



6B – Background Material

Textbook 6B: Hazardous Materials

6.B.1 What are hazardous materials?

Worldwide more than 100,000 different chemicals are in use. Not many of these chemicals are classified as pure substances – most are sold as mixtures or finished products. Irrespective of the source of chemical substances and preparations used or produced or emitted by the company, it is clear that many substances are a potential health and/or environmental hazard.

The damaging impact of chemicals on the environment and human health is often a combined effect. Organic solvents, for instance, contribute to the formation of ozone near the ground level, but if handled carelessly they can also cause severe health damage. With some substances, the (human) health hazard is the major concern (e.g. cyanide), with other substances it is the environmental impact (for instance the ozone depleting effects of CFCs).

Although chemicals are a potential hazard for everyone throughout their life cycle, starting from production to their handling, transport and use, workers are more often exposed to hazardous chemicals due to their daily contact with these substances. Therefore the use and handling of hazardous chemicals has to be regulated.

A chemical or product used in a company is considered a hazardous substance if it poses a risk to worker safety. Products classified as “hazardous” bear a label on the packaging and/or container. Dangerous properties are identified by a danger symbol (e.g. exclamation mark), a signal word (e.g. “Danger”) and hazard statements (e.g. “May cause severe eye damage”). Many working materials combine several hazardous properties.

As a general rule, the exposure of workers to hazardous chemicals should be avoided or at least reduced to a minimum. The employer has the duty to take appropriate technical, organizational or personnel measures to minimize the risk for workers.

To identify possible risks and take appropriate measures it is crucial to have information on the hazardous properties and safe handling of chemicals. Therefore chemicals have to be classified according to their hazardous properties and labelled correspondingly. Additionally, further information, e.g. on safe handling, storage or disposal, is essential. Based on this information, a risk evaluation can be carried out to establish appropriate measures for the protection of workers.

Worker safety regulations typically prescribe the necessary measures according to the hazardous properties of the chemicals.



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The following safety measures can be taken to reduce the exposure of workers to hazardous materials:

Technical:

- Exhaust systems;
- Closed (encapsulated) systems;
- Surveillance of exposure limits.

Organizational:

- Special labelling of workplaces;
- Reduction of the number of workers exposed to chemicals;
- Segregation of working areas with hazardous chemicals;
- Safe storage.

Personal

- Personal protection equipment;
- Training of workers;
- Raising the awareness on the handling of dangerous chemicals.

Currently the legal situation with respect to the classification and labelling of hazardous substances and mixtures differs from country to country. Whereas some countries have very strict legal provisions with respect to the classification, labelling and handling of hazardous chemicals, other countries have no legal requirements at all. Moreover, the classification criteria related to the hazardous properties are very inhomogeneous with the consequence that in one country a chemical is classified as hazardous and in other countries it is classified as non-hazardous.

To harmonize communication on hazard information and facilitate global trade the United Nations decided together with the ILO, the International Labour Organization, the OECD and various other governments and stakeholders to develop a "Globally Harmonized System of Classification and Labelling of Chemicals (GHS)".

The GHS includes the following elements:

- (a) Harmonized criteria for classifying substances and mixtures according to their health, environmental and physical hazards; and
- (b) Harmonized hazard communication elements, including requirements for labelling and safety data sheets.

The GHS addresses classification of chemicals by types of hazard and proposes harmonized hazard communication elements, including labels and safety data sheets. The major objective of the GHS is to ensure that information on physical hazards and toxicity from chemicals is available in order to enhance the protection of human health and the environment during the handling, transport and use of these chemicals. Target audiences for the GHS are consumers, workers, transport workers and emergency responders.



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Additionally the GHS also provides a basis for the harmonization of rules and regulations on chemicals at national, regional and worldwide level, which is an important factor for trade facilitation. The UN aims at implementing this harmonized system as a worldwide standard. Currently many national governments are adopting their current legislation completely or partly to the GHS system. A list of the countries which have fully implemented GHS and the present status of implementation can be viewed on the following web page: http://www.unece.org/trans/danger/publi/ghs/implementation_e.html

6. B. 2 Hazardous properties and their identification

According to the GHS, the hazardous properties can be differentiated into the following hazard classes:

- Physical hazards:
 - o Explosives;
 - o Flammable gases;
 - o Flammable aerosols;
 - o Oxidizing gases;
 - o Gases under pressure;
 - o Flammable liquids;
 - o Flammable solids;
 - o Self-reactive substances and mixtures;
 - o Pyrophoric liquids;
 - o Pyrophoric solids;
 - o Self-heating substances and mixtures;
 - o Substances and mixtures which emit flammable gases in contact with water;
 - o Oxidizing liquids;
 - o Oxidizing solids;
 - o Organic peroxides;
 - o Corrosive to metals.
- Health hazards:
 - o Acute toxicity;
 - o Skin corrosion/irritation;
 - o Serious eye damage/eye irritation;
 - o Respiratory or skin sensitization;
 - o Germ cell mutagenicity;
 - o Carcinogenicity;



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- Reproductive toxicity;
- Specific target organ systemic toxicity-single exposure;
- Specific target organ systemic toxicity-repeated exposure;
- Aspiration hazard.
- Environmental hazards:
 - Aquatic toxicity (acute, chronic).

These hazard classes are in most cases further divided into hazardous categories (1 – 5) or divisions (e.g. explosives) depending on the severity of the hazard.

The classification criteria (e.g. the flash point for flammable liquids) which determine if a substance has to be classified as dangerous and the corresponding cut-off values/concentration limits for the classification of mixtures are laid down in the GHS. Based on the classification criteria the corresponding labelling has been defined.

The main hazard communication elements to describe the possible risks within the GHS are pictograms, signal words and hazard statements.

The following GHS symbols (pictograms) are allocated to the different hazard classes:

Exploding bomb	Flame	Flame over circle
		
Explosives Self-reactives Organic peroxides	Flammables Self-reactives Pyrophorics Self-heating Emission of flammable gases	Oxidizers Organic peroxides
Gas cylinder	Corrosion	Skull and crossbones
		
Gases under pressure	Corrosives	Acute toxicity (severe)



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Exclamation mark	Health hazard	Environment
		
Irritant Dermal sensitizer Acute toxicity (harmful)	Carcinogen Respiratory sensitizer Reproductive Target organ toxicity Mutagenicity	Environmental toxicity

Depending on the severity of the risk, different symbols can be used for a hazard class, e.g. "Skull and crossbones" and "Exclamation mark" for the hazard class "Acute toxicity".

The hazard statement can also specify possible risks (e.g. "Heating may cause an explosion").

In the following chapters, the physical, health and environmental hazards according to the GHS are described in more detail and examples including the classification criteria and the hazard communication elements are provided.

6.B.2 Flammable and explosive materials

Flammability and explosiveness of chemicals are severe safety hazards. Many fires in industry were caused by improper handling and storage of flammable working materials.

For a fire or an explosion to occur, the following three conditions must be fulfilled simultaneously:

- Presence of an ignitable (i.e. flammable) material;
- Sufficient concentration of oxygen (air) or another substance to accelerate the combustion or explosion ("fire promoter");
- Presence of an ignition source (heat, sparks, open flame, electrostatic charge).

While fire promoters do not burn themselves, they are capable of keeping a fire alive. Their function with regard to flammable materials is very much the same as that of oxygen. Fires involving fire promoters thus cannot be extinguished simply by cutting off the oxygen supply.



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Explosives

The hazard class “explosives” is subdivided into the following divisions:

- 1.1 Mass explosion hazard
- 1.2 Projection hazard
- 1.3 Fire hazard and minor blast and/or projection hazard
- 1.4 No significant hazard in case of ignition/initiation
- 1.5 Insensitive substances/mixtures with mass explosion hazard
- 1.6 Extremely insensitive substances/mixtures with no mass explosion hazard

The different identification elements for explosive materials specify the possible sources of danger.

The hazard communication of an explosive chemical of the division 1.2, for instance, should contain the following elements:

Classification according to GHS	Explosive material, Division 1.2
Symbol	
Signal word	Danger
Hazard statement	Explosive; severe projection hazard
Precautionary statements (examples)	Keep away from ignition sources such as heat/sparks/open flame. No smoking. DO NOT fight fire when fire reaches explosives.

Depending on their properties self-reactive materials or organic peroxides can also have an explosive potential (classification according to the GHS). Therefore these materials can be classified as explosives with the corresponding labelling.

Examples of hazard communication elements:

Classification according to GHS	Self-reactive substance (Type A)	Organic peroxides (Type A)
Symbol		
Signal word	Danger	Danger
Hazard statement	Heating may cause an explosion	Heating may cause an explosion



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Flammable gases:

Flammable gases are subdivided into extremely flammable gases (Category 1) and flammable gases (Category 2) depending on their physical properties. The gases are allocated to the different categories according to the following classification criteria:

Category 1: Extremely flammable gas:

Gases ignitable when in mixture of $\leq 13\%$ with air or having a flammable range with air of $\geq 12\%$ (regardless of the lower flammable limit); (at 20 °C, normal pressure).

Category 2: Flammable gases, other than those of Category 1 having a flammable range while mixed with air (at 20 °C, normal pressure).

Classification according to GHS	Flammable gas, Category 1	Flammable gas, Category 2
Symbol		No pictogram
Signal word	Danger	Warning
Hazard statement	Extremely flammable gas	Flammable gas

Flammable aerosols:

The following table includes the classification criteria and the corresponding hazard communication elements for flammable aerosols. The classification of flammable aerosols depends on their concentration of flammable components.

Classification according to GHS	Flammable aerosol, Category 1	Flammable aerosol, Category 2
Classification criteria according to GHS	Concentration of flammable components $> 85\%$ and heat of combustion ≥ 30 kJ/g	Concentration of flammable components $> 1\%$ and heat of combustion > 20 kJ/g
Symbol		
Signal word	Danger	Warning
Hazard statement	Extremely flammable gas aerosol	Flammable aerosol



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Flammable liquids

Liquids with a flash point of not more than 93°C are classified as flammable liquids within the GHS. They are allocated to the different categories according to their flash point or initial boiling point:

Classification according to GHS	Flammable liquid, Category 1	Flammable liquid, Category 2	Flammable liquid, Category 3	Flammable liquid, Category 4
Classification criteria according to GHS	Flash point < 23 °C and initial boiling point ≤ 35 °C	Flash point < 23 °C and initial boiling point > 35 °C	Flash point ≥ 23 °C and ≤ 60 °C	Flash point > 60 °C and ≤ 93 °C
Symbol				No symbol
Signal word	Danger	Danger	Warning	Warning
Hazard statement	Extremely flammable liquid and vapour	Highly flammable liquid and vapour	Flammable liquid and vapour	Combustible liquid

Flammable solids

Flammable solids are defined as solids which are readily combustible, or may cause or contribute to fire through friction. Readily combustible solids are powdered, granular or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly. The categorization is based on a burning rate test.

Classification according to GHS	Flammable solid, Category 1	Flammable solid, Category 2
Classification Criteria according to GHS	Burning rate test: Substances and mixtures other than metal powders: - wetted zone does not stop fire and - burning time < 45 seconds or burning rate > 2.2 mm/s Metal powders: - burning time ≤ 5 minutes.	Burning rate test: Substances and mixtures other than metal powders: - wetted zone stops the fire for at least 4 minutes and - burning time < 45 seconds or burning rate > 2.2 mm/s Metal powders: - burning time > 5 minutes and ≤ 10 minutes.



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Symbol		
Signal word	Danger	Warning
Hazard statement	Flammable solid	Flammable solid

Oxidizing gases, liquids and solids

According to the GHS, an oxidizing gas is a gas which may, generally by providing oxygen, cause or contribute to the combustion of other materials more than air does. For this hazard class only one category exists.

Oxidizing liquids or solids are defined as chemicals which, while in themselves necessarily combustible, may, generally by yielding oxygen, cause or contribute to the combustion of other materials. For this hazard class three categories (1-3) exist.

Classification according to GHS	Oxidizing gas Category 1	Oxidizing liquid Category 1
Classification criteria according to GHS	Gas contributes to the combustion of other material more than air does.	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of substance and cellulose is less than that of a 1:1 mixture, by mass, of 50% of perchloric acid and cellulose.
Symbol		
Signal word	Danger	Danger
Hazard statement	May cause or intensify fire; oxidizer	May cause fire or explosion; strong oxidizer



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6.B.2 Gases under pressure

Within the GHS, gases under pressure are defined as gases contained in a receptacle at a pressure of ≥ 280 kPa at 20°C or as a refrigerated liquid.

Depending on their physical state when packaged they are classified according to the following hazard categories as:

Compressed gas	A gas entirely gaseous at -50 °C; (includes all gases with a critical temperature of ≤ -50 °C).
Liquefied gas	Partially liquid at temperatures of > -50 °C: (a) High pressure liquefied gas: critical temperature between -50 °C and $+65$ °C; and (b) Low pressure liquefied gas: a gas with a critical temperature of $> +65$ °C.
Refrigerated liquefied gas	Partially liquid because of its low temperature.
Dissolved gas	Dissolved in a liquid phase solvent.

Examples for hazard communication elements:

Classification according to GHS	Compressed gas	Refrigerated liquefied gas
Symbol		
Signal word	Warning	Warning
Hazard statement	Contains gas under pressure; may explode if heated	Contains refrigerated gas; may cause cryogenic burns or injury

Self-reactive substances and mixtures

Self-reactive substances and mixtures are thermally unstable liquid or solid substances or mixtures liable to undergo a strongly exothermic decomposition even without participation of oxygen (air).

Pyrophoric liquids/solids

Pyrophoric liquids/solids are liquids/solids which, even in small quantities, are liable to ignite within five minutes after coming into contact with air.



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Examples for hazard communication elements according to their classification:

Classification according to GHS	Pyrophoric liquid, Category 1	Pyrophoric solid, Category 1
Classification criteria according to GHS	The liquid ignites within 5 minutes when added to an inert carrier and exposed to air, or it ignites or chars a filter paper within 5 minutes of coming into contact with air.	The solid ignites within 5 minutes of coming into contact with air.
Symbol		
Signal word	Danger	Danger
Hazard statement	Catches fire spontaneously if exposed to air	Catches fire spontaneously if exposed to air

Self-heating substance or mixture

According to the GHS classification, self-heating substances or mixtures are solid or liquid substances or mixtures other than pyrophoric chemicals which, by reaction with air and without energy supply, are liable to self-heat.

Examples for hazard communication elements according to their classification:

Classification according to GHS	Self-heating substance or mixture, Category 1
Classification criteria according to GHS	A positive result has been obtained in a test using a 25 mm sample cube at 140 °C.
Symbol	
Signal word	Danger
Hazard statement	Self-heating; may catch fire



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Substances and mixtures which emit flammable gases in contact with water

The substances or mixtures which, in contact with water, emit flammable gases are defined within the GHS as solid or liquid substances or mixtures which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

Examples for hazard communication elements according to their classification:

Classification according to GHS	Substances and mixtures which in contact with water, emit flammable gases, Category 1
Classification criteria according to GHS	Any substance which reacts vigorously with water at ambient temperatures and generally demonstrates a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance in any one minute.
Symbol	
Signal word	Danger
Hazard statement	In contact with water releases flammable gases which may ignite spontaneously

Corrosive to metals

This hazard class includes substances or mixtures which by chemical action can materially damage or even destroy metals.

Classification according to GHS	Corrosive to metals, Category 1
Classification criteria according to GHS	Corrosion rate on steel or aluminium surfaces exceeding 6.25 mm per year at a test temperature of 55 °C.
Symbol	
Signal word	Warning
Hazard statement	May be corrosive to metals



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6.B.2.2 Substances with a damaging effect on human health

Working materials with a potentially damaging effect on human health have to be clearly labelled according to the classification criteria laid down in the GHS.

The GHS prescribes the following four pictograms for chemicals with a potential risk to human health:



These symbols together with the hazard statement and the signal word describe the possible health effects.

Generally the "Exclamation mark" is used for chemicals with less severe risks to human health whereas the "Skull and crossbones" and the "Exploding man" indicate higher risks.

Skull and crossbones

This symbol is only used for chemicals classified as acutely toxic either due to oral, dermal or inhalative exposure. The hazard statement further specifies the risk. The allocation to the 5 different categories is based on the LD₅₀¹ (lethal dose) or LC₅₀² (lethal concentration).

Example:

Classification according to GHS	Acute toxicity; Category 1
Classification criteria according to GHS	LD ₅₀ ≤ 5 mg/kg bodyweight (oral) LD ₅₀ ≤ 50 mg/kg bodyweight (skin/dermal) LC ₅₀ ≤ 100 ppm (gas) LC ₅₀ ≤ 0.5 (mg/l) (vapour) LC ₅₀ ≤ 0.05 (mg/l) (dust, mist)
Symbol	

¹ LD₅₀ (Lethal Dose₅₀): is the amount of a substance that, when administered by a defined route of entry (e.g. oral or dermal) over a specified period of time, is expected to cause the death of 50% of a defined animal population.

² LC₅₀ (Lethal Concentration₅₀) is the amount of a substance in air that, when administered by inhalation over a specified period of time, is expected to cause the death in 50% of a defined animal population.



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Signal word	Danger
Hazard statement	Fatal if swallowed (oral) Fatal in contact with skin (dermal) Fatal if inhaled (gas, vapour, dust, mist)

Exploding man

This symbol is used for chemicals which have the potential to cause severe damage to human health:

- Respiratory sensitizer (Category 1)
- CMR (carcinogenic, mutagenic and reprotoxic) chemicals (Category 1A, 1B, 2)
- Specific target organ systemic toxic chemicals (STOST), (Categories 1 and 2)
- Aspiration hazards (Categories 1 and 2)

Examples:

Classification according to GHS	Carcinogenicity, Category 1A and 1B	Toxic to reproduction, Category 2
Classification criteria according to GHS	Known or presumed human carcinogen including mixtures containing $\geq 0.1\%$ of such a substance.	Suspected human reproductive toxicants (see criteria in section 3.7.2 of Chapter 3.7 of the GHS) or mixtures containing $\geq 0.1\%$ or $\geq 3.0\%$ of such a substance (see section 3.7.3 and Notes 3 and 4 of Table 3.7.1, Chapter 3.7 of the GHS).
Symbol		
Signal word	Danger	Warning



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Hazard statement	May cause cancer (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard).	Suspected of damaging fertility or the unborn child (state specific effect if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
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Corrosive

Depending on the severity of the hazard the corrosive symbol or the exclamation mark is used for substances classified as "Skin corrosive/irritant" or causing serious eye damage or eye irritation. The same symbols as for substances corrosive to metals are used (see physical hazards).

Examples:

Classification according to GHS	Serious eye damage/eye irritation Category 1 (irreversible effects)	Skin corrosion/irritation Category 1A, 1B, 1C
Symbol		
Signal word	Danger	Danger
Hazard statement	Causes serious eye damage	Causes severe skin burns and eye damage



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Exclamation mark

The exclamation mark is used for chemicals with less severe impacts on human health.

Classification according to GHS	Acute toxicity Category 4	Specific target organ systemic toxicity following single exposure Category 3
Classification criteria according to GHS	LD ₅₀ between 300 and less than 2000 mg per kilogram of bodyweight (oral) LD ₅₀ between 1000 and less than 2000 mg per kilogram of bodyweight (skin/dermal) LC ₅₀ between 2500 and less than 5000 ppm (gas) LC ₅₀ between 10.0 and less than 20.0 (mg/l) (vapour) LC ₅₀ between 1.0 and less than 5.0 (mg/l) (dust, mist)	(a) Respiratory tract irritation Evidence on the substance or mixture of transient irritant Effects on respiratory tract in humans; or (b) Narcotic effects Evidence on the substance or mixture of transient narcotic Effects from animal studies and in humans.
Symbol		
Signal word	Warning	Warning
Hazard statement	Harmful if swallowed (oral) Harmful in contact with skin (dermal) Harmful if inhaled (gas, vapour, dust, mist)	Respiratory tract irritation: May cause respiratory irritation or Narcotic effects: May cause drowsiness or dizziness



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6.B.2.3 Environmentally harmful effect

In addition to the physical and health hazards environmental risks have to be taken into consideration for the classification of chemicals. Damage to the environment is caused by substances which, when released into the environment, contaminate environmental media such as water, air, soil or endanger the health of organisms such as man, animals, plants or micro-organisms. A separate danger symbol to indicate that a substance is "environmentally harmful" exists:



Depending on the expected risk of the substance or mixture the GHS differentiates between the following hazard classes:

- a) Acute hazards to the aquatic environment, with the following hazard statements:
 - o Very toxic to aquatic life;
 - o Toxic to aquatic life;
 - o Harmful to aquatic life.

- b) Chronic hazards to the aquatic environment:
 - o Very toxic to aquatic life with long lasting effects;
 - o Toxic to aquatic life with long lasting effects;
 - o Harmful to aquatic life with long lasting effects;
 - o May cause long lasting harmful effects to aquatic life.

The corresponding classification criteria are laid down in Part 4 "Environmental Hazards" of the GHS.

6.B.3 Health hazards caused by dangerous substances

Depending on the substance, quantity, quality, intake route, duration and person affected, the effect of a substance can be more or less hazardous or damaging to human health.

6.B.3.1 How are substances dangerous to human health absorbed by the body?

Generally, there are three possible routes of exposure:

- Inhalation;
- Ingestion (oral);
- Skin and eye contact (dermal).



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Inhalation – absorption through the respiratory tract

When exposed to an atmosphere of harmful gases, volatile liquids, aerosols (minute liquid droplets in the air, e.g. mist) and dust the body may absorb harmful substances through the respiratory tract and the lungs (inhalation). The harmful substances mix with the inhaled air, enter the blood stream through the lungs and can cause damage to the respiratory organs or other organs downstream of the breathing apparatus.

The risk is acute in the following cases:

- If gas escapes due to a failure to close connections or through a leak in a pipe or tubing;
- Handling of chemicals (e.g. decanting of solvents);
- If paints, varnishes and adhesives containing solvents are used in closed, badly ventilated work areas;
- During sand blasting;
- If paint is removed with a sander or by burning;
- If welding operations are performed without air removal equipment and breathing mask.

Depending on the duration of the exposure the effects to human health may differ. Possible measures to avoid exposure by inhalation are:

- Implementation of exhaust gas systems, ventilation;
- Use of closed (encapsulated) systems;
- Use of PPE (personal protection equipment), e.g. dust masks;
- Segregation of dusty areas.

Ingestion – absorption through the oesophagus (oral exposure)

The second way of absorbing hazardous materials, especially liquids and solids, is by swallowing. This may occur as a result of:

- Misuse or improper handling, for instance when a product is decanted or if an attempt is made to orally pipette acids, alkaline solutions or solvents;
- Storage of hazardous products in drink bottles or food boxes;
- Eating, drinking or smoking with contaminated, unwashed hands;
- Accumulation of hazardous substances in food (e.g. air saturated with solvents, dust).



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Possible measures to avoid oral exposure of chemicals are:

- Clear spatial separation of working and eating areas (adequate labelling of areas);
- Use of PPE, e.g. gloves;
- Clear labelling of contents.

Skin and eye contact – absorption through the skin (dermal exposure)

The possibility of absorbing hazardous substances through the skin is often underestimated. When it comes to injuries caused by skin contact, one tends to think of irritating or caustic substances acting locally at the point of contact with the skin, the mucous membranes or the eyes. Nevertheless, a number of gases, vapours, liquids and solids are also capable of entering the body through the unprotected skin – without any visible signs of absorption!

A dermal exposure may occur in the following situations:

- Contact with readily liposoluble solvents (both as a liquid and as vapour);
- Disinfection of rooms with products containing phenol and formaldehyde;
- Spraying of paint through spray guns;
- Dusty operations.

As many organic solvents are capable of degreasing the skin and affecting the kidneys, the liver and the nervous system, do not under any circumstances use technical solvents or fuels (e.g. diesel) to clean dirty skin.

Possible measures to avoid dermal exposure of chemicals are:

- Implementation of exhaust gas systems;
- Use of PPE (e.g. protective cloth, goggles).

6.B.3.2 What is the effect of harmful substances on the body?

Whether a substance remains in the body and has a detrimental effect on the health of the victim or whether it simply passes through the body before being excreted depends on the type, quantity, way of absorption and toxicity of the substance. A substance can be removed from the body *via* the respiratory tract (for instance by breathing out solvents or minute solid particles), the intestines or the bladder. Sometimes, the substances are broken down or transformed before excretion. In other cases, the toxic substance is the very product of the transformation in the body. The detrimental effect of working materials can take many forms:



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Acute intoxication: e.g. by swallowing methanol, by inhaling chlorine gas;

Chronic intoxication: e.g. ingress of lead compounds in the blood, damage to the central nervous system caused by solvents;

Local effect: e.g. acid or alkali burn, caused by strong agents (sulphuric acid);

Resorptive and systemic damage: e.g. paralysis of the respiratory muscles as a result of a major intake of solvents;

Allergy inducing effect: e.g. illnesses of the respiratory tract as a result of exposure to isocyanates in two-component paint and adhesives, nickel induced skin allergy;

Carcinogenic effect: e.g. benzene in combustion engine fuels, nickel dust, chromates;

Mutagenic effect (corruption of genes): e.g. benzene, cyanacrylates in adhesives;

Embryotoxic effect (teratogenity): e.g. methyl mercury;

Neurotoxic effect: e.g. heavy metals (mercury, lead), organic solvents.

The possible effects as well as the relevant route of exposure are described by the pictograms (e.g. "Acute toxicity") and the hazard statement (e.g. "Fatal if swallowed"). Therefore chemicals have to be labelled very carefully.

Although the labels provide a quick overview of the main hazardous properties and risks of a chemical, in many cases further detailed information is required, for example the necessity of carrying out a workplace risk assessment and of taking appropriate safety measures. The GHS therefore includes the safety data sheet as a further hazard communication element (see next chapter).



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6.B.4 Information sources for hazardous working materials

The most important channels of information about hazardous working materials in the company are:

- Product data sheets;
- List of MCW³ (maximum concentration at the workplace) or OEL (occupational exposure limit) values;
- Product labels;
- Safety data sheets.

This information should be available at all times in any company.

Product data sheet

The product data sheet mainly contains the technical specification of the product. Information on possible risks to human health or the environment are in most cases not covered.

List of MCW or OEL values

Many countries have regulated the occupational exposure of workers to hazardous chemicals by prescribing maximum concentrations of hazardous chemicals at the workplace which have to be monitored. These limit values may vary between countries due to different classification and evaluation systems. A list of the national limit values should be available at the national ministry responsible for the safety at workplaces.

According to the national evaluation system different types of limit values exist:

- Threshold Limit Value/Time Weighted Average (TLV-TWA)

The average concentration under which most people can work consistently for eight hours, day in, day out, with no harmful effects. Gas or vapours are expressed in parts per million (ppm), while solids, mist or floating dust particles are expressed in milligrams per cubic metre (mg/m³).

- Threshold Limit Value – Short Term Exposure Level (15 minutes) (TLV-STEL)

The TLV-STEL is defined as a fifteen minute TWA exposure which will not be exceeded at any time during the workday even if the 8 hour TWA is within the TLV-TWA.

³ The MCW values (maximum concentration at the workplace) are defined as the maximum admissible concentration of a working material – a gas, vapour or solid – which, based on the currently available knowledge, does not generally put the health of an employee at risk, even if he/she is exposed to the chemical repeatedly and for an extended period of time.



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A threshold limit value is defined as an exposure limit “to which it is believed nearly all workers can be exposed day after day for a working lifetime without ill effect” for CMR (carcinogenic, mutagenic, reprotoxic) substances. Therefore often no limit values exist, as in many cases a minimum level without adverse effects cannot be defined.

An overview of existing national lists for OEL values can be found on the following homepage:

http://osha.europa.eu/good_practice/risks/ds/oel



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6.B.4.1 Product identification using product labels

The product label is an important information source on possible hazardous properties of a chemical. According to the GHS the label has to comprise the following information:

- Product identifier;
- Chemical identity;
- Pictograms (symbols);
- Signal word;
- Hazard statements;
- Precautionary statements;
- Supplier identifier.

Product identifier

A product identifier should be used on a GHS label and it should correspond to the product identifier used on the SDS. A product identifier can be a specific code, number or name. If the substance or mixture is covered by the UN Model Regulations on the Transport of Dangerous Goods, the UN proper shipping name should also be indicated on the package;

Chemical identity

The label for a substance should include the chemical identity of the substance (if possible the CAS number or other reference numbers). For mixtures or alloys, the label should also include the chemical identities of those ingredients or alloying elements which contribute to the hazardous properties of the mixture.

Pictograms (symbols)

The GHS label should contain the hazards symbols corresponding to the classification of the chemical.

Signal words

A signal word is a word used to indicate the relative level of severity of hazard and alert the reader to a potential danger on the label. The signal words used in the GHS are "Danger" and "Warning". "Danger" is used for the more severe hazard categories (hazard categories 1 and 2), while "Warning" is used for the less severe categories. If the signal word "Danger" is used, the signal word "Warning" should not appear.

Hazard statements

A hazard statement is a phrase assigned to a hazard class and category which describes the nature, and if appropriate, the degree of the hazards a product presents. The tables of label elements in the individual chapters for



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each hazard class detail the hazard statements which have been assigned to each of the hazard categories of the GHS.

Precautionary statements

A precautionary statement is a phrase (and/or pictogram) describing recommended measures to be taken in order to minimize or prevent adverse effects in case of exposure to a hazardous product, or improper storage or handling of a hazardous product. The GHS label should include appropriate precautionary information, which can either be provided by the labeller or the competent authority.

Supplier identification

The label should include name, address and telephone number of the manufacturer or supplier of the substance or mixture.

Example for GHS labelling:

Epichlorohydrin XP	Epichlorohydrin (1-Chloro-2,3-epoxypropane) CAS No. 106-89-8 UN No. 2023
	
Danger	
Flammable liquid Toxic if swallowed Toxic if contact with skin Fatal if inhaled May cause an allergic skin reaction May cause genetic defects May cause cancer Causes severe skin burns and eye damage Causes serious eye irritation Toxic to aquatic life	
Precautions: Avoid exposure – obtain special instructions before use. In case of an accident or if you feel unwell, seek medical advice immediately.	
Suppliers: Company Ltd Street 23, Town, Country Tel: 234, Fax: 567	



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Transport labelling

For transport labelling two parallel systems exist: labelling according to the GHS and labelling according to the transport regulations. The classification criteria of the GHS are based on the UN "Recommendations on the Transport of Dangerous Goods".

Within the UN classification system for the transport of dangerous goods, products (including mixtures and solutions) and articles subject to these regulations are assigned to one of nine classes according to the hazard or the most predominant of the hazards they present. Some of these classes are subdivided into divisions. These classes are:

- Class 1: Explosives (Divisions 1.1 – 1.6)
- Class 2: Gases (Divisions 2.1 – 2.3)
- Class 3: Flammable liquids
- Class 4: Flammable solids; substances liable to spontaneous combustion; substances which, in contact with water, emit flammable gases (Divisions 4.1 – 4.3)
- Class 5: Oxidizing substances and organic peroxides (Divisions 5.1 – 5.2)
- Class 6: Toxic and infectious substances (Divisions 6.1 – 6.2)
- Class 7: Radioactive material
- Class 8: Corrosive substances
- Class 9: Miscellaneous dangerous substances and articles

For transport the following symbols are used:

			
Explosives			
Class 1 Division 1.1	Class 1 Division 4	Class 1 Division 5	Class 1 Division 6
			
Flammable gases		Non-flammable non-toxic gases	Toxic gases
Class 2, Division 2.1		Class 2, Division 2.2	Class 2, Division 2.3
			

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Flammable liquids		Flammable solids	Spontaneous combustion
Class 3		Class 4, Division 4.1	Class 4, Division 4.2
			
Emits flammable gases in contact with water		Oxidizing substances	Organic peroxides
Class 4, Division 4.3		Class 5, Division 5.1	Class 5, Division 5.2
			
Class 6, Division 6.1	Class 8		
Toxic substances	Corrosive substances		

Additional symbols are available for radioactive chemicals (Class 7) and infectious substances (Class 6, Div. 6.2).

More detailed information is available under:
http://www.unece.org/trans/danger/publi/unrec/12_e.html

In addition, there are other transport classification systems besides the UN classification system. Within Europe the ADR/RID applies. The ADR/RID is the European Convention on the Transportation of Hazardous Goods by Road (ADR) and Rail (RID). Introduced in 1957, the ADR/RID applies to national and cross-border transport of goods. The classification criteria and the labelling correspond more or less to the UN classification system.



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Transport labels are typically attached to the packaging material (outer packaging) whereas GHS labels are directly applied to the container of the hazardous chemical (inner packaging). The following pictures demonstrate how the labelling should be used.

Example: Combination packaging for a Category 1 specific target organ/systemic toxicant and Category 2 flammable liquid (source: GHS, Annex 7).

Outer Packaging: Box with a flammable liquid transport label*
Inner Packaging: Plastic bottle with GHS hazard warning label**

**PAINT (FLAMMALINE,
LEAD CHROMIUM)** Product Identifier
(see 1.4.10.5.2 (d))



** SIGNAL WORD (see 1.4.10.5.2 (a))



Hazard Statements (see 1.4.10.5.2 (b))

Precautionary Statements (see 1.4.10.5.2 (c))

Additional information as required by the competent authority as appropriate.

Supplier Identification (see 1.4.10.5.2 (e))

Notes: * Only the UN transport markings and labels are required for outer packagings.
** A flammable liquid pictogram as specified in the UN Recommendations on the Transport of Dangerous Goods, Model Regulations may be used in place of the GHS pictogram shown on the inner packaging label.



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6.B.4.2 Safety data sheets

The material safety data sheet (SDS) is the basic means of communication for hazardous material between producers/suppliers and users. The SDS contains important information on the hazardous properties of the material as well as on its handling, use and disposal. Additionally more detailed information on physical and toxicological properties are covered. The SDS should enable users of chemicals to take the necessary measures to ensure workplace safety, the protection of health at the workplace and the protection of the environment.

In many countries the supplier is under legal obligation to provide the SDS for hazardous substances or mixtures. Some manufacturers also include an SDS for non-hazardous materials. The advantage of the SDS is that all relevant information is available in a clearly structured way.

The GHS lays down minimum requirements for SDS (Annex 4 of the GHS). Currently more and more countries implement the GHS standard with respect to the SDS requirements and the format. The new European legislation on chemicals (REACH), for instance, has adopted the GHS standard format.

The SDS has to be prepared by a competent person and written in a clear and concise manner. The date of issuance and, in case of a revised SDS, the revision date and the version should be indicated. In addition, the total number of pages (e.g. page 3 of 4) should be stated on each page.

Safety data sheets have to be delivered free of charge, and the supplier of the goods must distribute them to all users in trade and industry together with the first delivery of the hazardous working material, and on each occasion thereafter if requested by the receiver. A supplier, manufacturer or importer must also provide an updated safety data sheet each time the composition of the product changes, or if new information which may affect the risk management measures or new information on hazards becomes available.

With each delivery, the company should order the updated safety data sheets and have them collected by the responsible department (e.g. purchasing department or safety officer).

To ensure the safest and most efficient handling of chemicals the supplier's willingness to cooperate by providing the necessary information on potential health and environmental hazards should be an important factor when it comes to choosing among several products of comparable technical merit.



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6.B.4.3 Which information must be included in the safety data sheet?

According to the GHS, the SDS has to cover the following 16 sections:

1. Identification
2. Hazard(s) identification
3. Composition/information on ingredients
4. First-aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure controls/personal protection
9. Physical and chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information
16. Other information.

1	Identification of the substance or mixture and of the supplier
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Information provided:

- GHS product identifier;
- Other means of identification;
- Recommended use of the chemical and restrictions on use;
- Supplier details (including name, address, phone number, etc.);
- Emergency phone number.

This section should enable the user of a hazardous product to identify the product and obtain basic information on the manufacturer/supplier of the product in case further information is necessary.



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2	Hazard(s) identification
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Information provided:

- GHS classification of the substance/mixture and any national or regional information.
- GHS label elements, including precautionary statements. (Hazard symbols may be provided as a graphical reproduction of the symbols in black and white or the name of the symbol, e.g. flame, skull and crossbones.)
- Other hazards which do not result in classification (e.g. dust explosion hazard) or are not covered by the GHS.

This section should provide a short and precise overview of the most important hazards the chemical presents to human health and the environment.

3	Composition/information on ingredients
---	--

Information provided:

Substance

- Chemical identity;
- Common name, synonyms, etc.;
- CAS number and other unique identifiers;
- Impurities and stabilizing additives which are themselves classified and which contribute to the classification of the substance.

Mixture

- The chemical identity and concentration or concentration ranges of all ingredients which are hazardous within the scope of the GHS and are present above their cut-off levels.

This section is especially relevant to mixtures. It should provide an overview of the main hazardous substances of a mixture and their concentration range. The indicated classification only refers to the specific substance and not to the whole product.

4	First-aid measures
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Information provided:

- Description of necessary measures, subdivided according to the different routes of exposure, i.e. inhalation, skin and eye contact and ingestion;
- Most important symptoms/effects, acute and delayed;
- Indication of immediate medical attention and special treatment needed, if necessary.



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In case workers are exposed to a hazardous chemical this section provides important information on first aid measures at the workplace (e.g. using an eye-flushing bottle). It also indicates whether a doctor should be consulted. Therefore in case of an accidental exposure to a hazardous chemical it is important to show the SDS to the medical personnel.

5	Fire-fighting measures
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Information provided:

- Suitable (and unsuitable) extinguishing media;
- Specific hazards arising from the chemical (e.g. nature of any hazardous combustion products);
- Special protective equipment and precautions for fire fighters.

Within this section suitable extinguishing agents and the risks associated with the substance in case of fire (e.g. hazardous combustion gases) are described.

6	Accidental release measures
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Information provided:

- Personal precautions, protective equipment and emergency procedures;
- Environmental precautions;
- Methods and materials for containment and cleaning up.

This section describes the measures which should be taken in case of an accidental release of the hazardous material.

7	Handling and storage
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Information provided:

- Precautions for safe handling;
- Conditions for safe storage, including any incompatibilities.

This section is important for the safe handling and storage of the hazardous chemicals and should be taken into account very carefully. It also describes technical measures (e.g. local removal) to avoid the exposure of workers to chemicals.

8	Exposure controls/personal protection
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Information provided:

- Control parameters, e.g. occupational exposure limit values or biological limit values;
- Appropriate engineering controls;
- Individual protection measures, such as personal protective equipment.



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Within this section occupational exposure limit values or biological limit values are indicated which should be monitored and reduced in order to avoid or diminish the exposure for workers. Generally the national values of the country where the product is used apply. If no national limit values exist, limit values from other countries might be indicated, if appropriate.

This section also lists appropriate engineering controls and specific personal protective equipment. The personal protective equipment should be clearly described.

9	Physical and chemical properties
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Information provided:

- Appearance (physical state, colour, etc.);
- Odour;
- Odour threshold;
- pH;
- Melting point/freezing point;
- Initial boiling point and boiling range;
- Flash point;
- Evaporation rate;
- Flammability (solid, gas);
- Upper/lower flammability or explosive limits;
- Vapour pressure;
- Vapour density;
- Relative density;
- Solubility(ies);
- Partition coefficient: n-octanol/water;
- Auto-ignition temperature;
- Decomposition temperature.

This section provides an overview of the main physical and chemical properties of the chemical.

A low boiling temperature (e.g. < 80 °C) or boiling range or a high vapour pressure means that the product can easily evaporate at low temperatures. If the product is flammable, this may result in explosive gas/air mixtures.

The solubility of a substance in water is important if the product is spilled, the container leaks or the product is stored. The pH value indicates whether the product is an acid or an alkaline solution and whether the substance is likely to cause corrosion or irritation. Products with a pH of < 2 (highly acid) and a pH of > 12 (highly alkaline) are usually classified as corroding liquids while weaker acid and alkaline solutions are classified as irritating liquids.

The flash point is the temperature above which a substance can be ignited or caused to explode. Generally, the flash point of a substance is at least 50 °C below the boiling point. A substance with a boiling point of 65 °C is likely to be highly flammable (flash point < 21 °C), while a substance with a boiling point of 90 °C is likely to be flammable (flash point < 55 °C). The ignition temperature indicates the temperature the ignition source (flame, spark, embers, etc.) must have before it is able to ignite the substance. With



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liquids, the ignition temperature is usually high and far above the flash point. The explosion limits state the concentration range within which a mixture of air and the substance is potentially explosive.

The information about thermal decomposition should include the decomposition temperature and all potentially hazardous products of decomposition. For instance, chlorinated hydrocarbons (TRI, PER, 1,1,1-trichloroethane etc.) will decompose at as little as 200 °C and in the process form hazardous gases (hydrochloric acid, phosgene gas, etc.). Hot parts of machinery or the tip of a lit cigarette will easily reach this temperature. Therefore, refrain from smoking in rooms where PER or TRI are handled.

Dangerous reactions are reactions that can be triggered by light, heat or contact with other substances, for instance by introducing water into concentrated sulphuric acid (release of heat).

10	Stability and reactivity
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Information provided:

- Chemical stability;
- Possibility of hazardous reactions;
- Conditions to avoid (e.g. static discharge, shock or vibration);
- Incompatible materials;
- Hazardous decomposition products.

11	Toxicological information
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Information provided:

- Concise but complete and understandable description of the various toxicological (health) effects;
- Available data used to identify those effects, including:
 - Information on the likely routes of exposure (inhalation, ingestion, skin and eye contact);
 - Symptoms related to the physical, chemical and toxicological characteristics;
 - Delayed and immediate effects and also chronic effects from short and long-term exposure;
 - Numerical measures of toxicity (such as acute toxicity estimates).

12	Ecological information
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Information provided:

- Ecotoxicity (aquatic and terrestrial, if available);
- Persistence and degradability;
- Bioaccumulative potential;
- Mobility in soil;
- Other adverse effects.



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13 Disposal considerations

Information provided:

- Description of waste residues and information on their safe handling and methods of disposal, including the disposal of contaminated packaging.

In this section a description of the waste (including waste codes) and recommendations for proper disposal are provided. In addition, specific national disposal requirements should be indicated.

14 Transport information

Information provided:

- UN number;
- UN proper shipping name;
- Transport hazard class(es);
- Packing group, if applicable;
- Marine pollutant (Yes/No);
- Special precautions which a user needs to be aware of or needs to comply with in connection with transport or conveyance, either within or outside their premises.

The transport of hazardous goods is subject to binding national and international rules. Hazardous goods are categorized according to hazard classes. The information may refer to road transport (e.g. ADR/GGSt), rail transport (e.g. RID) and marine transport (e.g. IMDG).

The UN number identifies hazardous substances during transportation. It is derived from the United Nations (UN) recommendations and part of a worldwide numbering system for hazardous goods.

Examples: Tetrachloroethylene; UN no. 1897, methanol: UN no. 1230

The ADR/RID is the European Convention on the Transportation of Hazardous Goods by Road. Introduced in 1957, the ADR/RID applies to the national and cross-border transport of goods. When last amended on 1 January 1997, a distinction between so-called "Only Classes" and "Free Classes" was introduced. The "Only Classes" control only the transportation of specifically listed hazardous substances, which is allowed subject to compliance with certain specified conditions. All other substances of this hazard class not specifically listed are excluded from transportation. In the "Free Classes", not specifically mentioned substances may be transported as well.

Comment [S. B. 1]: Per = perchloroethylene bzw. tetrachloroethylene (hier noch besser)

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The ADR comprises the following the hazard classes:

ADR Class		Properties of the hazardous good
ONLY	FREE	
1		Explosives and objects with explosives
	2*	Gases
	3	Flammable liquids
	4.1	Flammable solids
	4.2	Self-igniting substances
	4.3	Substances producing flammable gases when in contact with water
	5.1	Substances with igniting or oxidizing effect
	5.2	Organic peroxides
	6.1	Toxic substances
	6.2	Nauseating substances or substances carrying a risk of infection
7		Radioactive substances
	8	Corroding substances
	9**	Several other hazardous substances and objects

***Class 9 includes all substances that cannot be assigned to any of the other 8 classes.*

15	Regulatory information
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Information provided

- Safety, health and environmental regulations specific to the product in question.

This section provides specific legal information on safety, health and the environment. In addition, it includes special import requirements for substances/mixtures (e.g. TSCA list) and national information, e.g. specific labelling.



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16	Other information including information on preparation and revision of the SDS
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Space for additional information, such as training instructions, recommended use and application, etc.

This section should provide information which is not contained in Sections 1 to 15 of the SDS, for example:

- Date of the latest revision of the SDS;
- Indication of changes made to the previous version of the SDS, if not previously mentioned;
- Key/legend to abbreviations and acronyms used in the SDS;
- Key literature references and sources for data used to compile the SDS.

6.B.4.4 What can safety data sheets do for the company?

The safety data sheet is important for assessing the risk potential of hazardous working materials. Even if the safety data sheet does not list all relevant ingredients of the product, it often includes hidden references of the individual ingredients. For instance, the transport section often states ADR or UN code numbers which, interpreted together with other information, such as the MCW value, ID or danger symbols, can easily reveal the presence or absence of a certain ingredient.

Safety data sheets do not always reflect the full scope of potential environmental or health hazards, but if they are correctly prepared and interpreted together with other documentation, they can make a valuable contribution to human health and the protection of the environment.

Check whether the safety data sheets of the company are fit for use.

Estimate the risk potential of hazardous working materials used by the company based on the information included in the safety data sheet and the product identification.

For practical use and information dissemination among employees, the safety data sheets should be regularly revised, for instance, by issuing written internal instructions. These should provide easily understandable information at the workplace, advising the user of the risks associated with a certain product, and of the protective measures to be taken when processing the product. The internal instructions should be prepared in cooperation with the company's preventive services (occupational physician, safety experts, etc.).

Based on the information of the safety data sheet, it should be possible to carry out a risk evaluation of the workplace.

6.B.5 Safe storage of chemicals

Some basic rules and guidelines should be observed to minimize the risks associated with the storage of hazardous substances. Safety precautions are indispensable if a company uses a large number of different toxic substances, or if it stores large quantities of chemicals. The following issues need to be considered:

- **Spatial separation of stored chemicals according to their properties**

Substances which may cause a powerful reaction (e.g. strong acids and alkaline solutions) as well as substances capable of releasing toxic reaction products (acids + solution of chlorinated lime) must be stored separately.

The following illustration provides a simplified scheme for the storage of hazardous working materials.

	○	-	-	-	-	-
	-	+	-	-	○	-
	-	-	+	○	○	-
	-	-	○	+	+	○
	-	○	○	+	+	+
	-	-	-	○	+	+

+	Can be stored together.
-	Cannot be stored together.
○	Can be stored together if specific precautions are taken. Consult the safety data sheets.



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- **Storage of liquids in collection trays close to floor level**

In shelf-type racks, always store liquids on the lower shelves. If there is an accident (e.g. a container breaks or leaks), this will prevent the liquid from oozing into materials stored on the lower levels. Liquids kept in small tanks/containers (up to approximately 200 litres) must be stored in collection troughs suitable for their chemical properties.

- **Separate storage of substances that can be extinguished with water and substances that cannot be extinguished with water**

Chemicals which can be extinguished with water should be separated from chemicals that must not be extinguished with water. Wherever possible, store these two groups of substances in different rooms.

- **No storage of chemicals at the workplace**

Often large amounts of hazardous substances are (temporarily) stored at the workplace (e.g. solvent containers under worktops). In case of an accident these substances are a major source of danger. Do not keep more than one day's requirement of any hazardous substance at the workplace. Refill daily from the central storage point.

- **Keeping storage records**

At each storage point, the company must keep a storage list. The list should include the type, quantity and risk potential of the stored substance. If an accident occurs, the fire brigade will know how to fight the fire due to the information provided by the storage list.

- **Substitution of high risk substances**

The best way of avoiding risks associated with the storage of chemicals is to eliminate high-risk substances altogether from the company and replace them by less dangerous alternatives. In particular, substances with a high potential to cause a fire or damage to human health or the environment (e.g. chlorinated hydrocarbons, products containing heavy metals and water-soluble substances that will not readily degrade, such as non-degradable surfactants) should be substituted.