



Hydrogen Peroxide

Guideline document for safety measures



Preface

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This guideline document is supported and maintained by the Cefic Peroxygens Sector Group, which consists of the following member companies:

Arkema

Belinka Perkemija

Ercros

Evonik

Kemira

Nouryon

Solvay

The development of this guideline document is in accordance with our Responsible Care commitment to all stakeholders throughout the life cycle of hydrogen peroxide. Its purpose is to provide a single source of guidance for the domains of safe handling, storage and transport of hydrogen peroxide which is intended to be widely available to all stakeholders.

This document can also be found on our website: www.peroxygens.org

How to ensure safe handling, storage and transport of hydrogen peroxide (H₂O₂)



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Purpose and scope of this guideline document

For years now, the domains where hydrogen peroxide been used, have undergone major development. Indeed, the substance shows highly valuable properties as biocide or strong oxidiser but is also recognized as environmentally friendly as its breakdown products are oxygen and water.

Nevertheless, those major advantages have not to conceal the fact that its handling, storage and transport must be done in strictly controlled conditions to avoid any risk of accident. Hydrogen peroxide is, indeed, a dangerous good.

The European producers of hydrogen peroxide, members of the Cefic Peroxygens Sector Group have decided to combine their knowledge and experience in order to share with you, through this brochure, good practices and consistent recommendations on safety measures in the domains of safe handling, storage and transport.

Transport regulation is based on the UN orange book. This book complies with UN recommendations on the transport of dangerous goods model regulations. This is a guidance document developed by the United Nations to harmonize dangerous goods transport regulations. However, this document does not give any details on crucial domains like technical equipment, procedures for pre-loading and loading, emergency procedures, protective equipment, and other safety aspects.

The aim of this document is:

- To provide users, authorities and other stakeholders with information for the safe handling, storage and transport of hydrogen peroxide.
- To propose realistic and already applicable procedures to users of hydrogen peroxide in order to minimize safety risks in handling, storage and transport operations.
- To set up minimum harmonised requirements for the handling, storage and transport of hydrogen peroxide, accepted by all the hydrogen peroxide producers which are members of Cefic Peroxygens Sector Group.



I. What you need to know about H₂O₂

Hydrogen peroxide is a reactive oxygen species and the simplest peroxide chemical compound with the chemical formula H_2O_2 .



Hydrogen peroxide is a clear, colourless liquid. It is only used in aqueous solution and is miscible with water in all proportions.

At low concentrations, H_2O_2 is odorless.

Technical data and physical properties

PHYSICAL PROPERTIES OF TYPICAL HYDROGEN PEROXIDE:					
			*		
Concentration	Density at 20°C	Boiling point	Freezing point	Viscosity at 20°C	
weight %	kg/m³	°C	°C	Ns/m²	ср
0 (water)	1000	100	0	0.001002	1.002
35	1132	108	-33	0.00111	1.11
50	1196	114	-52	0.00117	1.17
70	1288	126	-40	0.00124	1.24

Hydrogen peroxide has miscible solubility in water in all proportions. In aqueous solutions, hydrogen peroxide differs from the pure substance due to the effects of hydrogen bonding between water and hydrogen peroxide molecules. The pure, undiluted hydrogen peroxide (i.e., 100 % w/w) exhibits a freezing point as -0.43 °C and a boiling point of 150.2 °C.

Chemical reaction

In its pure form and at low pH, hydrogen peroxide is a relatively stable compound. However, decomposition can be initiated and accelerated by light, heat, high pH or the presence of various impurities, such as organic matter and metals or by mixing with other oxidisers or reducing agents. Decomposition is an exothermic reaction, which means it liberates heat and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
.

Hydrogen peroxide is a powerful oxidising agent, because it readily takes electrons and is reduced in both alkaline and acidic environments. In an acidic medium, hydrogen peroxide can receive electrons and behave as an oxidising agent:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
.

In an alkaline medium, it can take electrons and operate as an oxidising agent:

$$H_2O_2 + OH^- + 2e \rightarrow 3OH^-$$
.

While in neutral medium, hydrogen peroxide oxidises a wide range of substances, for example, the oxidation of sulphites to sulphates:

$$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O.$$

It can however also act as a reducing agent for strong oxidants:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2.$$

Another ability of hydrogen peroxide is to form other per-compounds, both organic and inorganic by transfer of the O-O functional group. It is utilised according to the following stoichiometry:

$$H_2O_2 + 2RX \rightarrow ROOR + 2HX$$
.

2. Applications

Hydrogen peroxide can be used as an oxidiser, bleaching agent, biocide and antiseptic in a variety of ways.

To improve and accelerate processes, it is sometimes coupled with other agents. For consumer use it is usually diluted, while higher concentrations are intended for professional industrial use.

The following are some of its most common applications, grouped by industries:



Paper Industry (bleaching of paper pulp)



Textile Industry (bleaching of textile fibers)



Chemical Industry (manufacture of chemical compounds)



Cosmetic Industry (hair bleaching, health care, hygiene)



Medical and
Pharmaceutical
Industry
(disinfection, wound
healing)



Food Industry (food, feed and beverages packaging disinfection)

Hydrogen peroxide can work in all media, including water, air, wastewater, and soils.

See more applications below, grouped by industries:



Wastewater
Treatment
(decomposition of
pollutants and toxic
substances)



Agriculture
Industry
(farming – soil
treatment, fishkeeping,
horticulture,
disinfection)



Metal Industry (metal surface treatment, mining, metallurgy)



Aeronautic Industry (propellant)



Electronics
Industry
(etching of circuit
boards, semiconductor
chips manufacture)

3. Transportation

General information

Hydrogen peroxide is transported mostly by road and rail in bulk quantities but is also available in intermodal container (ISO containers), intermediate Bulk Containers (IBCs), drums and plastic jerry cans.







Railway tank

Road tanker

ISO containers



IBC



Drums and plastic jerry cans

Hydrogen peroxide is classified as dangerous good and is subject to international transport regulations and must carry the proper signs and labels when transported. Note that national regulations may differ from one country to another, see chapter 4 "The regulatory aspects of transport (ADR/RID/IMDG(IATA)".

In addition, regulations of explosive precursors EU 2019/1148 also require the investigation of parties that are involved in the use or transport of hydrogen peroxide.

Bulk Transportation

Requirements for transport containers

- Transport containers (of recommended stainless-steel quality, e.g., 304L and 316L) must be thoroughly cleaned, pickled and passivated prior to initial use.
- The transport containers must be equipped with venting devices (breathers) and pressure-relief devices (pressure-relief valve/burst disc).
- The transport containers must be used for hydrogen peroxide only.

Loading and unloading

Loading

• To ensure cleanliness, the transport containers must be inspected before hydrogen peroxide is loaded.

Loading & Unloading

- Ensure brakes are activated and wheels are chocked.
- Check and clear area of any combustible materials.
- Close off the loading/unloading area.
- Turn on a warning light or a sign indicating that loading/unloading is in progress.
- Verify that safety showers and eye wash stations are functional.
- Ensure a readily available water supply in case of a spill or fire.
- Visually check the flexible hoses used for operation before launching it.
- Install a remote emergency stop button for stopping operations at a distance in case of any issues.

Unloading

- Confirm enough capacity in the storage tank before unloading starts.
- The connection point for unloading should be clearly labelled "Hydrogen Peroxide".
- Tank cars are unloaded via a self-priming pump or with pressurized air (check national regulations).
- In order to prevent contamination (unloading of another product), a physical barrier must be established, for instance by a cap or a valve closed with a key.

On the road

- Bring personal protective equipment (PPE) specified in chapter 7 "Personal Safety Instructions".
- Driver should have knowledge of hydrogen peroxide properties, characteristics and hazards and be able to handle incidents during transportation.



Transportation of small containers

- When transporting small containers like drums or IBC, the hydrogen peroxide should be segregated from other chemicals.
- Do not use wooden pallets; instead, use plastic pallets.
- Each small container should be equipped with a continuous vent to prevent internal pressure buildup.
- Do not block the vents by stacking drums on top of each other.
- Do not reuse hydrogen peroxide small containers for other chemicals.

Hydrogen peroxide is classified according to the classification principles as laid down by UN, recommendations on the Transport of Dangerous Goods, Model regulations.

Hydrogen peroxide < 8% by weight: Not dangerous good

Hydrogen peroxide 8% to <20% by weight:

Hydrogen Peroxide Concentration	Transport Hazard Class	Labels	UN Number	Proper Shipping Name
Road/rail/sea transport	5.1	OTHERWS AGENT	2984	HYDROGEN PEROXIDE, AQUEOUS SOLUTION
Air transport	5.1	ONUMA MASS 1	2984	Hydrogen Peroxide, aqueous solution

Hydrogen peroxide 20% to < 60% by weight:

Hydrogen Peroxide Concentration	Transport Hazard Class	Labels	UN Number	Proper Shipping Name
Road/rail/sea transport	5.1+8	ODDING AGEST COMPOSING	2014	HYDROGEN PEROXIDE, AQUEOUS SOLUTION
Air transport	5.1+8 Only allowed for HP < 40 % by wt	DITIONAL AGEST	2014	Hydrogen Peroxide, aqueous solution

Hydrogen peroxide > 60% by weight:

Hydrogen Peroxide Concentration	Transport Hazard Class	Labels	UN Number	Proper Shipping Name
Road/rail/sea transport	5.1+8	OUDIANG AGENT	2015	HYDROGEN PEROXIDE, AQUEOUS SOLUTION, STABILIZED
Air transport	Not to be transported by air	Not to be transported by air	Not to be transported by air	Not to be transported by air

National regulations may differ from one country to another and are being revised continuously.

Customers who want to transport hydrogen peroxide within national boundaries should refer to the applicable national regulations.

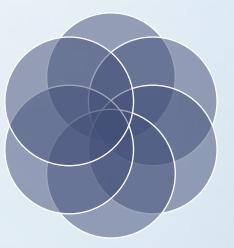
Everybody involved in transporting or handling hydrogen peroxide must ensure compliance with relevant regulations and take all actions and precautions to transport dangerous goods in a safe way.

In case of an accident or incident during the transportation of hydrogen peroxide, the following measures are recommended:

Switch off the motor

Never return leaked product back to the container due to the risk for decomposition/contamination

In case of a leakage, try to seal or stop



Smoking is prohibited and do not use any open flames

Mark the risk area and warn other road users

Contact the emergency service

Notice for use of "written instruction" can be found in chapter <u>5.4.3</u> and <u>8</u> on ADR

4. The regulatory aspects of transport

Useful reference of ADR / RID / IMDG / IATA



Road transport:

ADR - International Carriage of Dangerous Goods by Road is a 1957 United Nations treaty which governs transnational transport of hazardous materials.

Rail transport:

RID – Regulations concerning the International Carriage of Dangerous Goods by Rail. Various intergovernmental agreements and conventions set the regulations for international carriage by rail.





Sea transport:

 IMDG – Regulations concerning International Maritime Dangerous Goods set by the International Maritime Organization (IMO).
 IMO is the United Nations specialised agency with responsibility for safety and security of shipping and prevention of marine and atmospheric pollution by ships.

Air transport:

IATA DGR – The International Air Transport
Association Dangerous Goods Regulations
manual is a global reference for shipping
dangerous goods by air. IATA works closely
with local governments and International Civil
Aviation Organization (ICAO), a specialized
agency of the United Nations.



5. Precautions for safe handling

As a general rule, the following measures have to be taken when handling hydrogen peroxide, no matter its concentration, but having clearly in mind that the higher the concentration the higher the risk:

- Keep away from combustible materials and incompatible chemicals (e.g., alkali, acids and metals).
- Keep only in the original container.
- <u>Label</u> containers properly.
- Keep water accessible.
- Storage materials: passivated stainless steel, glass, polyethylene.
- Spilled product must never be returned to the original container for recycling. Reduce danger by dilution with large quantities of water.
- Handle samples in suitable containers.
- Avoid contact with skin, eyes and clothing.

4 GOLDEN RULES

Never confine

Never contact

Always have water available

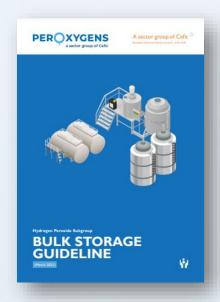
Never contaminate

As a logical exception, the last precautionary statement is not needed when dealing with hydrogen peroxide below 5% concentration, as it can be (and is usually) used for skin and wound disinfection.



6. Safe storage recommendations

For hydrogen peroxide storage it should be distinguished between intransit-storage and permanent storage. Additionally, a differentiation between bulk storage and packed material (IBC, drum and jerry can) storage should be highlighted.



For bulk storage facilities and associated aspects please refer to the <u>CEFIC Bulk</u> Storage Guideline, which can be found on our website.

With bulk storage being well covered in the mentioned document, the focus of this chapter will be on packed material storage and in-transit storage considerations for bulk material.

Generally, any in-transit storage of hydrogen peroxide should be limited as much as possible, as monitoring of the product condition by product-experienced and qualified personnel as well as all recommended safety measures for storage cannot always be ensured. If, however, especially extended, in-transit storage becomes necessary the same general practices as for regular storage should be applied.

Due to the potential for a self-accelerating decomposition reaction of any hydrogen peroxide, as outlined in Bulk Storage Guideline Appendix 2, storing of hydrogen peroxide should only take place in a well-controlled environment as described below.

The key factors for safe storage are:

Temperature:

Hydrogen peroxide should be stored in a cool, dry place. The temperature of any hydrogen peroxide, if not listed differently in the safety data sheet, should ideally be kept well below 40°C, as above this temperature the risk for self-accelerated decomposition increases. At the same time, a negative influence on packing material stability may become noticeable.

Other radiation influences:

Especially packed material should be kept out of any sunlight and away from any other potential heat radiation sources.

Moisture:

The storage areas should be dry, so potential leaks can be easily identified.

Packaging:

Only approved and dedicated bulk tanks are to be used for hydrogen peroxide storage. Packed material is to be kept in its original packaging, which is of special design with a degassing device in the closure. Any packaging is only to be stored in its correct upright position to ensure the proper function of the degassing device. The correct operation of these degassing devices should be checked periodically. Non-functioning of the degassing device can usually be noticed by a bulging package.

In order to prevent the container from rupturing, it is necessary to release pressure manually. If there is any doubt, please contact your vendor for additional guidance in advance.

In general, hydrogen peroxide must never be fully confined, but always have the opportunity to vent evolving oxygen gas to a safe location. This is also to be considered in equipment/pipework design.

Storage area and storage:



concrete floor and be well-ventilated. Within the same containment / fire protection zone, only compatible chemicals should be stored alongside with hydrogen peroxide. Especially any flammable materials are to be kept clear of the storage area for hydrogen peroxide.

Additionally, a **fire water sprinkler system** is advisable. During storage, a regular inspection of the area for potential leaks and/or bulging containers (malfunction of degassing device) or any other abnormalities, such as temperature increase of a single packaging, should take place.

The shelf life of each individual pack should be observed, as this is not only focusing on the product itself, but also the safety and integrity of its packaging.

Any leaked product must never be returned to its original packaging but be diluted and disposed of in a locally acceptable manner.

Joint storage advice:

Do not store together with:

- Alkalis, reductants, or metallic salts (risk of decomposition)
- Inflammable substances (risk of fire)
- Organic solvents (risk of explosion)
- Even though hydrogen peroxide itself is not flammable, ignition sources (e.g., wooden pallets) should be kept away, and smoking in storage areas is not permitted.

Additional hints for Bulk Storage:

- Only use tank installations made from compatible materials with adequate separation distance, adequate emergency venting capacity of the tank, suitable general venting devices, temperature monitoring, earthing (grounding), and barrier in case of leakage as well as emergency dilution and dumping plan.
- Erroneous filling of any other chemical into a hydrogen peroxide tank should be prevented by technical and organizational means.
- Prior to the first filling and operation of a tank installation all parts of the facility including all pipes must be thoroughly cleaned and flushed through for hydrogen peroxide service.
- Metal elements of the installation must first be pickled and passivated sufficiently. For detailed information on design specifications for the construction of tank and dosing installations ask the producer for advice.
- Regularly verify the availability of water to deal with emergencies (for cooling, tank flooding, fire fighting) and check correct operation periodically.

Regardless of the recommendations in this document, local laws and regulations must always be adhered to. In many cases, more stringent practices may apply.

7. Personal safety instructions

Hydrogen peroxide is a hazardous substance.

Protective measures must be applied to mitigate hydrogen peroxide hazard. Two kinds of protective measures exist: general protective measures and personal protective measures.

Carrying out an appropriate risk analysis allows for identifying which are the best suitable protective measures. Local regulations can also require some mandatory protective measures.

Personal safety instructions must be clearly available at the working place (dashboard, etc.).



General protective measures:

- Ensure sufficient air exchange and/or exhaust in work areas.
- Ensure safety shower and eye wash stations installed in work areas.

Personal safety instructions:

 Due to the classification of hydrogen peroxide as liquid oxidiser and the risk of spontaneous combustion, carbon-based textiles (such as leather, cotton, textile fibers, etc.) are forbidden.



Eye/face protection

- Eye protection is mandatory.
- Based on risk analysis and description of task to be done, different kind of eye
 protection can be used. Such as: safety glasses with side-shields, full-protection
 glasses or complete mask.

Respiratory protection

- If there is a risk of inhalation of hydrogen peroxide (insufficient ventilation, atomisation or aerosol-development of hydrogen peroxide, etc.), wear suitable respiratory equipment.
- In case of spillage, wear a mask.
- A full-face mask also acts as eye and face protection.

Hand, skin and body protection

- Due to the classification of Hydrogen Peroxide as liquid oxidiser and the risk of spontaneous combustion, carbon-based textiles (leather, cotton, textile fibers...) are forbidden. Use protective gloves (PVC, neoprene) complying with EN 374.
- Based on a hazard analysis, boots and full protective suits have to be worn. Allowed materials are natural rubber, PVC, neoprene or polyethylene.
- Be careful that no hydrogen peroxide can enter into boots from above.
- Boots and protective suits have to be checked on a regular basis.

PEROXYGENS

A sector group of Cefic *

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