

Hazard Symbols

Hazard symbols are used for the labeling hazardous substances according to the *Ordinance on Hazardous Substances*.

The *Ordinance on Hazardous Substances* is a regulation to safeguard versus hazardous substances and comprises primarily the field of occupational safety. The directions of the Ordinance on Hazardous Substances for the classification, packing, and labeling of chemicals are valid for all fields and areas and apply, therefore, also for environmental and consumer protection and human health.

The term *Hazardous Substances* is a generic name and is defined after the §19/2 of the *Chemicals Law* as

- Dangerous substances or formulations according to § 3a of the Chemicals Law,
- Substances, formulations or products they may form or release dangerous substances or formulations during their production or use,
- Explosive substances, formulations, and products.

Following are some definitions to better understand these legal issues:

- **Substances** are chemical elements or compounds how they occur in nature or produced in a synthetic way (e.g., asbestos, bromine, ethanol, lead, etc.).
- Formulations are blends, mixtures, or solutions of two or more substances (e.g., diluting agents, paints, formaldehyde solutions, galvanic bathes).
- **Products** are substances or formulations which obtained a specific shape, surface, or form during the production process. These properties determine the function of the products more than their chemical composition (e.g., nickel containing welding electrodes, pine wood shelves, plastic tanks).

Hazardous substances defined above possess one or more properties marked with danger symbols.



Since the adoption of the **GHS-Regulation** (GHS stands for "Globally Harmonised System of Classification and Labelling of Chemicals") in all countries of the European Union.20. January 2009, the previously used **Hazard symbols** have been replaced by the GHS-Regulation, **Hazard pictograms** are graphic depictions containing black signs on a white background, inside a diamond with red borders. Additionally, the labelling has a signal word associated with it that reflects the relative degree of the hazard. According to the GHS-Regulation there are only two signal words:

Danger - for more severe hazard categories, and

Warning – for less severe hazard categories.

Hazard categories for substances and formulations marked with Hazard pictograms are subdivided into

- Risks of fire and explosion (physical-chemical properties),
- Health risks (toxicological properties), or
- Combination of these both.

In the following paragraphs all **GHS-Pictograms** are listed (together with the old danger symbols).

Inflammable Substances:

Explosive

GHS-Pictogram





Substances and formulations marked with the hazard pictogram "explosive" can explode by hit, friction, heating, fire, and other ignition sources even without atmospheric oxygen. This includes

• unstable explosive substances and mixtures,



- explosive substances and mixtures, as well as products with explosives,
- self reactive substances and mixtures,
- certain organic peroxides

Explosion will be triggered by a vigorous reaction of the substance. High energy is released thereby along with propagation of shock waves. The risk of explosion can be determined after the methods given in the *Law for Explosive Substances*.

In the laboratory mixtures of strongly oxidizing compounds with flammable or reducing substances can be explosive. For instance, fuming nitric acid reacts with an explosion with solvents like acetone, diethyl ether, ethanol, etc. Production or working with explosives necessitates particular knowledge and practical experiences as well as special safety measures. While working with these substances the quantities must be kept small for handling as well as for stockpiling.

An example for the above described properties is **2,4,6-trinitrotoluene** (TNT).

Oxidizing

GHS-Pictogram



old danger symbol

Substances and formulations marked with the hazard notation "oxidizing" are usually not combustible. But in contact with combustible or highly flammable substances they can increase the risk and the violence of a fire significantly.

This includes

• oxidizing gases, liquids and solids

In many cases they are salt-like inorganic substances with strongly oxidizing properties and organic peroxides.



Examples for the above described properties are **potassium chlorate and potassium permanganate**, but also **concentrated nitric acid**.

Flammable

GHS-Pictogram



old danger symbols



Flammable substances and formulations, if they are liquids, are characterised by low flash points (below 60 °C).

This includes

- flammable gases, aerosols, liquids and solids,
- self reactive substances and mixtures,
- pyrophoric liquids and solids,
- self heating substances and mixtures,
- substances and mixtures that liberate flammable gases on contact with water

Flammable gaseous substances easily form an explosive mixture with air under normal conditions. Some highly flammable substances produce extremely flammable gases under the influence of humidity. Substances that may heat up in air at room temperature without additional energy supply and finally ignite are also labeled as flammable.

Examples for the above described properties are **diethyl ether** (liquid) and **hydrogen** or **propane** (gases), as well as **acetone** and **sodium metal**, which are regularly used in laboratories as solvent resp. drying agent..



Pressurized gases

GHS-Pictogram



old danger symbol none

This includes

- pressurized gases, liquefied gases
- refrigerated liquefied gases,
- dissolved gases

Substances Hazardous to Health:

The categorization of substances and formulations according to their toxicological properties comprises acute and long-term effects regardless whether these effects are caused from one single, repeated, or long-term exposition. An important parameter to assess the acute toxicity of a substance is its LD_{50} value determined in animal experiments. The LD_{50} value reflects the lethal dose in mg per kg body weight which would cause the death of 50% of the test animals within 14 days after one single administration. Due to the test design a distiction is made between LD_{50} oral (p. o. = per os) uptake and digestion through the gastrointestinal system, and LD_{50} dermal in the case of uptake through the skin. Besides these there also exists a lethal concentration LC_{50} pulmonary (inhalation). It reflects the concentration of a pollutant in air (mg/L) which would cause death of 50% of the test animals within 14 days after an exposition



Acutely toxic substances

GHS-Pictogram



old danger symbols



Substances and formulations that can cause significant acute health damage or even death at low or very low concentrations if taken up by inhalation, ingestion, or by contact with the skin.

This includes

• substances with oral, dermal or inhalative acute toxicity

Chemical substances are classified into one of the 4 acute toxicity hazard categories by acute toxicity estimates (ATE) defining the categories as follows:

Exposition route	category 1	category 2	category 3	category 4
oral [mg/kg body-weight]	$ATE \leq 5$	$5 < ATE \le 50$	50 < ATE ≤ 300	300 < ATE ≤ 2000
dermal [mg/kg body-weight]	ATE ≤ 50	50 < ATE ≤ 200	200 < ATE ≤ 1000	1000 < ATE ≤ 2000
Gase [ppmV]	$ATE \le 100$	100 < ATE ≤ 500	500 < ATE ≤ 2500	2500 < ATE ≤ 20000
Vapours [mg/L]	ATE ≤ 0,5	0,5 < ATE ≤ 2,0	2,0 < ATE ≤ 10,0	10,0 < ATE ≤ 20,0
Dusts and mists [mg/L]	ATE ≤ 0,05	0,05 < ATE ≤ 0,5	$0,5 < ATE \le 1,0$	$1,0 < ATE \le 5,0$

Examples for substances with an ATE category 1 are **hydrogen cyanide**, **dinitrobenzene isomers** or the naturally occurring **nicotine** from tobacco. Examples for substances with an ATE category 1 are **hydrogen sulfide**, the solvent **methyl alcohol = methanol**, or **bromine**.



Chronically toxic substances

GHS-Pictogram





This includes

- carcinogenic substances,
- substances that cause mutagenic effects (germ cell mutagens),
- substances that have toxic effects on reproduction,
- some substances that cause specific target organ toxicity with single or repeated doses
- substances that cause sensitization of the respiratory organs

Examples for substances with the above described properties are the former laboratory solvents **chloroform = trichloromethane** (carcinogenic), **benzene** (carcinogenic) and **1,2dimethoxyethane = ethyleneglycol dimethyl ether** (toxic to reproduction).

Harmful substances

GHS-Pictogram





Harmful substances have a moderate risk of health damages if taken up by inhalation, ingestion, or in contact with the skin.

This includes

- substances with relatively low oral, dermal or inhalative acute toxicity (category 4)
- substances with specific target organ toxicity on single exposure,
- narcotic substances,



Examples for substances with the above described properties are the laboratory solvents 1,2ethanediol = 1,2-ethylene glycol = glycol and cyclohexanol.

Tissue Destroying Substances:

The term "tissue destroying substances" includes the sub-groups "corrosive substances" and "irritant substances".

Corrosive substances

GHS-Pictogram





Substances and formulations that destroy living tissues. If a substance destroys the healthy and intact skin of test animals in its whole thickness or this property is predictable due to the chemical characteristics of the test substances, e.g., acids (pH < 2) and bases (pH > 11.5), then it will be marked as corrosive.

This includes

- corrosive substances,
- substances that cause irreversible eye damage,
- but also substances that are corrosive for metals

are labeled with his pictogram.

Examples for substances of this group are mineral acids like **hydrochloric acid** and **sulfuric acid** and **bases** like **sodium hydroxide solutions** (**caustic-soda** solutions).



Irritant substances

GHS-Pictogram



old danger symbol

Irritant substances and formulations are not corrosive. But they can cause inflammation in contact with skin or mucous membranes.

This includes

- skin irritants,
- eye irritants,
- respiratory irritants,
- substances that can sensitize the skin

Examples for such substances are **isopropylamine** and **calcium chloride**, and also more **diluted acids** and **diluted bases**.

Dangerous for the Environment:

Dangerous for the environment

GHS-Pictogram





Substances and formulations that can cause immediate or delayed adverse effects on one or more environmental compartments (water, soil, air, plants, micro organisms) and lead to ecological disturbances.

Examples for the above described properties are **tributyl tin chloride**, **tetrachloromethane**, and petroleum hydrocarbons like **pentane** and **petroleum benzine**.