Z-04030.06 Concentration of respirable dust Range: (0.15 - 16.6) mg/m<sup>3</sup> Filtration and weighing method

PN-75/Z-04101 Air purity protection. Determination of manganese and its compounds at work stations with the use of colorimetric method

PN-79/Z-04125/02 Air purity protection. Manganese and its compounds contents tests. Determination of manganese and its compounds with the use of atomic absorption spectrometry

PN-77/Z-04106/01 Air purity protection. Determination of copper and its compounds at work stations with the use of colorimetric method with sodium diethyldithiocarbamate

PN-79/Z-04106/02 Air purity protection. Copper and its compounds contents test. Determination of copper and its compounds with the use of atomic absorption spectrometry

# Acceptable exposure limits:

Biological limit values (DSB):none

Derived No-Effect Levels DNEL for SSP

Routes of exposure	Derived No-Effect Levels DNEL	
	Worker	General population
INHALATION	2.9 mg/m <sup>3</sup>	-
Systemic Effects Long-term		
DERMAL	4.2 mg/kg/b./day	2.08 mg/kg body weight/day
Systemic Effects Long-term		

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# Derived No-Effect Levels DNEL for Manganese sulphate:

Routes of exposure	Derived No-Effect Levels DNEL	
	Worker	General population
DERMAL	0,00414 mg/kg body weight/day	0,0021 mg/kg body weight/day
Systemic Effects Long-term		
INHALATION	0,2 mg/m <sup>3</sup>	0,043 mg/m <sup>3</sup>
Systemic Effects Long-term		

### Derived No-Effect Levels DNEL for Copper sulphate:

Routes of exposure	Derived No	Derived No-Effect Levels DNEL	
	Worker	General population	
ORAL	-	41 μg/kg /kg body weight/day	
Systemic Effects Long-term			
ORAL	-	82 μg/kg /kg body weight/day	
Acute Effects			
DERMAL	137 mg/kg masy ciała/dzień	-	
Systemic Effects Long-term			
INHALATION	1 mg/m <sup>3</sup>	-	
Systemic Effects Long-term			
INHALATION	1 mg/m <sup>3</sup>	-	
Local Effects Long-term	_		

# PNEC (Predicted No Effect Concentration)

Data for for Manganese sulphate::

Element (environment)	PNEC	
Fresh water	0,0128 mg/l	
Marine water	0,0004 mg/l	
Water intermittent release	0,03 mg/l	
Sediment (freshwater)	0,0114 mg/kg sediment	
Sediment (marinewater)	0,00114 mg/kg sediment	
Soil	25,1 mg/kg soil dw	
Waste water treatment plant	56 mg/l	

# Data for for Copper sulphate:

Data for for copper sulphate	
Element (environment)	PNEC
Fresh water	7,8 μg/l
Marine water	5,2 μg/l
Soil	65 mg/kg soil dw
Sediment (freshwater)	87 mg/kg sediment
Sediment (marinewater)	676 mg/kg sediment
Waste water treatment plant	230 μg/l

# 8.2. Exposure control

# 8.2.1 Appropriate engineering controls

Avoid high dust. Use adequate ventilation as needed. In addition, as part of good industrial practice, eye rinses and a safety shower may be used during storage and use of the mixture.

Hygiene: wash hands, forearms and face thoroughly after working with the substance and before eating, smoking and using the toilet

# 8.2.2 <u>Individual protection measures, such as personal protective equipment</u>

Respiratory protection: In case of insufficient ventilation and excessive dust, use respiratory protection (dust mask or respirator with appropriate filters, e.g. EN 143, 149, Filter P2, P3). Wear protective gloves (e.g. plastic, rubber, leather) in case of prolonged contact with the product.

Eye or face protection: In case of excessive dusting and exposure above the permissible level, the wearing of safety glasses or a face shield is required. In other cases, it is recommended to wear safety glasses.

Skin protection: Use workwear.

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# Protection against thermal hazards: not required

# 8.2.3 <u>Environmental exposure controls</u>

Dispose the water used for rinsing according to the local and national regulations.

### **SECTION 9: Physical and chemical proprieties**

# 9.1. Information on basic physical and chemical proprieties

Physical state	Solid body in the form of pellets
Colour	Grey-brown
Odour	No odour
Melting / freezing point	No data
Boiling point or initial boiling point and	No data
boiling range	
Flammability	Non-flammable mixture (on the basis of the composition and components)
Lower and upper explosion limit	Do not apply to solids
Flash point	Do not apply to solids
Auto-ignition temperature	Do not apply to solids
Decomposition temperature	Do not apply
pH	3,5-5,0 (10% solution)
Kinematic viscosity	Do not apply
Solubility	partially soluble in water, may create water slurries
Partition coefficient n-octanol/water	Not applicable, mixture of inorganic compounds
(log value)	
Vapour pressure	No data
Density and/or relative density	900-1100 kg/m <sup>3</sup>
Relative vapour density	Do not apply to solids
Particle characteristics	product in the form of granules

# 9.2. Other information

# 9.2.1 Information with regard to physical hazard classes :

The product is not considered to be explosive, has no oxidizing properties and does not contain organic peroxides. It is not self-reactive or self-heating, and is not self-igniting. The product is not classified as corrosive to metals. The product is not flammable. Risks related to the physico-chemical properties of the product are not expected

9.2.2 Other safety characteristics:none

# **SECTION 10: Stability and reactivity**

# 10.1. Reactivity

Product stable under recommended storage and handling conditions (see Section 7).

# 10.2. Chemical stability

Product stable under recommended storage and handling conditions (see Section 7).

# 10.3. Possible dangerous reactions

Dangerous reactions may occur during heating - decomposition products, see item 10.6

#### 10.4. Conditions to avoid

Heating, contact with alkalies

# 10.5. Incompatible materials

Alkalies, ammonium nitrate

#### 10.6. Hazardous decomposition products

Under normal storage and handling conditions no hazardous decomposition products should be produced. Production of poisonous gasses is possible during heating or in case of fire: e.g. phosphorous oxides (e.g.  $P_2O_5$ ), sulphur oxides (SOx), chloride, fluoride, hydrogen chloride

# **SECTION 11: Toxicological information**

# 11.1. Information on hazard classes as defined in Regulation (EC) No 1272/2008

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The mixture was not tested. Due to the ingredients contained, the preparation is dangerous for human health.

#### Acute toxicity:

ATE mix oral> 2000 mg/kg ATE mix skin > 2000 mg/kg ATE mix inhalation > 5 mg/l

Skin corrosion/irritation: based on available data, the classification criteria are not met

Serious eye damage/irritation: causes serious eye damage

Respiratory or skin sensitisation: based on available data, the classification criteria are not met

germ cell mutagenicity: based on available data, the classification criteria are not met carcinogenicity: based on available data, the classification criteria are not met reproductive toxicity: based on available data, the classification criteria are not met STOT-single exposure: based on available data, the classification criteria are not met STOT-repeated exposure: based on available data, the classification criteria are not met

Aspiration hazard: based on available data, the classification criteria are not met

### Toxicological data of the ingredients

Data for superphosphate:

Acute toxicity:

LD50 (orally) > 2000 mg/kg (OECD 425 test material: diammonium phosphate)
LD50 (skin) > 5000 mg/kg (OECD 402 test material : diammonium phosphate)

LC50 (inhalation) > 5 mg/l (OECD 403 test material: diammonium phosphate)

#### Data for Manganese sulfate

LD50 (oral, rat) 2150 mg/kg

LC50 (inhalation, rat) >4.45 mg/l/4h

Data for Copper sulfate
LDL50 (oral rat): 300 mg/kg
LDL50 (rat): 43 mg/kg
LDL50 (rat): 630 mg/kg
LD50 ( mouse): 18 mg/kg

Information on likely routes of exposure

Inhalation: probable similar exposure to dust

Skin: likely exposure Ingestion: no exposure

Symptoms related to the physical, chemical and toxicological characteristics

No detailed data.

### Delayed and immediate effects as well as chronic effects from short and long-term exposure

Health effects of short-term exposure: May cause eye irritation if it gets into the eye. There are no known symptoms of inhalation poisoning. Not harmful if swallowed. Health effects long-term exposure: Long-term contact with the preparation may cause slight skin irritation.

Interactive effects not known

Absence of specific data- substances: not known

# 11.2. Information on other hazard

11.2.1. Endocrine disrupting properties: no properties

11.2.2. Other information- no known

# **SECTION 12: Ecological information**

#### 12.1. Toxicity

# Acute toxicity indicator

Data for superphosphate

LC50 for freshwater fish: >100 mg/L

EC50/LC50 for freshwater invertebrates: 1790 mg/L

EC50/LC50 for freshwater algae: >100 mg/L EC10/LC10 or NOEC for freshwater algae: 100 mg/L

Data for copper sulfate:

LC50: 0.81 mg/l/96h (Cyprinus carpio)

LC50: 0.45 mg/l/96h (Pimephales promelas)

LC50: 0.0098 mg/l/96h (Daphnia magna)

EC10: 0.108 mg/l/72h (Pseudokirchneriella subcapitata

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# Data for manganese sulfate:

Acute (short-term) toxicity:

Fish: Salmo trutta, LC50 (96 h) = 49.9 mg Mn/l.

Aquatic invertebrates: Daphnia magna, LC50 (48 h) = 9.8 mg Mn/l. Algae/aquatic plants: Desmodesmus subspicatus, EC50 (72 h) = 61 mg/l.

Microorganisms: Activated sludge with domestic sewage, EC50 (3 h) > 1000 mg/L.

Chronic (long-term) toxicity:

Fish: Danio rerio, NOEC (30 d) = 2.78 mg Mn/l.

Aquatic invertebrates: Macrobrachium rosenbergii, NOEC (60 d) = 0.01 mg Mn/l.

#### 12.2. Persistence and degradability

Nitrogen undergoes natural nitrification or denitrification cycle, producing nitrogen or nitrogen oxides.

Phosphates are transformed into calcium, iron and aluminium phosphates, or combine with the organic matter of the soil. Potassium is absorbed by clay soils or exists in ionic form in soil solutions.

Product should not be released to sewage in large quantities, as it may cause eutrophication of closed water regions.

### 12.3. Bioaccumulation potential

Due to the properties of inorganic compounds - the potential is low

Data for Zinc Oxide: Partition coefficient n-octanol/water (Log Pow)1.53

### 12.4. Mobility in soil

Good solubility in water. Ammonium ion is absorbed by soil particles. Phosphates are transported in the soil for a short time and then are immobilized in the soil. Potassium ion is absorbed by clay soils. In soils light potassium may be washed out.

### 12.5. Results of PBT and vPvB assessment

Mixtures of inorganic compounds, therefore it is not assessed as PBT and vPvB.

# 12.6. Endocrine disrupting properties

The ingredients do not have endocrine-disrupting properties

# 12.7. Other adverse effects

none

# **SECTION 13: Disposal considerations**

# 13.1. Waste treatment methods

According to local and national regulations the waste is disposed by deposition or combustion. Prevent the substances from penetration to watercourses. Biodegradation control is possible under the process of waste water treatment.

Wastes and used packagings should be delivered to a company dealing with waste management.

Waste code number: 16 03 03 Inorganic wastes containing hazardous substances

Package waste code: 15 01 02 Plastic packages.

# **SECTION 14: Transport information**

May be transported with the use of any means of transportation provided that the product is protected against weather conditions and goods displacement.

# 14.1. UN number or ID numer

It is not classified as hazardous product according to ADR/RID regulations

#### 14.2. UN proper shipping name

It is not classified as hazardous product according to ADR/RID regulations

### 14.3. Transport hazards class(es)

It is not classified as hazardous product according to ADR/RID regulations

#### 14.4. Packaging group

It is not classified as hazardous product according to ADR/RID regulations

#### 14.5. Environmental hazards

Not labelled as dangerous for the environment

### 14.6. Special precautions for user

None

### 14.7. Maritime transport in bulk according to IMO instruments

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Not applicable

### **SECTION 15: Regulatory information**

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

#### **EC REACH Regulations**

Official Journal of the EU 2007 L 136, corrigendum to Official Journal of the EU 2006 L 396 + corrigenda (Official Journal of the EU L 36 of 5.2.2009)+ Official Journal of the European Union L 118 of 12.5.2010 as amended

Corrigendum to the Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

# **EC Regulations - CLP**

Official Journal of the European Union 2008 L 353 as amended

Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

# EC Regulations - export import

Official Journal of the EU 2012 L 201

Regulation (EC) No 649/2012 of the European Parliament and of the Council of 4 July 2012 concerning

the export and import of dangerous chemicals  $% \left\{ \left( 1\right) \right\} =\left\{ \left( 1\right)$ 

Other

Classification of dangerous goods according to ADR Agreement and RID Regulations

### 15.2. Chemical Safety Assessment

No chemical safety assessment has been carried out for the mixture.

# **SECTION 16: Other information**

MSDS prepared in the format of the card Commission Regulation (EU) 2020/878.

<u>Training:</u> Employees should be instructed within the scope of proper handling of the preparation. One should read the safety data sheet before use of the preparation.

Limitations of use: none

<u>Data sources</u>: Legal regulations listed under item 15.1, Chemical Safety Report for superphosphate, supplier's sheet, IUCLID database Change:

- updated of the safety data sheet format
- Section 1.4 update of emergency number
- update of data on hazardous ingredients (section 3, section 4, section 6, section 7, section 8, section 9, section 11, section 12)
- update of legal provisions

# Classification:

Mixture classification according to CLP was made with the use of classification criteria for each exposure class contained in parts 2–5 of the appendix I of the CLP Regulation and mixture classification criteria contained in parts 3-4 of the appendix I of the CLP Regulation (assessment method: Mixtures classification, in case there is data available for all components or only for some of the components) Classifications according to 67/548/EEC Directive was made according to calculation method

All data contained herein are consistent with the present knowledge and our experience. Safety data sheet is a description of products as regards safety requirements. It is not the intention of our data to ensure product's properties. Related documents:

Exposure scenario	Use
ES3 Superphosphate	Use at industrial site
ES4 Superphosphate	Consumer use of Superphosphates as granular fertilizer
ES5 Superphosphate	Use by professional worker - Professional use of Superphosphates as granular fertilizer