

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 solubilities 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, anthrahydroquinone, water, and hydrogen peroxide solubilities. The capacity is defined as the maximum amount of hydrogen peroxide in g/L 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 solubilities of the anthrahydroquinones and hydrogen peroxide and the distribution coefficient of the working solution-H<sub>2</sub>O<sub>2</sub>-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 (41-44) for use in autoxidation processes. Whereas the anthraquinones are usually monosubstituted at the 2-position, the literature includes examples of C-1 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 favorably partition so that a reasonably high strength hydrogen peroxide solution can be safely extracted. Alcohols, ureas, amides, caprolactams, esters, and pyrrolidones have been used or cited in the literature as usable polar solvents. Table 4 lists the working solution components of the principal U.S. producers. Although a high distribution coefficient increases the extraction step efficiency, if too high it creates potential safety problems; especially if a free phase forms as a result of slightly exceeding the water solubility of the oxidized but unextracted working solution. The distribution coefficient is defined as weight of solute per unit weight of extract, divided

Table 4. U.S. Hydrogen Peroxide Producers' Working Solution Components

Parameter	Producer				
	Degussa	Du Pont	EKA	FMC	Interox
RAQ	EAQ	EAQ/BAQ/AAQ	EAQ	EAQ	AAQ
solvent system <sup>a</sup>					
AQ	A/B	A/B	A/B	A/B	A/B
HAQ	TBU/TOP	DIBC	TBU/TOP	TOP	DIBC
Reference	45	46	47	48	49

<sup>a</sup>A/B = alkylated benzenes; TBU = tetrabutyl urea; TOP = triethyl phosphate; and DIBC = diisobutyl carbinol. See text.

by the weight of solute per unit weight of solvent. Table 5 shows the effect of the distribution coefficient (DC) on the maximum achievable aqueous hydrogen peroxide strength vs the working solution capacity (WSC).

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 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 psi/g)) 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<sub>2</sub>O<sub>2</sub> 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) (50,51) for a substantially tetrahydroalkylanthraquinone-free working solution (antra system) and the 60-75°C indicated by LaPorte Chemicals (Interox-Solvay), where the working solutions contain more tetrahydroalkylanthraquinone than alkylanthraquinone (tetra system) (52,53). Degussa apparently uses the highest operating pressure, near 300 kPa (43.5 psi) overpressure (54). The conversion of quinone to hydroquinone

Table 5. Maximum Hydrogen Peroxide Achievable, %

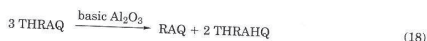
DC	WSC <sup>a</sup>			
	7.7	10.0	12.5	15.0
50	28.9	35.2	40.5	45.0
75	37.9	44.9	50.5	55.1
100	44.8	52.1	57.7	62.1
150	54.9	62.0	67.1	71.1
200	61.9	68.5	73.2	76.6

<sup>a</sup>Density of 0.93 g/mL.

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 (55).

**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 (56). To maintain a low tetra content, combinations of milder operating temperature and low hydrogen partial pressure, more selective catalysts and solvents, and 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, eg, ethylene, is converted to the corresponding alkane, eg, ethane (57–58). Some ring dehydrogenation of the tetra species to the anthra species per equation 2 is one of several functions performed by the basic alumina in the working solution regenerators. The reaction is reasonably slow.



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. The oxanthrone is readily regenerated by passing through activated alumina, but the anthrone is only marginally affected. Anthrone is subject to other reaction 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 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, the formation of the tautomer oxanthrone occurs.

Conventional continuous stirred-tank reactors (CSTRs), tubular, draft-tube agitated, and fixed-bed (59,60) hydrogenator designs have been patented, as has a special carbon candlefilter for use with fine palladium black catalyst (61). 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 life-span. 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 activity 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 suspension 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.

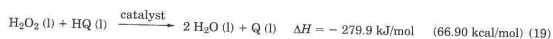
The Raney nickel catalyst used in the original Riedl-Pfleiderer process was active, caused excessive ring hydrogenation, was easily deactivated by oxygen or hydrogen peroxide, and was pyrophoric. The use of a palladium catalyst, used by all principal producers as of this writing, avoids the problems 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 a high crush strength and are reasonably smooth and rounded to resist attrition, abrasion, and fracturing. A truly round support with minimum asperities 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 (62). 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 (63).

**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 become 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 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 anthrahydroquinone, the actual oxygen concentration in the liquid, and the system temperature (64). 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  $\text{H}_2\text{O}_2$  and hydroquinone (HQ) at a catalytic site (eq. 19).



The oxidation of alkylanthrahydroquinones by forming noncoalescing foams (65) between the working solution and oxygen or oxygen-containing gas and continuous gas-liquid dispersions (66) has been patented. Minimized investment and energy consumption are claimed and the short contact time reportedly minimizes detrimental 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. Working solutions used by the principal producers are less dense than water so 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 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 (67). 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, 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, and unfilled 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 extractor the distance between trays (spacings) 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 (68,69). For most working solutions the optimum individual tray hole diameter is 2.5–3.0 mm. Tray spacings are 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 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 that containing aliphatic carboxylic acids to give peroxycarboxylic acid. Other patents describe transfer of hydrogen peroxide from one solvent to another.

**Working Solution Regeneration and Purification.** Economic operation of an anthraquinone autooxidation process mandates frugal 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) (70). 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. 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 upon addition of small amounts of *N,N*-di-*n*-butylaniline to the working solution is claimed (71).

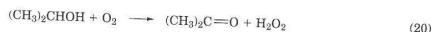
Recovery of working solution components includes recrystallization of the anthraquinones, extraction of crude mixtures with lower alcohols, use of anion-exchange resin, or isolation of the hydroquinones (71). Dilution of a heavily

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 (72). 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 (73).

The alumina or sodium aluminosilicate catalysts used to regenerate degraded working solutions lose activity with time as active soda sites are neutralized, but these too 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, carboxylic acids, hydrogen peroxide (74), organic solvents, 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 partial 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. A liquid-phase process based on the autoxidation of isopropyl alcohol [67-63-0] was operated for about 20 years at Norco, Louisiana, by Shell Chemical Co. (see PROPYL ALCOHOLS, ISOPROPYL ALCOHOL). The by-product acetone (qv) was marketed and most of the hydrogen peroxide was used captively to produce glycerol (qv).



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

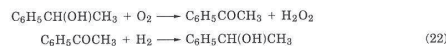
Alcohol autoxidation is carried out in the range of 70–160°C and 1000–2000 kPa (10–20 atm). These conditions maintain the product and reactants as liquids and are near optimum for practical hydrogen peroxide production rates. Several additives including acids, nitriles, stabilizers, and sequestered transition-metal oxides reportedly improve process economics. The product mixture, containing hydrogen peroxide, water, acetone, and residual isopropyl alcohol, is separated in a wiped film evaporator. The organics and water are taken overhead and further refined to recover by-product acetone and the isopropyl alcohol for recycle. The hydrogen peroxide is concentrated at the bottom and must be continuously diluted with water to maintain its concentration near 45% to avoid safety problems that result from hot, concentrated hydrogen peroxide in intimate contact with organic materials. The recovered hydrogen peroxide is

purified by scrubbing with solvent, passed through both anion- and cation-exchange resins, and stabilized. Several modifications, special materials of construction treatments, and use of other secondary reactions have been noted (75–77).

In the former USSR, there reportedly are two technologies in use; one is old anthrahydroquinone autoxidation technology and the other is closed-loop isopropyl alcohol oxidation technology. Production facilities include several smaller, 100–150-t/yr isopropyl alcohol oxidation plants and a larger, 15,000-t/yr plant, which reportedly is being expanded to 30,000-t/yr. Differences in this technology as compared to the Shell Chemical Co. process are the use of oxygen-enriched air in the oxidation step and, catalytic reduction of the coproduct acetone back to isopropyl alcohol per equation 21.



Alcohol oxidation patent activity in the 1980s and 1990s by ARCO (78–83) involved the oxidation of methylbenzyl alcohol [98-85-10] (*sec*-phenethylalcohol) to acetophenone [98-86-2] and hydrogen peroxide. Methylbenzyl alcohol is the main coproduct of propylene oxide [75-56-9] (qv) produced from propylene [115-07-1] (qv) and ethylbenzene hydroperoxide [3071-32-7]. The last is produced by the oxidation of ethylbenzene [100-41-7]. 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 22 and 23.



to give the net reaction



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.

**Hydrocarbon Autoxidation.** Hydrogen peroxide can be prepared directly by the vapor-phase partial oxidation of hydrocarbons and indirectly from several hydrocarbon hydroperoxides. Although many patents have been granted, non-processes are known to be practiced on a commercial scale. These vapor-phase oxidation processes generate a great number of by-products which complicate

the recovery, purification, and concentration of the hydrogen peroxide. Several methods for recovery have been listed in the literature, including extractive distillation of the crude reaction mixture using acetic acid.

Organic hydroperoxides can be prepared by liquid-phase oxidation of selected hydrocarbons in relatively high yield. Several cyclic processes for hydrogen peroxide manufacture from hydroperoxides have been patented (84,85), and others (86–88) describe the reaction of *tert*-butyl hydroperoxide with sulfuric acid to obtain hydrogen peroxide and coproduct *tert*-butyl alcohol or *tert*-butyl peroxide.

**Nitrogen Compound Autoxidation.** Cyclic processes based on the oxidation of hydrazobenzene and dihydrophenazine to give hydrogen peroxide and the corresponding azobenzene–phenazine were developed in the United States and Germany during World War II. However, these processes could not compete economically with the anthrahydroquinone autoxidation process.

**Hydrolysis of Peroxycarboxylic Systems.** Peroxyacetic acid [79-21-0] is produced commercially by the controlled autoxidation of acetaldehyde (qv). Under hydrolytic conditions, it forms an equilibrium mixture with acetic acid and hydrogen peroxide. The hydrogen peroxide can be recovered from the mixture by extractive distillation (89) or by precipitating as the calcium salt followed by carbonating with carbon dioxide. These methods are not practiced on a commercial scale. Alternatively, the peroxycarboxylic acid and alcohols can be treated with an esterifying catalyst to form  $H_2O_2$  and the corresponding ester (90,91) (see PEROXIDES AND PEROXY COMPOUNDS).

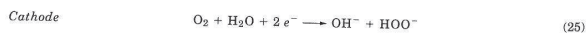
#### ELECTROLYTIC METHODS

The electrolytic processes for commercial production of hydrogen peroxide are based on (1) the oxidation of sulfuric acid or sulfates to peroxydisulfuric acid [13445-49-3] (peroxydisulfates) with the formation of hydrogen and (2) the double hydrolysis of the peroxydisulfuric acid (peroxydisulfates) 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

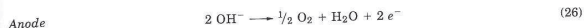


This electrolytic process technology is no longer used because of the extensive and continuous electrolyte purification needs, the high capital and power requirements, and economic inability to compete with large-scale anthrahydroquinone autoxidation processes.

**The Huron-Dow Process.** The Huron-Dow (H-D) process is a refinement of the cathodic reduction 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 (92). The two reactions involved are



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



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 (93–100). The newest cell design (94–96) consists of a porous cathode and a platinum-coated titanium anode separated by a diaphragm and an ion-exchange (qv) membrane (see MEMBRANE TECHNOLOGY; METAL ANODES). The diaphragm consists of multiple layers of a porous polypropylene composite, which assures uniform flow of the electrolyte. The electrolyte enters 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 made 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 which 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 (ethylenedinitro)tetraacetic acid (EDTA) is added at up to 0.5 g/L to protect against tramp metal ion induced decomposition (96). 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 (see ELECTROCHEMICAL PROCESSING, INORGANIC).

#### 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 (101–106). More recent investigations have included use of homogeneous catalysts such as organic complexes of palladium, iron and platinum, iridium, and the use of promoters (107–109); heterogeneous catalysts using acidic aqueous solutions and some additives (110–118); and those processes using heterogeneous catalysts and organic solvents including acetone, methanol, fluorocarbons, and acetonitrile (119–121). Platinum-group metal carriers have included hydrophobic materials such as Teflon, polyethylene, polypropylene, and polystyrene (109); silicic acid (106); and carbon, charcoal, silica, and alumina (116).

In Du Pont patents (116) 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