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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

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.

In case of fire, use only water. Deluge with large quantities. Foam is not effective because oxygen and heat continue to be generated under the foam blanket.

Hydrogen peroxide is used routinely for the bleaching of mechanical pulps. An alkaline bleach liquor is usually made up of sodium hydroxide, sodium silicate, and magnesium sulfate. Hydrogen peroxide used to be added directly to the bleach liquor make-up tank, but is now more typically added to the bleach liquor feed line just prior to the process application in order to mitigate the potential for excessive peroxide decomposition. Mechanical pulp bleaching requires the application of peroxide in excess of the actual consumption, with residual peroxide recycled back to the process. Loss of peroxide residual is often a result of the presence of catalase (in the case of recycle paper bleaching), an enzyme that consumes hydrogen peroxide. The addition of concentrated hydrogen peroxide to alkaline bleach liquor has not been associated with unmanageable hydrogen peroxide decomposition.

Since the time that hydrogen peroxide has been used routinely in chemical pulp bleaching there have been several catastrophic events resulting from explosions in pumps, mixers, and tanks. The incidents have involved the application of hydrogen peroxide at 50% concentration and alkali-catalyzed decomposition of peroxide has been implicated in the explosions. Kinetic modeling of the explosions has shown that addition of caustic to a pre-existing pool of high concentration hydrogen peroxide results in a sudden, and very substantial, pressure rise due to the rapid decomposition of hydrogen peroxide to form oxygen gas and steam, as a consequence of the sustained presence of peroxide in its acid form. The reaction is not self-limiting, as it is with the typical mechanical pulp situation. The consequence has been total destruction of the pump, severe damage to equipment and facility in the vicinity, and a high potential for injury.

Although a similar unmanageable decomposition problem has not been observed in mechanical pulp bleaching operations, the interruption in flow of the bleach liquor solution could result in a pool of concentrated hydrogen peroxide in the supply line and process receiving vessel. Re-establishment of the alkaline bleach liquor solution might result in similar decomposition kinetics to those observed in the chemical pulp explosion incidents. (High) pulp consistency is a key factor for optimizing bleaching performance with mechanical pulps, so hydrogen peroxide is typically added as a high concentration solution. Although addition of concentrated hydrogen peroxide solutions into bleach liquor delivery lines may result in improved bleaching performance, it presents the potential for increased safety risks (as described above).

In chemical pulp bleaching this hazard situation generally presents during process upset conditions, when pulp flow is interrupted, and peroxide continues to flow in the mixing chamber. It is recommended that hydrogen peroxide be diluted to <10% concentration prior to application in chemical pulp bleach plants and that appropriate process safety interlocks be installed to stop the flow of bleaching chemicals when pulp flow is interrupted. In addition to limiting the total amount of peroxide present, on a 100% basis, in the event of failure of the interlocks, peroxide additions often must overcome pump pressures or static head pressures so the use of peroxide solutions diluted to 5-10% concentration decreases the risk of personal injury in the event of a peroxide spray from a leaking gasket or seal.

Accidental release measures

Hydrogen peroxide storage should be located in an area that is diked, to eliminate the potential release of concentrated peroxide in case of catastrophic failure of the tank. In case of an accidental release outside of a containment area:

- Try to stop the release, if it can be done safely using proper personal protective equipment.
- Isolate the area to limit exposure to mill personnel.
- Contain large spills with temporary diking of sand, gravel, or dirt.
- Remove organic materials that may present a fire hazard.

Small spills should be diluted (to drain) with large quantities of water. Dilution with water is the solution for most spills. Hydrogen peroxide will react in a controlled manner with organics and other material on the ground, or in the sewer. Its decomposition products are pure water and oxygen (and heat). When heat can be released harmlessly to the surroundings and gaseous decomposition products are not confined, the safety hazards and environmental impact of small hydrogen peroxide spills are limited and manageable.

Decomposition inside of a storage tank can result in the release of oxygen, steam, and peroxide aerosol through the free-lift manway. The decomposition may be quenched by diluting the contents of the tank as quickly as possible. If the tank can be approached safely, consideration may be given to draining the tank into the containment area in order to decrease the potential for an explosive pressure rupture of the tank. The tank should be approached behind a water hose with a mist nozzle, and while wearing full protective gear, including self-contained breathing apparatus. A water spray can be applied to the outside of the tank to facilitate heat transfer to the surroundings.

The urgency and immediate hazard is controlled when a large release has been safely contained. The area should be isolated to limit exposure to mill personnel. The liquid can be diluted to the extent that the containment volume allows. There are methods for decreasing the concentration of hydrogen peroxide solutions in place. **Consult your hydrogen peroxide supplier for advice on disposal of large peroxide spills.**

Comply with all federal, state, and local regulations in the reporting and disposal of waste. In order to avoid the risk of contamination, the recovered product must not be returned to the original tank/container.

Storage and handling of hydrogen peroxide

Product delivery

Bulk delivery of hydrogen peroxide to the pulp industry in North America is generally of 50% and 70% concentration aqueous solutions. A 60% concentration is available from some hydrogen peroxide producers. Deliveries of 70% hydrogen peroxide solutions are generally diluted and stored at 50% concentration. The water used for dilution must be assessed for contaminants and tested to ensure that the diluted solution is sufficiently stable in storage.

Deliveries are made by tank truck and railcar, which are dedicated to hydrogen peroxide service. Tank truck unloading is generally handled by the hydrogen peroxide producer, or its carrier. The trucks are equipped with pumps and are top-unloaded.

Tank railcars are unloaded by pulp mill chemical handlers. The railcars should be spotted for unloading with brakes set, wheels chocked, blue warning sign displayed, and derailer installed along the track. All hydrogen peroxide railcars are top-unloading. Although dome arrangements will vary from railcar to railcar, each railcar is equipped with a manway (with hinged cover), combination safety vent/air (nitrogen) connection, flanged unloading eduction pipe, and rupture disc assembly.

A safety vent on tank trailers and railcars used in the transport of bulk hazardous chemicals is atypical and special permission must be granted by U.S. DOT or be compliant with Transport Canada regulations. The DOT competent authority approval number should be affixed to the tank trailer, near the trailer manufacturer's registration plate.

Due to the potential for leakage from the vent filter in the event of a railcar derailment the vent device must provide for a gas flux but prevent the passage of liquid. Some vent devices use a Goretex® membrane sandwiched between drilled PTFE plates. The Goretex® membrane is prone to perforation, so it should be checked for holes at the time of unloading. The latest vent design uses a porous stone filter medium, in conjunction with a check valve in the vent cap. In the event of a railcar overturn, the ball in the check valve will seat and prevent peroxide leakage through the vent. Regardless of the type of vent device, the gas flux rate through the vent media will be less than the unloading flow rate, so chemical unloaders are urged to open the manway prior to unloading, and to rest the hinged lid (in a closed position) on one of the lid bolts, in order to eliminate the potential for creating a negative pressure in the railcar.

Pump unloading of railcars is strongly recommended to minimize the potential for "run-on" leaks associated with pressure unloading. The preferred unloading method is by a self-priming centrifugal pump. Air padding is discouraged because of the potential to introduce contamination to the product. The unloading valve arrangement is bolted to the eduction pipe and connected to the unloading pump by a flexible steel hose. These fittings should be capped when not in use to prevent contaminants from entering the hydrogen peroxide storage system. Hydrogen peroxide railcars are not designed for pressure unloading, and this practice is not recommended.

Tank truck unloading connections are often of a non-standard size to ensure that other chemicals are not mistakenly unloaded into hydrogen peroxide systems. Extreme care must be taken in system design and operating practice to ensure that hydrogen peroxide in storage is not contaminated. Storage systems should be identified with labels that designate the UN TDG codes, product hazards, and NFPA ratings. The fill line connections should have similar placards, and bills of lading should be checked carefully prior to connection. The area around hydrogen peroxide unloading and storage areas, and especially within containment dikes, should be kept clear of combustible materials. In spite of these design precautions there have been examples of storage tanks being launched surprising distances due to the unloading of other chemicals into hydrogen peroxide storage tanks. The chemicals are typically the other common chemicals used in a bleach plant, i.e., sodium hydroxide and DTPA. Both of these chemicals are alkaline, and result in the sudden release of gas (and pressure) described in the previous section on 'Fire and Explosion Hazards'.

Storage tank design

Storage tanks should be located away from potential contaminants, with provision for suitable spill containment. It is recommended that storage tanks of hydrogen peroxide solutions, of 50% concentration or higher, be located out-of-doors to limit the high hazard potential to personnel and physical assets associated with decomposition in a tank located inside a building.

The materials of construction for storage tanks, suitable for most grades of hydrogen peroxide, are high purity aluminum, and 304 and 316 stainless steels (although 304L and 316L are recommended). The tanks are designed to be operated at atmospheric pressure. Tanks are equipped with a continuous filter vent to handle the generation of oxygen through the natural decomposition of hydrogen peroxide. Tanks are also equipped with a suitably sized top-mounted pressure-opening emergency release manway.

Hydrogen peroxide is not flammable, so the hazard of static charge build-up, due to droplet free-fall from a top discharge fill line is minimal. Nevertheless, it is often advisable to have the fill line extend below the liquid surface, terminating with a mixer/eductor nozzle, especially if the hydrogen peroxide is to be diluted in storage during the unloading process. Some means of siphon-breaking should be included in the design of those lines. All tank connections should be flanged.

Tanks should be equipped with a local level indication. A temperature monitoring system is recommended on tanks containing high strength hydrogen peroxide solutions. Temperature increase may be the first indication of product contamination. Monitoring algorithms, including temperature and rate of temperature increase, may provide alarms in sufficient time to investigate and remedy a contamination situation before it accelerates to the point of causing personal injury and damage to physical assets. A deluge system is recommended for storage of hydrogen peroxide solutions of greater than 60% concentration. Tanks and piping systems should be cleaned with detergent and passivated with an oxidizing acid prior to being put into service.

Piping systems

Pipe. All wetted surfaces must be made of materials that are compatible with hydrogen peroxide. **The hydrogen peroxide supplier should be consulted when making changes to hydrogen peroxide storage and handling systems.** 304L and 316L stainless steel is suitable for hydrogen peroxide service. Carbon steel and copper piping, and brass and bronze fittings must be avoided. Piping systems are preferably of butt-welded and flanged construction. Stainless steel bolting is desirable since carbon steel bolting and back flanges will rust, affording a source of possible contamination of the piping when flanges are opened. For low strength and low volume applications, stainless steel tubing and compression fittings are satisfactory. Polyethylene is compatible with hydrogen peroxide, but use in permanent systems should be avoided. Piping systems should be sloped to promote complete drainage when not in use.

Pressure relief. Hydrogen peroxide systems must be designed to avoid entrapment of hydrogen peroxide. It is normal for hydrogen peroxide to decompose at a very slow rate, so systems must be designed to prevent excess pressure build-up from oxygen evolution. The number of valves should be kept to a minimum, and pressure relief devices must be installed between valves, pumps, check valves, gauges, and wherever there is the potential for

pressurization due to hydrogen peroxide entrapment. The discharge of these safety relief devices should be directed in a safe manner, never back to bulk storage. Flanged ball valves are recommended for hydrogen peroxide service. The ball must be drilled in order to prevent pressure build-up in the valve cavity.

Hydrogen peroxide systems must be designed to prevent siphoning or back-flow of process fluids or water into hydrogen peroxide tanks. This can be done with appropriate engineering design, including redundant check valves, solenoid valves activated by liquid flow (or no-flow) sensors, etc. A method for ensuring that process and other product streams do not flow back into the hydrogen peroxide storage tank is the use of a (gravity) break tank. Hydrogen peroxide should not be returned to the storage tank.

Pump seals. A mechanical seal of stainless steel, with glass-filled polytetrafluoroethylene (PTFE) and ceramic (silicon carbide) faces, is recommended for centrifugal pumps. Metering pumps should have PTFE diaphragms or meshing gear and 304 or 316SS wetted parts.

Gaskets. Solid PTFE, PTFE impregnated with a variety of fillers, and PTFE envelope gaskets are acceptable for hydrogen peroxide service. Perfluoroelastomer or fluoroelastomer “O” rings are recommended.

Pump packing should not contain graphite, bronze, copper, lead, asbestos, lubricants, or other materials frequently used to modify or strengthen common packing. Threaded pipe fittings are not recommended. Most pipe dopes should be avoided. If threaded connections are required, use PTFE pipe joining tape and only those pipe sealants specifically recommended by the hydrogen peroxide supplier.

Gauges. Liquid pressure gauges should contain chlorotrifluoroethylene lubricating oil, similar specialty fluorinated lubricating oils, or similar inert liquids only. Silicone, mineral oils, and most other fluids are to be avoided. Bourdon tubes, with “dead ends,” should also be avoided.

Materials in pulp mill applications

The decomposition of hydrogen peroxide will be catalyzed by incompatible materials of construction in bleaching applications. Hydrogen peroxide reacts readily with organic materials in solutions. Therefore, chemical residual and organic carryover from previous bleaching stages can decrease the efficiency of hydrogen peroxide bleaching applications. These decomposition reactions are accelerated by alkali addition and increased temperature. Handbook data indicate significant corrosion effect of hydrogen peroxide on titanium in alkaline environments. This corrosion effect is inhibited by the presence of calcium and magnesium ions. Although caution must be taken when planning to refit hydrogen peroxide applications into bleaching stages designed for chlorine dioxide, with titanium process elements, practical experience has shown that titanium corrosion is not a serious issue at typical process conditions; even for totally chlorine free, TCF, bleaching.

Definition

Hydrogen peroxide, especially in higher concentrations, is a strong oxidant. Hydrogen peroxide is available commercially as aqueous solutions ranging from 3% concentration, for household antiseptic purposes, to concentration greater than 90%, for military purposes. In North America, hydrogen peroxide solutions of 50% and 70% concentration (some availability at 60% concentration) are delivered in bulk by tank truck and railcar. Hydrogen peroxide shipped at 70% concentration is normally diluted to 50% concentration during unloading, for safe storage. Hydrogen peroxide is primarily used as an oxidizing agent in the bleaching of pulp. However, it can also be used as a reducing agent, as in the preparation of chlorine dioxide. Other uses include destruction of total reduced sulfur (TRS), and a variety of environmental applications. Hydrogen peroxide is an inorganic peroxide, primarily used in pulp bleaching. Commonly, it is referred to as peroxide.

Material

Although pure hydrogen peroxide is very stable, many contaminants, even in very minute amounts, can catalyze its decomposition. Most standard peroxide grades are protected from excessive decomposition by the addition of stabilizers that control the effects of incidental metallic ion contaminants. Nevertheless, hydrogen peroxide solutions do decompose at a very slow rate under normal conditions and prolonged storage. Hydrogen peroxide becomes

unstable when heated or contaminated with heavy metals, such as iron, lead, manganese, cobalt, copper and its alloys, reducing agents, rust, dirt, or organic materials. It is not compatible with cyanides, hexavalent chromium compounds, nitric acid, and potassium permanganate.

Table 2 shows some of the physical and chemical properties of hydrogen peroxide at different concentrations.

Table 2. Properties

Chemical name	Hydrogen peroxide		
Chemical formula	H ₂ O ₂		
Molecular weight	34		
Physical state	Liquid		
Color	Clear, colorless, water white		
Odor	Slightly pungent		
Solubility in water	100%		
% Content (by weight) H ₂ O ₂	35	50	70
Active oxygen, weight %	16.5	23.5	32.9
Freezing point, °C	-33	-52	-40
°F	-27	-63	-40
Boiling point, °C @ 760 mm Hg	108	114	125
°F	226	237	258
Density, g/mL @ 20°C	1.13	1.20	1.29
lb/gallon @ 68°F	9.44	9.98	10.75
Viscosity, mPa·s @ 20°C	1.11	1.17	1.24
Viscosity mPa·s @ 0°C	1.81	1.87	1.94
Total vapor pressure, mm Hg @ 30°C	23	18	11
Heat of decomposition, Kcal/mole H ₂ O ₂	22.7	22.8	23.4
Heat of decomposition BTU/lb Sol'n @ 77°C	420	603	852
Volume expansion ratio @ 20°C, 760 mm Hg	700	1300	2500

Keywords

Hydrogen peroxide, Safety, Materials handling, Storage, Environments

Additional information

Effective date of issue: April 15, 2010

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