

13.7 MPa (140 kg/cm²) with 60–70% of the hydrogen feed selectively forming hydrogen peroxide.

Interest has continued in on-site manufacture of hydrogen peroxide from the elements, particularly for remote sites located considerable distances from world-scale anthraquinone processes. However, no commercial-scale direct combination plants have been constructed as of this writing.

Inorganic Methods. Before the development of electrolytic processes, hydrogen peroxide was manufactured solely from metal peroxides. Early methods based on barium peroxide, obtained by air-roasting barium oxide, used dilute sulfuric or phosphoric acid to form hydrogen peroxide in 3–8% concentration and the corresponding insoluble barium salt. More recent patents propose acidification with carbon dioxide and calcination of the by-product barium carbonate to the oxide for recycle.

Acid ion-exchange resins have been proposed for sodium peroxide-based processes. Alternatively, use of an acid and a water-insoluble organic has been suggested to avoid the hydrogen peroxide recovery problems otherwise encountered in using the more soluble sodium salts. A cyclic synthesis of hydrogen peroxide and hydrazine has been proposed, using an alkali metal and alkali metal peroxide as the common electron donor-acceptor pair (122).

PURIFICATION AND CONCENTRATION

The crude product from any hydrogen peroxide process can be used as such, but commercial grades are further purified, concentrated, and stabilized. Crude products from organic-based processes contain organic impurities which affect color, odor, surface tension, and stability, and are normally pretreated to reduce the carbon content before final purification and concentration by various distillation methods.

Procedures include solvent extraction followed by optional air stripping to remove residual solvent and treatment with synthetic resins, polyethylene, waxes, carbon, and aluminum and magnesium hydroxides and alumina. Active ion-exchange resins have been used to remove both metallic and acidic impurities. More recent patented methods for purifying crude hydrogen peroxide include further contact with an aromatic gasoline in static mixers, followed by a series of coalescing steps to effect phase separation (123), passing the solution through columns packed with halogen-containing porous styrene-divinylbenzene copolymer resin (124), and passing the solution through an anion-exchange resin which has been pretreated with various chelating agents to remove metal ions and organics (125). The amount of nonvolatile organic impurities present in extracted crude hydrogen peroxide from anthrahydroquinone autoxidation processes may be reduced by washing the working solution either continuously or batchwise with water or dilute caustic and discarding the washings.

Concentration of hydrogen peroxide prepared by the autoxidation processes can be carried out safely and conveniently by distillation at reduced pressure. The distillations include liquid or vapor feed to columns consisting of stripping and rectification; vapor feed to columns consisting of rectification only, with or without reboil; or combinations involving both liquid and vapor feeds. General procedures analogous to those developed for concentrating electrolytic process

product are used to alleviate yield problems and assure safe operations with heating and concentrating hydrogen peroxide with organic materials.

The hydrogen peroxide is concentrated during distillation and is usually marketed as a 50–70-wt % product. It can be concentrated to higher strengths by redistillation or through freeze–melt techniques. A procedure for concentrating very dilute solutions via formation of organic nitrogen-compound peroxyhydrates has been patented (126). Other patents describe the production of a nearly water-free organic solution of hydrogen peroxide by mixing aqueous hydrogen peroxide with alkyl or cycloalkyl esters of saturated aliphatic carboxylic acids and separating by azeotropic removal of water (127), and production of water-free hydrogen peroxide for nuclear hydroxylation of phenols by mixing the phenol with 70-wt % aqueous hydrogen peroxide and dichloromethane followed by removing water and the dichloromethane through azeotropic distillation (128).

Economic Aspects

U.S. production of hydrogen peroxide is shown in Table 6 (129). The driving influence on H₂O₂ capacity and production has come from the pulp and paper sector, as this industry converts from chlorine bleaching and the attendant dioxin and chloroform formation to the environmentally more benign peroxide chemistry. Since the 1970s, U.S. and North American production has increased significantly owing to start-up of nine new plants and expansions to existing plants. Table 7 lists all North American manufacturers and their estimated capacities.

Total U.S., North American, and both Americas capacities for 1993, as estimated from commissioning notices and public announcements by the manufacturers, are 355–360 × 10³, 505–515 × 10³, and 555–565 × 10³ t/yr,

Table 6. U.S. Production of Hydrogen Peroxide^{a,b}

Year	Production, t × 10 ³
1960	26.0
1970	55.7
1980	105.8
1982	98.5
1984	126.3
1986	138.0
1988	161.0
1990	216.6
1992	271.8
1994	360 ^c
1996	470 ^c
1998	580 ^c
2000	700 ^c

^aRef. 129. Courtesy U.S. Department of Commerce, Bureau of the Census.

^b100% basis.

^cValue is estimated.

Table 7. U.S. and North American Manufacturers of Hydrogen Peroxide^{a,b}

Manufacturer	Site	Capacity, t $\times 10^3$ /yr	
		U.S.	N.A.
Chempro ^c	Becancour, P.Q.		30
Degussa ^d	Theodore, Ala.	75	75
Du Pont	Memphis, Tenn.	64	64
	Maitland, Ont.		36
	Gibbons, Alta.		36
Eka Nobel	Columbus, Miss.	35	35
FMC Corp.	Spring Hill, W.Va.	38	38
	Bayport, Tex.	43	43
	Prince George, B.C.		41
	Santa Clara, Mexico		10
Fort Howard ^e	Muskogee, Okla.	3	3
Solvay Interlox	Deer Park, Tex.	50	50
	Longview, Wash.	50	50
Total		358	511 ^f

^a100% basis.^bAll producers use the alkylanthraquinone autoxidation process except where noted.^cChempro (Oxysynthese) is considering building a 20×10^3 t/yr plant at Portland, Oreg. or Tacoma, Wash. Estimated start-up in 1995 or 1996.^dDegussa is considering adding a 50×10^3 t/yr plant in North America in the 1997–1998 time frame.^eUses the Huron-Dow process.^fKemira has announced plans for a 34 kt/yr plant at a site in the U.S. or Canada, with estimated start-up to be in late 1995.

respectively. Worldwide capacity is estimated at $1.8\text{--}1.9 \times 10^6$ t/yr, of which one-half is in Europe.

The January 1993 price for technical-grade H_2O_2 is shown in Table 8. Because of overcapacity and slower growth during the mid-1991 through 1993 recession period, prices, especially to large accounts, had declined significantly as the manufacturers bid for market share to maintain volume. Somewhat higher pricing reflected a more typical marketplace with increasing demand for the last half of 1994 when prices rose about \$0.05/kg. Capacity increases are forecast to be required starting in the 1995–1996 period.

Table 8. 1993 Technical-Grade Hydrogen Peroxide Price Schedule^a

Concentration, wt %	Price, \$/kg	
	Commodity basis	100% basis
35	0.541	1.543
50	0.755	1.510
	1.091 ^c	2.182 ^c
70	1.052	1.503

^aRef. 130.^bFob nearest producer, material in tank cars or trailers unless otherwise noted.^cMaterial in 0.208-m³ drums.

Specifications and Standards

Aqueous hydrogen peroxide is sold in grades ranging from 3 to 86 wt %, most often containing 35, 50, and 70 wt % H_2O_2 . In the United States, the only use for 86% H_2O_2 (ca 1994) is for attitude (flight path behavior) control of space craft, etc. This minor amount is imported.

The 3–6% H_2O_2 solutions for cosmetic and medicinal use are obtained by diluting a more concentrated grade, usually with the addition of extra stabilizer. The 3% grade has a USP specification (131) (see COSMETICS).

The 30% reagent-grade hydrogen peroxide is purer than the industrial grades, is covered by ACS reagent specification, and is used as a laboratory reagent and in some specialty uses (see FINE CHEMICALS). Several grades are also marketed for electronics use and thus have exceptionally low impurity levels. Some of these latter contain very little or no stabilizers (see ELECTRONIC MATERIALS).

The 35 and 50% H_2O_2 concentrations are used for most industrial applications. The standard grades contain sufficient stabilizers to ensure safety. Grades having lower stabilizer content and evaporative residue are available for specialty uses and for aseptic cleansing of containers in food processing and marketing.

The 70% H_2O_2 concentration is used in chemical processing and for certain organic oxidations. Dilution-grade 70% H_2O_2 is stabilized to allow for later dilution to 35–50% storage concentration.

Concentrations over 8 wt % are classified as corrosive liquids by the Department of Transportation (DOT). The Bureau of Explosives regulation (132) classifies all solutions containing 20 wt % and greater as oxidizers and corrosives. The product containers must have identifying labels (drums) or placards (tank cars, tank trailers) indicating that the contents are an oxidizer and corrosive material, UN 2014 or UN 2015. Bills of lading must also be so identified. Tank cars and tank trailers are constructed from high purity aluminum or 300 series stainless steel.

Up to 52 wt % is permitted to be shipped in uv light-protected polyethylene drums. Double headed aluminum drums are permitted for 70% shipments but have not been used for some years.

Analytical and Test Methods

Analytical methods for the qualitative or quantitative determination of hydrogen peroxide are based on its redox or physical properties. Aqueous hydrogen peroxide solutions are usually titrated with potassium permanganate, a strong oxidizer capable of oxidizing many organic materials. Therefore, titrations of hydrogen peroxide in the presence of organic matter may be biased on the high side. Colorimetric and specific procedures are available (133,134), as are other procedures (impurities and stability) (131,135–137).

High pressure liquid chromatography (qv) (138) and coulometry can be used to detect and quantify anthraquinones and their derivatives in a hydrogen peroxide process working solution.

Health and Safety Factors

Hydrogen peroxide, especially in high concentrations, is a high energy material and a strong oxidant. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) reportable spill quantity for greater than 52% hydrogen peroxide is 1 lb (0.45 kg). It is considered an acute, reactive, and pressure hazard under Superfund and Reauthorization Amendments (SARA) Title III. However, it can be handled safely if proper personal protective equipment is worn and the proper precautions are observed (136). Some generally applicable control measures and precautions for handling hydrogen peroxide include the use of adequate ventilation to keep airborne concentrations below exposure limits, 8 h TWA, 1.4 mg/m³, use of overall chemical splash goggles in combination with a full-length face shield if spraying is a potential occurrence, use of a NIOSH/MSHA-approved respirator if airborne concentration can exceed exposure limits, and use of neoprene or other impervious and compatible gloves. Other clothing items such as impervious aprons, pants, jackets, hoods, boots, and totally encapsulating chemical suits with breathable air supply should be available for use as necessary. Leather (qv) gloves and shoes (uppers or soles) should not be worn because these can ignite within three minutes following contact with 50% hydrogen peroxide or greater. Cotton (qv) items should be avoided for the same reason.

Health and Physiological Effects. Hydrogen peroxide is irritating to the skin, eyes, and mucous membranes. However, low concentrations (3–6%) are used in medicinal and cosmetic applications. Precautions should be taken with higher strengths to prevent inhalation of the vapors, ingestion, or splashing into the eyes. In case of accidental contact with hydrogen peroxide, the affected area should be washed immediately with excess water.

Tests using rabbits indicate that transition from an eye irritant to a corrodant occurs at about 10% H₂O₂. At strengths 10% and above, a splash in the eye can cause severe ulceration and irreversible corneal damage unless flushed immediately with water. Inhalation of concentrated vapors can cause irritation of the nose and throat with chest discomfort, cough, difficult breathing, and shortness of breath. Ingestion can cause irritation of the gastrointestinal tract with pain, bleeding, and, distension of the stomach and esophagus, resulting from the liberation of oxygen. Gross overexposure by ingestion may be fatal. No component in industrial hydrogen peroxide solutions is listed as a carcinogen.

Decomposition and Explosive Hazards. The principal hazards associated with hydrogen peroxide include (1) decomposition of H₂O₂ with unrelieved pressure buildup; (2) spontaneous combustion of mixtures of H₂O₂ and readily oxidizable material; (3) inadvertent admission of incompatible materials into a tank containing H₂O₂ or vice versa; (4) decomposition of H₂O₂ to form an oxygen-rich vapor phase; (5) deflagration, detonation of a condensed-phase mixture of H₂O₂ and organics initiated by shock or thermal effects; and (6) explosive reaction of H₂O₂ vapor.

Hydrogen peroxide decomposes with the generation of heat and oxygen. The decomposition is promoted by catalytic impurities and its rate increases by a factor of about 2.2–2.3 for each 10°C rise in temperature over the range of 20–100°C (136). If the system is contained, and decomposition starts, the

temperature increases and the volume of oxygen released increases the pressure so that the rate becomes self-accelerating. Pressures reaching several thousand kPa are achievable and ruptures of tanks, valves, piping, etc., occur. The hazard from decomposition increases with increasing concentration because of relative gas generation. Aqueous solutions containing more than 65 wt % can totally vaporize by adiabatically absorbing the heat of decomposition, resulting in much higher system temperature. For example, under ideal adiabatic conditions 1 m³ of 70% H₂O₂ can generate 2545 m³ of gas and reach 233°C, but 1 m³ of 50% H₂O₂ can generate 1280 m³ of gas at close to 100°C. Thus it is imperative that decomposition be controlled for safe storage and handling. Containers and equipment must be constructed from compatible materials, be adequately vented, and maintained free of contaminants (136). Drums and other portable shipping containers should preferably be stored or shipped alone; so, in the event of an accident, the H₂O₂ cannot mix with common combustibles or flammable liquids and gases.

In organic processes, such as organic oxidations using high strength hydrogen peroxide, decomposition can result in an oxygen-enriched organic vapor space. The higher oxygen content has little effect on the lower explosive limit but significantly lowers the required ignition energy. Another potential is the formation of a condensed-phase organic–hydrogen peroxide mixture at or near the stoichiometric ratio. Such a stoichiometric mixture can deflagrate or detonate if the mixing is sufficient to approach emulsification and sufficient external energy in the form of heat or shock is added. The external energy requirement is usually quite large, so condensed-phase explosions would be rare. A vapor-phase explosion could possibly propagate to the condensed phase by this mechanism.

Many inorganic reagents are incompatible with hydrogen peroxide. Among these are nitric (139) and sulfuric acid (67) above certain concentrations, and mercurous oxide (140), which can react with explosive violence. Many organic compounds can form unstable peroxides during reaction with hydrogen peroxide. The most frequent explosive rupture incidents involve strong bases and hydrogen peroxide. Hydrogen peroxide is less stable at high pH; thus the inadvertent admission of caustic into a tank of hydrogen peroxide could result in runaway decomposition and tank destruction. A review of each installation should be made to assure that design features are in place so as to avoid such contamination. A thorough safety review is a must for all new use applications, and explosion testing may be required.

Hydrogen peroxide concentrations of 35% and above may, and 50% and above do, cause spontaneous combustion of dry grasses, wood, and leaves. Spills of concentrated hydrogen peroxide should be diluted with excess amounts of water immediately. Practically all solid combustible materials contain sufficient quantities of catalytic impurities to rapidly decompose hydrogen peroxide, especially at 70% concentration and above.

It is impossible to obtain a propagating detonation of commercial hydrogen peroxide at ambient temperature under normal conditions of storage (141). Concentrations of 86% and above can detonate, but only if subject to a high energy source. In the vapor phase, explosions occur under certain conditions. The lower explosive limit at atmospheric pressure is about 26 mol % H₂O₂, which is close to the equilibrium vapor concentration above boiling 75% hydrogen peroxide.

Explosive vapor concentration above 90% hydrogen peroxide is avoided by maintaining its temperature below ca 115°C. Under vacuum, the lower explosive concentration limit increases, which provides a safe route to concentrating by fractionation.

Uses

Hydrogen peroxide is used in many applications throughout a wide variety of industries. The principal use areas are shown in Table 9. Most are based on the oxidizing properties of hydrogen peroxide. Some are derived from substitution, decomposition, or the formation of perhydrates.

Bleaching. The largest single use for hydrogen peroxide in the United States and North America is wood pulp bleaching, but consumption for the manufacture of chemicals, environmental applications, and for bleaching cotton (qv), wool (qv), and other textiles (qv) is significant.

Environmental concerns have led the pulp and paper industry to turn to alkaline solutions of hydrogen peroxide as a replacement for chlorine and, in some cases, for hypochlorite and chlorine dioxide in bleaching applications (143–152). These include mechanical and kraft pulp bleaching and deinking (153) of recycled paper (see RECYCLING, PAPER). Kraft pulp bleaching is the largest application in the United States, where hydrogen peroxide has been used in the final bleaching sequence to obtain very white product having maximum color stability. A variety of bleaching sequences are in use and hydrogen peroxide is now being used in a multiple number of the steps. The annual growth rate of hydrogen peroxide in this industry through the early 1990s has been about 12–16%. Future growth rate is expected to depend on how fast and how far the pulp manufacturers move toward chlorine-free bleaching. Most of the hydrogen peroxide use in Canada is at more recently constructed large chemithermal mechanical pulp (CTMP) mills. These modern mills can consume 5000–10,000 t/yr of hydrogen peroxide.

The bleaching of cotton textiles was once the single largest use for hydrogen peroxide, with lesser quantities used to bleach wool, silk (qv), cotton–synthetic blends and some vegetable and animal fibers (qv). The stabilized alkaline hydrogen peroxide bleaching of cotton and cotton blend fabrics is done in continuous processes. A primary advantage for hydrogen peroxide in this industry is that

Table 9. Usage of Hydrogen Peroxide in North America

Use area	H ₂ O ₂ , t × 10 ³ /yr ^a					
	1978		1980		1991	
pulp and paper	10.2	(10.0)	31.4	(29.1)	144	(49.1)
textiles	25.5	(25.0)	17.1	(15.8)	24	(8.2)
chemicals ^b	28.6	(28.0)	30.0	(27.7)	44	(15.0)
environmental	10.2	(10.0)	18.1	(16.7)	43	(14.7)
all others	27.5	(27.0)	11.6	(10.7)	38	(13.0)
Total	100.2		108.2^c		293.0^c	

^aValues in parentheses are percentages.

^bIncludes plasticizers.

^cRef. 142.

it has no effect on many modern dyes. It has been estimated that 85% of all cotton fabrics are bleached with hydrogen peroxide. Added to its other advantages, hydrogen peroxide is a nonpolluting oxidant which is of significant and increasing importance.

Hydrogen peroxide is also used to bleach solid surfaces such as wood (qv) or linoleum, and to improve the color of oils and waxes.

Environmental Applications. Hydrogen peroxide is an ecologically desirable pollution-control agent because it yields only water or oxygen on decomposition. It has been used in increasingly greater amounts to convert domestic and industrial effluents to an environmentally compatible state (see WASTES, INDUSTRIAL; WATER).

Hydrogen peroxide is used to treat wastewaters (144–161) and sewage effluents, and to control hydrogen sulfide generated by the anaerobic reaction of raw sewage in sewer lines or collection points, thus minimizing or eliminating disagreeable odors. It has been proposed as a supplemental oxygen source for overloaded activated sludge plants, and reportedly controls denitrification in secondary clarifiers and improves bulking conditions. It also has been used as a flotation (qv) assistant (162–163). Activated sludge-treated wastewater chemical oxygen demand (COD) values have been decreased using hydrogen peroxide with an iron salt catalyst (162–163). It has also been generated *in situ* in wastewater reservoirs by the cathodic reduction of oxygen (164).

Industrial liquid and gaseous detoxification systems based on hydrogen peroxide have been developed (149,150,157–161,165–173). H₂O₂ is reported to be especially suitable for cyanide-containing wastes having high free cyanide concentration or those also containing organic impurities (173). Hydrogen peroxide systems with formaldehyde (169), copper salt, water glass, or iodide and silver ion added to increase reaction rates and efficiency have been described or patented. A method and apparatus for cyanide destruction by monoperoxy-sulfuric acid generated as needed from hydrogen peroxide and sulfuric acid has been claimed. Procedures have been described for removing nitrite ion from waste streams and for recovering arsenic acid or arsenates. Similar procedures using hydrogen peroxide have been developed for detoxifying organic pollutants (168), including formaldehyde (qv), phenol mixtures (169), acetic acid, lignin sugars, surfactants (qv), amines and glycol ethers (159–161), and sulfur derivatives (170–172). Most recently, there has been interest in using hydrogen peroxide as an *in situ* oxygen source for maintaining aerobic bacteria needed for the bioremediation of organics, eg, gasoline that has leaked into the soil from underground tanks.

Toxic or malodorous pollutants can be removed from industrial gas streams by reaction with hydrogen peroxide (174,175). Many liquid-phase methods have been patented for the removal of NO_x gases (138,142,174,176–178), sulfur dioxide, reduced sulfur compounds, amines (154,171,172), and phenols (169). Other effluent treatments include the reduction of biological oxygen demand (BOD) and COD, color, odor (142,179,180), and chlorine concentration.

Chemical Uses. Hydrogen peroxide or a peroxycarboxylic acid made from H₂O₂ is used in the manufacture of a number of organic and inorganic chemicals (181). The electrophilic epoxidation of soybean oil, linseed oil, and related unsaturated esters with peroxyformic or peroxyacetic acid formed *in situ* from