HYDROGEN PEROXIDE

1. Introduction

Hydrogen peroxide [7722-84-1], H_2O_2, mol wt 34.016, is a strong oxidizing agent commercially available in aqueous solution over a wide range of concentrations. It is a weakly acidic, nearly colorless clear liquid that is miscible with water in all proportions. The atoms are covalently bound in a nonpolar H−O−O−H structure having association (hydrogen bonding) somewhat less than that found in water. Thenard discovered hydrogen peroxide in 1818, producing it by the reaction of dilute acids on barium peroxide BaO_2. Hydrogen peroxide has been an article of commerce since the midnineteenth century, initially as unstable, weak (3–7%) solutions. In 1900 the worldwide production was about 2000 toney H_2O_2 on a 100% basis (1). Its scale of manufacture and use has increased markedly since 1905, when electrolytic processes were developed in Europe (Degussa Weissenstein process, 1905–1908; Electrochemical Works/Munich, 1910; Riedel de Haen, 1924). Introduced to the United States (FMC/Buffalo Electrochemical Co., Buffalo, N.Y., 1925; Degussa/Roessler & Hasslacher Co., Niagara Falls, N.Y., 1926; DuPont, 1930) and development of industrial bleach applications increased the world production in 1950 to 30,000 t of H_2O_2 on an 100% basis. Today it is manufactured primarily in large, strategically located anthraquinone autoxidation processes. Its many uses include bleaching wood pulp and textiles, preparing other peroxygen compounds, and serving as a nonpolluting oxidizing agent (see also PEROXIDES AND PEROXIDES COMPOUNDS, INORGANIC; PEROXIDES AND PEROXIDES COMPOUNDS, ORGANIC).

2. Occurrence

H_2O_2 is ubiquitous in the environment. In surface water H_2O_2 is generally produced by photochemical processes. Surface water levels range from 0.34 to 109 $\mu g/m^3$. In the atmosphere H_2O_2 is generated by photolysis of O_3 (2) or aldehydes (3). An overview of of H_2O_2 levels in the environment is given in Reference 4.

H_2O_2 also occurs is living organisms. Examples are blue-green algae (5) and the bombardier beetle, *Brachinus crepitans* (L.), which produces H_2O_2 solutions of up to 28.5% (6).

H_2O_2 has also been detected in the exhale breath of humans at concentrations of 300–1000 $\mu g/m^3$ (7).

3. Physical Properties

Hydrogen peroxide is a clear, colorless liquid that is miscible with water in all proportions. Hydrogen peroxide and concentrated aqueous solutions >65% are soluble in a variety of organic solvents such as carboxylic esters. Hydrogen peroxide and water do not form an azeotropic mixture and in theory can be separated by distillation. In practice 100 wt% hydrogen peroxide is obtained by fractional crystallization of 85–90 wt% aqueous solutions. The most important physical properties of pure hydrogen peroxide and aqueous H_2O_2 solutions are summarized in Tables 1 and 2.

Numerous other physical property data appear in the literature, including approximation coefficients for free-energy function calculations, coefficients of diffusion, partition coefficients, spectroscopic studies, thermodynamic properties, Henry's law constant, vapor density, and third-law entropy (8–14).

In aqueous solution the hydrogen bonds (association) between water and H_2O_2 molecules are appreciably more stable than those between molecules of the individual species do. This increase in attraction forces is evidenced from many properties such as heat of mixing, vapor pressure, viscosity, and dielectric constant. Physical constants of H_2O_2 and H_2O are compared in Table 3.

Mathematical correlations for vapor pressure, surface tension, heat of vaporization, heat capacity, liquid density, thermal conductivity, and viscosity values have been established for the 0–450°C range, as well as heat and free energy of formation, vapor heat capacity, thermal conductivity, and viscosity values for the 0–1200°C range (15).

4. Chemical Properties

4.1. Dissociation. Hydrogen peroxide is a weak acid, having a pK_a of 11.75 at 20°C.

$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^- \tag{1}$$

Dissociation of the second proton is insignificant. The pH of its aqueous solutions can be measured reproducibly with a glass electrode, but a correction dependent on the concentration must be added to obtain the true pH value. Correction values for the most common commercial solutions are listed in Table 4. The type and amount of stabilizers added can affect the apparent pH of commercial product solutions.

4.2. Decomposition. The decomposition of hydrogen peroxide may be homogeneous or heterogeneous and can occur in the vapor or the condensed phase. Although there is considerable evidence that the decomposition occurs as a chain reaction involving free radicals, the products of the decomposition are water and oxygen gas. For the decomposition of pure hydrogen peroxide at 298.16 K (Eq. 2), $\Delta H = -105.26$ kJ/mol when H_2O_2 is in the vapor state, and $\Delta H = -98.20$ kJ/mol when H_2O_2 is in the liquid phase.

$$2\,H_2O_2 \rightarrow H_2O + O_2 \tag{2}$$

The mechanism and rate of hydrogen peroxide decomposition depend on many factors, including temperature, pH, and presence or absence of a catalyst (16–19), such as metal ions, oxides, and hydroxides. Some common metal ions that actively support homogeneous catalysis of the decomposition include ferrous, ferric, cuprous, cupric, chromate, dichromate, molybdate, tungstate, and vanadate. For combinations, such as iron and copper together, the decomposition rate is greater than for the individual components. A key factor is that copper reduces iron and thus assures a greater concentration of the more active ferrous ions. Other combinations yield similar results. Catalase enzyme and the halide ions except for fluoride also can be active. Active common catalytic surfaces include copper, mild steel, iron, silver, palladium, platinum, and oxides of iron, lead, nickel, manganese, copper, mercury, and activated carbon.

The stability of pure hydrogen peroxide solutions increases with increasing concentration and peaks at pH 3.5–4.5. The decomposition rate of ultrapure hydrogen peroxide increases 2.2–2.3-fold for each 10 K rise in temperature from ambient to about 100°C. This approximates an Arrhenius-type response with activation energy of about 58 kJ/mol (13.9 kcal/mol). However, an increase of the decomposition rate as low as 1.6-fold for each 10 K rise has been noted for impure, unstabilized solutions.

Various purification steps during manufacture, use of clean passive equipment, control of contaminants, and the addition of stabilizers minimize the decomposition of aqueous hydrogen peroxide. The decomposition is zeroth-order with respect to hydrogen peroxide concentration.

4.3. Free-Radical Formation. Hydrogen peroxide can react directly or after it has first ionized or dissociated into free radicals. Often, the reaction mechanism is extremely complex and may involve catalysis. Enhancement of the oxidizing action of H_2O_2 is accomplished in the presence of metal catalysts (20). The redox system Fe(II)–Fe(III) is the most widely used catalyst, which, in combination with hydrogen peroxide, is known as *Fenton's reagent* (21,22). In 1894, H.J. H. Fenton discovered that ferrous ion promoted the oxidation of maleic acid by H_2O_2. Subsequent studies showed that this combination is able to oxidize a variety of organic compounds, but it was not until 1934 that the mechanism of the reaction was elucidated and the hydroxyl radical was identified as one of the reactive species (22). The hydroxyl radical is one of the strongest oxidants (Table 5). Hydrogen peroxide can form free radicals by homolytic cleavage of either an O–H or the O–O bond.

$$\mathrm{HOOH} \rightarrow \mathrm{H}^{\cdot} + \mathrm{OOH}^{\cdot} \qquad \Delta\mathrm{H} = 380\,\mathrm{kJ/mol} \tag{3}$$

$$\mathrm{HOOH} \rightarrow 2\,\mathrm{OH}^{\cdot} \qquad \Delta\mathrm{H} = 210\,\mathrm{kJ/mol} \tag{4}$$

Equation 3 predominates in uncatalyzed vapor-phase decomposition and photochemically initiated reactions. In catalytic reactions, and especially in solution, the nature of the reactants determines which reaction is predominant.

Fenton chemistry is dependent on the formation of free radicals.

$$\begin{aligned} \mathrm{Fe}^{2+} + \mathrm{H_2O_2} &\rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-} + \mathrm{OH}^{\cdot} \\ \mathrm{Fe}^{3+} + \mathrm{H_2O_2} &\rightarrow \mathrm{Fe}^{2+} + \mathrm{OOH}^{\cdot} + \mathrm{H}^{+} \end{aligned} \tag{5}$$

The radicals are then involved in oxidation reactions such as formation of ketones (qv) from alcohols. Similar reactions are finding commercial application in the treatment of wastestreams (see also section on environmental applications, below). These reactions normally are conducted in an aqueous acid medium at pH00 1–4 to minimize the catalytic decomposition of the hydrogen peroxide. More information on metal and metal oxide–catalyzed oxidation reactions (Milas' oxidations) is available (16,20–22) (see also PHOTOCHEMICAL TECHNOLOGY, PHOTOCATALYSIS).

4.4. Stabilization. Pure hydrogen peroxide solutions are relatively stable and can be stored for extended periods in clean passive containers. Commercial solutions, however, invariably contain or may be exposed to varying amounts of catalytic impurities and must therefore contain reagents that deactivate these impurities, either by adsorption (qv) or through formation of complexes (see CHELATING AGENTS). For example, sodium pyrophosphate $Na_2H_2P_2O_7$, added to acidic hydrogen peroxide solutions, acts as a complexing agent, whereas sodium stannate trihydrate $Na_2SnO_3 \cdot 3\,H_2O$, forms protective colloids (qv). Alkaline solutions of hydrogen peroxide are inherently less stable than acidic solutions, and often magnesium or silicate ions are added to alkaline solutions to form soluble or colloidal compounds that deactivate tramp metal ions. Additionally, the use of amine-substituted organophosphonic acids or their alkali metal salts for stabilizing weak hydrogen peroxide solutions (0.01–5.0%) in the pH range of 7–12.5 has been patented (23).

Many stabilizer systems have been tailored to a particular industry need or for particular areas where dilution water quality is poor. These grades are heavily stabilized and may contain organic sequestering agents, such as stannate, phosphates, and nitrate ions, so that the weak solutions produced by dilution from hard water retain acceptable stability. The nitrate is not a stabilizer, but it inhibits corrosion of aluminium storage tanks by chloride ion.

Several patents (24–26) claim that adding small amounts of organic sequestering agents to aqueous hydrogen peroxide solutions containing normal stabilizers, such as stannates and phosphates, improves the resistance against polyvalent metal cation-induced decomposition. Other patented stabilizer packages include combinations of organic compounds and organometallic salts with or without stannates and phosphates (27–34).

Special hydrogen peroxide stabilizer packages have been tailored for uses such as metal etching, chemical synthesis, detergents, cosmetics, food processing, cleaning high-capacity semiconductor chips, and other critical electronic components for the computer industry (see SEMICONDUCTORS). Electronic grades require extremely low metal ion content and, in some cases, the use of all-organic stabilizers (35–41) is cited. Some very pure, unstabilized 30% hydrogen peroxide containing <1 ppb of total metal ions has reportedly been used in this market. Because container corrosion would be a source of metal ion contamination, the containers are either special glass or are lined.

4.5. Molecular Addition. Oxyacid salts, metal peroxides, nitrogen compounds, and others form crystalline peroxohydrates in the presence of hydrogen peroxide. When dissolved in water, the peroxohydrates react as solutions of their components. The peroxohydrates formed from sodium carbonate and urea are commercially available. Examples of peroxohydrates can be found in the literature (42,43).

Sodium perborate tetrahydrate [10486-00-7] is formed from hydrogen peroxide and sodium borate [1303-96-4] and, although cited often as an example of a peroxohydrate, has been shown to be a true peroxo compound, disodium-di-μ-peroxo-bis(dihydroxoborate) hexahydrate (44,45). The peroxoborate salts are a key bleaching ingredient in laundry detergent formulations (see BLEACHING AGENTS).

4.6. Substitution. A variety of peroxygen compounds can be formed through substitution reactions of hydrogen peroxide with organic reagents. These compounds are commercially useful as catalysts for polymerization reactions and oxidizing agents for a number of specialized reactions. The reactant and principal product of such reactions include alkylating agents (ie, alkylhydroperoxides), carboxylic and peroxy acids, acid anhydrides or chlorides (ie, diacyl peroxides), and ketones and ketone peroxides. These derivatives are considerably more hazardous than hydrogen peroxide and should be handled with extreme care, according to manufacturer instructions.

Inorganic peroxygen compounds can be prepared through similar reactions with inorganic reagents. Alkaline-earth metal peroxides are prepared from hydrogen peroxide and the corresponding hydroxide, and monoperoxosulfuric acid is prepared by reacting hydrogen peroxide and sulfur trioxide or sulfuric acid (see PEROXIDE AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES).

4.7. Oxidation. Hydrogen peroxide is a strong oxidant. Most of its uses and those of its derivatives depend on this property. Depending on the pH, the following redox equations can be formulated:

$$\mathrm{H_2O_2} + 2\,\mathrm{H}^+ + 2\,e^- \rightarrow 2\,\mathrm{H_2O} \quad \mathrm{E_0(pH0)} = +1.80\,\mathrm{V} \tag{6}$$

$$\mathrm{H_2O_2} + 2\,e^- \rightarrow 2\,\mathrm{OH}^- \quad \mathrm{E_0(pH14)} = +0.87\,\mathrm{V} \tag{7}$$

Hydrogen peroxide oxidizes a wide variety of inorganic compounds. Examples are given in Table 6. The rate of these reactions may be quite slow or so fast that the reaction occurs on a reactive shock wave. The mechanisms of these reactions are varied and dependent on the reductive substrate, the reaction conditions and catalysis. Specific reactions are discussed in several publications (20,21,47–50).

Numerous oxidation reactions of organic molecules with H_2O_2 are also known from the literature (20,51–53).

Examples are the oxidation of mercaptans to disulfides (eq. 8), thioethers to sulfoxides or sulfones (eqs. 9 and 10), thiourea to formamidine sulfinic acid (eq. 11), ketones to carboxylic acid esters (Baeyer–Villinger reaction; eq. 12), and primary amines to the corresponding oximes (eq. 13). Interesting is the oxidation of formaldehyde, which yields formic acid and hydrogen gas (eq. 14).

$$\mathrm{R-SH} + \mathrm{H_2O_2} \rightarrow \mathrm{R-S-S-R} + 2\,\mathrm{H_2O} \tag{8}$$

$$\mathrm{R-S-R} + \mathrm{H_2O_2} \rightarrow \mathrm{R-S(O)-R} + \mathrm{H_2O} \tag{9}$$

$$\mathrm{R-S-R} + 2\,\mathrm{H_2O_2} \rightarrow \mathrm{R-S(O_2)-R} + 2\,\mathrm{H_2O} \tag{10}$$

$$\mathrm{NH_2-C(S)-NH_2} + \mathrm{H_2O_2} \rightarrow \mathrm{NH=C(SO_2H)-NH_2} \tag{11}$$

$$\mathrm{R-CO-R} + \mathrm{H_2O_2} \rightarrow \mathrm{R-C(O)OR} + \mathrm{H_2O} \tag{12}$$

$$R - CH_2 - NH_2 + H_2O_2 \rightarrow R - CH = N = OH + H_2O \qquad (13)$$

$$2\,CH_2O + H_2O_2 \rightarrow 2\,HC(O)OH + H_2 \qquad (14)$$

4.8. Reduction. Hydrogen peroxide reduces stronger oxidizing agents (see examples in Table 7) such as sodium hypochlorite, potassium permanganate, and ceric sulfate. The last two are used for the volumetric determination of hydrogen peroxide. The ability of hydrogen peroxide to reduce hypochlorite is the basis for the use of H_2O_2 in treatment for industrial wastestreams (see WASTES, INDUSTRIAL) containing hypochlorite or in electrolytic production processes for chlorine/caustic or sodium chlorate to remove the corrosive and electrode/membrane damaging hypochlorite.

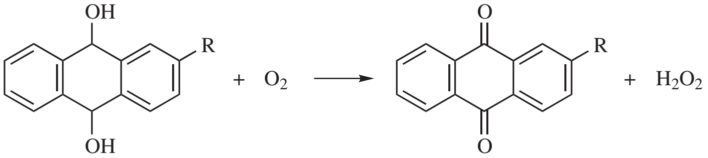
4.9. Antimicrobial Properties. Hydrogen peroxide exhibits good bacteriostatic at 20–40 ppm (54), but only moderate bactericidal properties. High concentrations (0.1–3%) and/or high temperatures (up to 80°C) are required to get good kill rates for bacteria, yeasts, and viruses. An overview on the antimicrobial properties of H_2O_2 is given in Reference 55.

5. Manufacture

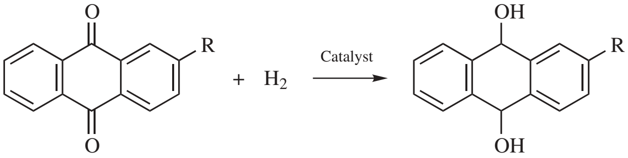
Hydrogen peroxide is composed of equimolar amounts of hydrogen and oxygen and can be formed directly by catalytically combining the gaseous elements. It can also be formed from compounds that contain the peroxy group; from water and oxygen by thermal, photochemical, electrochemical, or similar processes; and by the uncatalyzed reaction of molecular oxygen with appropriate hydrogen-containing species. It has been manufactured commercially by processes based on the reaction of barium peroxide or sodium peroxide with an acid; the electrolysis of sulfuric acid and related compounds; the autoxidation of 2-alkylanthrachinones, isopropyl alcohol, and hydrazobenzene; and more recently by the Huron–Dow (56–58) process through the cathodic reduction of oxygen in an electrolytic cell using dilute sodium hydroxide as the electrolyte. By far, the majority of hydrogen peroxide produced since 1957 has been based on the autoxidation of 2-alkylanthrahydroquinones.

5.1. Autoxidation Methods. *Anthraquinone Autoxidation.* It was discovered in 1901 that hydroquinone would each react with O_2, forming H_2O_2 quantitatively. Then in 1935 it was found that 2-alkylanthraquinones (2-alkyl-9,10-anthracenediones) were well suited for use as the reaction hydrogen carrier in a cyclic process (59). I. G. Farben in Germany operated the first large-scale anthrahydroquinone autoxidation plant, producing H_2O_2 at a rate of 30 t/mo, as a production unit during World War II (60). All subsequent anthrahydroquinone autoxidation processes retain the basic features of this, the Riedl–Pfleiderer process, shown in Figure 1.

A 2-alkylanthraquinone (RAQ) (**1**) dissolved in a suitable solvent or solvent mixture is catalytically hydrogenated to the corresponding 2-alkylanthrahydroquinone (RAHQ) (**2**), namely, 2-alkyl-9, 10-anthracenediol or 2-alkylanthraquinol (eq. 15). The 2-alkylanthraquinone is commonly called the reaction carrier, hydrogen carrier, or working material; the 2-alkylanthraquinone-solvent mixture is called the *working solution*. Carriers in industrial use include 2-*tert*-amylanthraquinone [32588-54-8], 2-*iso-sec*-amylanthraquinone [68892-24-4], 2-*tert*-butylanthraquinone [84-47-9], and 2-ethylanthraquinone [84-51-5].



(15)

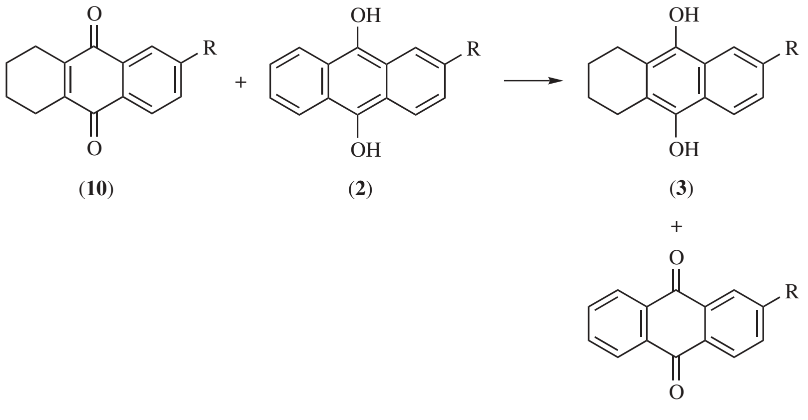


(16)

All have the alkyl group in the 2 position; thus the terms alkylanthrahydroquinone and alkylanthraquinone are taken to mean C2 substitution herein. The working solution containing the carrier product alkylanthrahydroquinone is separated from the hydrogenation catalyst and aerated with an oxygen-containing gas, usually compressed air, to re-form the alkylanthraquinone carrier while simultaneously producing hydrogen peroxide (eq. 16). The hydrogen peroxide is then extracted from the oxidized working solution using demineralized water, and the aqueous extract is purified and concentrated by fractionation to the desired strength. The extracted working solution is dried and recycled back to hydrogenation.

When the process is first started, the working solution contains only the alkylanthraquinone species. The alkylanthraquinone (RAQ) acts in close concert with the catalyst, which is usually palladium metal, and can be envisioned as Pd:RAQ. The complex reacts with hydrogen, yielding Pd:RAHQ. The alkylanthrahydroquinone is subject to many other secondary reactions that occur continuously during each process cycle. During the short time that the alkylanthrahydroquinone is in contact with the catalyst, a minor amount of catalytic reduction of the unsubstituted aromatic ring occurs at the 5, 6, 7, and 8 positions, yielding the tetrahydroalkylanthrahydroquinone (**3**) shown in Figure 2. Further ring reduction may occur in the 1, 2, 3, and 4 positions of the substituted ring, yielding octahydroalkylanthrahydroquinone (**4**). Once this compound is formed, it remains until purged owing to its essentially nonexistent oxidation rate. Transannular tautomerization of the alkylanthrahydroquinone also yields the hydroxyanthrones (oxanthrones) (**5** and **6**), which can be reduced to the anthrones (**7** and **8**). Another possible chemical route to the oxanthrone is via the formation and subsequent breakup of a quinhydrone-type charge-transfer complex. Although the formation of tetrahydroalkylanthrahydroquinones (**3**) is slow, these oxidize yielding H_2O_2 and the corresponding tetrahydroalkylanthraquinones, which are the apparent precursors to the tetrahydroalkylanthraquinone epoxide (**9**). This series of reactions repeats with each subsequent cycle of equations 18 and 19,resulting in a continuing buildup of the tetrahydroalkylanthraquinones, until these secondary products could become the dominant anthraquinone species if not reverted.

These compounds react directly with alkylanthrahydroquinone species accepting its hydrogen to form the tetrahydroalkylanthrahydroquinone (THRAQ) (**10**) and thus freeing the alkylanthraquinone (eq. 17) to continue the hydrogenation cycle.



(**10**) (**2**) (**3**) (**1**)

(17)

(18)

Although considered an active participant in the process cycle, the tetrahydroalkylanthraquinone (**10**) may not be a significant part of the catalytic hydrogenation because, dependent on the concentration in the working solution, these could all be converted to the hydroquinone by the labile shift per equation 20 and not be available to participate. None of the other first- or second-generation anthraquinone derivatives produce hydrogen peroxide, but most are susceptible to further reaction by oxidative or reductive mechanisms.

The chemical yield of hydrogen peroxide and the anthraquinone per process cycle is very high, but other secondary reactions necessitate regeneration of the working solution and hydrogenation catalyst, and the removal of organic material from the extracted hydrogen peroxide.

The first commercial-scale anthrahydroquinone autoxidation process in the United States was put into operation by E. I. du Pont de Nemours & Co., Inc. (Memphis, Tennessee) in 1953, followed by FMC Corporation (West Virginia), Laporte Chemicals, Ltd. (U.K.), Degussa (Germany), Mitsubishi-Gas Chemical Co. (Japan), and others.

Working-Solution Composition. The working solution in an anthraquinone process is composed of the anthraquinones, the by-products from the hydrogenation and oxidation steps, and solvents. The solvent fraction usually is a blend of polar and aromatic solvents, which together provide the needed solubility and physical properties. Once the solution has been defined, its composition and physical properties must be maintained within prescribed limits for achieving optimum operation.

Each working solution has an inherent maximum capacity, which depends on the anthraquinone, water, and hydrogen peroxide solubility. The capacity is defined as the maximum amount of hydrogen peroxide in grams per liter of working solution that can be produced per process cycle. The theoretical production capability of the process is the product of this capacity and the working solution flow rate. Usually the limiting factors are the solubility of the anthrahydroquinones and hydrogen peroxide and the distribution coefficient of the working solution H_2O_2 water system. The capacity can be altered somewhat by using various substituent groups on the anthraquinones or a combination of them with various solvents. The working solution and each of its individual ingredients should be chemically stable throughout the process cycle. Although the principal hydrogen peroxide producers have only used 2-ethylanthraquinone (EAQ), 2-*tert*-butylanthraquinone (BAQ), and a mix of branched isomers 2-*tert*- and 2-iso-*sec*-amylanthraquinones (AAQs), other compounds have been patented (62–64) for use in autoxidation processes. Whereas the anthraquinones are usually monosubstituted at the 2 position, the literature includes examples of C1 substituents as well as 1,2-disubstituted alkylanthraquinones and naphthoquinones.

The solvents must be nontoxic and reasonably high boiling to minimize vapor emissions and the subsequent effect on the environment, possess a flash point and physical properties (density, viscosity, diffusivities) consistent with planned operating conditions, have reasonable solvency for hydrogen and oxygen, be relatively nonreactive and resistant to oxidative attack, and be nearly insoluble in the aqueous extract, yet favorable be partitioned so that a reasonably high-strength hydrogen peroxide solution can be safely tolerated by the weight of solute per unit weight of solvent. Table 8 shows the effect of the distribution coefficient (DC) on the maximum achievable aqueous hydrogen peroxide strength versus the working-solution capacity (WSC) (see also Table 9).

In extraction (qv), the distribution coefficient value is the slope of the equilibrium line. In practice, the slope of the operating line is set at a value somewhat less than the distribution coefficient to provide a driving force and fix the required theoretical extraction stages at some reasonable number.

Hydrogenation and Catalyst. The carrier alkylanthraquinone is catalytically reduced by hydrogen to the corresponding anthrahydroquinone (anthraquinol) in the hydrogenator. The reaction is carried out at slightly elevated [100–400 kPa/g (14.5–58 psig), (pounds per square inch gauge)] pressure, and below 75°C. Most patent examples cite temperatures in the 40–50°C range. The exothermic hydrogenation reaction accounts for nearly 55% of the 188.7 kJ/mol (45.1 kcal/mol) heat of formation of H_2O_2 from the elements. The excess heat is removed by conventional means such as precooling the working-solution feed, cooling jackets or internal cooling, recirculating a cooled stream from the outlet to the inlet, or by combinations of these.

The extremes appear to be the 25–40°C operating temperatures proposed by Mitsubishi Gas-Chemical (MGC) (70,71) for a substantially tetrahydroalkylanthraquinone-free working solution (anthra system) and the 60–75°C indicated by Laporte Chemicals (Interox-Solvay), where the working solutions contain more tetrahydroalkylanthraquinone than alkylanthraquinone (tetra system) (72,73). Degussa apparently uses the highest operating pressure, near 300 kPa (43.5 psi) overpressure (74). The conversion of quinone to hydroquinone or degree of hydrogenation is normally 45–50% to minimize secondary reactions, but conversions above 80% have been cited.

The hydrogenation rate is maintained nearly constant by either the periodic addition or exchange of catalyst. The rate can also be varied somewhat by adjusting the hydrogen partial pressure and the temperature between certain limits. However, the rate apparently is not affected by pressures greater than 405 kPa (4 atm). Ammonia (qv) gas added to the hydrogenator, or water-soluble amines or ammonium salts added to the working solution, have been cited as effective ways to increase the hydrogenation rate (75).

Anthra System. Operating in the all-anthraquinone–anthrahydroquinone system provides benefits in the oxidizer because the anthra species oxidize 5–10 times faster than the tetra species (76). To maintain a low tetra content, combinations of milder operating temperature and low hydrogen partial pressure, more selective catalysts and solvents, as well as special reaction carriers have been proposed. MGC proposed the continuous dehydrogenation of the tetra species using a high-temperature catalytic technique in which an olefin gas, for example, ethylene, is converted to the corresponding alkane, such as ethane (77,78). Some ring dehydrogenation of the tetra species to the anthra species is one of several functions performed by the basic alumina in the working-solution regenerators. The reaction is reasonably slow.

$$3\ \text{THRAQ} \xrightarrow{\text{basic } Al_2O_3} \text{RAQ} + 2\ \text{THRAHQ}$$

Increased temperature and low initial hydroquinone content favor reversion. The main anthraquinone degradation route in the anthra system is the formation of anthrone, presumably by reduction of oxanthrone, the transannular tautomer of the alkylanthrahydroquinone. Passing through activated alumina readily regenerates the oxanthrone, but the anthrone is only marginally affected. Anthrone is subject to other reactions such as formation of nonregenerable dianthrone.

Tetra System. Most principal producers operate within the tetra mode because no specific measures are taken to either suppress the formation of tetra during hydrogenation or to substantially revert it back to anthra as it forms. With time, the working solution contains more tetra than do anthra species, and the hydrogenated anthraquinone occurs exclusively as the 2-alkyltetrahydroanthrahydroquinone (**3**) (see eq. 17). This mode of operation is known as the all-tetra system. If the concentration of tetra species increases much above 75% of the total quinone content, further hydrogenation of the substituted ring may occur and lead to octahydroanthrahydroquinone (**4**) formation. Regardless of the operating mode, formation of the tautomer oxanthrone occurs.

Continuous stirred-tank reactors (CSTRs), tubular, draft-tube agitated, and fixed-bed (79,80) hydrogenator designs have been patented, as has a special candlefilter for use with fine palladium black catalyst (81). Reduction methods involving other than catalytic fixing of hydrogen have been proposed but have little value in large commercial plants.

The catalyst must be active, selective, and stable over a rather long lifespan. Slurry-type catalysts are easy to remove and add without need for a process shutdown. These can therefore be rejuvenated by various external means and returned to maintain average catalytic function at a reasonably high level. Alternatively, the hydrogenation system can be started at relatively low catalyst concentration and more catalyst added as necessary to maintain the desired result. As long as the deactivated catalyst does not adversely impact the chemistry, this type of operation can continue until the concentration of catalyst reaches a level where maintaining suspensions is limited by system energy input. The catalyst is then removed, rejuvenated, or processed for metal recovery and the cycle repeated (see CATALYSTS; REGENERATION). A fixed-bed-type hydrogenator is not burdened by suspension difficulties. If the palladium remains fixed and the support resists attrition, the preoxidation filtration needs should be less stringent. Maintaining favorable chemistry impact as the bed slowly deactivates is a prime consideration, given the high cost of the anthraquinone species. Periodically the hydrogenator must be shut down either to replace a portion of the bed or for *in situ* rejuvenation of the entire bed.

The Raney nickel catalyst used in the original Riedl–Pfleiderer process was active, caused excessive ring hydrogenation, was easily deactivated by oxygen or hydrogen peroxide, and was pyrophoric. The use of a palladium catalyst, used by all principal producers as of this writing, avoids the problems associated with Raney nickel. It can be used as palladium black, as wire screen or gauze, or supported on a carrier for use in slurry or fixed-bed applications. The activity and selectivity of supported catalyst are influenced by both chemical and physical properties of the support and perhaps even more by the preparation procedure. The supports generally have high crush strength and are reasonably smooth and rounded to resist attrition, abrasion, and fracturing. A truly round support with minimum asparities and with an aspect ratio near 1.0 would be ideal to avoid attrition. Treating the palladium-supported catalysts with hydrogen at high temperature or adding other platinum group metals to the palladium reportedly improves selectivity.

The most recent and novel fixed-bed-type hydrogenator utilizes a honeycomb monolith having alumina- and silica-modified surfaces on which palladium has been deposited (82). The design is claimed to offer excellent long-term stability and mass-transfer characteristics. A hybrid tubular design incorporating static mixing to improve hydrogen mass transfer has also been claimed (83).

Oxidation. The hydrogenated working solution, which has been filtered or in some other manner freed of catalyst, is oxidized by the noncatalytic reaction with an oxygen-containing gas, which is usually filtered and compressed ambient air. Oxygen or oxygen-enriched air can be used, but avoidance of the obvious hazards becomes more complicated. (None of the principal producers use oxygen or oxygen-enriched air). Either co- or countercurrent flow of gas and liquid in a single- or multistage system with or without packing or trays can be employed. With coflow up, liquid holdup is maximized, but the design may permit high-strength aqueous-phase hydrogen peroxide that separates from the solution to drain back down the vessel walls and collect in the base. Such a solution can approach the theoretical maximum concentration as controlled by the system operating titer and distribution coefficient and could become a serious safety concern. Using countercurrent flow liquid holdup is less, but because the working solution flows down the column, a separate phase, if formed, is flushed out with the working solution into the extractor, where it is safely diluted.

Because the reaction takes place in the liquid, the amount of liquid held in the contacting vessel is important, as are the liquid physical properties of the liquid such as viscosity, density, and surface tension. These properties affect gas bubble size and therefore phase boundary area and diffusion properties for rate considerations. Chemically, the oxidation rate is also dependent on the concentration of the anthrahydroquinon, the actual oxygen concentration in the liquid, and the system temperature (84). The oxidation reaction is also exothermic, releasing the remaining 45% of the heat of formation from the elements. Temperature can be controlled by the various options described under hydrogenation. Added heat release can result from decomposition of hydrogen peroxide or direct reaction of H_2O_2 and hydroquinone (HQ) at a catalytic site:

$$\mathrm{H_2O_2(l) + HQ(l) \rightarrow 2\,H_2O(l) + Q(l)} \qquad \Delta H = -279\mathrm{kJ/mol}(66.90\mathrm{kcal/mol}) \tag{19}$$

The oxidation of alkylanthrahydroquinones by forming noncoalescing foams (85) between the working solution and oxygen-containing gas and continuous gas–liquid dispersions (86) has been patented. Minimized investment and energy consumption are claimed and the short contact time reportedly minimizes deterimental effects on working solution components.

Hydrogen Peroxide Recovery. Hydrogen peroxide formed in the oxidation step is usually recovered by countercurrent extraction of the oxidized working solution, using demineralized water in liquid–liquid sieve tray columns. As working solutions used by the principal producers are less dense than water these would enter near the base of the column and flow upward as the dispersed phase. Water enters the column at the top and increases in hydrogen peroxide content and density as it flows downward as the continuous phase. All known principal producers use sieve tray columns having these flow paths for extraction. Dependent on the type and composition of the working solution, concentrations of hydrogen peroxide of up to 45 wt% are obtained by extraction. For safety reasons, 45 wt% aqueous hydrogen peroxide extract is a reasonable limit for nonmiscible organic systems (87). The columns and trays are usually constructed from 304 or 316 stainless-steel or low-carbon equivalents. Aluminum and high-grade aluminum alloys are also adequate materials. The sieve tray extractor's particular advantages are high throughput and reasonably high tray efficiency, and, because they have no moving parts, they are economically maintained. Rate turndown is about 2:1, limited by the dispersed phase droplet size or tray stability. Other extract methods involving use of rotating mechanical devices, packed columns, spray columns, have been claimed.

The tray-free area can be decreased at intervals from top to bottom as the density differential between the aqueous phase and the working solution widens. This adjustment maintains a nearly constant depth of coalesced working solution beneath each tray. For this type of extractor the distance between trays (spacing) is constant from top to bottom. Alternatively, the tray area can be held constant and the height of the coalesced layer beneath the tray permitted to vary, thus providing the needed pressure drop for flow.

Liquid system properties including density, viscosity, and interfacial tension, together with design factors including orifice size and mass flow rate, influence droplet formation, transport surface area, and droplet coalescence.

Considerable engineering research has been conducted in Europe on sieve tray column performance and design factors (88,89). For most working solutions the optimum individual tray hole diameter is 2.5–3.0 mm. Tray spacing is best determined experimentally. Hydrophobic netting made from polyethylene, polypropylene, poly(vinyl chloride), and polytetrafluoroethylene has been used in the working-solution layer beneath the trays to aid aqueous droplet coalescence and separation.

Hydrogen peroxide can also be recovered directly from the working solution by vacuum distillation or by stripping with organic solvents. The organic solutions obtained by the solvent stripping can be used to prepare peroxycarboxylic acids, or they can be extracted with water to obtain aqueous hydrogen peroxide of higher strength. The use of extract water containing sodium metaborate has been claimed to give sodium perborate, or those containing aliphatic carboxylic acids to give peroxycarboxylic acid. Other patents describe transfer of hydrogen peroxide from one solvent to another, or separation within an integrated membrane-based process (90).

Working-Solution Regeneration and Purification. Economic operation of an anthraquinone autoxidation process mandates restrictive use of the expensive anthraquinones. During each reduction and oxidation cycle some finite amount of anthraquinone and solvent is affected by the physical and chemical exposure. At some point, control of tetrahydroanthraquinones, tetrahydroanthraquinone epoxides, hydroxyanthrones, and acids is required to maintain the active anthraquinone concentration, catalytic activity, and favorable density and viscosity. This control can be by removal or regeneration.

Treating the working solution or isolated quinone mixtures with a dehydrogenation catalyst converts the tetrahydroanthraquinones to the corresponding anthraquinone. Treating with an olefin in the presence of hydrogenation catalysts converts oxanthrones and minor amounts of tetrahydroanthraquinones back to the corresponding anthraquinone (**1**) (91). Treating the working solution with activated alumina or sodium aluminum silicate at moderate temperature (60–90°C) in the presence of a proton source such as the anthrahydroquinone (**2**) converts some of the tetrahydroanthraquinone (**3**) to the corresponding anthraquinone, tetrahydroanthraquinone epoxide (**9**), to the corresponding tetrahydroanthraquinone epoxy alcohol, and oxanthrone to the corresponding anthraquinone (92). Total conversion of the tetrahydroanthraquinone epoxide also requires dehydration of the intermediate epoxy alcohol. Other procedures for working-solution regeneration include treatment with alkali, acids, metal oxides, chlorides, silicates or aluminosilicates, and dithionates, with oxygen, ozone, or purifying by washing with water. *In situ* oxidative regeneration of anthrone on addition of small amounts of *N,N*-di-*n*-butylaniline to the working solution has been claimed (93).

Recovery of working-solution components includes recrystallization of the anthraquinones, extraction of crude mixtures with lower alcohols, use of anion-exchange resin, or isolation of the hydroquinones (93). Dilution of a heavily degraded working solution with *n*-heptane is claimed to form two separate phases where most of the degraded products are in the heptane phase. The low-boiling heptane is recovered by distillation (94). Another method used to separate the degradation products from the working solution involves extraction with a C-9-alkylated aromatic and a carbon dioxide fluid at 10–20 MPa (1450–2900 psi) and −4 to 10°C (95).

The alumina or sodium aluminosilicate catalysts used to regenerate degraded working solutions lose activity with time as active soda sites are neutralized, but these also can be regenerated.

Hydrogenation Catalyst Regeneration. Procedures for recovering palladium from spent catalyst as well as methods for *in situ* or external regeneration have been developed. These latter methods include treating with wet steam, strong oxidants, liquid ammonia or concentrated ammonium hydroxide, other highly alkaline solutions, inorganic acids (96) carboxylic acids, hydrogen peroxide (97), organic solvents, oxidized working solution (98), or heating in air at temperatures ranging from 250 to 700°C. Many of the methods involve multiple steps having various sequential treatments with polar solvents, aqueous ammonium hydroxide, steam, and oxygen-containing gases to remove adsorbed organic matter prior to palladium dissolution and deposition. Periodic reduction of the hydrogen partial pressure and treatment with an inert gas tends to prolong catalyst life by stripping catalyst poisons. Only those treatments, which essentially reconstitute the catalyst, return it to near-original activity. Other methods improve economics or prolong catalyst life by stripping catalyst poisons.

Alcohol Autoxidation. The noncatalytic oxidation of primary and secondary alcohols using air or oxygen in liquid phase gives hydrogen peroxide and the corresponding aldehydes or ketones in good yield. If not operated closed loop, the economics of this process depends on the value of the by-product aldehyde or ketone. Shell Chemical Company operated a liquid-phase process based on the autoxidation of isopropyl alcohol for about 20 years at Norco, Louisiana. The by-product acetone (qv) was marketed, and most of the hydrogen peroxide was used captively to produce glycerol (qv).

$$(CH_3)_2CHOH + O_2 \rightarrow (CH_3)_2C = O + H_2O_2 \tag{20}$$

This process was discontinued in the late 1970s for economic reasons.

Alcohol oxidation patent activity in the 1980s and 1990s by ARCO (99–104) involved the oxidation of methylbenzyl alcohol (*sec*-phenethylalcohol) to acetophenone and hydrogen peroxide. Methylbenzyl alcohol is the main by-product of propylene oxide (qv) produced from propylene (qv) and ethylbenzene hydroperoxide [3071-32-7]. The latter is produced by the oxidation of ethylbenzene. Methylbenzyl alcohol has no significant market value, and as of this writing is dehydrated to styrene (qv). Acetophenone is the main by-product and is catalytically hydrogenated back to methylbenzyl alcohol. In the process, ethylbenzene hydroperoxide is catalytically decomposed to methylbenzyl alcohol and hydrogen peroxide, which is then separated by distillation and extraction. The methylbenzyl alcohol is oxidized by molecular oxygen in liquid phase, giving acetophenone and hydrogen peroxide. After separating the hydrogen peroxide, the acetophenone is hydrogenated back to methylbenzyl alcohol completing the cycle, as shown in equations 21 and 22.

$$\begin{gathered} C_6H_5CH(OH)CH_3 + O_2 \rightarrow C_6H_5COCH_3 + H_2O_2 \\ C_6H_5COCH_3 + H_2 \rightarrow C_6H_5CH(OH)CH_3 \end{gathered} \qquad (21)$$

to give the net reaction

$$H_2 + O_2 \rightarrow H_2O_2 \qquad (22)$$

As of this writing, the process has not been commercialized, but apparently the alcohol can be separated from its propylene oxide coproduct process to maintain an economically competitive position. The formation of organic hydroperoxides is a concern, as it was in the Shell process.

5.2. Electrolytic Methods. The electrolytic processes for commercial production of hydrogen peroxide are based on the oxidation of sulfuric acid or sulfates to peroxodisulfuric acid [13445-49-3] (peroxodisulfates) with the formation of hydrogen and the double hydrolysis of the peroxodisulfuric acid (peroxodisulfates) to Caro's acid and then hydrogen peroxide. To avoid electrolysis of water, smooth platinum electrodes are used because of the high oxygen overvoltage. The overall reaction is

$$2\,H_2 + O + \text{electrical energy} \rightarrow H_2O_2 + H_2 \qquad (23)$$

This electrolytic process technology is no longer used because of the extensive electrolyte purification needs, the high capital and power requirements, and economic inability to compete with large-scale anthrahydroquinone autoxidation processes.

The Huron–Dow Process. The Huron–Dow (H-D) process is a refinement of the cathodic reducion of oxygen in an alkaline electrolyte yielding low-strength hydrogen peroxide directly. Earlier attempts relied on neutralizing the excess caustic or forming insoluble metal peroxides (105). The two reactions involved are

$$\text{cathode } O_2 + H_2O + 2\ e^- \rightarrow OH^- + HOO^- \qquad (24)$$

where oxygen is reduced, giving hydroxyl and perhydroxyl ions, and

$$\text{Anode } 2\,OH^- \rightarrow 1/2\ O_2 + H_2O + 2\ e^- \qquad (25)$$

where hydroxyl ion is oxidized, giving oxygen and water. The net reaction, in absence of losses, requires passing 2 F of electricity (192,978 C) through the solution to produce 1 mol of hydrogen peroxide.

The H-D process development, begun in the early 1980s, is intended for on-site production of dilute alkaline hydrogen peroxide for direct use in the pulp-and-paper industry. Operated on a pilot scale for many years, it was commercialized in 1991 when improvements in the electrolytic cell design and its current efficiency were achieved (107–113). The newest cell design (107–109) consists of a porous cathode and a platinum-coated titanium anode separated by a diaphragm and an ion-exchange (qv) membrane. The diaphragm consists of multiple layers of a porous polyropylene composite, which assures uniform flow of the electrolyte. The electrolyte enter near the base of the anode, and the product solution exits near the base of the cathode. Oxygen gas enters near the top of the porous cathode, and oxygen formed through the anodic oxidation of hydroxyl ion exits the top of the anode compartment. The ion-exchange membrane is claimed to control the migration of ions into and out of the cathode compartment, reducing peroxide losses and improving the current efficiency. This latter is claimed to be 95% for the electrolysis.

Because the electrolyte contains excess alkali that could cause spontaneous decomposition of the hydrogen peroxide, the H_2O_2 in the product solution is limited to 30–40 g/L. The chelating agent (ethylenediamine) tetraacetic acid (EDTA) is added at up to 0.5 g/L to protect against tramp-metal-ion-induced decomposition (114). For use in a pulp (qv) mill, it may be necessary to blend with purchased hydrogen peroxide to achieve the proper ratio of caustic to hydrogen peroxide.

5.3. Other Methods.

Direct Combination of Hydrogen and Oxygen. Hydrogen peroxide can be formed directly by thermal, electric discharge, or metal-activated reaction between hydrogen and oxygen. Silent electric discharge processes have been patented, but the power requirements are too high for commercial use. Since about 1910, the study of forming hydrogen peroxide by directly combining the elements has challenged researchers. Investigations during the 1960s and 1970s focused on platinum-group metal-catalyzed processes (115–120). More recent investigations have included use of homogeneous catalysts such as organic complexes of palladium, iron and platinum, iridium, and the use of promoters (121–123); heterogeneous catalysts using acidic aqueous solutions and some additives (124–132); and those processes using heterogeneous catalysts and organic solvents including acetone, methanol, fluorocarbons, and acetonitrile (133–135). Platinum-group metal carriers have included hydrophobic materials such as Teflon, polyethylene, polypropylene, and polystyrene (123); silicic acid (120); and carbon, charcoal, silica, and alumina (131).

In Du Pont patents (302), the catalyst is prepared by spray-drying a mixture of colloidal silica or other carriers and Pt/Pd salts. Aqueous hydrogen peroxide solutions up to 20 wt% are reported for reaction conditions of 10–17°C and 13.7 MPa (140 kg/cm^2) 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.

5.4. 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 (136), passing the solution through a hydrocyclone (137) packed with halogen-containing porous styrene–divinylbenzene copolymer resin (138) passing the solution through an anion-exchange resin pretreated with various chelating agents to remove metal ions and organic impurities (139) and passing the solution through a zeolite (140). Washing the working solution either continuously or in batches with water or dilute caustic and discarding the washings may reduce the amount of nonvolatile organic impurities present in extracted crude hydrogen peroxide from anthrahydroquinone autoxidation processes.

Concentration of hydrogen peroxide prepared by the autoxidation processes can be carried out safely and conveniently by distillation at reduced pressure. The distillations incude 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 (141). 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 (142), 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 (143).

6. Storage and Transportation

Materials of construction suitable for transport and storage of concentrated H_2O_2 are stainless steel DIN 1.4306 (ANSI 304), DIN 1.4435 (ANSI 3161), DIN 1.4401 (ANSI 316) DIN 1.4571 (ANSI 316 Ti), aluminum (99.5% min), and certain aluminum–magnesium alloys. At this point it should be noted that contamination of the H_2O_2 with even small quantities of chloride ion (eg, from dilution water) might cause severe pitting of aluminum. Stainless steel must be passivated before use by a special treatment with HF/HNO_3. Aluminum passivation is conducted by a two-stage treatment with dilute sodium hydroxide solution followed by dilute nitric acid. Up to 60% H_2O_2 concentration can also be stored in polyethylene (PE) tanks. Other compatible materials are poly(vinylidene fluoride) (PVDF), Teflon, poly(vinyl chloride) (PVC), and glass.

Commercial H_2O_2 solution are supplied in bulk by railroads cars (20–50 tons) by trucks (20 tons) and ISO container (20 tons). Also PE containers with 5-, 30-, 60-L, and 220-L plastic drums and 1-m^3 IBCs are available.

Transportation and storage of H_2O_2 solution is regulated by UN/DOT (United Nations/U.S. Department of Transportation) and by the regulations of dangerous substances according to EEC (European Economic Community) directive 67/548 in Europe and by the Bureau of Explosives Regulations in North America, respectively.

Up to a concentration of 8%, H_2O_2 solutions are not regulated by DOT. Concentrations >8% are classified as 5.1. oxidizer. Solutions of H_2O_2 >40% concentration is prohibited from air transport. In the U.S. shipment of H_2O_2 in polyethylene drums is permitted up to a concentration of 52% only. H_2O_2 solutions with <20% concentration are not considered dangerous substances according to EEC 67/548 in Europe. H_2O_2 solutions with 8–19% concentration are classified as irritant (Xi), 20–60% H_2O_2 as corrosive (C), and H_2O_2 >60% is also oxidizing (C, O).

The Bureau of Explosives regulation in the United States classifies all H_2O_2 solutions >20% as oxidizing and corrosive (144).

Transport regulations, classification, and labeling are summarized in Tables 10 and 11.

7. Economic Aspects

The world and North American (Canada, Mexico, USA) market demand (apparent consumption) for hydrogen peroxide is summarized in Table 12 (145–150).

The driving force for the accelerated growth since the mid-1970s has been the pulp-and-paper industry, with its demand for an environmentally sound replacement for chlorine and chlorine dioxide bleaching of chemical pulps, the growth of recycled fiber processing, and the establishment of bleached chemo-thermo mechanical pulp (BCTMP), which can only be bleached with hydrogen peroxide. Other growth segments include the textile industry (cotton bleaching), chemical industry (epoxidized soybean oils, organic peroxides, amine oxides, specialty chemicals, and intermediates, downstream peroxide products), environmental applications and specialty markets such as food processing, cosmetic industries, liquid nonchlorine detergent bleaches, and the electronics industry (for details, see the section on uses and market demand, below). The overall growth of the hydrogen peroxide market in the developed economies after the year 2000 is expected to drop to the GDP growth, whereas developing countries with emerging pulp-and-paper and chemical industries may still see growth rates of about 5% per year in the decade from 2001 to 2010.

The worldwide installed nameplate capacity in 1998 is estimated to be 2600×10^3 t. Even for world-class plants the available capacity rarely exceeds 90% average per year, due to the nature of the production process, which results in 2340×10^3 t available capacity for 1998. Table 13 shows the worldwide and North American production nameplate capacity by major producer.

There are 13 production sites for hydrogen peroxide in North America (see Table 14).

The 1998 North American hydrogen peroxide prices have dropped to an historical low as a result of a significant oversupply in the market. Some producers have started rationalizing their production capacity, which eliminates about 100,000 t/yr and may bring the supply and demand back in balance by 1999. Published prices for technical-grade hydrogen peroxide are shown in Table 15 (151).

8. Grades, Specifications, and Quality Control

Aqueous hydrogen peroxide is sold in concentrations ranging from 3 to 86 wt%, most often containing 35, 50, and 70 wt% H_2O_2. Small quantities of concentrations >70% are sold into specialty applications or are captively used in the manufacturing of H_2O_2 derivatives.

The 35, 50, 60, and 70% (wt%) H_2O_2 concentrations are used for most industrial applications. The 3–6% H_2O_2 solutions for consumer products and medicinal use are obtained by diluting a more concentrated grade, containing extra stabilizer. The 3 and 30% topical solutions have a United States pharmacopeia (USP) specification (152).

Cosmetic-grade H_2O_2 contains sufficient amounts of special stabilizers that allow the preparation of stable diluted solutions and formulations. In the United States and EU countries, cosmetic-grade H_2O_2 complies with the USP and *Pharmacopee Europeenne/Colipa* (153) specifications for 3 and 30% H_2O_2, respectively.

The 30% reagent-grade hydrogen peroxide is purer than the industrial grades 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).

Specialty grades with tailored stabilizer combinations have been developed for applications in chemical synthesis, where standard stabilizers may cause interference with catalysts and thus affect yields and selectivity.

Other specialty grades are employed in metal etching, detergents, and the food industry. Food-grade H_2O_2 (30–50%) meets the *U.S. Food Chemical Codex* requirements and contains <60-mg nonvolatile compounds (154,155).

The most important quality parameter for H_2O_2 is stability. All major producers check the stability of their products before shipment by running an accelerated decomposition test at elevated temperatures (96–100°C). Other standard specification parameters are concentration and pH (see section on health and safety factors, below).

Typical shelflife and stability data for technical grade H_2O_2 solutions are given in Table 16.

9. Analytical and Test Methods

Analytical methods for the qualitative or quantitative determination of hydrogen peroxide are based on its redox (reduction–oxidation) or physical properties.

Aqueous hydrogen peroxide solutions are usually titrated with potassium permanganate (156). Density measurement is an alternative method for determinations of pure aqueous H_2O_2 solutions. For analysis of the hydrogen peroxide content in the presence of organic matter, the iodometric titration method should be employed because of side reactions of permanganate with organic compounds, resulting in a higher consumption of titer solutions (157). Another titrimetric method is based on the reduction of Ce(IV). H_2O_2 froms with Ti(IV) in a very specific reaction a yellow-orange $[Ti(O_2)OH]^+$ complex, which can be quantitatively determined by colorimetry (158–161). Other analytical methods use chemoluminescence of H_2O_2 with luminol and fluorescence reaction with scopoletin and peroxidase. An overview on different methods for the measurement of trace quantities of H_2O_2 in air, water, and biological media is given in Ref. 162.

High-pressure liquid chromatography (qv) (163) and coulometry can be used to detect and quantify anthraquinones and their derivatives in a hydrogen peroxide process working solution. Atomic absorption and induced coupled plasma spectroscopy are used for determination of metals and inorganic impurities. Stabilizers and inorganic anions can be determined by ion chromatography (152,164,165).

The pH of H_2O_2 solution can be measured with a glass electrode (see section on chemical properties, dissociation, following Table 3,above). Values given by the producers on certificates of analysis and product information are typically not connected. Stability of concentrated H_2O_2 solutions (35–70%) is determined by conducting accelerated decomposition tests at 96–100°C for 16 min to 24 h. For testing high-performance grades, such as cosmetic H_2O_2 or dilution grades, the H_2O_2 solution is spiked with metal salts to account for metal contamination by dilution water, storage or packaging material, and other compounds of the formulation. Depending on the H_2O_2 grade, decomposition rates up to a maximum of 5% are acceptable. H_2O_2 containing formulations such as those for consumer products are tested for long-term-stability at 40–50°C for several weeks.

10. 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 (166). Some generally applicable control measures and precautions for handling hydrogen peroxide include the use of adequate ventilation to keep airborne concentrations below occupational exposure limits, 8 h TWA, 1 ppm (1.4 mg/m^3), use of coverall 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. Short-term exposure should not exceed 3 mg/m^3 for 15 min. 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) must not be worn because these can ignite within 3 min following contact with $\geq$50% H_2O_2. 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. In contact with eyes, H_2O_2 solutions of more than 10% cause irreversible corneal damage. Solutions less than 6% are considered as nonirritant according EEC classification (167,168). 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.

The acute toxicity of H_2O_2 is moderate. The LD_{50} for mice is 800–5000 mg/kg body weight depending on the concentration of the applied H_2O_2 solution. 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. Inhalation of concentrated vapors can cause irritation of the nose and throat with chest discomfort, cough, difficult breathing, and shortness of breath. No component in industrial hydrogen peroxide solutions is listed as a carcinogen. For a review and assessment of the current available toxicological data, see Ref 4.

Hydrogen peroxide is moderately toxic to aquatic organisms. Acute ecotoxicity data are available for fish, daphnia, and algae (162).

Decomposition and Explosive Hazards. The principal hazards associated with hydrogen peroxide are

1. Decomposition of H_2O_2, with unrelieved pressure buildup
2. Spontaneous combustion of mixtures of H_2O_2 and readily oxidizable material
3. Inadvertent admission of incompatible materials into a tank containing H_2O_2 or vice versa
4. Decomposition of H_2O_2 to form an oxygen-rich vapor phase
5. Deflagration or detonation of a condensed-phase mixture of H_2O_2 and organic compounds initiated by shock or thermal effects
6. Explosive reaction of H_2O_2 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 K rise in temperature over the range of 20–100°C (166). Stabilizers have only little effect on this characteristic. 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 thousands of kilopascals are achievable, and ruptures of tanks, valves, piping, and other components may 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 m^3 of 70% H_2O_2 can generate 2545 m^3 of gas and reach 233°C, but 1 m^3 of 50% H_2O_2 can generate 1280 m^3 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 contaminats (14,166) (see Table 17).

Drums and other portable shipping containers should preferably be stored or shipped alone, so, that in the event of an accident, the H_2O_2 cannot mix with common combustibles or flammable liquids and gases.

In organic processes 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 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 (169) and sulfuric acid (87) above certain concentrations, mercurous oxide (170) and permanganate, 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 peroxides of concentrations of 35%, 50%, and above may cause spontaneous combustion of dry grasses, wood, and leaves. Spills of concentrated hydrogen peroxide should be diluted with excess amounts of water immediately. Practically every solid combustible material contains 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 (171). 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% H_2O_2, which is close to the equilibrium vapor concentration above boiling 74% hydrogen peroxide.

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

11. Uses

Hydrogen peroxide is used in many applications throughout a wide variety of industries. The principal use areas and consumption of H_2O_2 in North America and Europe are shown in Table 18 and 19.

11.1. Bleaching. The largest single use for hydrogen peroxide worldwide is wood pulp bleaching (172,173). Environmental concerns have led the pulp-and-paper industry in Europe and North America to turn to alkaline solutions of hydrogen peroxide as a replacement for chlorine and hypochlorite and chlorine dioxide in bleaching applications (174–183). These include mechanical (184–190) sulfite (191–197), kraft pulp bleaching (198,199), and deinking (200–204) of recycled paper (see RECYCLING, PAPER).

Kraft pulp bleaching is the largest application in the United States and Scandinavia, where hydrogen peroxide has been used in the final bleaching sequence and/or E_{op} stage to obtain a high-brightness product having maximum color stability. Most of the hydrogen peroxide use in Canada is at the large chemothermo mechanical pulp (CTMP) mills. In mechanical pulp bleaching strong oxidants such as chlorine or chlorine dioxide cannot be used economically because of the high residual lignin content of the raw pulp. High brightness numbers (75–80% ISO brightness) and good yields can be obtained with H_2O_2 because of the selective oxidation of the chromophores. H_2O_2 charges of up to 5% are employed. Sulfite pulps can easily be bleached to high brightness levels with H_2O_2 as the only bleaching chemical. Because of stringent regulations, this technology has been completely implemented in continental Europe for many years. The annual growth rate of hydrogen peroxide in this industry through the early 1990s has been about 12–16%. The future growth rate is expected to depend on implementation of environmental regulations on AOX discharge, the demand on chlorine-free bleached pulp, and the economical advantages of hydrogen peroxide over chlorine dioxide bleaching.

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 or batch processes. Primary advantages for hydrogen peroxide in this industry is that it has no effect on many modern dyes and does not cause fiber damage. In denim finishing H_2O_2 is employed as a dechlorination agent. It has been estimated that 85% of all cotton fabrics are bleached with hydrogen peroxide.

Hydrogen peroxide is used to bleach solid surfaces such as wood (qv) or linoleum, and to improve the color of oils, surfactants, and waxes. Food-grade H_2O_2 is employed as bleaching agent for certain vegetable fibers, which are used in the manufacture of noncaloric flour.

11.2. Environmental Applications. Hydrogen peroxide is an ecologically desirable pollution-control agent because it does not form toxic by-products and yields only water or oxygen on decomposition. It has been used in increasing amounts to convert domestic and industrial effluents to an environmentally compatible state (see WASTES, INDUSTRIAL; WATER).

Hydrogen peroxide is used to treat wastewater (206–212) 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 clarifies and improves bulking conditions. It also has been used as a flotation (qv) assistant (213,214).

Industrial liquid and gaseous detoxification systems based on hydrogen peroxide have been developed (208–212,215–225). H_2O_2 is reported to be especially suitable for cyanide-containing wastes having high free-cyanide concentration or those also containing organic impurities (225). Hydrogen peroxide systems with formaldehyde (221,226–228), copper salt, silicates (229), or iodide and silver ion added to increase reaction rates and efficiency have been described or patented. Procedures have been described for removing nitrite ion from wastestreams and for recovering arsenic acid or arsenates. Similar procedures using hydrogen peroxide have been developed for detoxifying organic pollutants, including formaldehyde (qv), phenol mixtures (221), acetic acid, lignin sugars, surfactants (qv), amines, glycol ethers (210–212), and sulfur derivatives (222–224). Hydrogen peroxide is also being used as an *in situ* oxygen source for enhanced aerobic degradation of organic pollutants by bacteria in the bioremediation of contaminated soils, such as from gasoline that has leaked into the soil from underground tanks (230,231).

Toxic or malodorous pollutants can be removed from industrial gas streams by reaction with hydrogen peroxide (232,233). Many liquid-phase methods have been patented for the removal of NO_x gases, sulfur dioxide, reduced sulfur compounds, amines (205,223,224), and phenols (221). Other effluent treatments include the reduction of biological oxygen demand (BOD) and COD, color, odor (235,243,244), and chlorine concentration.

Certain pollutants can not be destroyed by H_2O_2 alone. H_2O_2 must be activated by Fe^{2+} (Fenton's reagent), uv radiation, or in combination with ozone-forming hydroxyl radicals.

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^- + Fe^{3+} \tag{26}$$

$$H_2O_2 \rightarrow 2\,OH^{\cdot} \tag{27}$$

$$O_3 + H_2O_2 \rightarrow 2\,OH^{\cdot} \tag{28}$$

The hydroxyl radical is one of the strongest oxidants and reacts with all types of organic substrates via the splitting of hydrogen atoms or by the addition to C–C double bonds (243). The final reaction products are water and carbon dioxide.

A review of the literature reveals a number of basic investigations using Fenton's reagent for the oxidation of organic compounds (244,245). Examples of the application of Fenton's reagent for oxidation of phenols, benzene derivatives, the reduction of BOD/COD, (biological/chemical oxygen demand) and destruction of dyestuffs from textile mill effluents have been published (246,247).

Numerous investigations show that chloroalkanes (eg, TCE, vinyl chloride), benzene, dioxane, dimethyhydrazine and certain pesticides (eg, DDT, DCT) can cost-effectively be destroyed using uv and H_2O_2 (248).

Advanced oxidation processes using H_2O_2 in combination with ozone or uv light are under investigation in the laboratory and on full scale as a possible primary treatment of drinking water for the removal of organic compounds (247–252). A critical issue is the formation of organobromine, bromate, and other halogenated compounds, which can be formed in the presence of bromide and iodide (241). H_2O_2 alone is used for the removal of iron and managanese (250). In Germany the addition of H_2O_2 for drinking water pretreatment is limited to 17 mg/L, and a residual H_2O_2 concentration of less than 0.1 mg/L must be obtained (242).

Dioxins can also be destroyed in the gas phase by H_2O_2 in combination with a silica catalyst (253).

11.3. Chemical Uses. Hydrogen peroxide or a peroxycarboxylic acid made from H_2O_2 is used in the manufacture of a number of organic and inorganic chemicals (52,254). The electrophilic epoxidation of soybean oil, linseed oils, and related unsaturated esters with peroxyformic or peroxyacetic acid formed *in situ* from aqueous hydrogen peroxide has been used to prepare plasticizers (qv) and stabilizers.

The catalyzed hydroxylation of phenols yields catechol and hydroquinone (52,254–259). $HClO_4$ and H_3PO_4, iron or cobalt salts, and titanium silicate can be employed as catalysts.

Another large-scale application is in the synthesis of hydrazine from ammonia replacing the old Raschig and Bayer processes (see HYDRAZINE AND ITS DERIVATIVES) (254,260,261).

Hydrogen peroxide or its derivatives have been used to prepare long-chain amine oxides for detergent use (262,263), thiourea dioxide (254) used for bleaching of deinked pulp (264–266) and as a reducing and dye-stripping agent in textile finishing (267–273).

H_2O_2 in the form of peroxy acetic acid is employed in the synthesis of caprolactone (274,275), a raw material for polyurethanes and biodegradable plastics (276).

H_2O_2 is also used to produce other compounds (277–279), including magnesium silicate sols (169) for fiber coating and forming, hydroxyimidazoles (279) for use as antimycotics (see ANTIPARASITIC AGENTS) and herbicides (qv), and 5-hydroxyhydantoin (279) for use in penicillin and cephalosporin synthesis (see ANTIBIOTICS; HYDANTOIN AND ITS DERIVATIVES). A new route for the manufacturing of adipic acid by direct oxidation of cyclohexene with H_2O_2 in the presence of a tungsten catalyst has been described in the literature (277).

Other chemical uses for hydrogen peroxide include the preparation of cyanogen, cyanogen chloride (254,280), bromine (281), and iodic acid (282). H_2O_2 finds increasing use in bromination reactions as an alternative to chlorine for the regeneration of Br_2 from HBr, such as in the manufacture of the flame-retardant tetrabromobisphenol A (283,284) and to avoid methylbromide by-product formation. H_2O_2 is also employed in the manufacture and regeneration of *N*-methylmorpholine N-oxide which is used as a solvent for cellulose in the manufacture of cellulose fibers (285,286).

Interest in hydrogen peroxide as an active chemical ingredient for preparing other large-volume chemicals is growing. Processes have been developed for the preparation of caprolactam with H_2O_2 in the presence of tungstate as a catalyst (52), and propylene oxide (qv) (280,287–291) using water-immiscible organic solutions of a peroxycarboxylic acid. However, for cost reasons these processes have not gained large-scale applications.

The discovery of titanium silicate (292–295) for the activation of H_2O_2 has been a major breakthrough in the development of heterogeneous catalysts for the synthesis of caprolactam (296–301) and propylene oxide with H_2O_2 (302–304). Minimization of waste and by-products are the major advantages of the titanium silicate catalyzed processes; 1.8–4.4 kg of ammonium sulfate by-product can be avoided in the direct ammoximation of cyclohexanone using H_2O_2 and titanium silicate. Propylene oxide can be obtained in high yields and good selectivity from propene with H_2O_2/Ti silicate under mild conditions in methanol as solvent. Titanium silicate catalysts have also been described for the synthesis of hydrazine (305) and hydroxylamines (306) and for the hydroxylation of phenol (259).

Other heterogeneous catalysts for H_2O_2 in chemical synthesis have been reviewed in References 307 and 308.

The epoxidation of water-soluble olefins by hydrogen peroxide with metal or fluoroketone catalysts has also been described (309) in the literature.

11.4. Derivative Formation. Hydrogen peroxide is an important reagent in the manufacture of organic peroxides, including *tert*-butylhydroperoxide, benzoylperoxide, di-*tert*-butylperoxy cyclohexanes, peroxyacetic acid, esters such as *tert*-butyl peroxyacetate, and ketone derivatives such as methyl ethyl ketone peroxide. These are used as polymerization catalysts, crosslinking agents, and oxidants. Equilibrium peroxy acetic acid finds increasing use as disinfectant, slimicide, and sterilant (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES).

Zinc, calcium, and magnesium peroxides prepared from hydrogen peroxide are used as specialized oxidants where a slow release of hydrogen peroxide is desired. Calcium peroxide is used as a peroxide source in dentifrice products and a dough conditioner in the bakery industry (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES).

Hydrogen peroxide is used, particularly in Europe with the hotter wash temperatures and extended washing cycles, to manufacture sodium peroxoborate for household use and detergent bleach applications. Sodium carbonate peroxohydrate is used in simiar applications. Urea peroxide finds applications in cosmetic and pharmaceutical products. Potassium peroxomonosulfate is manufactured for uses in denture cleansers, automatic dishwashing detergents, hard-surface cleansers, and swimming-pool chemicals. (See PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES).

11.5. Mining and Hydrometallurgy. The largest application for hydrogen peroxide in the mining industry is the treatment of cyanide containing effluents from gold and silver ore leaching. Processes using H_2O_2 in combination with various catalysts (229,310–312) or as Caro's acid (313–318) (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES) have been described and are practiced at numerous mills around the world. H_2O_2 is also being employed for the enhanced cyanidation of gold and silver ores (319–323).

Hydrogen peroxide, in combination with various carbonates or bicarbonates, is used as an oxidant for the in-place solution mining of low-grade uranium ores (324–327). It is also used to precipitate uranium from ion-exchange eluates and solvent-extraction strip liquors and has been proposed as a fracturing agent in the *in situ* mining of low-grade copper (qv) ores and residues. Procedures for leaching copper, manganese, and zinc (328), from milled ore using hydrogen peroxide and for the recovery of ruthenium (329,330) and uranium (331,332) have been patented.

Small amounts of H_2O_2 are used for clarification of by-product sulfuric acid (qv), purification of selenium, in the separation of cobalt and nickel, and as a depressant and redox modifier in the flotation of copper and molybdenum ores (333,334).

11.6. Propellant. The catalytic decomposition of hydrogen peroxide 70% or greater proceeds rapidly and with sufficient heat release that the products are oxygen and steam (see eq. 2). The thrust developed from this reaction can be used to propel torpedoes and other small missiles (see EXPLOSIVES AND PROPELLANTS). An even greater amount of energy is developed if the hydrogen peroxide or its decomposition products are used as an oxidant with a variety of fuels.

Some publications suggest the use of highly concentrated hydrogen peroxide as mono or bipropellant for launching of smaller rockets (335,336). No practical application has been reported so far.

11.7. Other Uses. There are numerous small specialty uses for hydrogen peroxide. These include oxidizing metal ions to a higher valence state to facilitate subsequent removal, chemical polishing metal surfaces, and other metal surface treatments (qv). By catalytically decomposing hydrogen peroxide, the oxygen can be used as an *in situ* blowing agent for preparing certain foam rubbers and plastics (see FOAMED PLASTICS). Minor amounts are also used to prepare aseptic packaging for foods, tripe bleaching (see FOOD PACKAGING), and as a direct human food ingredient (337). In the United States the residual level in food immediately after aseptic packaging must not exceed 0.5 ppm. Under the "generally recognized as safe" (GRAS) regulation, the maximum treatment level for food applications can be up to 1.25% depending on the use.

Patents have been granted claiming the use of hydrogen peroxide as an oxygen source for various purposes, including the maintenance of breathable concentrations (see OXYGEN-GENERATING SYSTEMS).

Hydrogen peroxide is found in a variety of consumer products. It is used as a topical disinfectant (see DISINFECTANTS AND ANTISEPTICS) and antimycotic to sterilize contact lenses (qv). Small amounts are used in cosmetic preparations such as hair colorations and bleaching formulations. H_2O_2 is the active ingredient in color-safe household bleaches and carpet and hard-surface cleaners. H_2O_2 and other inorganic peroxo compounds are employed as a peroxide source in dentifrice products (338). 3% H_2O_2 USP topical solutions are sold in North America as over-the-counter drug for disinfection.

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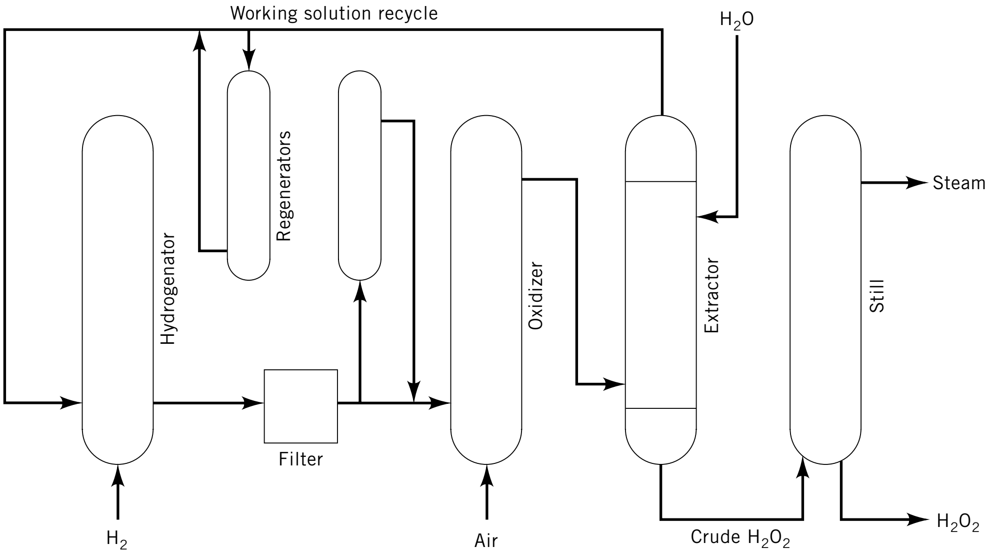

Fig. 1. Anthrahydroquinone autoxidation, Riedel–Pfleiderer process.

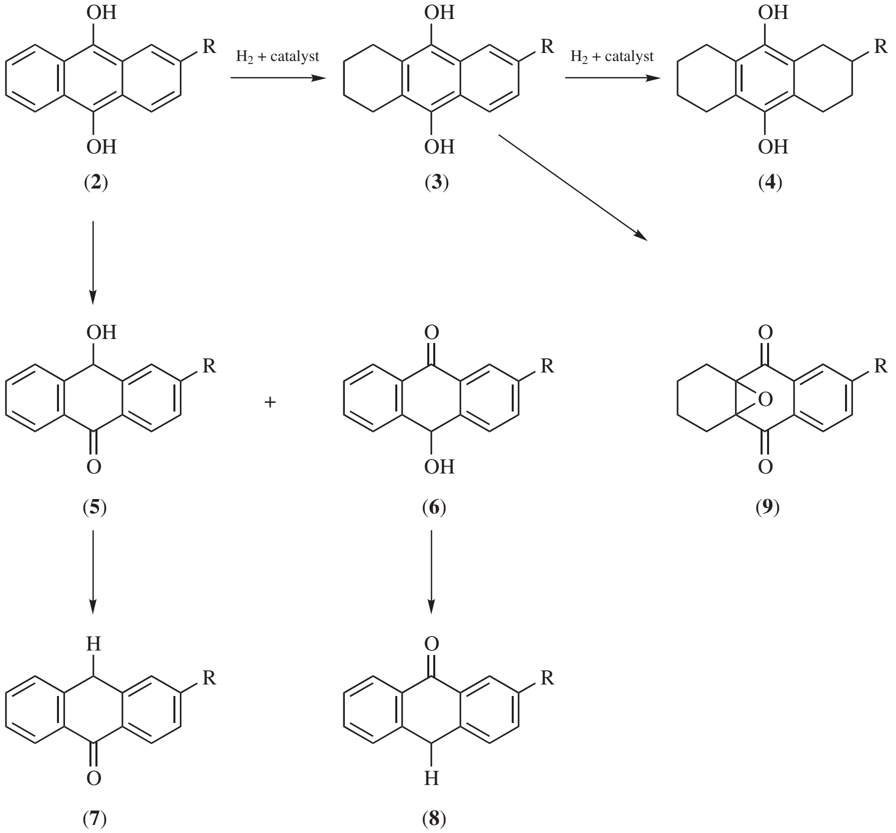

Fig. 2. Possible secondary reactions of 2-alkylanthrahydroquinones.

Table 1. **Properties of Pure Hydrogen Peroxide**

Property	Value
mp, °C[a]	−0.41
bp, °C	150.2
density at 25°C, g/mL	1.4425
viscosity at 20°C, mPa · s (=cP)	1.245
surface tension at 20°C, mN/m (=dyn/cm)	80.4
specific conductance at 26°C, $(\Omega \cdot \text{cm})^{-1}$	4×10^{-7}
heat of fusion, J/g[b]	367.52
specific heat at 25°C, J/(g · K)[b]	2.628
heat of vaporization at 25°C, kJ/g[b]	1.517
dissociation constant[c] at 20°C	1.78×10^{-12}
heat of dissociation, kJ/mol[b]	34.3
refractive index, mp^{20}	1.4084

[a] Tendency to supercooling.

[b] To convert J to cal, divide by 4.184.

[c] At zero ionic strength.

Table 2. **Physical Properties of Commercial Hydrogen Peroxide Solutions**

	Concentration of H_2O_2 (by weight)					
Parameter	10%	35%	50%	60%	70%	90%
density at 20°C, kg/m^3	1.034	1.113	1.195	1.2364	1.288	1.387
freezing point, °C	−6.0	−33.0	−52.2	−55.5	−40.3	−11.9
boiling point, °C	102	108	114	119	125	141
viscosity at 20°C, mPa · s	1.01	1.11	1.17		1.24	1.26
surface tension at 20°C, N/m	0.0731	0.0746	0.0757		0.0773	0.0792
$\Delta H_{\text{vap.}}$ at 25°C, kJ/mol	2.357		2.017	1.928	1.832	1.627
total vapor pressure at 30°C, Pa		3.200	2.400	1.867	1.467	0.667
partial vapor pressure at 30°C, Pa		48	99	120	175	333
Henry's law constant at 20°C, Pa · m^3/mol			1×10^{-3}			
refractive index n_D^{20}		1.3563	1.3672	1.3745	1.3827	1.3995

Table 3. **Physical Properties of Hydrogen Peroxide and Water**[a]

Property	Value H_2O_2	Value H_2O
mp, °C	−0.43	0
bp (101.3 kPa), °C	150,2	100
heat of melting, J/g	368	334
heat of vaporization, J/g		
at 25°C	1519	2443
at bp	1387	2258
specific heat, J g^{-1} K^{-1}		
liquid (25°C)	2.629	4.182
gas (25°C)	1.352	1.865
relative density, g/m^3		
at 0°C	1.4700	0.9998
at 20°C	1.4500	0.9980
at 25°C	1.4425	0.9971
viscosity, mPa · s		
at 0°C	1.819	1.792
at 20°C	1.249	1.002
critical temperature, °C	457	374.2
critical pressure, MPa	20.99	21.44
refractive index n_D^{20}	1.4084	1.3330

[a] Ref. 14.

Table 4. **pH Correction**

H_2O_2 conc, wt%	Equivalence point	True pH	Correction factor
35	3.9	4.6	+0.7
50	2.8	4.3	+1.5
70	1.6	4.4	+2.8
90	0.2	5.1	+4.9

Table 5. **Oxidation Potentials of Various Oxidants in Acidic Solution**

Compound	Potential, V
fluorine (F_2)	3.06
hydroxyl radical ($OH^{\cdot}$)	2.80
ozone (O_3)	2.07
hydrogen peroxide (H_2O_2)	1.81
perhydroxyl radical ($OOH^{\cdot}$)	1.70
chlorine (Cl_2)	1.36

Table 6. **Hydrogen Peroxide as an Oxidizing Agent**[a]

Redox reaction	Standard potential E_{O}, V
pHO	
$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$	+1.80
$HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3\,H^+ + 2\,e^-$	−0.17
$NO_2^- + H_2O \rightarrow NO_3^- + 2\,H^+ + 2\,e^-$	−0.94
$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	−1.36
$2\,Br^- \rightarrow Br_2 + 2\,e^-$	−1.07
$2\,I^- \rightarrow I_2 + 2\,e^-$	−0.54
pH 14	
$H_2O_2 + 2\,e^- \rightarrow 2\,OH^-$	+0.87
$Mn(OH)_2 + 2\,OH^- \rightarrow MnO(OH)_2 + H_2O + 2e^-$	+0.05

[a] Ref. 46.

Table 7. **Hydrogen Peroxide as a Reducing Agent**[a]

Redox reaction	Standard potential E_0, V
pH 0	
$H_2O_2 \rightarrow 2\,H^+ + O_2 + 2\,e^-$	−0.66
$5\,e^- + MnO_4{}^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$	+1.51
$1\,e^- + Ce^{4+} \rightarrow Ce^{3+}$	+1.61
pH 14	
$H_2O_2 + 2\,OH^- \rightarrow 2\,H_2O + O_2 + 2\,e^-$	+0.08
$1\,e^- + ClO_2 \rightarrow ClO_2{}^-$	+1.16
$2\,e^- + ClO^- + H_2O \rightarrow Cl^- + 2\,OH^-$	+0.89

[a] Ref. 46.

Table 8. **U.S. Hydrogen Peroxide Producers Working-Solution Components**[a]

	Producer				
Parameter	Degussa	OCI	EKA	FMC	Interox
RAQ solvent system[a]	EAQ	EAQ/BAQ/AAQ	EAQ	EAQ	AAQ
AQ	A/B	A/B	A/B	A/B	A/B
HAQ	TBU/TOP	DIBC	TBU/TOP	TOP	DIBC
reference	65	66	67	68	69

[a] Abbreviations: A/B = alkylated benzene; TBU = tetrabutyl urea; TOP = trioctyl phosphate; DIBC = diisobutyl carbinol.

Table 9. **Maximum Hydrogen Peroxide Achievable, %**

	WSC[a]			
DC	7.7	10.0	12.5	15.0
50	28.9	35.2	40.5	45.0
75	37.9	44.9	50.5	55.1
100	44.8	52.1	57.7	62.1
150	54.9	62.0	67.1	71.1
200	61.9	68.5	73.2	76.6

[a] Density of 0.93 g/mL.

Table 10. **Transport Regulations for Hydrogen Peroxide**

	H_2O_2 concentration, wt%		
Regulation	8–20	20–60	>60
RID/ADR	8, No. 62c	8, No. 62c	5.1., No. 1
IMDG Code	5.1.	5.1.	5.1.
UN No.	2984 package group III	2014 package group II	2015 package group I

Table 11. **Classification and Labeling of Hydrogen Peroxide**

	5–19%	20–59%	>60%
danger symbol	Xi	C	C, O
risk phrase	R 36/38	R 34	R 8–34
safety phase	S 28–36/39–45	S 28–36/39–45	S 28–36/39–45

Table 12. **World and North American Market Demand (Apparent Consumption) of Hydrogen Peroxide (100% Basis)**

Year	World, t×10^3	Annual growth rate, %	North America, 10^3t	Annual growth rate, %
1960	100	N/A	57	N/A
1965	173	14.6	106	17.2
1970	305	15.3	126	3.8
1975	393	5.8	132	1.0
1980	620	11.6	144	1.8
1985	712	14.8	162	12.5
1990	902	3.0	292	16.0
1995	1632	16.2	511	15.0
1998[a]	1970	6.9	595	5.5
2000[a]	2150	4.6	681	7.2

[a] Estimate.

Table 13. **Worldwide and North American Hydrogen Peroxide (100%) Nameplate Capacity by Major Producer**

Manufacturer[a]	Country of world headquarters	Worldwide, 10^3 t	Capacity[b] %	North American, 10^3 t	Capacity,[b] %
Solvay	Belgium	598	23	201	25
Degussa	Germany	364	14	162	20
FMC	USA	286	11	192	24
Elf Atochem	France	298	12	137	18
Akzo Nobel	Netherlands	208	8	64	8
Kemira	Finland	170	7	40	5
OCI	Korea	78	3		
Ausimont	Italy	78	3		
Mitsubishi Gas Chemicals	Japan	78	3		
Others		442	16	3	<1
Total		*2600*	*100*	*799*	*100*

[a] Includes all joint ventures with a controlling share of >50.0%.

[b] About 200,000 t of the worldwide capacity were mothballed in 1998 because of oversupply in the market in an attempt by the producers to improve their cost structure. DuPonts H_2O_2 plants have been sold to Degussa, Kemira, and Atochem.

Table 14. **North American Hydrogen Peroxide Plants**

Manufacturer	City	State or Province	Country	Nameplate capacity[a]
Akzo Nobel (Eka)	Columbus	Mississppi	USA	64
Degussa	Mobile	Alabama	USA	80
	Gibbons[b]	Alberta	Canada	82
Elf Atochem	Woodstock[b]	Tennessee	USA	64
Kemira	Maitland[b]	Ontario	Canada	40
Elf Atochem	Becancour	Quebec	Canada	73
FMC	Bayport	Texas	USA	109[c]
	Spring Hill	West Virginia	USA	25
	Prince George	British Colombia	Canada	48
	Santa Clara	Mexico D.F.	Mexico	10
Fort James	Muskogee	Oklahoma	USA	3[d]
Solvay	Deer Park	Texas	USA	136[c]
	Longview	Washington	USA	65
Total				*799*

[a] 100% basis; available production estimated to be 90% of published nameplate capacity.

[b] Former DuPont Plant.

[c] In 1998 approximately 50,000 tonne capacity were mothballed because of market oversupply.

[d] Uses electrochemical Dowradian process; all other producers use anthraquinone autoxidation process.

Table 15. **1998 Technical-Grade Hydrogen Peroxide Price Schedule, U.S. \$/kg**[a]

Concentration, wt%[b]	Commodity basis	100% basis
35 bulk	0.54	1.54
50 bulk	0.75	1.50
70 bulk	1.05	1.49
35 drum	0.79	2.18
50 drum	1.09	2.18

[a] Free on board nearest producing plant.

[b] Bulk = full-tank trucks/trailers or railcars, drum=full truckload of 0.208-m^3 (55-U.S. gal) drums.

Table 16. **Shelflife of Commercial H_2O_2 Solutions**

Temperature, °C	Decomposition rate
20	<2%/year
70	<2%/week
95	<5%/24 h

Table 17. **Adiabatic Decomposition of H_2O_2 Solutions**[a]

H_2O_2 content, % by wt	Adiabatic decomposition temperature (°C)	Evaporation of water, %	Gas volume developed	
			L/kg solution	L/L solution
10	89	1.0	44	45
20	100	12.1	276	296
30	100	27.9	542	602
40	100	45.5	808	931
50	100	65.5	1076	1286
60	100	88.3	1347	1672
65	109	100.0	1508	1906
70	233	100.0	1974	2544
75	360	100.0	2439	3202
80	487	100.0	2893	3874
85	613	100.0	3331	4547
90	740	100.0	3761	5235
95	867	100.0	4179	5934
100	996	100.0	4592	6649

[a] Ref. 14.

Table 18. **Consumption of Hydrogen Peroxide in North America, 10^3 t**

Use Area	1980	1990	1995	2000[a]
pulp and paper	32	144	340	410
textile	28	34	40	63
chemicals[b]	44	52	59	75
environmental[c]	10	23	31	66
other	30	39	41	67
Total	*144*	*292*	*511*	*681*

[a] Estimate.

[b] Includes captive use.

[c] Includes mining industry.

Table 19. **Consumption of Hydrogen Peroxide in Western Europe, 10^3 t/yr**

	Year	
Use area	1991	1997
pulp and paper	156	320
textiles	40	43
chemicals[a]	280	255
environmental[b]	19	33
all others	8	12
Total	*503*	*663*

[a] Includes captive use.

[b] Includes mining industry.