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Hydrogen peroxide (H₂O₂) safe storage and handling

Scope

This TIP provides basic information on measures to protect personnel and equipment in the handling and storage of bulk aqueous solutions of hydrogen peroxide. It is vitally important that any new hydrogen peroxide facility design be undertaken with advice from a supplier of hydrogen peroxide in order to cover all of the unique design parameters associated with hydrogen peroxide.

Safety precautions

Hazards classification

CAS Registration 7722-84-1. Hydrogen peroxide at 20-60% concentration is identified as UN2014, and is classified as an oxidizer and corrosive. Hydrogen peroxide at greater than 60% concentration is identified as UN2015, and is classified as an oxidizer and corrosive. See Table 1.

Table 1. Hazard classification summary

Concentration:		50%	70%
UN No.		2014	2015
TDG Hazard Class		5.1	5.1
Subsidiary Hazard Class		8	8
Packing Group		II	I
NFPA Rating:	Health -	3	3
	Flammability -	0	0
	Reactivity -	1	3
	Special -	OXY	OXY
Exposure Limits:			
	ACGIH® TLV®	1 ppm TWA	1.4 mg/m ³ TWA
	OSHA PEL	1 ppm TWA	1.4 mg/m ³ TWA
	NIOSH REL (1994)	1 ppm TWA	1.4 mg/m ³ TWA

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Workplace Hazard: (Health Canada WHMIS Classification)

C – Oxidizing material

D1B – Toxic material, with immediate and serious toxic effects

E – Corrosive material

F – Dangerously reactive material

TIP Category: Automatically Periodically Reviewed (7-year review)



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Health hazards

Eye: Contact of all industrial grades of hydrogen peroxide with the eyes can cause severe irritation and burns, including ulceration of the cornea and may even lead to blindness. Hydrogen peroxide at concentrations above 6% can cause permanent eye damage, without prompt first aid treatment. Medical attention must be sought immediately after peroxide contact with eye(s).

Skin: Contact of 70% hydrogen peroxide with the skin can cause severe burns. If the peroxide is not washed out, redness and blister formation may result. The injury should be treated as an ordinary heat burn. If the contact time is relatively short, especially for concentrations of 50% and lower, a temporary whitening or bleaching, accompanied by a tingling sensation, may result. The whitening of the skin is caused partially by decomposition of hydrogen peroxide after diffusion through the skin. The whiteness, due to oxygen microbubbles, disappears as the oxygen diffuses from under the skin. The bleaching of the skin is not as damaging as the injury from contact with acid. The skin soon returns to normal if it is washed promptly after contact.

Inhalation: Inhalation of hydrogen peroxide vapor or mist at high concentrations may cause extreme irritation and inflammation in the nose and throat.

Ingestion: If swallowed, peroxide may cause injury to the mouth, throat, esophagus, and stomach. Decomposition will cause the rapid evolution of oxygen, which may distend the esophagus or stomach and cause internal injury.

Chronic and acute toxicity: No chronic systemic or local effects from exposure to hydrogen peroxide are known. It has no known acute systemic toxicity.

Personal protective equipment (PPE)

Personal protective equipment must be worn when opening storage tanks, vessels and piping systems containing hydrogen peroxide. When working in the vicinity of high concentration hydrogen peroxide, or whenever exposure to hydrogen peroxide is possible, the PPE must be worn.

Minimum protection when working in the vicinity of hydrogen peroxide systems:

- close-fitting, splash-proof chemical monogoggles at all times
- neoprene or butyl rubber gloves, loose fitting for ease of removal, for operation of valves on hydrogen peroxide systems.

When opening vessels and piping systems containing hydrogen peroxide, and whenever exposure to hydrogen peroxide is possible, wear the above equipment, plus...

- acid-resistant coveralls (place sleeves and legs outside to keep liquid from flowing into the gloves and boots)
- rubber boots
- hard hat

Leather gloves and boots should not be worn when working on hydrogen peroxide systems. They present a significant burn hazard to the wearer, if they contact hydrogen peroxide. If contaminated by hydrogen peroxide, leather apparel presents a fire hazard and should be rinsed with water and then discarded. They should not be re-used. Any other clothing that has come in contact with hydrogen peroxide should be washed thoroughly and immediately, to avoid the potential of a delayed ignition.

Safety equipment

Ensure that a safety shower, eye wash fountain, and one additional source of water are readily accessible in the unloading area. Water lines should be protected against freezing, and should be tested frequently. The water supply should be tempered. Safety showers and eye wash stations should be readily accessible at hydrogen peroxide storage, pumping, and application locations. Activation of the shower or eyewash station should trigger an alarm to summon help.

First aid

- Contact with eyes: - Irrigate immediately and freely with water for at least 15 minutes, while holding the eyelids apart. Obtain medical attention immediately.
- Contact with the skin: - Flush immediately with plenty of water for at least 15 minutes. Obtain medical attention after contact with hydrogen peroxide at above 50% concentration. Remove eye protection only after under a safety shower. Remove contaminated clothing and shoes quickly after commencing water flush. After first aid measures are complete, contaminated clothing should be washed thoroughly in order to eliminate a delayed potential fire hazard.
- Ingestion: - Do not induce vomiting. Give large volumes of water. Do not give anything by mouth to an unconscious person. Obtain medical attention immediately.
- Inhalation: - Remove immediately to fresh air. Obtain medical attention if nose and throat are irritated.

Fire and explosion hazards

Hydrogen peroxide, by itself, is nonflammable. However, it is a strong oxidizer and contact with oxidizable organic material may cause spontaneous combustion. Hydrogen peroxide is catalytically decomposed by many common materials, resulting in the evolution of heat and oxygen, which can support the burning of combustible materials.

Contamination of hydrogen peroxide has the potential to yield a self-accelerating decomposition reaction, depending on the relative rate of heat loss and the rate of decomposition, which are affected by vessel size, ambient temperature, insulation, initial concentration, amount of contamination, etc. Although high concentration hydrogen peroxide solutions can be stored safely, with special engineered safety precautions and tight control of procedures and the immediate environment, the accelerated reaction kinetics associated with higher concentration solutions provides an increased risk for the storage of high concentration hydrogen peroxide solutions, therefore Hazard and Risk Assessment processes typically lead most industrial users to avoid storage at concentrations greater than 50%. Mills can receive hydrogen peroxide at 70% concentration, and dilute for storage at 50% concentration. This may trigger an OSHA requirement for a full Process Hazards Assessment. Combustible material in the presence of high concentration hydrogen peroxide may quickly burst into flame. Ignition, with lower concentration hydrogen peroxide solutions, may be delayed after initial contact.

At ambient temperature it has been impossible to obtain a propagating detonation in commercial hydrogen peroxide solutions. Organic material dissolved in hydrogen peroxide, especially in stoichiometric amounts, may form an explosive mixture. Under ordinary storage and handling conditions there is no hazard of a vapor phase explosion. Vapors can reach explosive conditions in the head space of a confined space as a result of the heat of an external fire. The explosive decomposition of vapor requires an ignition source.

The more common hazard is an “explosive” pressure rupture due to a gas generation rate exceeding the vent capacity of a container. Catalytic decomposition results in the liberation of oxygen and heat. One liter of 50% hydrogen peroxide yields approximately 200 liters of oxygen and additional volumes of steam. In concentration above 65%, a catalytic decomposition can become self-accelerating because the rate of heat evolution exceeds the rate of heat loss to the surroundings. Vaporization of solution water results in further concentration of the hydrogen peroxide solution. Under typical circumstances, hydrogen peroxide at mills is stored at 50% concentration. There is sufficient water present to absorb any heat evolved due to normal slow (unaccelerated) peroxide disproportionation. There is also capacity in the ‘system’ to absorb the heat of a moderate degree of product contamination, and provide sufficient time to undertake actions that might safely avoid the system going ‘critical’ in a self-accelerating decomposition reaction.

Hydrogen peroxide storage temperature should be monitored. The decomposition process is usually slow at first, and may take days or weeks to become ‘critical’. In case of extreme contamination in storage, the decomposition can reach dangerous proportions quickly. A temperature increase of 1-2°C per hour, at 30-35°C, is indicative of a decomposition event. Decomposition reactions in storage can be quenched by external cooling or dilution.