

PREPARING TO MANUFACTURE HYDROGEN PEROXIDE



Part of the [Hydrogen Peroxide Propulsion Guide](#)

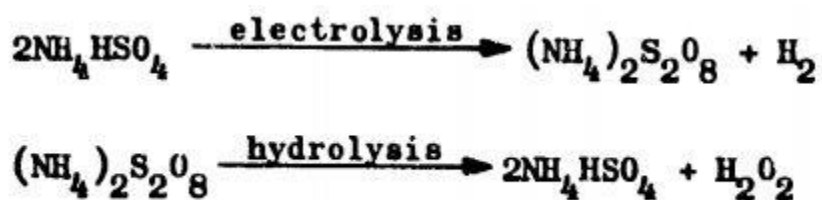
The early laboratory preparation of hydrogen peroxide was based on the technique that Thenard used during the initial preparation of hydrogen peroxide. In this technique, barium nitrate, purified by recrystallization, was decomposed by heating in air in a porcelain retort. The resulting oxide was further oxidized by heating in a stream of oxygen to a dull red heat. The barium peroxide which formed was then dampened, ground, and dissolved in hydrochloric acid (nitric acid was used in Thenard's initial experiments). A slight excess of sulfuric acid was then added to precipitate barium sulfate and regenerate hydrochloric acid. The procedure of barium peroxide solution and sulfate precipitation was repeated several times in the same solution to increase the peroxide concentration (concentrations of up to 33 percent by weight hydrogen peroxide could be achieved in this manner).

The concentrated solution containing water, hydrogen peroxide, and hydrochloric acid, along with accumulated impurities, was cooled with ice and saturated with barium peroxide; iron and manganese impurities in the solution were then precipitated out as phosphates. The hydrochloric acid was removed by the addition of silver sulfate and the sulfate ion was removed by the subsequent addition of barium oxide. Further concentration was accomplished by vacuum distillation until "no further density increase occurs." Thenard reported that 100 w/o

hydrogen peroxide (on the basis of density data and the measurement of the volume of oxygen released) could be obtained by this technique.

The first record of commercial production of hydrogen peroxide appeared in the 1865 to 1875 period. The first commercial production in the United States was by the Oakland Chemical Company, Brooklyn, New York, in 1881. Laporte Chemicals Ltd. established a factory in Yorkshire, England in 1888. With the exception of substitution of fluorosilicic acid for the hydrochloric acid, Thenard's process was used essentially unchanged for the manufacture of hydrogen peroxide until nearly 1900. The formation of hydrogen peroxide in the electrolysis of sulfuric acid was first reported in 1853; later developments made the manufacture of hydrogen peroxide by an electrolytic process possible in 1908. By 1939, only 10 percent of the world's production was by the barium peroxide process.

Currently, hydrogen peroxide is commercially manufactured either by an electrolytic (inorganic) method or one of two organic processes. The electrolytic process (Ref. 1) involves the electrochemical formation of either peroxydisulfuric acid or peroxydisulfate (from an ammonium bisulfate solution), their subsequent hydrolysis, and separation of hydrogen peroxide by distillation. The basic equations for these reactions may be summarized as follows:

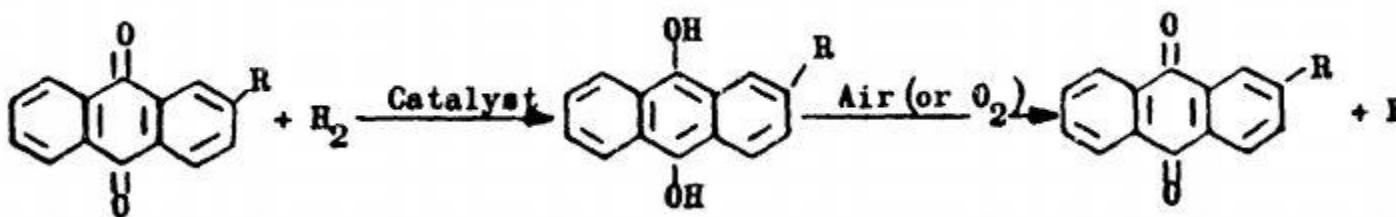


Although sulfuric acid may be used as the starting material, the ammonium bisulfate process is cheaper and has a higher cell efficiency.

The electrolysis is carried out in stoneware tanks with platinum electrodes; conversion of bisulfate to the persulfate takes place at the anode. After hydrolysis of the persulfate (with steam) in an evaporator, the resulting dilute aqueous solution of H₂O₂ is separated from the bisulfate and further distilled in a stoneware distillation column. The resulting solution is approximately 30 w/o H₂O₂. Both the cathode liquor (after purification) and the bisulfate from the evaporator (and separator) are recycled back to the cells.

One of the organic processes used commercially for the manufacture of hydrogen peroxide involves the catalytic reduction of a substituted anthraquinone and subsequent oxidation back to the quinone structure with the production of H₂O₂ (Ref. 2). Although the process may vary

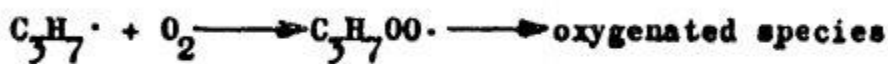
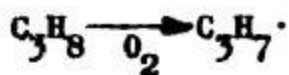
slightly among the several commercial manufacturers who use it, the basic reactions can be summarized as follows:



Where R may be ethyl, t-butyl, etc.

The reduction of the substituted anthraquinone with hydrogen is accomplished from room temperature to 40 C or more and at 1 to 3 atmospheres of pressure in the presence of a Raney nickel, nickel, palladium, or platinum catalyst. The catalyst is separated from the hydroquinone solution and recycled to the hydrogenator. After oxidation of the hydroquinone by either air or oxygen, the resulting quinone solution containing 0.5 to 1 w/o H₂O₂ is extracted with water at 25 to 40 C. The aqueous solution of hydrogen peroxide (~ 15 to 35 w/o H₂O₂) is cleaned of organic contamination and vacuum distilled to ~70 w/o H₂O₂. The organic phase from the extractor is evaporated from entrained water, partially dried, cleaned of H₂O₂ (by a decomposition catalyst), and recycled as the work solution to the hydrogenator.

The second organic process used in the present commercial manufacture of hydrogen peroxide is based on the oxidation of propane or a propane derivative (such as isopropyl alcohol). Although the actual details of hydrogen peroxide manufacture by these processes are not defined, the basic reactions of the propane oxidation are postulated as follows (Ref. 3):



As noted, the side products in this reaction series are a variety of oxygenated organic species, propylene, methane, and ethylene.

The oxidation of isopropyl alcohol may occur as follows (Ref. 3):



It is reported that the latter reaction can be conducted in either the liquid or vapor phases. Hydrogen peroxide concentrations of 15 to 17 w/o H₂O₂ and 25 to 30 w/o H₂O₂ are obtained from the propane and isopropyl alcohol oxidations, respectively.

Source : <http://www.diyspaceexploration.com/preparing-manufacture-hydrogen-peroxide/>