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18062

Ms. Christina RUIZ-CORTES (CLT 89/600); Backstopping Officer: Mr. Herce, IPCT/TP/INF

PREFACE

This information package has been prepared to respond to the con-
siderable interest in hydrogen peroxide production shown by INTIB
users in developing countries.

The most important areas that are raising the demand for this pro-
duct are the new and wider applications in waste treatment and in
the pulp and paper industry.It is also important to note that hy-
drogen peroxide is one of the most non-polluting oxidizing agents
a factor that is becoming increasingly important.

Worldwide demand is increasing by almost 5% per year and by about
10% per year in North America.

The minimum size for hydrogen peroxide plant is about 2000t/year;
the largest plant (Oxosynthesis) is 30000t/year.

Although the anthraquinone autoxidation process for hydrogen per-
oxide manufacture is the most widely used commercial process,this
information package is devoted to the electrochemical process
(peroxydisulphate process) since there are many plants which are
usually small,using this process throughout the world.Neverthe -
less,there are other factors to be considered by individuals in-
volved in the development of this product and these are discuss-
ed in this package.

An information package is intended as a time-saving tool for
people involved in chemical industries since it supplies them
with primary information selected from a wide variety of exist-
ing sources,which usually is not readily accessible to developing
countries.

INTRODUCTION

Hydrogen peroxide (H_2O_2) is the most widely used peroxide compound. It is of considerable importance in connection with its numerous applications.

The technology of both manufacture and utilization of hydrogen peroxide is comparatively new. Its scale of manufacture and use increas ed markedly since about 1925 when electrolytic processes were intro duced to the U.S. and industrial bleach applications were developed. Three commercial processes have been employed to manufacture hydrogen peroxide :

- Electrosynthesis

- Oxidation of isopropyl alcohol

- Anthraquinone process

The third process, often commonly referred to as the quinone process is the most predominant commercial process in use in the 1980s. Nevertheless worldwide, a number of plants (usually small plants) pro produce hydrogen peroxide by electrolytic methods.

In the first process, hydrogen peroxide can be produced electrochemi cally by the anodic oxidation of sulphuric acid or its salts (ammonium or potassium sulphate) to produce persulphuric acid or persulphates as anode products, which are subjected to hydrolysis and subsequently distilled to produce a 30 - 40% hydrogen peroxide solu - tion.

Sulphuric acid electrolyte has a low current efficiency (70-75%) but the use of ammonium sulphate causes crystallization problems, so a mixture is used to obtain a current efficiency of 80% or high

er and crystallization troubles are eliminated.( )

At least during the 80's decade,although equi_____
'ydrogen gas are coproduced,recovery is not practiced in the U.S.
The crude product from any hydrogen peroxide process can be used
as such,but commercial grades are further purified,concentrated
and stabilized. Especially concentrated hydrogen peroxide requires
great care in handling and storing.

According to literature,some disadvantages are the following :

- extensive and continuous purification of the electrolyte is re-
  quired

- high capital

- high power requirements

- maintenance of sophistificated apparatus is required,together
  with highly qualified personnel

Because of these facts,electrolytical processes cannot compete e-
conomically with anthraquinone process. Nevertheless,electrolyti-
cal plants may have benefits such as protective tariffs or serve
a local market,thus saving on transportation costs,which allows
them to compete with the lower-cost anthraquinone process ( ).
Additionally there are two relevants facts that could promote in-
terest in an electrolytic process : increasing amounts are used
in wastewater treatment and in the pulp and paper industry. These
uses require dilute peroxide solutions and about 40% of the ener-
gy requirement (peroxydisulphate process) is used to concentrate
the peroxide product to 50% hydrogen peroxide. Despite this sa -
ving more innovation for this process is required in order to ma-
ke it more energy competitive ( ).

Hydrogen peroxide is sold in aqueous solutions ranging from 3% to
to 9% by weight.

The main fields of applications for hydrogen peroxide are in che-
micals,textiles,pulp and paper industry,pollution control,metal -
lurgy and miscellaneous uses.Generally,most applications make use
of its properties as a strong oxidizing or bleaching agent.

In the United States of America the two major markets for hydro -
gen peroxide have historically been textile bleaching and chemi -
cal manufacturing.At present increasing amounts are used in the
pulp and paper industry,especially in Canada and the U.S.A. by re
placing chlorine as a bleaching agent. Hydrogen peroxide has the
advandtage of its milder action on fibres and it leaves no envi -
ronmentally undesirable residue compared to chlorine and its com-
pounds.Furthermore hydrogen peroxide produces an improves the qua
lity of paper ( ).

In Europe,hydrogen peroxide is employed,in particular,to manufac-
ture perborates and others persalts for household and detergent
bleach applications. This market in Europe accounts for 40% of hy
drogen peroxide utilization.

Concentrated (90-100%) hydrogen peroxide is used as a source of e
nergy in both military and civil use.

Besides its uses in bleaching and deodorizing textiles,mainly co-
tton and other fibres,natural or synthetic,wood pulp and in the
pulp and paper industry,it is also a source of organic and inorga
nic peroxides,plasticizers,laboratory reagents,refining and clea-
ning metals,bleaching and oxidizing agent in foods.

In the near future one can expect new applications for this pro -

duct : sanitation and deodorization of liquid and gaseous effluents, soil regeneration, epoxidation of natural rubber, and as a substitute for chlorine in water and sewage treatment ( ).

The use of hydrogen peroxide in wastewater treatment could represent a significant new market since one pound of hydrogen peroxide can be substituted for 3 or 4 pounds of chlorine, nevertheless, its use depend on economic considerations as hydrogen peroxide is more expensive hypochlorites.

1.—

111: 99751r Hydrogen peroxide. Savostianoff, D. (Fr.). *Inf. Chim.* 1989, 304, 117-18 (Fr). A review with 2 refs. of the manuf. and use, as oxidant, of H_2O_2.

2.—

108: 28553e **An electrode.** Nakamura, Kenichi; Nankai, Shiro; Iijima, Takashi (Matsushita Electric Industrial Co., Ltd.) Jpn. Tokkyo Koho JP 62 40,437 [87 40,437] '''. C25B11,04), 28 Aug 1987. Appl. 79, 78,748, 21 Jun 1979; 3 pp. A durable electrode having a long service lifetime is comprised of a metal oxide, redox compd. immobilized on the metal oxide. and conductor. Optionally, the metal oxide may be comprised of SnO_2. WO_3. RuO_2. MnO_2. TiO_2. MoO_3... or IrO_2. The electrode is useful as a H_2O_2 manufg. electrode and enzyme sensor.

3.—

104: 189158a **Effect of impurities in peroxymonosulfuric acid on the yield of hydrogen peroxide.** Smirnov, G. I.; Chernyak, A. S.; Chernysheva, O. N.; Shepot'ko, M. L. (Irkutsk. Univ., Irkutsk, USSR). *Zh. Prikl. Khim. (Leningrad)* 1986, 59(3), 662-4 (Russ). The effect of the concn. of impurities in H_2SO_5 was studied on the H_2O_2 yield in the electrolytic hydrolysis of H_2SO_5. The H_2O_2 yield decreased from 70.7 to 54.8 and 72.2 to 45.8% with the increase of the concn. of Fe and Cu from 15.5 to 99.0 and 0.04 to 2.74 mg/L, resp. The effect of the simultaneous presence of Fe, Ti, Al, and Si; of Na, Pt, Mg, and Ca; and of Pb, Cu, and Pt on the yield was studied with a math. model. The results can be used for the improvement of H_2O_2 prepn.

4.—

103: 195562k **Hydrogen peroxide [as a reagent].** Pandiarajan, K. (Dep. Chem., Annamalai Univ., Annamalainagar, 608002 India). *Synth. Reagents* 1985, 6, 60-155 (Eng). Edited by Pizey, James S. Horwood: Chichester, UK. A review with 426 refs. on the uses of H_2O in org. chem.

5.—

101: 113178m **Comparision of experimental and calculated data on hydrogen peroxide conversion for a commercial reactor.** Brounshtein, B. I.; Zharikov, Yu. N.; Krichevskava, O. P. (USSR). *Issled. po Apparaturno-tekhnol. Oformleniyu i Avtomatiz. Khim. Protsessov*, L. 1983, 41-7 (Russ). From *Ref. Zh., Khim.* 1984, Abstr. No. 10I121. Title only translated.

6.—

97: 63037r **Electrochemical production of hydrogen peroxide by the Lowenstein method in a bipolar electrolyzer.** Spiral, Jiri; Musil, Josef; Balej, Jan; Thiele, Wolfgang; Matschiner, Hermann (Chem. Zavody, N. P., Sokolov, Czech.). *Chem. Prum.* 1982, 32(6), 287-91 (Czech). The long term electrolytic prodn. of concd. solns. of $(NH_4)_2S_2O_8$ as a byproduct of electrolytic prodn. of H_2O_2 by the Loewenstein-Riedel method in bipolar electrolytic cells type EZ II consumes 1/3 less elec. energy as comparedwith the old plant with the original monopolar-type cells. The cost of energy consumed for mech. cooling of the new link is practically cancelled out by the saving of cooling water. From the hygienic viewpoint the operation of 3 exptl. EZ II (S) cells without exhausting pollutants into the atm. may be regarded as a remarkable advance in comparison to the org. uncovered cells.　　　　　　　　　　　　　　E. R. Holman

7.—

90: 102832y **Hydrogen Peroxide and Its Derivatives: Chemistry and Uses.** (Wassers'offperoxid and Seine Derivate: Chemie and Anwendung) Weigert, Wolfgang M.; Editor (Huethig: Heidelberg. Ger.). 1978. 205 pp.

3.—

90: 45814t **Electrosynthesis of hydrogen peroxide and peroxydisulfates. Part III. Mechanism of anodic formation of peroxydisulfates.** Balej, Jan; Matschiner, Hermann; Thiele, Wolfgang (Inst. Inorg. Chem., Czech. Acad. Sci., Prague, Czech.). *Chem. Tech. (Leipzig)* 1978, 30(11), 578–81 (Ger). A review with 55 refs.

9.—

88: 172842j **The electrosynthesis of hydrogen peroxides and peroxodisulfates. Part II. Optimization of electrolysis cells using an electrolyzer for peroxodisulfuric acid as an example.** Schleiff, Martin; Thiele, Wolfgang; Matschiner, Hermann (VEB Eilenburger Chem.-Werk, Eilenburg, E. Ger.). *Chem. Tech. (Leipzig)* 1977, 29(12), 679–83 (Ger). A combination statistical and phys. model is developed and evaluated for the title electrolyzer. An anal. of all of the costs affecting the electrolysis process is presented and tech. and economic optimization performed. A math. anal. of the model yields generally valid conclusions concerning the shifting of the optimum in relation to the different target functions investigated when certain design and economic parameters are varied.

L. Rajkay

10.—

035732 **PERSPEKTIVY PRIMENENIYA PEREKISI VODORODA V NARODNOM KHO- ZYAISTVE. [Prospects of Using Hydrogen Peroxide in the National Economy].** The use of hydrogen peroxide as a bleaching agent and in the synthesis of organic chemicals is discussed. Particular attention is paid to the use of hydrogen peroxide in epoxydation and hydroxyl- ation processes and in the production of synthetic fibers. The need for wider use of cheaper and more convenient methods of producing hydrogen peroxide in the USSR is stressed, in particular, the use of a method based on the oxidation of secondary alcohols. 54 refs. In Russian.

Pneva. E.Ya. *Khim Prom* n 2 1976

11.—

88: 138629k **Development of the production of hydrogen peroxide outside of the Soviet Union.** Pneva, E. Ya. (USSR). *Proizvod. Perekisi Vodoroda Zhidkofazn. Okisleniem Izopropilovogo Spirta* 1975, 2, 4-12 (Russ). A review with 51 refs.

J. Jarzebowska

12.—

87: 126429m **Hydrogen peroxide: preparation and properties.** Osteroth, D. (Witten, Ger.). *Chem. Labor Betr.* 1975, 26(8), 310–11 (Ger). A review on the prepn. and properties of H_2O_2 since 1818 with 2 refs.

13.—

87: 87103d **Preparation and purification of hydrogen peroxide by the hydrolysis of persulfate. Part 7.** Choe, Il Dong; Kim, Man Su; Sim, Myong Gil (N. Korea). *Huahak Kwa Huahak Kongop* 1977, 20(3), 130-3 (Korean). The effects of factors that affect the prepn. of H_2O_2 from $(NH_4)_2S_2O_8$ and H_2SO_4 were detd. and the hydrolysis conditions for obtaining a max. yield of H_2O_2 were established. The concn. of H_2SO_4 was 22 M and that of $(NH_4)S_2O_8$ was 3.2 M; the reaction temp. for the first 30 min. was 70° and that for the second 60 min. was 80°. The H_2O_2 yield was 80% and 99% of the $(NH_4)S_2O_8$ was hydrolyzed. When the Cu and Fe^{3+} concns. were > 10⁻¹%, the H_2O_2 yield decreased

87: 74039n On the formation reaction velocity of hydrogen peroxide from ammonium persulfate. Part 6. Choe, Il Dong; Kim, Man Su; Pak, Hwa Suk; Sim, Myong Gil (N. Korea). *Hwahak Kwa Hwahak Kongop* 1977, 20(2), 75–80 (Korean). The effect of H_2SO_4 acid concn. on the rate of H_2O_2 formation from $(NH_4)_2S_2O_8$ was studied along with the rates of side reactions with impurities such as Cu^{2+} and Fe^{3+}. The rate of H_2O_2 formation is limited by the reaction $SO_5^{2-} + H_2O = H_2O_2 + SO_4^{2-}$, with product $[H_2O_2]$ at time t and 70 °C of $[H_2O_2]_t = [S_2O_8^{2-}]_0\{1 - \exp -(k^{e''} + 0.0101\Delta c)t\}$ with initial $[H_2SO_4]_0 > 1.2$ mol/L, where Δc stands for change in $[H_2SO_4]$ during the designated reaction period and k_0'' represents the rate constant when initial $[H_2SO_4]$ is 1.2 mol/L. The secondary side reactions by impurities can be reduced if the hydrolysis rate of $S_2O_8^{2-}$ is increased by increasing the catalytic acid concn. Impurities affect the decompn. rates of both SO_5^{2-} and H_2O_2.   J. S. Yoo

87: 41264d Distillation of hydrogen peroxide from persulfuric acid solutions. Markov, S. S.; Smirnova, M. A.; Trokhova, L. S.; Tyminskii, V. N. (USSR). *Khim. Prom-st. (Moscow)* 1977, (3), 204-5 (Russ). The distn. of H_2O_2 from persulfuric acid solns. was studied at 100° and 80 mm Hg, for which the vapor pressure of 70-2% H_2SO_4 is ~0. The dependence of the distribution coeff. (ratio of H_2O_2 concn. in soln. to H_2O_2 concn. in condensate) on the H_2SO_4 concn. in the soln. is demonstrated. The H_2O_2 yield increases with increasing H_2SO_4 final concn.
          A. Fucs

86: 92539j Technical-economical evaluation of hydrogen peroxide preparation processes. Rubinchik, A. M.; Pneva, E. Ya. (USSR). *V sb., Proiz-vo Perkisi Vodoroda Zhidkofaznym Okisleniem Izopropil. Spirta* 1976, (3), 4-8 (Russ). From *R./Zh., Khim.* 1976, Abstr. No. 21L55. Title only translated.

85: 199028y Studies of preparation and purification of hydrogen peroxide by hydrolisis of ammonium persulfate. Com. 4. Mutual solubility of ammonium persulfate-ammonium sulfate-sulfuric acid-water systems. Choe, Il Dong; Kim, Man Su; Sim, Myong Gil (N. Korea). *Hwahak Kwa Hwahak Kongop* 1976, 19(1), 46-52 (Korean). Mutual solubilities were detd. in the $(NH_4)_2S_2O_8$-$(NH_4)_2SO_4$-H_2SO_4-H_2O system at 5, 20, and 35°. Optimum H_2SO_4 and $(NH_4)_2SO_4$ concn. ranges were detd. for continuous electrolyris and for $(NH_4)_2S_2O_8$ crystn.

84686y Hydrogen peroxide manufacture by distillation of aqueous solutions of peroxodisulfuric acid and/or peroxodisulfates. Thiele, Wolfgang Ger. (East) 92,432 (Cl. C 01b), 12 Sep 1972, Appl. WP C 01b/155 249, 21 May 1971; 12 pp. By injecting the hot condensate (from the evaporator) immediately at the bottom of the last distn. stage, the concd. circulating acid is recycled at reduced pressure without prior cooling. The amt. of steam formed during the diln. is conducted countercurrently to the concd. circulating acid for stripping the residual H_2O_2.
          M. Knaack

19.—

66542v Determination of losses in platinum used as an anode material in the preparation of Perhydrol. Aleksandrova, L. G.; Zhitarev, G. A. (USSR). *Tr. Inst. Fiz. Metal., Ural. Nauch. Tsent., Akad. Nauk SSSR* 1971, No. 28, 348–50 (Russ). From *Ref. Zh., Khim.* 1972, Abstr. No. 16L211. The detn. of trace amts. of Pt in solns. by inverse voltammetry with a C paste electrode is described. Pt is concd. at a controlled potential (-1.0 V) on the electrode surface as a metallic film and anodically oxidized with linearly changing potential (scan rate 1 V/sec); the dissoln. curves are monitored oscillog. The anodic peak height for Pt dissoln. at 1.5 V is directly proportional to the Pt concn. Cu^{2+}, Mn^{2+}, Al^{3+}, SO_4^{2-}, and Cl^- do not interfere with the detn. of Pt. The sensitivity of the method is $5 \times 10^{-8}\%$; the error is 7.9%.

20.—

61464v Hydrogen peroxide. Thiele, Wolfgang Ger. (East) 78,229 (Cl. C 01b), 12 Dec 1970, Appl. 31 Jul 1969; 19 pp. H_2O_2 is produced by the hydrolysis of H_2SO_5 or its salts followed by distn. in an evap. app. contg. a heating surface of graphitic carbon impregnated with a phenol-HCHO resin The app. for the prepn. is described.

21.—

45817y Hydrogen peroxide from aqueous acidic solution obtained by hydrolysis. Harper, William Sheridan; Daigler, David Wayne (FMC Corp.) U.S. 3,694,154 (Cl. 423–585; C 01b, B 01d), 26 Sep 1972, Appl. 699,958, 23 Jan 1968; 5 pp. In the manuf. of H_2O_2 from a soln. obtained by electrolysis of an aq. $(NH_4)_2SO_4$-H_2SO_4 mixt. greater yields are obtained by careful control of temp. and concn. to assure max. hydrolysis of $S_2O_8^{2-}$ to SO_5^{2-} and finally to H_2O_2. Thus, an electrolyzed soln. had its water content reduced from 45 to 30% by removing part of the water by evapn. without loss of H_2O_2. The resulting soln. had a compn. of: H_2SO_4 30–45; $(NH_4)_2SO_4$ 20–35; active O tied up as $S_2O_8^{2-}$ and SO_5^{2-} 0.5–2.5%. This soln. was heat treated at const water content by refluxing the soln. at 105–130° at atm. pressure. The length of heating depended on the concn. and temp. of the soln. Residence time of 5 to 15 min gave good results. The partial pressure of H_2O_2 formed in the soln. is considerably below the prevailing pressure. The H_2O_2 is then steam stripped from the soln. to give a product contg. 4–10% H_2O_2. The uncondensed vapors are returned to the stripping column at a point below the point of introduction of heat treated soln. to assure min. loss of product. R. A. Coad

22.—

24044h Removal of a finely divided coating from a porcelain surface in Perhydrol production. Khramov, A. V.; Mikhailov, V. A.; Planina, L. S. (USSR). *Sin., Ochistka Anal. Neorg. Mater., Tr. Konf. "Nauka-Proizvod."* 1965 (Pub. 1971), 225–9 (Russ). Edited by Nikolaev, A. V. "Nauka," Sib. Otd.: Novosibirsk, USSR. The dark coating deposited on porcelain Raschig rings in the production of H_2O_2 from H_2SO_4 by electrolysis contained graphite 28, SiO_2 36, and M_2O_3 36% (where M was sesquioxidic metals). Its dissoln. in 25% NH_4OH, concd. Trilone B (pH 9) soln., and in NaOH (1–40% soln.) at the b.p. of the soln. was studied. The 1st two agents were ineffective and complete removal of the coating was reached only after boiling in NaOH solns. at all concns., varying only the time of boiling. Concns. $\leq 10\%$ of NaOH were suitable; at higher concns., the glazed surface of the rings was attacked. For industrial purposes, 1% soln. of NaOH and 4 hr boiling was recommended. Hanus Landspersky

2. AVAILABLE BOOKS AND REPORTS FOR HYDROGEN PEROXIDE AND RELATED SUBJECTS

2.1 Electrochemical synthesis of inorganic compounds : A bibliography
ed. Zoltan Nagy 455p. 1985

2.2 Electrochemical processes,industrial:A comprenhensive review of
past and present industrially scaled processes
ed. Kuhn. Elsevier

2.3 Final report on survey of electrochemical production of inorganic
compounds
Castle Technology Co. 1980, U.S Dpmt.of Energy

2.4 Wasserstoffperoxide und seine derivade.Chemie und Anwendungen
Hrsg. v. Weigert, Wolfgang, 1978, 205p.

2.5 Complements au nouveau traite de chimie minerale
P.Pascal, 1975, P.A.Giguere, Masson et Cie.

2.6 Hydrogen peroxide
W.C. Schumb et al.,American Chemical Society
Monograph series № 128

2.7 Hydrogen peroxide manufacture
R. Powell, Noyes,Chemical Process Review

2.8 Hydrogen peroxide handbook
Technical report AFRPL-TR-67-144, 1967
North American Aviation, Inc. Cal.

2.9 Handbook of inorganic chemistry
Gmelin, 1966, 430p.

Dr 2280

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MASTER

Final Report on
SURVEY OF ELECTROCHEMICAL PRODUCTION
OF INORGANIC COMPOUNDS
Contract No. 31-109-38-5054

by

Castle Technology Corporation

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LABORATORY

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Wolfgang Weigert

Wasserstoffperoxid und seine Derivate

Chemie und Anwendung
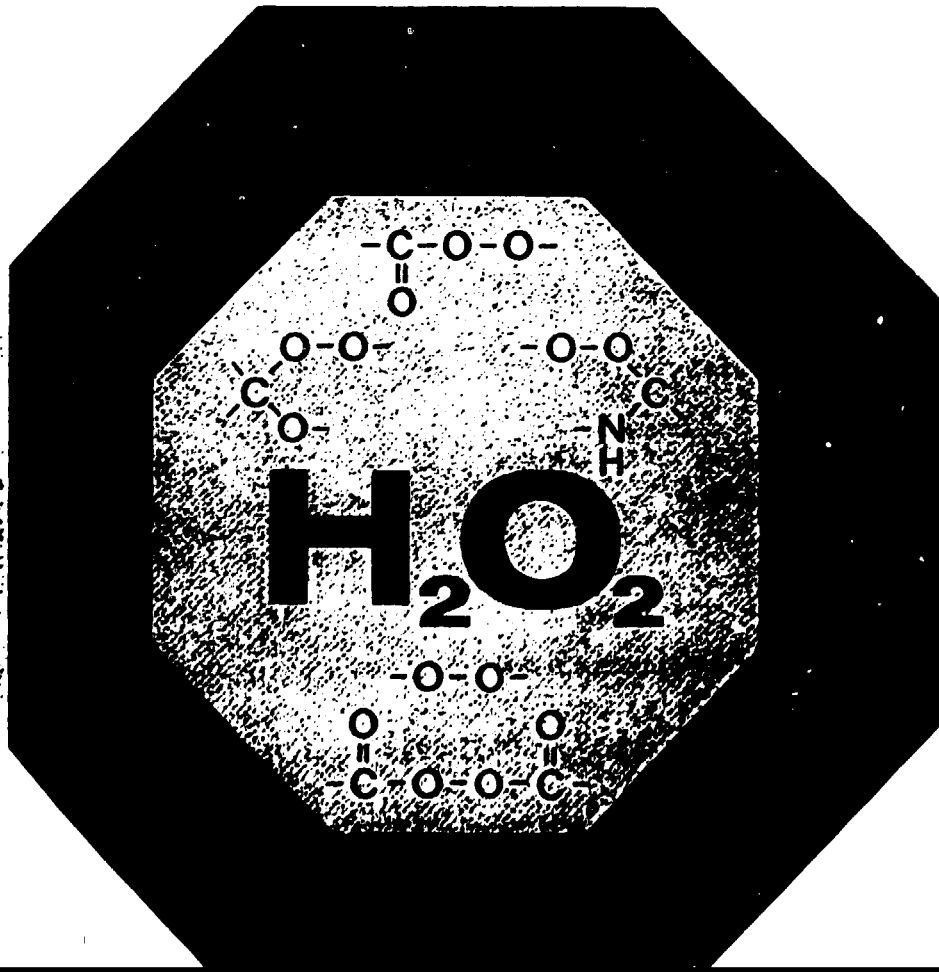
P. PASCAL

COMPLÉMENTS
au nouveau traité
de
CHIMIE MINÉRALE

sous la direction de
L. PACAULT et G. PANNETIER

PEROXYDE D HYDROGENE
POLYOXYDES D HYDROGENE **4** P. A. GIGUERE

TABLE DES MATIÈRES

HYDROGEN PEROXIDE HANDBOOK

1968

by

...Apartment
...American Aviation, Inc
...California

3. SOME WORLDWIDE HYDROGEN PEROXIDE PRODUCERS

3.1 IMPORTANT WEST EUROPEAN PRODUCERS:

Hydrogen peroxide (Peroxide)		Annual Capacity (Thousands of Metric Tons)
AUSTRIA		
Biochemie Gesellschaft mbH Alpine Chemische division	KUFSTEIN–SCHAFTENAU, (Tirol)	2
Österreichische Chemische Werke Ges.mbH – ÖCW	WEISSENSTEIN OB DER DRAU, (Kärnten)	25
BELGIUM		
Degussa Antwerpen nv	ANTWERPEN, (Antwerpen)	48
Interox sa	JEMEPPE SUR SAMBRE, (Namur)	20
FINLAND		
Oy Finnish Peroxides Ab	VOIKKAA, (Kymi)	15
FRANCE		
L'Air Liquide SA Chemical Department	CHALON SUR SAÔNE, (Saône et Loire)	na
Interox Chimie SA	TAVAUX, (Jura)	25
Oxysynthèse SA	JARRIE, (Isère)	90
GERMANY		
Degussa AG Chemicals Sector Industrial and Fine Chemicals Division	RHEINFELDEN, (Baden–Württemberg)	25
Peroxid–Chemie GmbH	BAD HÖNNINGEN, (Rheinland–Pfalz)	20
	HÖLLRIEGELSKREUTH, (Bayern)	12
ITALY		
Interox Chimica SpA	ROSIGNANO–SOLVAY, (Livorno)	25
Montefluos SpA	BUSSI SUL TIRINO, (Pescara)	30
THE NETHERLANDS		
Interox Chemie BV	HERTEN, (Limburg)	9
PORTUGAL		
Interox Portuguesa – Produtos Quimicos, Lda	PÓVOA DE SANTA IRIA, (Lisboa)	4
SPAIN		
Foret, SA	LA ZAIDA, (Zaragoza)	30
Interox Química, SA	TORRELAVEGA, (Santander)	14
SWEDEN		
Eka Alby Kemi AB	ALBY, (Västernorrland)	25
Eka Nobel AB	SURTE, (Göteborg–Bohus)	25
UNITED KINGDOM		
Interox Chemicals Ltd.	WARRINGTON, (Cheshire)	50
	ADD TOTAL	494

Source: SRI International estimates as of January 1, 1987.

Belgium

Solvay & Cie S.A., Rue du Prince
Albert 33, B-1050 Bruxelles T: (00)
5188111, Tx: 21337

Degussa: Antwerp

Interox S.A.
rue du Prince Albert 33, 1050 Bruxelles
Te: (2) 516-6111
Tx: 21337

Finland

Kemira Oy, P.O. Box 330, SF-00101
Helsinki -10, T: (00) 13211, Tx: 123033

Finnish Peroxides: Voikkaa

France

Solvay & Cie S.A., 5 rue François-Ier,
F-75008 Paris -Cédex 08, T: (33)
1/00000011
ATOCHEM, Tour ATO, La Défense 10,
Cédex 42, F-92091 Paris-la-Défense
T: (33) 1/40000000, Tx: 611922

Interox: Taveux

PCUK - Produits Chimiques Ugine Kuhlmann
Tour Manhattan, Cédex 21, 92087 Paris-La Défense
Te: (1) 773-3456
Tx: 611922

Germany, Federal Republic of-

FEDDERSEN & CO. (GmbH & Co.) K.
D., Postfach 111753, D-2000 Hamburg
-11, T: (040) 3618-1, Tx: 2163081

E. Merck
Postfach 4119, 6100 Darmstadt 1
Te: (6151) 720
Tx: 4193280
Ca: Emerck

Dr. Theodor Schuchardt & Co.
Eduard-Buchner-Strasse 14-20, 8011 Hohenbrunn
Te: (8102) 4092
Tx: 528315
Ca: Tchaschuchardt
(Primarily a producer of laboratory chemicals)

Great Britain and N.I.

Laporte Industries Ltd., Hanover Ho.,
14, Hanover Sq, GB- London
-W1R 0BE, T: (01) 000000, Tx: 02221
Laporte Industries Ltd., P.O. Box 8, GB-
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Tx: 00201
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Greece

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Piraeus T: (01) 4525551, Tx: 212388

ITALY

Eurobase S.p.A.
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Te: (2) 988-0395
Tx: 312888

Farmitalia Carlo Erba S.p.A.
Casella postale 10519, 20100 Milano
Te: (2) 69951
Tx: 330314
Ca: Erbacar

Industria Italiana Petroli S.p.A.
1 Piazza della Vittoria, 16121 Genova
Te: (10) 5994
Tx: 270107

Natronchemie B.V.
P.O. Box 1321, 3000 BH Rotterdam
Te: (10) 360122
Tx: 22444

Norway

Norsk Hydro A/S, P.O. Box 2594 Solli,
N-0203 Oslo -2, T: (02) 432100,
Tx: 18300

Spain

Martin F. Villaran S.A.
Centro Directivo Mercabarna, Zona Franca, Sector "C"
Barcelona 4, Spain
Te: (3) 336-5511
Tx: 97456

Solvay & Cie. S.A.
269 Mallorca, Barcelona 8, Spain
Te: (3) 215-3258
Tx: 54665
Ca: Solvay

Sweden

Eka Nobel AB, S-445 01 Surte T: (0000)
00000, Tx: 2000

Switzerland

ELFA AG, Bahnstr. 70, CH-5000 Aarau
T: (064) 225551, Tx: 00200
Du Pont de Nemours International S.A.
, Postfach, CH-1211 Genève -24,
T: (022) 500031, Tx: 02002

Hetaco S.A.
34 Avenue du Tribunal, 1005 Lausanne
Te: (21) 209301
Tx: 25548
Ca: Hetaco

3.2 EAST EUROPEAN PRODUCERS:

CZECHOSLOVAKIA
Chemicke Zavody Sokolov: Sokolov

GERMANY   (G.D.R.)

Chemie-Export-Import
133 Storkowerstrasse
1055 Berlin, German Democratic Republic
   Te: (2) 43220
   Tx: 112171
   Ca: Ahbchemie

HUNGARY
Budapest: Vegymuvek: Budapest

USSR

SOJUZCHIMEXPORT V/O,
Smolenskaja-Sennaja 32/34,
SU-121200 Moskau T: (0095) 2442204,
Tx: 411200

Yugoslavia

HEMPRO, Terazije 8, YU-11000
   Beograd T: (011) 334751, Tx: 11161
JUGOLABORATORIJA, RO,
   Postfach 217, YU-11001 Beograd
   T: (011) 682088, Tx: 12062
BELISKA, P.O. Box 73, YU-61231
   Ljubljana -Crnuce, T: (061) 371322,
   Tx: 34200
CENTROHEMIJA, P.O. Box 91,
   YU-61001 Skopje T: (091) 235033,
   Tx: 51200
JUGOSANITARIJA, P.O.Box 1002,
   YU-41001 Zagreb T: (041) 432000,
   Tx: 21600
KEMIKALIJA, P.O. Box 1002, YU-41001
   Zagreb T: (041) 514000, Tx: 21120

3.3 IMPORTANT U.S.A. PRODUCERS:

Manufacturer	Site	Process	Capacity*, thousand metric tons
DuPont	Memphis, Tenn.	anthraquinone	56.7
FMC	S. Charleston, W. Va.	anthraquinone	36.2
	Bayport, Texas	anthraquinone	27.2
	Vancouver, Wash.	electrolytic	8.1
Interox	Deer Park, Texas	anthraquinone	39.9
Shell	Norco, La.	2-propanol	16.3
PPG	Barberton, Ohio	anthraquinone	4.5

* 100% Basis.

3.3.1 Supplementary list:

Manufacturer:	address
Allied Chemical	P. O. Box 2064R, Morristown, NJ 07960, U.S.A. Te: (201) 455-2000 Tx: 136410 TWX: 710-986-7482
J.T.Baker	223 Red School Lane, Dpmt.LA-TR
Chemserve Corp.,	2505-T Copland, Detroit, Mi 48209
Mallinckrodt Inc.	P. O. Box 5439, St. Louis, MO 63147, U.S.A. Te: (314) 895-2000
PPG Industries Inc.	One Gateway Center, Pittsburgh, PA 15222, U.S.A. Te: (412) 434-3131 Tx: (WUT) 866570; (WUI) 6848005; 6848008 TWX: 710-664-2043

3.4 MAIN PRODUCERS:

JAPAN

The following table lists the producers of hydrogen peroxide in Japan, as of year-end 1979.

Company and Plant Location	Annual Capacity (thousands of metric tons, 100% H_2O_2)	Process Remarks
Mitsubishi-Gas Chemical Co., Ltd.		
Kashima, Chiba Prefecture	23	2-Amyl anthraquinone
Yokkaichi, Mie Prefecture	36	2-Amyl anthraquinone
Nippon Peroxide Co., Ltd.		
Kohriyama, Fukushima Prefecture	31	2-Ethyl anthraquinone
Tokai Electro Chemical Co., Ltd.		
Fuji, Shizuoka Prefecture	18	2-Ethyl anthraquinone
Total	108	

SOURCE: Communication with industry.

Source : CTH Product Review 1980
SRI INTERNATIONAL

CHUGAI BOYEKI CO., LTD.

Dainippon Ink & Chemicals/Oxysynthese.
Tomakomai
Fuji Hydrogen Peroxide. Itami

OSAKA GODO CO., LTD

Santoku Chemical Industries Co. Ltd.
10-2 Aza Otakeshinden, Imozawa, Miyagi-machi
Miyagi-gun, Miyagi Pref. 989-32, Japan
Te: (2239) 42171

INDIA

INDIA
Arat Electrochemical: Ahmedabad, Guj
National Peroxide Ltd.
Neville House, J.N. Heredia Marg, Ballard Estate
Bombay 400.038, India
Te: 268071
Tx: 112572
Ca: Naperol
- Sarabhai M. Chemicals
P. O. Box 80, Baroda 390.001, India
Te: 82821
Tx: 175473
Ca: Sarchem

CHINA

China National Chemicals Import & Export Corporation
Erh-Li-Kou, Hsi Chiao
Peking, People's Republic of China
Tx: 22243
Ca: Sinochem

ISRAEL:

Oxidon Israel Oxidation Co. Ltd.
P. O. Box 175, Holon 58101, Israel
Te: (3) 803257; 802504
Ca: Corbut

KOREA:

- Oriental Chemical Industry Co. Ltd.
C. P. O. Box 781, Seoul, Korea
Te: (2) 781-7211
Tx: 24114
Ca: Orienchem

Pakistan
Dawood Cotton Mills   Karachi

PHILIPPINES
Peroxide Philippines: Manila

SINGAPORE

National Oxygen Pte.L
National Oxygen Pte.Ltd.
21,Tg Kling Road

TAIWAN :

Chang Chun Petrochemical Co. Ltd.
301 Songkiang Road, 7th floor, Taipei, Taiwan
Te: (2) 561-8131
Tx: 22535
Ca: Longlite

3.5 AUSTRALIAN, AFRICAN AND LATINAMERICAN PRODUCERS:

Australia:

Interox Chemicals Pty. Ltd.
P. O. Box 18, Botany, N.S.W. 2019, Australia
   Te: (2) 666-8000
   Tx: 20628
   Ca: Peroxide

South Africa
Peroxide Chemicals   **Sasolburg**

Egypt
Misr Chemicals

ARGENTINA
Atanor: Rio Tercero, Cordoba

BRAZIL
Electroquimica Rio Cotia: Cotia, SP
Peroxidos do Brasil: Elclor, SP

CHILE

Farmoquimica del Pacifico SA

COLOMBIA:

Electroquímica Colombiana S.A.
Apartado aereo 4728, Medellín, Colombia
   Te: (4) 810599; 778752
   Tx: 6550
   Ca: Electroquimica

MEXICO:

FMC de Mexico S.A.
Apartado postal 7-1446, 06700 Mexico, D.F., Mexico
   Te: (5) 533-2405
   Tx: 1761095

4. SOME EQUIPMENT SUPPLIERS AND CONSULTANCY SERVICES: A TENTATIVE LIST

4.1 AUSTRALIA:

	ADDRESS
-Simon Carver	Div. of Simon Eng.(Aust)Pty POBox No 364 Nth Ryde NSW 213

4.2 GERMANY:

-Bamag Davy	Wetzlarerstr.136,D6303, Butzbach
-Krebskosmo Ges. fur Chemie Ingenieur Technic m.b.H.	Zeltinger Platz 16,D 1000 Berlin 231
-Lurgi G.m.b.H.	POBox 111231,Lurgy-Alle 5,D-6000 Frankfurt

4.3 JAPAN:

Matsushita Elec. Ind. Co. Ltd.	1006, Kadoma,Kadoma, Osaka-Pref. 571

4.4 SWITZERLAND:
-Krebs & Co.Ltd.   Claridenstr. 20
                                   CH.3002 Zurich

4.5 UNITED KINGDOM:
-CJB Developments Ltd.   Airport Services Rd.,Portsmouth
                                   Hants PO3 5PG,U.K.

-Engelhard Ltd.   Chancery House,ST, High. way
                                   Sutton,Surrey SM1 1ED,U.K.

5. R & D INSTITUTS

5.1 BULGARIA:
-Higher Institute of Chemical   J Jeln Voivoda, Darvenitza,56
 Technology   Sofia
 Dep. of Inorganic Technology

5.2 FRANCE:
-Laboratoire des sciences   Irve Grandville,54042,Nancy
 du genie chimique   CEDEX

5.3 GERMANY:
-Degussa AG.   Postfach 11 05 33, D-6000
                                   Frankfurt AM Main 11

-Dortmund University   Postfach 50 05 00
                                   August Schmidt str. D-4600
                                   Dortmund 50

5.4 INDIA:
-Central Electrochemical   Karaikudu 623 006
 Research Institute (CECRI)   Tamil Nadu

5.5 ITALY:
-Electrode Processes Re-   Piazza Leonardo Da Vinci 32
 search Center   20133 Milan
 Milan Polytechnic

5.6 UNITED KINGDOM:
-University of Southampton   High Field,Southampton SO9 5NH
 Wolfson Centre For Elec-
 trochemical Science

5.7 U.S.A:
-Association of Consulting   50 E 41 St. New.York N.Y. 10017
 Chemists and Chem.Engrs.

—Charles Davidoff Association

5 Seatong Ave.
Port Washington,N.Y. 11050

—Electrochemical Society (ECS)

10 S.Main ST,Pennington
N.J. 03534

—Electrochemical Technology
Corp.

1601 Dexter Ave.,North
Seattle,Wa 93019

5.8 U.S.S.R.:
—Electrochemistry Institute

Leninsky Prospekt 31
Moscow 11 70 71

—Institute of Physical Che-
mistry

Leninsky Prospekt 31
Moscow 11 73 12

Company and location	Capacity (ton/year)	Process	Engineers/contractors	Cost	Start-up/ status
HYDROGEN PEROXIDE					
Eka Nobel/Norsk Hydro Rjukan, Norway	5 000	Eka Nobel			suspended
Kemira Oulu, Finland	15 000 - 20 000	Kemira		$19m	1988U
Oxynor Rjukan, Norway	3 000	Eriksson Services		$8.4m	Oct 1987
Oy Finnish Peroxides Voikkaa, Finland	(x) 15 000 20 000T				1988U
Saudi Industrial Resins Saudi Arabia	15-25 000				P

Companies buying or investing/companies acquired or set up	Location	Products/business	Status	Cost
Nobel Industries/Eka	Sweden/Sweden	Supply of hydrogen peroxide and chloralkali	acq	$77m
Nokia and Nobel Industries/Kenox	Finland/Finland	Manufacture of hydrogen peroxide	jv	—
Norsk Hydro and Eka Nobel/jv	Norway and Sweden/Norway	Production and marketing of hydrogen peroxide	51:49 jv	—

Company and location	Capacity (ton/year)	Process	Engineers/contractors	Cost	Start-up/ status
HYDROGEN PEROXIDE					
KemaNord Stockvik, Sweden	10 000	—	—	US$3m	1986
KemaNord Bleaching Chems Trollhätten, Sweden	10 000	—	—	—	P
Laporte Warrington, UK	50 000	Interox	Matthew Hall	US$25.7m	1986 U
Oy Finnish Peroxides Kuusankoski, Finland	(x) 150 000T	. .	—	—	—
Poland Poland	2 plants	-	. .	—	P

New projects summarized below appeared in *ECN* on 17 July and 24 July 1989

Company	Location	Product	Capacity ton/year	Process	Contractor	Total erected cost	Start-up date/ status
Solvay	Rotterdam, the Netherlands	hydrogen peroxide	20 000			$46.5m	1991

ECN PROJECT SUMMARY

New projects summarized below appeared in *ECN* on 26 June, 3 July, 10 July and 17 July 1989

Company	Location	Product	Capacity ton/year	Process	Contractor	Total erected cost	Start-up date/ status
Eka Nobel/ Du Pont/ Mitsubishi Gas Chemical	Santa Cruz, Aragua state, Venezuela	hydrogen peroxide	10 000	Eka			1991

ECN PROJECT SUMMARY

New projects summarized below appeared in *ECN* on 26 June and 3 July 1989

Company	Location	Product	Capacity ton/year	Process	Contractor	Total erected cost	Start-up date/ status
Oxysynth Canada	Canada	hydrogen peroxide	(x) 40 000T			$15.2m	

ECN PROJECT SUMMARY

New projects summarized below appeared in *ECN* on 12 June 1989

Company	Location	Product	Capacity ton/year	Process	Contractor	Total erected cost	Start-up date/ status
Du Pont Canada	Gibbons, Alta, Canada	hydrogen peroxide	36 000	Du Pont			

ECN INTERNATIONAL PROJECT REVIEW

ECN International Project Review, March 1989

Company and location	Capacity (ton/year)	Process	Engineers/contractors	Cost	Start-up/ status
Hydrogen peroxide					
Czechoslovakia Sokolov, Czechoslovakia	4-6 000	–	–	–	P
Interox Chemie Finland	–	–	–	–	1988 C
Kemira Oulu, Finland	15 000 - 20 000	Kemira	–	$19m	1988 C
Oy Finnish Peroxides Kuusankoski, Finland	15 000	Linde/Interox	Laporte/PT Consulting	–	1988 C
Saudi Industrial Resins Saudi Arabia	15-25 000	–	–	–	P

7. BIBLIOGRAPHY:

7.1 BOOKS, REPORTS AND JOURNAL ARTICLES:

7.1.1 Encyclopedia of chemical processing and design
J.J. McKetta, 1983

7.1.2 Mc Graw-Hill Encyclopedia of science and technology
1987

7.1.3 Encyclopedia of chemical technology
Kirk Othmer, 33d. 1981

7.1.4 Chemical economic handbook
SRI International 1980

7.1.5 Industrial chemicals
Faith,Keyes,Clark 3ed. 1965

7.1.6 Chemical process industries
Shreve and Brink 1977

7.1.7 Complements au nouveau traite de chimie mineral
P.Pascal 1976

7.1.8 Comprehensive inorganic chemistry
ed. Board, Pergamon press 1973

7.1.9 Hydrogen peroxide handbook
Technical report AFRPL-TR-67-144 1967

7.1.10 Survey of electrochemical production of inorganic compounds
Final Report Argonne National Laboratory

7.1.11 Inorganic chemical and metallurgical process encyclopedia
Noyes Development Co. 1963

7.1.12 Peroxide d'hydrogene
Informations chimie No 204

7.2 ON LINE SEARCH : 1970-1989
7.2.1 DATA BASE : CA SEARCH (chemical abstracts)

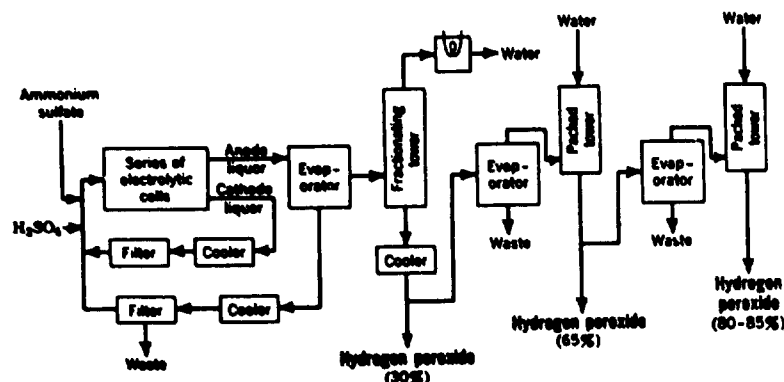7.3 DIRECTORIES :
7.3.1 Chemical industry directory 1989
7.3.2 ABC 1989 .The universal register of european exports
7.3.3 Chemical industry catalog
7.3.4 Pulp and paper 1980
7.3.5 Directory of chemical producers western Europe 1987
7.3.6 Directory of World Chemical producers 1985/86
7.3.7 The chemical industry,Africa & Asia
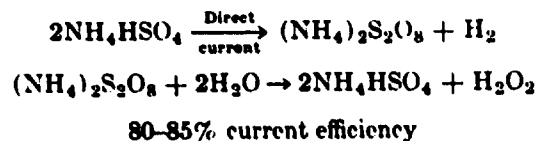7.3.8 Research services directory,1989
7.3.9 Books in print 1987-88, etc.

HYDROGEN PEROXIDE

H₂O₂

From Ammonium Bisulfate by Electrolysis

Reaction

$$2NH_4HSO_4 \xrightarrow[\text{current}]{\text{Direct}} (NH_4)_2S_2O_8 + H_2$$

$$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$$

80–85% current efficiency

Material and Energy Requirements

Basis—1 ton 30% hydrogen peroxide

Ammonia	50 lb
Sulfuric acid	60 lb
Demineralized water	215,000 gal
Electricity	5,700 kwhr
Steam	16,800 lb
Platinum	Very small

458

Process

Hydrogen peroxide is manufactured by the hydrolysis of a solution containing the persulfate ($S_2O_8^=$) ion. The particular solution used (persulfuric acid, ammonium persulfate, or potassium persulfate) is prepared in an electrolytic cell in which the corresponding sulfate is oxidized anodically. Hydrolysis of the persulfate (outside the cell) is carried out under conditions that regenerate the sulfate and vaporize a mixture of water and hydrogen peroxide. The latter are separated and the peroxide concentrated by vacuum distillation.

In the embodiment of the process as shown in the flowsheet, a regenerated solution of ammonium sulfate and sulfuric acid (equivalent to ammonium bisulfate) is adjusted to proper concentration and fed to a series of electrolytic cells. In one plant the porcelain cells are 70 cm wide and 95 cm deep. The platinum anodes and graphite cathodes are so arranged that water in cooling tubes may keep the electrolyte temperature below 35°C. The potential drop across each cell, operated at 5,400 amps, is 5.7 volts. Ammonium thiocyanate (0.1 g per liter) is usually added to the electrolyte to increase oxygen overvoltage. Anode current density is 0.4 to 1.1 amperes per sq cm. A current of air is swept continuously through the cell to keep the hydrogen concentration below 5 per cent so as to avoid explosion.

The persulfate solution leaving the cells goes to an evaporator, where it is heated by both live steam and by means of steam coils. Hydrogen peroxide and water vapors go overhead. The ammonium bisulfate solution is cooled, filtered to remove any sediment, adjusted in concentration, and returned to the cells. The cathode liquor is similarly cooled, filtered, and reused. The hydrogen peroxide–water vapor mixture is sent to stoneware distillation towers which are operated under vacuum (40 mm Hg). A 30 to 40 per cent hydrogen peroxide solution is removed from the bottom of the tower. This solution may be concentrated to 80 to 85 per cent or 90 to 98 per cent H₂O₂ in two stages.

The 30 to 40 per cent H₂O₂ solution recovered from the cell liquors is adjusted with sulfuric acid (about 0.5 g per liter) and fed to a stoneware or porcelain evaporator, where the solution is heated to 65°C at 40 to 50 mm Hg. The vapors evolved are scrubbed in a packed tower with distilled or demineralized water in such ratio to the peroxide vapors that a 65 per cent hydrogen peroxide solution leaves the bottom of the tower. This product may be fed to a second evaporator (at 75°C and the same pressure) and a second packed tower to produce an 80 to 85 per cent solution of hydrogen peroxide. The product is cooled, stabilized with acids or an organic oxidation inhibitor, and sent to storage.

This concentration process may be run continuously by fractionating and recycling the vapors from the first evaporator. The resulting 70 per cent H₂O₂ solution may be concentrated to a 90 to 98 per cent solution in a similar second stage. From time to time, liquid bottoms from the first evaporator must be drawn off to remove impurities. One manufacturer has

recently produced 100 per cent hydrogen peroxide (anhydrous) by a continuous fractional distillation process.

The ammonium persulfate process described differs only in details from the persulfuric acid process and the potassium persulfate process. All three are used commercially. The pure acid process has a lower current efficiency (70 to 75 per cent) but has the advantage that crystallization troubles within the system are eliminated.

In the potassium persulfate process, an ammonium bisulfate solution is electrolyzed as before. After electrolysis potassium acid sulfate is added to the electrolyte:

$$(NH_4)_2S_2O_8 + 2KHSO_4 \rightarrow K_2S_2O_8 + 2(NH_4)HSO_4$$
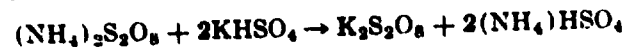
The potassium salt is crystallised and separated by filtration. The solid potassium salt is then added to a sulfuric acid solution to produce a slurry. On heating with live steam, the persulfate hydrolyzes to produce H_2O_2 vapors. As in the other processes, the potassium salt may be recovered and recycled.

By Oxidation of Alkylhydroanthraquinones

Typical Reaction

Ethylanthraquinone   Ethylhydroanthraquinone
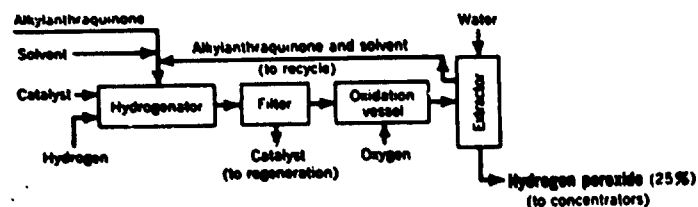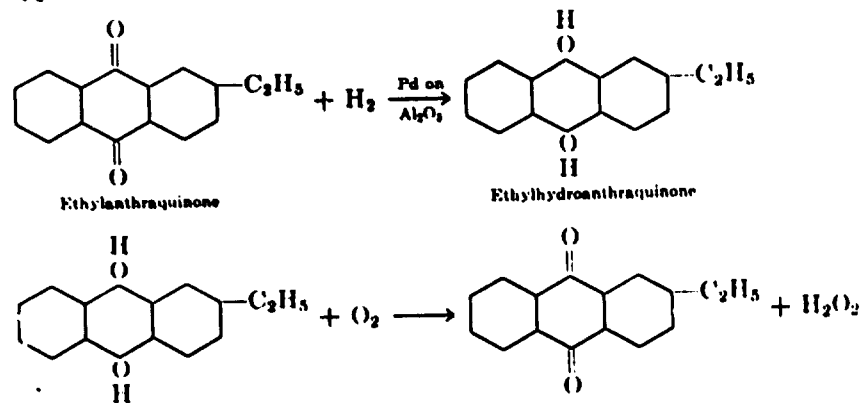
90% yield (based on hydrogen)

Material Requirements

Basis—1 ton hydrogen peroxide (25%)

Oxygen	5,280 cu ft (STP)
Hydrogen	5,870 cu ft (STP)
Ethylanthraquinone	Mechanical losses only
Solvent	Mechanical losses only
Palladium (catalyst)	Mechanical losses only
Water	180 gallons

Process

The modern chemical method for manufacturing hydrogen peroxide is an organic autoxidation process in which a suitable organic compound (usually a hydroquinone type) in solution is oxidized to the quinone form with the concurrent formation of hydrogen peroxide. The peroxide is extracted and concentrated; the oxidized organic compound is reduced catalytically and reused.

In one adaptation of this process, the raw material is a 10 per cent solution of mixed alkylated anthraquinones and their tetrahydro derivatives. The solvent is a mixture of primary and secondary nonyl alcohols with methyl or dimethylnaphthalene. This mixture is reduced with hydrogen in the presence of a catalyst of activated alumina coated with 0.7 per cent palladium. The reduction may be carried out at 40°C and under hydrogen pressures of 1 to 3 atm.

After removal of the catalyst granules by filtration, the resulting hydroanthraquinone still in solution is blown with oxygen or an oxygen-nitrogen mixture at 30 to 60°C to produce hydrogen peroxide (5 to 6 g per liter) and regenerate the original anthraquinones. The hydrogen peroxide is extracted with a sufficient quantity of water to yield a 20 to 25 per cent H_2O_2 solution. The anthraquinones are recycled. The hydrogen peroxide may be concentrated as described in the previous process.

This process is similar to a process developed in Germany and used there during World War II. The German process made use of ethylanthraquinone in a benzene-cyclohexanol solvent and used Raney nickel as a hydrogenation catalyst. High losses of Raney nickel and the partial solubility of the solvent in water led to the economic modifications of the process described.

From Barium Peroxide

A process formerly widely used, but currently only of limited interest involves the following reaction:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$
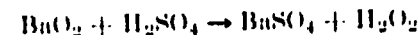
The barium sulfate precipitate is a valuable by-product. The barium peroxide is prepared as follows:

$$BaO + \tfrac{1}{2}O_2 \xrightarrow{\ 600\ C\ } BaO_2$$
(as dry air)
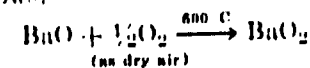
Miscellaneous

Properties. 100 per cent hydrogen peroxide is a water-white syrupy liquid with oxidizing properties.

Mol. wt.	34.02	M.P.	$-0.461°C$
Sp. gr.	1.438 20°C/4	B.P.	155.5°C

Miscible with water in all proportions. Soluble in ether. Insoluble in hydrocarbons.

In pure form, either as is or in solution, hydrogen peroxide is quite stable. It decomposes, sometimes violently, in the presence of even traces of metallic impurities. In contact with readily oxidizable organic substances it may cause spontaneous combustion.

Grades. Hydrogen peroxide is sold as a water solution, according to both percentage peroxide by weight and by "volume strength" (the volume of oxygen gas in milliliters that can be liberated from one milliliter of solution). The most common grades are: 3 per cent (10 volume strength), 6 per cent (20 volume strength), 27.5 per cent (100), 30 per cent (110), 35 per cent (132), 50 per cent (208), 70 per cent (264), and 90 per cent (415). The USP grade is 10 volume strength. All grades contain a small amount of stabilizer (usually 0.1 to 0.2 grains acetanilid per fluid oz). Sometimes small amounts of pure hydrochloric acid are also used.

Containers and Regulations. Vented all-aluminum tank cars, aluminum drums, glass carboys, and brown or amber-colored bottles. White ICC "Corrosive Liquid" label required. Manufacturing Chemists Association requires warning label. All pipes for transfer should be Pyrex, ceramic, or 99.6 per cent aluminum.

Economic Aspects

The technology of both the manufacture and utilization of hydrogen peroxide is comparatively new. Prior to World War II hydrogen peroxide was generally considered an unstable compound, too hazardous for ordinary chemical use. Military demands, particularly for rockets, torpedoes, and submarines, led to improvements in manufacturing and handling techniques and subsequently to stable high-purity solutions of high concentration. After the war this availability led to increased use of hydrogen peroxide for the bleaching of textiles and paper pulp. In the near future one can expect even greater advances in the fields of epoxidation (addition of an oxygen atom to the olefinic linkage), the manufacture of peroxy-acid catalysts for polymerization reactions, the oxidation of organic compounds, as a blowing agent (for foamed gypsum, plastics, and resins), and as a source of energy in both military and civilian use. Because of security regulations, no estimate of present military demands can be made.

All new plants use the chemical rather than the electrolytic process. It

placed. Present plants vary in size from 2 million to 32 million lb annual capacity (calculated as 100 per cent H_2O_2).

Manufacturers and Plant Sites

Allied Chemical Corp., Syracuse, N. Y.
E. I. du Pont de Nemours & Co., Inc., Memphis, Tenn.
FMC Corp., Vancouver, Washington; Buffalo, N. Y.; So. Charleston, W. Va.
Pennsalt Chemicals Corp., Wyandotte, Mich.
Pittsburgh Plate Glass Co., Barberton, Ohio
Shell Chemical Co., Norco, La.

HYDROGEN PEROXIDE FROM PERSULFURIC ACID
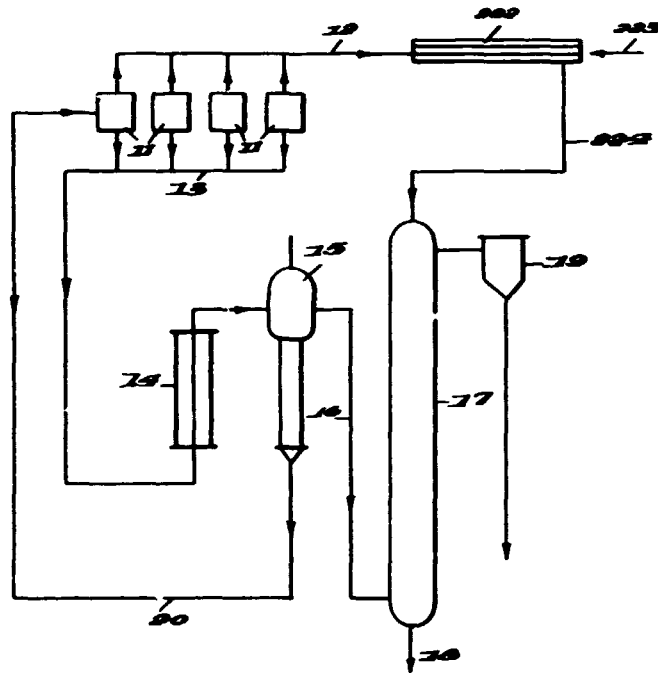
This is a process for the production of hydrogen peroxide by electrolytic oxidation of an anolyte containing SO_4 anions to produce a solution of a per-compound selected from the group consisting of persulfuric acid and its salts with simultaneous production of cathodic hydrogen as a by-product.

It further involves decomposing said per-compound solution to produce a hydrogen peroxide solution and recovering hydrogen peroxide from such solution by distilling off hydrogen peroxide with the aid of a fractionating column operating with reflux. This specific process further involves collecting the by-product cathodic hydrogen, employing said cathodic hydrogen for the chemical production of a dilute solution of hydrogen peroxide and supplying at least a portion of said dilute hydrogen peroxide solution to said fractionating column as reflux.

In the figure, 11 designates the electrolytic cells in which persulfuric acid is produced by anodic oxidation of sulfuric acid. The cathodic hydrogen produced is collected in conduit 12. The anolyte produced in the electrolytic cells flows to the distillation column 14 through conduit 13, and then to column 15 in which the H_2O_2 produced is blown out with direct steam. The resulting H_2O_2 vapors are supplied to condenser 17 through conduit 16, whereas the sulfuric acid separated in column 15 is recycled to the electrolytic cells, through conduit 20. The hydrogen peroxide vapors are fractionally condensed in condenser 17 and the condensed hydrogen peroxide withdrawn at 18. The water vapors are condensed at 19.

The cathodic hydrogen produced may be used to form H_2O_2 by catalytic combustion employing palladium metal as a catalyst as shown diagrammatically. The cathodic hydrogen collecting in conduit 12 is supplied to the catalytic furnace 222 into which oxygen or air is introduced for the catalytic combustion through conduit 223. The resulting H_2O_2 is supplied together with water as reflux to the head of condenser 17 over conduit 224 and is concentrated in such condenser and withdrawn at 18 jointly with electrolytically produced H_2O_2.

4.4.5 Conclusions

The total quantity of energy required for electrolytic manganese dioxide production in the year 2000 is estimated to be 6.1×10^{12} Btu. Substantial process heat is required for the ore leaching step, so that only about one-half or 3.1×10^{12} Btu, will be used by the electrolytic cells. These cells run at about 40% efficiency. The total potential target for energy savings is, therefore, about 1.8×10^{12} Btu/yr, a value too small to recommend government funding.

4.5 Hydrogen Peroxide

4.5.1 Introduction

Hydrogen peroxide first gained industrial significance in the early 1900's when the first electrolytic cells were invented. Three commercial processes have been employed to manufacture hydrogen peroxide:

- electrosynthesis

- oxidation of isopropyl alcohol

- the anthraquinone process

Virtually all the hydrogen peroxide produced in the world today is made by the anthraquinone process. The only alcohol oxidation plant that was ever built was shut down. Those electrolytic plants still in operation have been fully depreciated and have the use of low cost hydroelectric power. Electrolytic plants may have further benefits such as protective tariffs, or serve a local market saving on transportation costs, which allows them to compete with the lower cost anthraquinone process. Nevertheless, there have been a number of novel approaches appearing in the recent literature on the electrosynthesis of hydrogen peroxide that makes this route worth re-examining.

Hydrogen peroxide is sold as an aqueous solution and is available in a variety of strengths ranging from 3 to 90% by weight. Most industrial applications use the 35% and 50% solutions. High strength peroxide (90%) is used in military and space programs.

Production figures for hydrogen peroxide since 1943 are given in Figure 25. Estimates for 1980 put production at about 125,000 tons. The use of this chemical is expected to grow at about 6 percent per year which would lead to a production rate of 400,000 tons/yr by the year 2000 requiring an energy input of 13.4×10^{12} Btu/yr. The consumption pattern for the year 1974 is given in Table 12.

About 85 to 90 percent of all cotton bleaching processes use hydrogen peroxide and this is the major textile use. Hydrogen peroxide is used in the epoxidation of oils and fatty acid esters mainly for plasticizers and for various organic and inorganic peroxides. The use of hydrogen peroxide in wastewater treatment could represent a significant new market since one pound of peroxide can be substituted for three to four pounds of chlorine, and chlorine is believed to have environmental problems associated with its use.'

TABLE 12

Hydrogen Peroxide Consumption Pattern for the Year 1974

	Thousands of Short Tons
Textiles	27.7
Plasticizers	25.8
Glycerin	8.3
Pulp and Paper	7.4
Wastewater Treatment	3.5
Miscellaneous	19.6
Total	92.3

4.5.2 Mechanism

4.5.2.1 Standard Potentials

The standard potential of the peroxide-water couple (64) in acid solution is

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \qquad E^O = 1.763 \text{ V} \qquad (31)$$

and in alkaline solutions

$$HO_2^- + H_2O + 2e \longrightarrow 3OH^- \qquad E_B^O = 0.867 \text{ V} \qquad (32)$$

These high positive potentials cause peroxide to be unstable with respect both to the oxidation of water and its own oxidation and reduction in acid and alkaline solutions. Many redox systems and metal surfaces act as catalysts for peroxide decomposition.

4.5.2.2 Anodic Oxidation of Sulfate

Hydrogen peroxide is produced electrochemically by the anodic oxidation of sulfate to peroxydisulfate which is then hydrolyzed. Peroxydisulfate is formed electrochemically by the anodic oxidation of ammonium sulfate (6) according to the reactions

$$2HSO_4^- \longrightarrow 2HSO_4 + 2e \qquad (33)$$

$$2HSO_4^- \longrightarrow 2SO_4^- + 2H^+ + 2e \qquad (34)$$

$$2SO_4^{2-} \longrightarrow 2SO_4^- + 2e \qquad (35)$$

$$2SO_4^- \longrightarrow S_2O_8^{2-} \qquad (36)$$

$$2HSO_4 \longrightarrow S_2O_8^{2-} + 2H^+ \qquad (37)$$

The overall reactions are

$$2HSO_4^- \longrightarrow S_2O_8^{2-} + 2H^+ + 2e \qquad\qquad E^O = 2.123 \text{ V} \qquad (38)$$

$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e \qquad\qquad E^O = 2.010 \text{ V} \qquad (39)$$
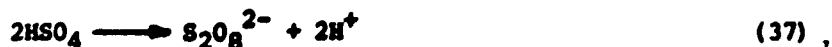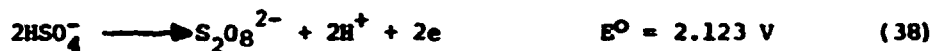
Oxygen evolution is thermodynamically preferred over peroxydisulfate formation and in order to obtain reasonable yields a number of criteria should be met (65):

● An anodic material is required on which oxygen will dissociate at high current densities. Shiny platinum is the most suitable.

● With increasing current density the Tafel slope changes due to the formation of surface oxides of platinum. Only above this transition region, at sufficiently high current densities, will peroxydisulfate form.

● The transition region occurs at lower current densities with increasing sulfuric acid concentration. This is believed due to the adsorption of sulfate ions on the platinum surface thereby inhibiting oxygen evolution.
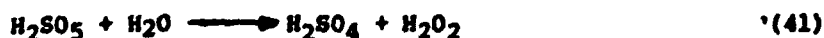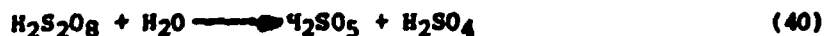
● Peroxydisulfate formation kinetics, relative to oxygen evolution kinetics, is enhanced at lower temperature.

● Halogenide, cyanide and thiourea additions help raise the anode potential to a suitable region.

The cathodic reaction is the discharge of hydrogen ions to form gaseous hydrogen. The overpotential, which should be kept low, is influenced by the cathode material, surface condition and current density. Only lead and graphite are cheap enough and have the necessary chemical stability. Lead has better electrical conductivity and is more readily fabricated; graphite has a lower hydrogen evolution overpotential and better heat conduction.

Optimization of output requires balancing high current yield with low cell potential. High current yield requires high anodic current densities $(0.5-1.0 \text{ A/cm}^2)$. Low electrolyte potential loss requires low current densities on the cathode, in the electrolyte and in the diaphragm, as well as a homogenous current distribution. Cooling the anode chamber contributes to higher anodic potential and decreases the formation of peroxymonosulfuric acid by hydrolysis. On the other hand, the specific conductivity of sulfuric acid decreases at lower temperature. Since cooling costs money, an optimum temperature is between 15 and 25° depending on cell design.

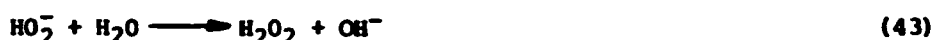Hydrolysis of peroxydisulfate to form hydrogen peroxide occurs in sulfuric acid solutions according to the reactions

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4 \qquad\qquad (40)$$

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2 \qquad\qquad '(41)$$

with Eq (40) believed to be the rate controlling step. Secondary side reactions are controlled by operating at sufficiently high acid concentration.

4.5.2.3 Cathodic Reduction of Oxygen

An alternate method of producing hydrogen peroxide electrochemically which has not achieved commercial significance is the cathodic reduction of oxygen in alkaline solution by the reactions

$$O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^- \qquad E_B^O = -0.076 \text{ V} \qquad (42)$$

$$HO_2^- + H_2O \longrightarrow H_2O_2 + OH^- \qquad (43)$$

Cathodic loss reactions are the direct reduction of oxygen to the hydroxyl ion

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \qquad E_B^O = 0.401 \text{ V} \qquad (44)$$

hydrogen evolution

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad E_B^O + -0.83 \text{ V} \qquad (45)$$

and reduction of hydroperoxide ion

$$.HO_2^- + H_2O + 2e \longrightarrow 3OH^- \qquad E_B^O = 0.867 \qquad (46)$$

Equations (44) and (45) result in reduced current efficiencies and Eq (45) has the added disadvantage of forming a potentially explosive mixture of hydrogen and hydrogen peroxide.

4.5.3 Industrial Processes

4.5.3.1 Peroxydisulfate Process

Hydrogen peroxide has been produced commercially by the hydrolysis of peroxydisulfates formed by electrosynthesis as discussed in Section 4.5.2.2. The three processes based on peroxydisulfate are the Weissenstein process using peroxydisulfuric acid, the Loewenstein/Laporte process using ammonium peroxydisulfate and the Pietzsch and Adolph process using potassium peroxydisulfate precipitated from ammonium peroxydisulfate. Peroxydisulfate hydrolysis is carried out in a separate vessel under conditions which permit regeneration of the sulfate and separation of the product hydrogen peroxide as a mixture of hydrogen peroxide and water vapor. Operating data for the three above mentioned processes are given in Table 13. Of these processes, the one based on the ammonium salt has been favored because it is an all liquid process (66). As shown in the schematic flowsheet, Figure 26, a solution of ammonium sulfate and sulfuric acid, equivalent to ammonium bisulfate, is fed to a series of electrolytic diaphragm cells generally using platinum anodes and either graphite or lead cathodes. In the Pietzsch and Adolph cell (63), the diaphragm consists of an asbestos rope wrapped around the graphite cathode. This eliminates the need for a catholyte. The diaphragm is required to prevent cathodic destruction of the peroxydisulfate ion formed at the anode.

TABLE 13. Hydrogen Peroxide Cell Data (63)

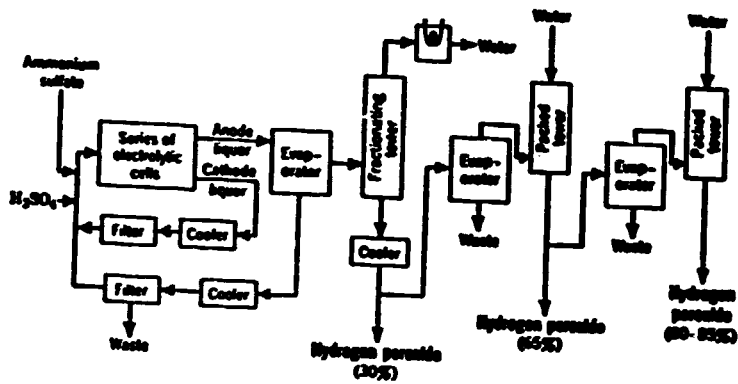|	Weissenstein	Pietsch-Adolph	Löwenstein Laporte
Catholyte, g/l:			
H_2SO_4	200	65–70	200
$(NH_4)_2SO_4$		261	200
K_2SO_4		35	
NH_4CNS	0.15	0.1	
$KCNS$		2.5	
$(NH_4)_2S_2O_8$		63	0
HCl	0.01		
H_2SO_5	35		
Anolyte, g/l:			
H_2SO_4	330–400	30–50	160
$(NH_4)_2SO_4$		22	70
K_2SO_4		35	
NH_4CNS		0	
$KCNS$		2.5	
K_2SO_4		137	2–22
$(NH_4)_2S_2O_8$	220–300		
H_2SO_5	21–25		
Cells in series			
Cell dimensions, cm	100 × 15 × 25		
Cooling tubes		160	Lead ends
Cathodes	Lead tubing water-cooled	Graphite rod	Lead plates
Number		150	
Number of sets		15	
Diaphragms	Porcelain	Asbestos cups	Ceramic
Number	10		
Anodes	Platinum strips, tantalum tags	Aluminum rod platinum wire	Platinum
Number	10	70	
Number of sets	11	14	
Fuses per anode	1	1	
Anode, cathode connection			
Catholyte:			
Flow	Through cathodes thru anodes in series		Through cathodes thru anodes in series 29–33
Temperature, °C	5° lower than anolyte		
Anolyte:			
Flow	Through cathodes thru anodes in series 29–30		Through cathodes thru anodes in series 29–33
Temperature, °C			
Voltage per cell:			
Platinum anode	5.6–5.7	5.2–6.3	5.0–6.3
Platinum-tantalum anode	5.2–5.3	(100 × 5)	230
Current per cell, amp			
Current density:			
Anode	0.06	0.04–0.05	0.4–1.1
Total	600		
Current concentration, amp/l	72–78	18	17
Current efficiency, %		63–64	63–64
Cell volume, l		340	
Flow rate, l/hr		1,600	110
Platinum life, yr		3–6	
Power:			
Kwh/kg equivalent to 100% H_2O_2	11–16.2	12.9–13.2	13.4
Do	21.5	17–18	17.0
Ac total			
Kwh/lb equivalent to 100% H_2O_2	6.6–7.3	6.6–6	6.1
Do	9.6	7.7–6.2	7.7
Ac total			
Platinum consumption:			
G/kg equivalent to 100% H_2O_2	0.0025–0.004	0.004–0.004	0.005
G/lb equivalent to 100% H_2O_2	0.001	0.004–0.0045	0.0025
Steam:			
Kg/kg equivalent to 100% H_2O_2	27.5	50–60	50–75
Lb/lb equivalent to 100% H_2O_2	27–30	25–30	50–75

Figure 26.   Flow Diagram for the Production of Hydrogen
            Peroxide by Ammonium Bisulfate Electrolysis (67)

The Lowenstein-Laporte cell employs unglazed porcelain diaphragms to separate the anolyte and catholyte. The solution flows through all of the catholyte compartments and then through the anolyte compartments of the electrolytic cells. As the solution flows through the cathode chambers, hydrogen is evolved and any residual active oxygen in the recycled sulfate is destroyed. Diffusion through the diaphragm and evaporation of water causes changes in the electrolyte composition. During passage of the solution through the anode chambers, sulfate is oxidized to peroxydisulfate. The porcelain cells contain platinum anodes and graphite cathodes arranged so that cooling coils may be used to keep bath temperatures below 35°C. The cells operate at about 5.7 volts. In order to prevent the formation of oxygen, ammonium thiocyanate at about 0.1 gm/liter (67) is added to the electrolyte to increase oxygen overvoltage. The anode current density ranges from 0.4 to 1.1 A/cm^2. The hydrogen evolved is diluted with air to prevent formation of an explosive atmosphere. Power consumption is about 12,200 kwh/ton. The oxidized solution containing peroxydisulfate is sent from the cells to an evaporator where a mixture of peroxide, formed by hydrolysis of the peroxydisulfate and water is vaporized by steam. The vapors are sent to a stoneware-filled distillation tower operated under a vacuum that produces a 30-40% hydrogen peroxide solution. The sulfate solution remaining in the evaporator is cooled and filtered to remove any sediment and then returned to the cells. The concentration is adjusted as required.

The recovered peroxide is acidified with sulfuric acid (0.5 g/l) and fed to a second evaporator-distillation tower system operating at 65°C and 0.06 atm which further increases the concentration of hydrogen peroxide to about 70%. This product may be further concentrated to about 85% by processing in a third evaporator-tower system.

Although the process described above uses an ammonium bisulfate feed, a similar process using sulfuric acid is also used to produce hydrogen peroxide. This process, known as the Weissenstein process and a modification, the Eilenburg process (65), oxidizes sulfuric acid directly to peroxydisulfate. In the Weissenstein cell a lead coil serves both as cathode and cooling coil. Inside the coil are ten vertical porcelain diaphragms spaced equidistantly. Each diaphragm serves an anode consisting of thin platinum strips with tantalum tops. This cell operates at about 5.7 volts.

Improvements in cell design have led to cell potentials on the order of 3.7 volts, mainly by reduction in the cathodic and anodic overpotentials. A comparison of the potential drops within the Eilenburg and Weissenstein cells is shown schematically in Figure 27. The Eilenburg cell is designed on the principle of a filter press. Figures 28A and B show the flowchannels through the electrodes. The anode compartment (Figure 28A) consists of two sections through which anolyte flows. The anode consists of tantalum foil with platinum strips attached. The cathode plate (Figure 28B) has milled channels through which the catholyte flows. The cell body, gaskets and spacers are made of PVC. The hydrogen evolved is rapidly removed through the narrow flow channels and serves as a gas lift pump for circulating the catholyte.

In a third modification of the peroxydisulfate process, potassium bisulfate is added to the ammonium peroxydisulfate solution to precipitate
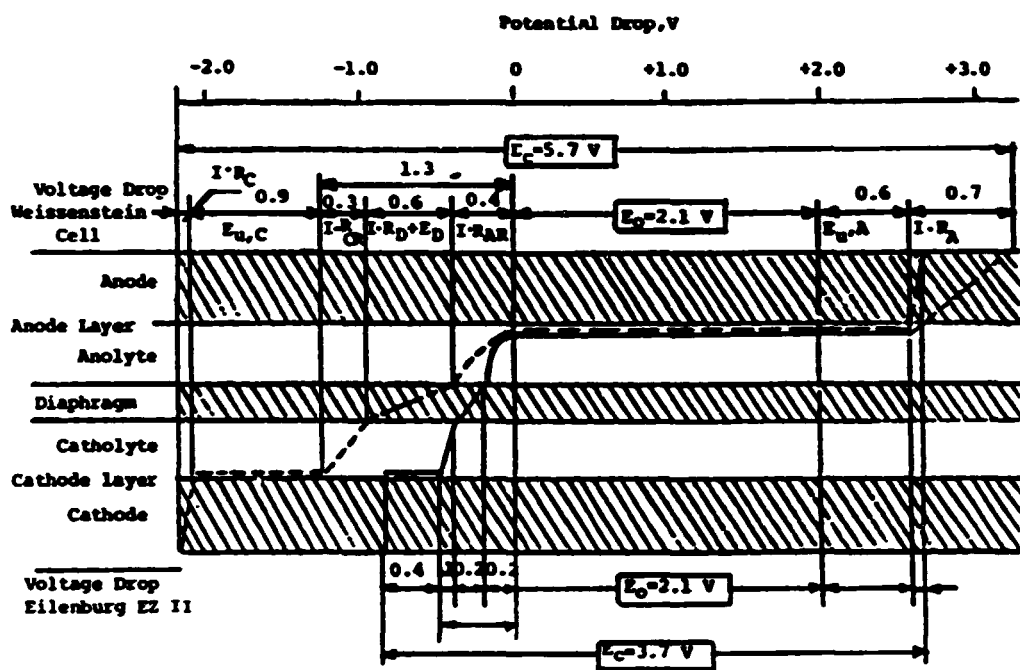
Figure 27. Potential Drop in Weissenstein and Eilenburg Cells (65)

E_C=cell voltage $E_{U,C}$=cathode overpotential E_0=theoretical voltage
E_{UA}=anode overpotential I=current R_{CR}=cathode layer resistance
R_D=diaphragm resistance E_D=diaphragm voltage drop R_{AR}=anode layer resistance
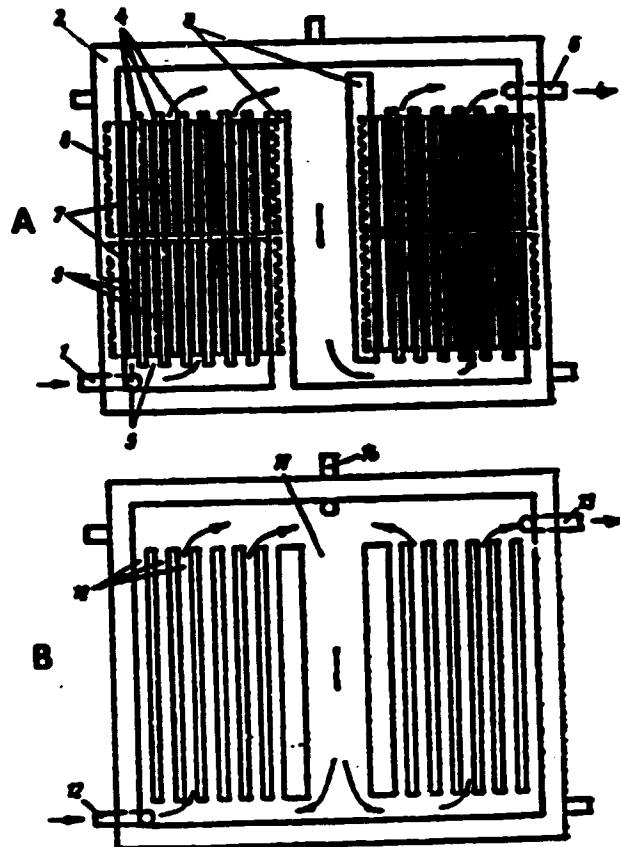R_A=anode resistance R_C=cathode resistance

Figure 28. Electrodes of Eilenburg EZ II Electrolyzer (65)
A. Anode B. Cathode

potassium peroxydisulfate. The potassium salt is separated from the electro-
lyte and then hydrolyzed. This process is shown in Table 13 as the Pietsch
and Adolph process.

4.5.3.2 Peroxydisulfate Process - Energy Requirements

The energy required to produce hydrogen peroxide as shown in
Figure 29, is used in two major process steps. Electrical energy is used to
produce peroxydisulfate and thermal energy, in the form of steam, is used to
separate and concentrate the peroxide.

The overall reaction is

$$2H_2O \longrightarrow H_2O_2 + H_2 \tag{47}$$

The heat of reaction is $\Delta H_R = 90.83$ kcal/mole and the heat of reaction
for the cell reaction

$$2 NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2 \tag{48}$$
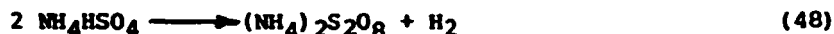
is $\Delta H_R = 99.16$ kcal/mole. As shown in Table 13, the cell energy required
ranges from 11,600 to 14,600 kwh/ton with the Loewenstein-Laporte cell
(ammonium bisulfate) at 12,200 kwh/ton or 128 x 10^6 Btu/ton. The Eilenberg
cell, with its lower cell voltage, uses about 9,000 kwh/ton or 95 x 10^6
Btu/ton.

The steam required for separation and concentration of the peroxide,
ranges from about 27.5 lb/lb to 75 lb/lb, depending on product strength
(30-70% H_2O_2). Using 32.5 lb/lb for a 50% product, at a boiler efficiency
of 82.5%, steam represents an additional 79 x 10^6 Btu/ton of peroxide.
Miscellaneous electrical power, for pumps and other equipment, and for
rectifier losses, amounts to an additional 3200-4000 kwh/ton or 14 x 10^6
Btu/ton. This gives a total energy input of about 15,400 kwh/ton for elec-
trical energy, and 79 x 10^6 Btu/ton for thermal input. The energy efficien-
cies, as previously defined are for electric energy

$$\text{cell efficiency} = E_c = .252*$$

$$\text{plant efficiency} = E_p = .073**$$

$$\text{fossil fuel efficiency} = E_f = .040**$$

The total fossil fuel equivalent energy required is 240 x 10^6 Btu/ton H_2O_2.

4.5.4 New Electrochemical Process Development

4.5.4.1 Alkaline Electrolysis

The cathodic reduction of oxygen in alkaline solution to hydrogen
peroxide was discussed previously in Section 4.6.2.3. In order for the

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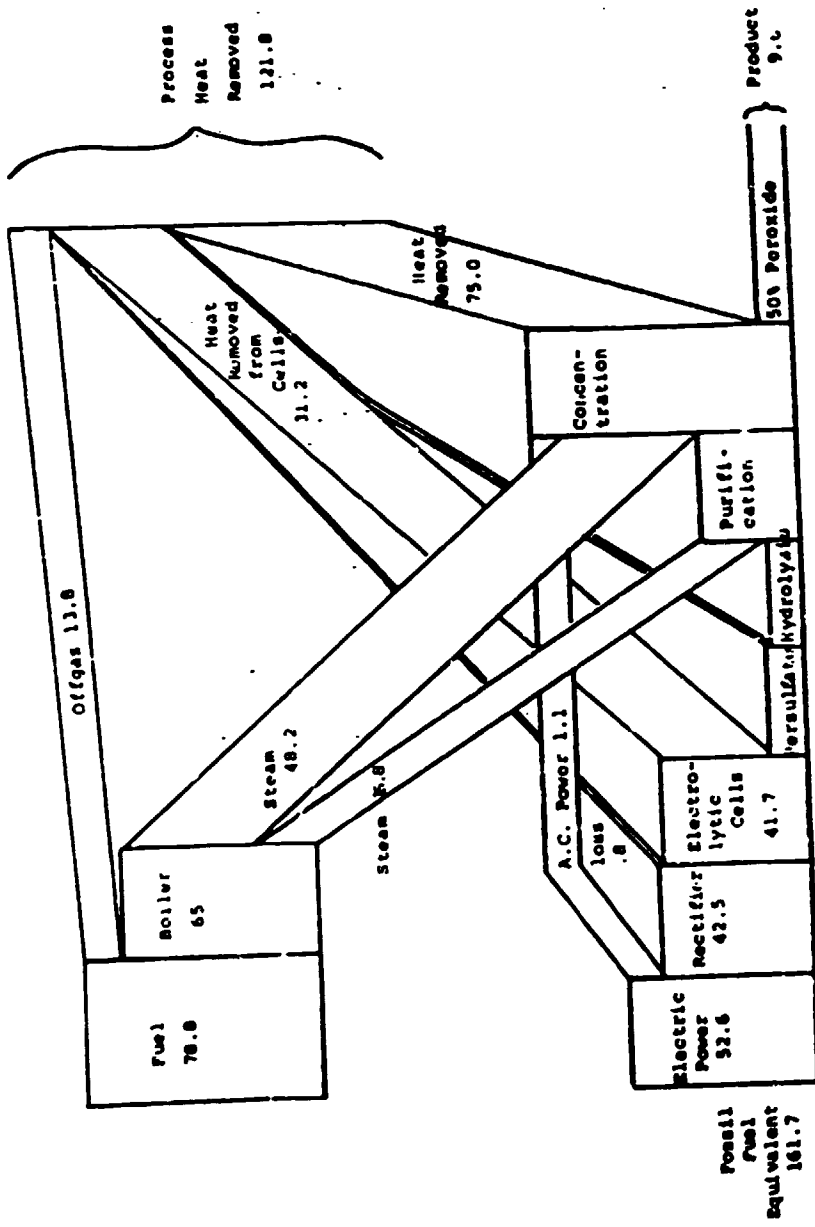
* based on Eq. (48)
** based on Eq. (47)

Figure 29. Energy Flow Diagram - Hydrogen Peroxide, Persulfate Process

Units are 10^6 Btu/ton 100% Peroxide

of 5:1 to 10:1 overall, with ratios in the individual stages of 10:1 to 25:1.
Three to eight stages are normally employed.

The feed material may either be anhydrous alcohol or the alcohol water
azeotrope and oxygen is supplied either as air or pure oxygen. The effluent
from the reactor, consisting of unreacted alcohol, diluent, acetone and
hydrogen peroxide, is cooled by reducing the pressure and condensing. The
peroxide and acetone are separated from the reaction mixture by distilla-
tions, as in the liquid phase process.

Energy Requirements

The major use of energy in the alcohol oxidation process is in the
steam required to separate the hydrogen peroxide and acetone products from
the recirculating alcohol/water mixture. It is estimated that approximately
36.6×10^6 Btu/ton peroxide are required. An additional 26.5×10^6 Btu/ton
of peroxide in the form of steam is required to concentrate the peroxide
solution to 50%. At a steam generating efficiency of 82.5%, this amounts to
a fuel input of 76.5×10^6 Btu/ton. In addition, fuel is required to vapor-
ize the reaction mixture (about 4.6×10^6 Btu/ton) and electrical energy for
pumps (400 kwh/ton). The total fossil fuel equivalent of the process energy
required is 85.3×10^6 Btu/ton H_2O_2. This does not include any energy
associated with the feed isopropanol or the by-product acetone. The heats
of reaction for both the liquid phase and the vapor phase oxidations are
exothermic: $\Delta H_R = -30.8$ and -21.9 Kcal/mole respectively. Therefore, the
energy efficiencies are meaningless.

4.5.6 Conclusions

The anthraquinone process for hydrogen peroxide manufacture uses only
about 45.6×10^6 Btu/ton, or one-fifth of the 240×10^6 Btu/ton required by
the peroxydisulfate electrolytic process. Although further improvements can
be projected for the peroxydisulfate process, there is no possibility that
it can become competitive on an energy use basis with the anthraquinone
process. There are however, several scenarios that could promote interest
in an electrolytic process. First, since there is a rapidly increasing
demand for peroxide in wastewater treatment and pulp and paper bleaching, it
may be desirable to consider on-site generation much as on-site hypochlorite
generation is used (see Section 4.3.1). Secondly, the above uses require
dilute peroxide solutions and about 40% of the energy requirement in the
peroxydisulfate process is used to concentrate the peroxide product to 50%
H_2O_2. Removal of steam requirements for an upgraded peroxide would decrease
the energy requirement to 150×10^6 Btu/ton. Despite this saving it is
apparent that a major innovative approach to electrolytic peroxide manufac-
ture is required in order to make it more energy competitive. Such a possi-
bility exists by the use of a coupling reaction cell where peroxydisulfate is
formed at the anode according to Eq. (38) and hydroperoxide ion at the
cathode according to Eq. (42). This process will be examined in detail in
Section 5.3.

PRODUCTION INDUSTRIELLE

Tel qu'expliqué dans l'introduction, la production du peroxyde d'hydrogène à l'échelle industrielle a connu jusqu'ici trois périodes. D'abord, vers la fin du siècle dernier, l'application de la méthode originale de Thenard à partir du peroxyde de baryum et d'un acide fort (sulfurique ou phosphorique) a permis de fabriquer une solution aqueuse assez stable, mais peu concentrée : de 3 à 6 pour 100 au plus. Ensuite, est venu le procédé électrolytique d'oxydation anodique des sulfates suivie de l'hydrolyse des peroxysulfates, qui donne des solutions plus concentrées; de l'ordre de 30 pour 100. Ce procédé a été supplanté à son tour par celui, plus économique et techniquement plus simple, de l'o-ydo-réduction cyclique des anthraquinones, procédé employé presque exclusivement de nos jours dans toutes les nouvelles installations. Il n'est pas impossible que lui aussi soit un jour remplacé par un quatrième, encore plus avantageux. Comme les deux premiers procédés sont maintenant désuets, ils ne seront décrits que très sommairement ici; d'autant plus qu'on en trouve des descriptions très détaillées dans les monographies déjà citées ([18, 20]).

I. — PROCÉDÉ AU PEROXYDE DE BARYUM

Bien que basé sur des réactions de chimie minérale assez simples en principe ce procédé présente de nombreuses difficultés en pratique. Disons d'abord que le peroxyde de baryum est le seul utilisable en pratique, ceux de calcium et de strontium ayant des pressions de dissociation beaucoup trop élevées aux températures où la réaction d'oxydation par l'air est suffisamment rapide pour être pratiquable.

La réaction

$$BaO + \frac{1}{2} O_2 \rightarrow BaO_2,$$ [120]
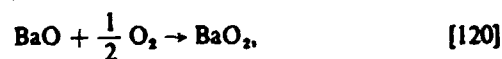
qui est exothermique de 17 kcal.mole^{-1}, a aux environs de 800 °C une pression de dissociation à l'équilibre égale à la pression partielle de l'oxygène dans l'air. En pratique on se contente de températures de l'ordre de 500 °C qui donnent quand même des taux de réaction suffisamment rapides.

La fabrication de l'oxyde de baryum de qualité appropriée présente encore plus de problèmes que la peroxydation, ou l'attaque subséquente par les acides.

En effet, le succès de tout ce procédé repose sur la texture de l'oxyde employé, qui doit être assez poreuse pour faciliter l'accès de l'oxygène de l'air. Le produit de départ est la baryte, ou spath lourd, le carbonate naturel étant trop impur pour servir à cette fin. La suite des opérations peut se résumer comme suit :

a) Réduction de la baryte en sulfure par le charbon pulvérisé dans un four à environ 1 000 °C :

$$BaSO_4 + 4C \rightarrow BaS + 4CO \qquad [121]$$
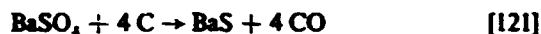
b) Dissolution du sulfure dans l'eau pour la carbonatation

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S \qquad [122]$$

c) Le carbonate, filtré au filtre-presse, puis séché, est transformé en oxyde par réduction avec le noir de fumée, le coke ou des hydrocarbures volatils. Cette opération, la plus délicate de toutes, exige un contrôle rigoureux afin d'obtenir un oxyde poreux et léger. En particulier, il faut prévenir la fusion de la masse solide, qui forme des agglomérats, enrobant ainsi une partie du carbonate non dissocié. L'opération se fait dans des cornues chauffées à plus de 1 000 °C pendant quelque 12 h. Le gaz dégagé, du monoxyde de carbone à 80 pour 100, sert à chauffer les cornues.

d) L'oxyde de baryum encore chaud est ensuite peroxydé par un courant d'air à 300 ou 400 °C dans des fours rotatoires. Cette opération dure de 14 à 16 h et donne un produit contenant jusqu'à 88 pour 100 de BaO_2, de 3 à 5 pour 100 de $BaCO_3$ et 1 pour 100 de $BaSO_4$. Les autres impuretés, silice, alumine, etc., ne doivent pas contenir trop de métaux lourds pour minimiser la décomposition catalytique du peroxyde d'hydrogène.

e) Le peroxyde de baryum, refroidi et pulvérisé, est traité par une solution d'acides minéraux dans des cuves munies d'un serpentin réfrigérant et d'agitateurs.

On a aussi préconisé la fabrication à partir du peroxyde de sodium, qui est beaucoup plus pur que celui de baryum, mais aussi plus coûteux. Cependant, l'obstacle principal vient de ce que les sels de sodium sont très solubles dans l'eau, en sorte que leur séparation d'avec le peroxyde d'hydrogène n'est plus possible. Ce procédé a servi à l'occasion pour fabriquer une solution de peroxyde utilisable sur place, quand la présence de sels de sodium n'offrait pas d'inconvénients : par exemple, dans le blanchiment de la pâte à papier. On a également obtenu du peroxyde d'hydrogène comme sous-produit dans la production de la cryolithe artificielle $Na_3(AlF_6)$ à partir de l'acide fluorhydrique.

## II. — PROCÉDÉS ÉLECTROLYTIQUES

La production électrochimique du peroxyde d'hydrogène est basée sur l'oxydation à l'anode de solutions concentrées d'acide sulfurique ou de sulfates alcalins. Il ne faut pas la confondre avec la réduction cathodique de l'oxygène qui a été décrite ci-haut (p. 114). C'est Meidinger ([14]) qui le premier

Bibl. p. 140. [*P. A. GIGUÈRE*]

en 1853 a rapporté la formation directe du peroxyde d'hydrogène à l'anode dans l'électrolyse d'une solution fortement acidifiée par l'acide sulfurique. Cette explication a prévalu jusqu'en 1878, alors que Berthelot ([15]) a démontré, qu'en fait, c'est d'abord de l'acide peroxydisulfurique $H_2S_2O_8$, qui se forme. L'hydrolyse subséquente donne du peroxyde d'hydrogène.

En principe cette méthode repose sur les équilibres déjà vus (p. 33). D'après ces équilibres il ne devrait se former que de l'oxygène à l'anode. En pratique, on peut produire du peroxyde ou des peroxysulfates, qui exigent un potentiel d'électrode plus élevé, en augmentant la densité de courant, et en choisissant une électrode avec une forte surtension pour le dégagement de l'oxygène. Le platine métallique est le seul à posséder cette caractéristique. Aussi, son emploi pour la fabrication de l'anode est-il indispensable. Comme c'est, en même temps, un bon catalyseur de la décomposition du peroxyde d'hydrogène, on ne pourrait obtenir plus que des traces de ce dernier en milieu neutre ou alcalin. Les peroxysulfates, au contraire, ne se décomposent pas de façon appréciable dans ces conditions. Les équations qui représentent leur formation sont

$$2\,HSO_4^- + 2\,H_2O \rightarrow S_2O_8^{2-} + 2\,H_3O^+ + 2\,\varepsilon^- \qquad [123]$$
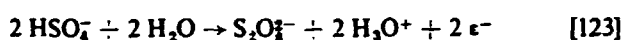
dont le potentiel d'électrode normal est de $-2{,}18$ v, et

$$2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,\varepsilon^-, \qquad [124]$$
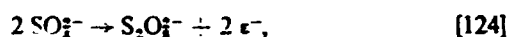
avec un potentiel assez voisin, $-2{,}06$ v.

Le mécanisme de la réaction anodique n'est pas encore parfaitement connu. Ainsi, certains auteurs ont prétendu qu'il se formait du peroxyde d'hydrogène, soit comme intermédiaire ([132]), soit concurremment avec la formation des peroxysulfates ([134]). Cette hypothèse apparaît cependant peu probable, comme l'a maintenu Haïssinsky, tant pour l'oxydation des sulfates ([135]), que pour celle des carbonates et des borates ([136]). On a aussi suggéré que l'oxydation se faisait par l'intermédiaire de l'oxygène naissant

$$2\,HSO_4^- + O + H_2O \rightarrow H_2S_2O_8 + 2\,OH^- \qquad [125]$$
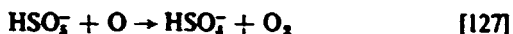
mais il n'y a aucune justification pour une telle hypothèse. Évidemment, il se dégage toujours un peu d'oxygène à l'anode, les conditions étant favorables du point de vue thermodynamique. Mais en pratique cette action peut être minimisée; le rôle de l'oxygène se borne effectivement à la polarisation de l'électrode.
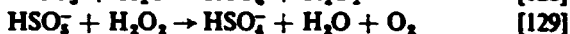
Il existe trois variantes du procédé au peroxysulfate selon que l'électrolyte est l'acide sulfurique, le sulfate de potassium ou celui d'ammonium. Chacun offre des avantages et des inconvénients. Aussi a-t-on essayé diverses combinaisons et modifications. Par exemple, l'acide peroxydisulfurique ne se décompose que très lentement à température ordinaire, mais il s'hydrolyse facilement pour donner l'acide permonosulfurique, ou acide de Caro,

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad [126]$$

Bibl. p. 140.   [P. A. GIGUÈRE]
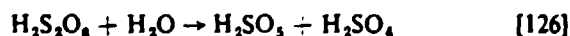
Or la formation d'acide de Caro est nuisible pour deux raisons. D'abord, il est détruit à l'anode

$$HSO_5^- + O \rightarrow HSO_4^- + O_2 \qquad [127]$$

et il s'hydrolyse sans donner de peroxyde d'hydrogène

$$HSO_5^- + H_2O \rightarrow HSO_4^- + H_2O_2 \qquad [128]$$
$$HSO_5^- + H_2O_2 \rightarrow HSO_4^- + H_2O + O_2 \qquad [129]$$
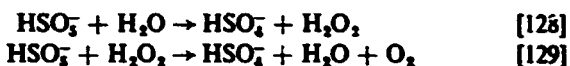
Comme cette hydrolyse se passe en solution on s'efforce de la minimiser en réduisant le volume de la solution par rapport à la surface de l'électrode. Pour la même raison il faut empêcher la température de s'élever au cours de l'électrolyse, malgré la forte densité de courant électrique nécessaire pour un bon rendement. En pratique on emploie une cathode creuse, avec circulation d'eau froide.

Les procédés au sulfate de potassium ou d'ammonium ne présentent pas ces inconvénients. Ce dernier surtout, qui est plus soluble que le premier, est particulièrement avantageux. Il s'agit, en réalité, du bisulfate, NH_4HSO_4, car la solution doit être gardée assez acide pour éviter la formation d'ammoniac par réduction à la cathode suivant la réaction globale

$$2(NH_4)_2SO_4 \rightarrow (NH_4)_2S_2O_8 + 2\,NH_3 + H_2 \qquad [130]$$
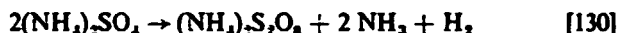
Diverses modifications ont été apportées à ce procédé. Ainsi, le peroxysulfate d'ammonium, très soluble, est converti en peroxydisulfate de potassium peu soluble par addition de bisulfate :

$$(NH_4)_2S_2O_8 + 2\,KHSO_4 \rightarrow K_2S_2O_8 + 2\,NH_4HSO_4 \qquad [131]$$

Le précipité est filtré, puis hydrolysé. La solution électrolytique peut alors être purifiée, puis recyclée. Une autre modification consiste à ajouter un sulfate alcalin à celui d'ammonium, ce qui permet de doubler la concentration de la solution, et partant, la capacité d'une usine d'électrolyse.

Quant à l'hydrolyse, celle de l'acide peroxysulfurique est beaucoup plus facile que celle des persulfates. En effet, ces derniers tendent à précipiter au cours de l'opération. Pour contourner cette difficulté on a eu recours à divers stratagèmes; soit des évaporateurs de construction spéciale, du type à « film grimpant », soit une opération en deux temps, comprenant une première concentration sous vide, suivie d'une hydrolyse rapide par la vapeur.

Étant donné leur complexité technique, les procédés électrolytiques ont donné lieu au cours des années à toutes sortes d'études et de développements dont la plupart sont restés secrets à cause de la concurrence. Ils ont pris énormément d'ampleur, surtout en Allemagne et en Autriche, entre les deux guerres mondiales; si bien qu'en 1950 ils assuraient, tant en Amérique qu'en Europe, 90 pour 100 de la production mondiale ([827]). Le fonctionnement de l'industrie allemande des peroxydes a été décrit dans les rapports des missions scientifiques des Alliés ([424, 703, 838, 839]).

En résumé, ces procédés sont avantageux en ce qu'ils fournissent directement un produit pur et assez concentré, de 30 à 35 pour 100. Par contre, ils

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exigent un investissement de capital considérable, et la consommation d'énergie électrique est élevée. Le bon fonctionnement et l'entretien d'un appareillage délicat et complexe requièrent une main-d'œuvre assez coûteuse. C'est peut-être ce dernier facteur qui a le plus contribué à leur désuétude.

III. — OXYDO-RÉDUCTION DES QUINONES

Les procédés modernes de fabrication du peroxyde d'hydrogène sont basés sur la réduction catalytique de composés organiques de la famille des quinones, suivie de l'autoxydation par l'air des hydroquinones ainsi formées. Ce sont des procédés cycliques, qui se font en milieu exclusivement organique. L'extraction par l'eau du peroxyde d'hydrogène dissous dans ces solvants organiques donne directement une solution de 25 à 35 pour 100.

On savait depuis longtemps que l'oxydation lente de certains composés organiques donne du peroxyde d'hydrogène ou des peroxydes organiques. Cependant, c'est à Walton et Filson ([640]) que l'on doit la première préparation en 1932 de H_2O_2 en quantités substantielles par oxydation de l'hydrazobenzène en solution alcoolique. Leur découverte, brevetée peu après ([641]), a donné naissance au procédé industriel connu sous le nom d'autoxydation des anthraquinones. Une compilation des nombreux brevets couvrant les diverses modifications de ce procédé a été publiée récemment ([642]).

La chimie de ce procédé peut se résumer dans l'équation suivante :

$$\text{(A)} \xrightarrow{+ H_2} \text{(B)} \xrightarrow{+ O_2} \text{(A)} - H_2O_2 \quad [132]$$
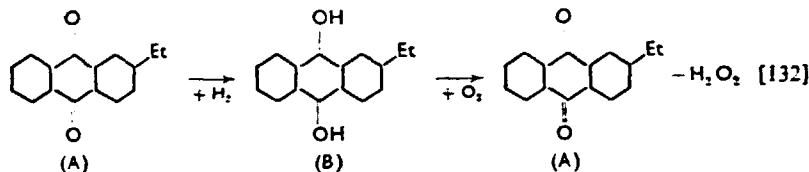
L'anthraquinone (A), dissoute dans un mélange de solvants organiques, est réduite par l'hydrogène à pression ordinaire en présence d'un catalyseur. Dans une seconde étape l'hydroanthraquinone (B) est oxydée par l'air, régénérant l'anthraquinone de départ, et formant du peroxyde d'hydrogène qui doit être extrait de la solution organique. Outre cette réaction principale, il se produit des réactions secondaires qui viennent malheureusement compliquer le système.

a) Anthraquinone. — Comme substance de travail on emploie de préférence l'éthyle-2 anthraquinone (A) à cause de sa solubilité favorable et sa résistance aux opérations répétées d'oxydo-réduction. On a aussi employé des mélanges d'alkyl-2 anthraquinones et de tétrahydroalkyle-anthraquinones. Ces dernières, de toute façon, se forment graduellement par hydrogénation de l'anthraquinone de départ. Parmi les autres composés décrits récemment dans des brevets on note : i) des mélanges eutectiques d'anthraquinones ([643]), plus solubles que les composés purs; ii) la tétrahydroanthraquinone pure à 85 pour 100 ([644]), qui permet d'opérer à des températures plus élevées avec de

wie längere Zeit bei eingeschalteter Heizung sorgfältig gespült. Sollte einmal durch unvorsichtiges Arbeiten. z. B. beim Aufheben eines Vakuums oder durch Bruch. Luft in die Anlage gelangt sein, so ist diese Spülung mit Inertgas zu wiederholen. Das gleiche gilt für den Fall, daß die Apparatur längere Zeit außer Betrieb war. Störungen durch Sauerstoff und Feuchtigkeit sind meistens auf Bedienungsfehler oder auf unsachgemäßes Arbeiten zurückzuführen.

Reduktion des Katalysators

Die Reduktion des BTS-Katalysators geschieht durch Einleiten von Wasserstoff oder Kohlenmonoxid bzw. durch Einleiten eines Gemisches der beiden Gase in das Absorptionsrohr (D) bei Temperaturen von 100 bis 150°C. Hierbei ist der Hahn 2 zu schließen, während der Hahn 1 zur Ableitung des überschüssigen Gases und des entstehenden Wassers geöffnet bleibt. Es ist selbstverständlich darauf zu achten, daß der überschüssige Wasserstoff gefahrlos abgeleitet wird.

Bei der Reduktion kann die Temperatur so stark ansteigen, daß die Bildung von inaktivem Kupfer statt der hochaktiven, schwarzen Form begünstigt wird. Zweckmäßig wird der Katalysator zunächst im Inertgasstrom auf 100 bis 120°C erhitzt, danach gibt man dem Inertgas reduzierendes Gas in dem Maße zu. daß 150°C nicht überschritten werden. Zuletzt sollte bei dieser Temperatur und völliger Schwarzfärbung die Reduktion mit unverdünntem Gas beendet werden. Die erstmalige Reduktion nimmt bei der angegebenen Menge etwa 10 bis 12 Stunden in Anspruch. Eine unbeabsichtigte kurze Temperatursteigerung auf 250°C beeinträchtigt gewöhnlich die Wirksamkeit nicht.

Die Regeneration des graugrünen, erschöpften Katalysators verläuft unter gleichen Bedingungen wie die erste Reduktion, jedoch in wesentlich kürzerer Zeit.

(Nach Unterlagen der Fa. NORMAG. Hofheim/Ts.)

# Wasserstoffperoxid: Herstellung und Eigenschaften

Von Dr. D. Osteroth, Witten an der Ruhr

Im Jahre 1818 gelang erstmals dem französischen Chemiker *Thénard* die Gewinnung einer zwar noch sehr verdünnten wäßrigen Lösung von Wasserstoffperoxid durch Einwirkung von Schwefelsäure auf Bariumperoxid:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

Auf diese Weise lassen sich nur Lösungen mit etwa 3 bis 6 Gew.% Gehalt an H_2O_2 erhalten. Trotzdem war diese Reaktion nahezu einhundert Jahre lang die einzige Möglichkeit zur Gewinnung dieses Peroxids und wurde sogar im technischen Maßstab angewendet.

Erst 1908 wurde in Österreich ein Elektrolyse-Verfahren zur Gewinnung von H_2O_2 entwickelt, das nach folgendem Schema abläuft:

$$H_2S_2O_8 \xrightarrow{2H_2O} 2H_2SO_4 + H_2O_2$$
$$H_2 \xleftarrow{\quad Elektrolyse \quad}$$
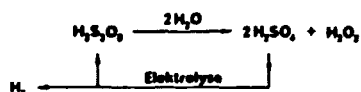
Dieses Verfahren wurde später u.a. von der *Degussa* zum sog. *Degussa-Weißensteiner*-Verfahren ausgebaut und im *Degussa*-Werk in Rheinfelden in einer Großanlage betrieben, in der 35%iges H_2O_2 anfiel.

Während des Zweiten Weltkrieges erlangte die Herstellung von hochprozentigem, etwa 85%igem H_2O_2 im damaligen Deutschen Reich sehr große Bedeutung. Dieses Produkt diente unter dem Decknamen „T-Stoff" als synthetischer Treibstoff für Raketentriebwerke (u. a. in V-Raketen. Torpedos, Raketenflugzeugen usw.). Die *Elektrochemischen Werke München (EWM)* besaßen in ihrem Werk Höllriegelskreuth eine Anlage, die am Ende des Krieges eine Kapazität von 400 moto hochprozentigem H_2O_2 erreichte. Zulieferwerk für 35%iges H_2O das die *EWM* nicht selbst in ausreichenden Mengen produzieren konnten, war das *Degussa*-Werk Rheinfelden. Eine weitere Produktionsstätte, die gleichfalls nach dem damals in der Welt einmaligen Konzentrationsverfahren der *EWM* arbeitete und deren Bau im Auftrage der damaligen Luftwaffe erfolgt war, befand sich in Bad Lauterberg im Harz; diese Anlage wies am Ende des Krieges eine Kapazität von 1100 moto auf. Weitere kleinere Anlagen befanden sich u. a. bei *Henkel* in Düsseldorf. Die größte Anlage zur Herstellung von hochprozentigem H_2O_2, das *T-Stoff-Werk Rhumspringe* im Vorharzland, war am Ende des Krieges im Bau; ferner war auch im *IG*-Werk Heydebreck in Oberschlesien eine neue Großanlage im Bau, die nach einem neuen *IG*-Verfahren produzieren sollte. Planmäßig wollte man im damaligen Deutschen Reich am 1.4.45 über eine Kapazität von 2770 moto, am 1.7.45 über 3770 moto und am 1.10.45 schließlich über 5200 moto verfügen, jedoch setzte das Kriegsende dieser Entwicklung ein Ende. Die Produktion von H_2O_2 wurde verboten und die Anlagen wurden demontiert.

Das *EWM*-Verfahren, nach den beteiligten Erfindern auch *Pietzsch-Adolph*-Verfahren genannt, beruhte auf der Elektrolyse von Ammoniumhydrogensulfat zu Ammoniumsulfat und dessen anschließender Umsetzung mit festem Kaliumhydrogensulfat zu Kaliumpersulfat. Nach Versetzen mit 60%iger Schwefelsäure und anschließendem Einleiten von Wasserdampf bildete sich durch Hydrolyse eine etwa 35%ige wäßrige Lösung von H_2O_2, aus der durch Destillation und Fraktionierung im Vakuum eine 80- bis 85%ige wäßrige Lösung von H_2O_2 von hoher Reinheit und Stabilität erhalten wurde.

Bereits im Jahre 1942 war von der damaligen *IG-Farbenindustrie Aktiengesellschaft* das sog. AO-Verfahren (Anthrachinon-Verfahren) entwickelt worden und wurde damals in einer Versuchsanlage im Pilot-Maßstab (30 moto) betrieben. Dieser von *Riedl* und *Pfleiderer* entwickelte Prozeß kam jedoch während des Krieges nicht mehr in Großproduktion. Heute stellt er jedoch den wichtigsten technischen Weg zum H_2O_2 dar, und die Hauptmenge der jährlich in der Welt hergestellten rund 400000 t wird so gewonnen. Folgender Prozeß läuft hierbei ab:
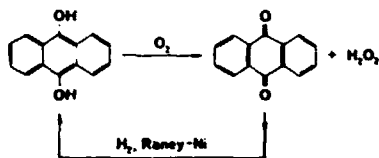
Beim AO-Verfahren wird eine sog. „Arbeitslösung" mit etwa 10 bis 20% des sog. „Reaktionsträgers" (z. B. 2-Äthylanthrachinon) in einem Lösungsmittel über mehrere Reaktionsstufen im Kreis geführt; als „Chinonlöser" dienen Aromaten im Siedebereich von etwa 160 bis 240°C. Der Lösung muß ferner ein „Hydrochinonlöser" zugesetzt werden, der verhindern soll, daß im Kreislauf gebildetes Äthylanthrahydrochinon auskristallisiert. Man verwendet hierfür Trioctylphosphat, Diisobutylcarbinol oder Methylcyclohexanolacetat. Für die Hydrierung verwendet man Raney-Nickel als Katalysator.

Das von der Firma Shell entwickelte Isopropanol-Verfahren arbeitet nach folgendem Prinzip:
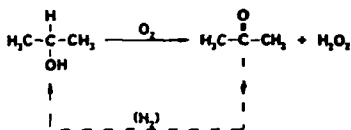
Bei der Oxidation von Isopropanol mit Luft entstehen Aceton und H_2O_2. Zwar ist es technisch durchaus möglich, das Aceton zu Isopropanol zurückzuhydrieren und im Kreislauf in den Prozeß einzuschleusen, doch wird dieser Kreisprozeß offenbar aus wirtschaftlichen Gründen nicht durchgeführt. Dieses Shell-Verfahren ist ein Basisprozeß für die Herstellung von synthetischem Glycerin, wobei H_2O_2 an Allylalkohol angelagert wird:
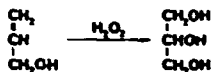
Das heute in den AO-Anlagen gewonnene H_2O_2 fällt in der Regel als 70%ige Ware an, die im Labor leicht durch Destillation und anschließende fraktionierte Kristallisation in wasserfreies H_2O_2 übergeführt werden kann; hierbei handelt es sich um eine sirupöse Flüssigkeit vom Fp $-0,43°C$ und vom Kp 150 bis 158°C. Obwohl H_2O_2 nach folgender Gleichung zerfallen kann,

$$H_2O_{2(fl)} \longrightarrow H_2O_{(fl)} + \tfrac{1}{2}O_{2(g)}$$

$$\Delta H = -23,5 \ kcal/mol$$
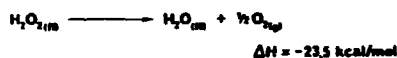
ist im Hinblick auf sicherheitstechnische Überlegungen die Tatsache sehr wichtig, daß wäßriges 90%iges H_2O_2 bei Normaltemperatur nicht zur Explosion gebracht werden kann, und zwar auch nicht durch Initialzündung. Die Zersetzungsneigung nimmt jedoch mit steigender Temperatur sowie insbesondere bei Gegenwart von Katalysatoren rasch zu. Bei Beachtung der einschlägigen Sicherheitsbestimmungen ist der Umgang mit H_2O_2 ungefährlich. Lösungen höherer Konzentration (auch die handelsübliche 35%ige Ware) können jedoch schwere Verätzungen hervorrufen, wobei insbesondere die Augenschleimhäute gefährdet sind. H_2O_2-Dämpfe führen ferner zu Reizungen der Augen sowie der Atemwege und der Lunge. In der Technik kommt H_2O_2 in Konzentrationen von 50 bis 70 Gew.% in Straßentankern oder Kesselwagen zum Versand an Großverbraucher. Der Umgang ist problemlos, wenn das H_2O_2 in hoher Reinheit vorliegt und ausreichend stabilisiert ist. Es muß ferner beachtet werden, daß Schwermetallspuren die Zersetzung des H_2O_2 katalysieren und wegen der Bildung von Sauerstoff durch Zersetzung die Lagertanks mit Entlüftungseinrichtungen ausgerüstet sein müssen. Als Werkstoffe für Tanks, Pumpen usw. eignen sich Chrom-Nickel-Stähle sowie Aluminium (99,5), ferner Al/Mg-Legierungen.

Hauptanwendungsgebiete für H_2O_2 in der Technik sind die Herstellung von Bleichmitteln für die Textil-, Papier- und Waschmittel-Industrie (Natriumperborat: $NaBO_2 \cdot H_2O_2 \cdot H_2O$), ferner die Herstellung von Glycerin und Weichmachern.

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Zur betrieblichen Bewältigung von Reglerstörungen

1. Einleitung

Wie an anderen verfahrenstechnischen Elementen innerhalb einer Prozeßanlage, so können auch an den Regeleinrichtungen Störungen auftreten. Da derartige Störungen häufig ein absolutes „Fehlverhalten" des betroffenen Instruments zur Folge haben, ist ihre frühzeitige Erkennung und die Einleitung geeigneter Maßnahmen eine wesentliche betriebliche Aufgabe.

Wenn einmal von den weniger häufigen Fällen abgesehen wird, bei denen die Energieversorgung für sämtliche Regelkreise einer Anlage ausfällt, so hat der Betriebsmann es normalerweise mit einer Einzelstörung zu tun, die er bei einiger Erfahrung leicht und schnell in den Griff bekommen sollte. Dazu ist es nicht zwingend notwendig, jedoch in jedem Fall nützlich, wenn er zumindest die Funktionsabläufe in einem Regelkreis kennt.

2. Schematischer Aufbau eines Regelkreises

Als Beispiel dient uns eine pneumatische Mengenregelung. Diese besteht aus der durchflossenen Rohrleitung, in die – in Flußrichtung gesehen – im allgemeinen zuerst die Meßblende und dann das Regelventil eingebaut sind.

Zwei Impulsleitungen führen von der Meßblende zum Transmitter, in dem der Meßwert pneumatisch verstärkt wird. Dazu braucht der Transmitter Druckluft, die ihm durch eine Versorgungsleitung zugeführt wird. Vom Transmitter führt eine Meßwert-Übertragungsleitung zum unter Umständen weit entfernten Regler. Im schreibenden Regler wird der Meßwert sowohl auf das Schreibwerk als auch auf den eigentlichen Regler gegeben. Im Regler, der ebenfalls eine eigene Druckluftzuführung hat, erfolgt die Umformung des Meßwertes in den Steuerimpuls, der durch eine weitere Leitung in Richtung Regelventil geleitet wird. Unmittelbar vor dem Regelventil trifft die Leitung auf ein Stellwerk („Positioner"), das die Aufgabe hat, den ankommenden Luftstrom zu verstärken. Auch hier gibt es eine Versorgungsluftzuleitung (im Meß- und Regeljargon: „Zuluftleitung"). Der verstärkte Luftstrom wird auf die unmittelbar benachbarte Membrane

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CHEMICAL PROFILE

Hydrogen Peroxide

SUPPLY

PRODUCER	CAPACITY*
Du Pont, Memphis, Tenn.	125
FMC, Bayport, Tex.	60
FMC, South Charleston, W. Va.	85
Interox, Deer Park, Tex.	88
Total	358

*Millions of pounds per year, 100 percent basis. FMC will expand its Bayport plant to 80 million pounds in the fourth quarter of 1984. Profile last published 4/20/81; this revision, 10/3/83.

DEMAND

1982: 218 million pounds; 1983: 235 million pounds; 1987: 307 million pounds.

GROWTH

Historical (1973-1982): 3.2 percent per year; future: 6 to 9 percent per year through 1987.

PRICE

Historical (1952-1983): High, 43c. per pound, 70 percent, tanktrucks tankcars, f.o.b. frt. equald.; low, 17c. per pound, dlvd. Current: 43c. per pound, f.o.b. frt. equald.

USES

Chemical synthesis, 28 percent; pulp and paper, 20 percent; textiles, 18 percent; environmental uses (including water treatment and geothermal steam treatment), 15 percent; mining, 5 percent; miscellaneous, 14 percent.

STRENGTH

Hydrogen peroxide is said to be non-polluting, non-corrosive and easy to handle. It has gained a larger share of the pulp and paper market partially because it is reportedly less energy-intensive than chlorine dioxide.

WEAKNESS

Hydrogen peroxide production fell substantially in 1981 and 1982 because of the effects the recession had on the chemical and textile industries. Demand for hydrogen peroxide in mining has been dropping steadily in recent years due to the poor state of the uranium market and oxygen's displacement of peroxide in certain mining applications.

OUTLOOK

Hydrogen peroxide is expected to grow two to three times faster than GNP through the next five years. The highest growth will be in the less cyclical end-use market — pulp and paper and environmental uses.

PRICE AND UNIT SHIPMENT VALUES

The following table lists price data for hydrogen peroxide of various strengths (by weight) from 1965 through 1979.

	35% H_2O_2		50% H_2O_2		70% H_2O_2 [b]	
	Cents per Pound	Cents per Kilogram	Cents per Pound	Cents per Kilogram	Cents per Pound	Cents per Kilogram
1965	17.00	37.48	—	—	—	—
1966	17.00	37.48	24.25	53.46	32.00	70.55
1967	17.00	37.48	24.25	53.46	32.00	70.55
1968	17.00	37.48	24.25	53.46	32.00	70.55
1969	17.00	37.48	24.25	53.46	32.00	70.55
1970	16.00	35.27	21.70	47.84	28.80	63.49
1971	16.00	35.27	21.70	47.84	28.80	63.49
1972	13.75	30.31	18.25	40.23	23.00	50.71
1973	13.75	30.31	18.25	40.23	23.00	50.71
1974	13.75	30.31	18.25	40.23	23.00	50.71
1975	13.75	30.31	18.25	40.23	23.00	50.71
1976	15.50	34.17	21.25	46.85	26.00	57.32
1977	15.50	34.17	20.75	45.75	26.00	57.32
1978	15.50	34.17	21.25	46.85	28.00	61.73
1979 [c]	16.25	35.82	24.00	52.91	32.50	71.65

Prices [a]

See MANUAL OF CURRENT INDICATORS – SUPPLEMENTAL DATA for additional information.

a. Prices are list prices taken on or near July 1 of each year. Whenever a range of prices was given in the source, the lowest was used. The price bases are:

35% H_2O_2

1965-1971	Tanks, delivered
1972-1977	Tanks, works, freight equalized
1978-1979	Tanks, works, technical, freight equalized.

50% and 70% H_2O_2

| 1966-1971 | Tanks, delivered |
| 1972-1979 | Tanks, freight equalized. |

b. On a 100% basis, 70% H_2O_2 solutions are usually the lowest in list price. Such prices have been as follows (100% basis):

	Cents per Pound	Cents per Kilogram
1966-1969	45.71	100.77
1970-1971	41.14	90.70
1972-1975	32.86	72.44
1976-1977	37.14	81.88
1978	40.00	88.18
1979	46.43	102.36

c. The prices for 1979 were listed by the source after midyear, but according to industry sources were in effect before midyear.

SOURCES: (A)   Chemical Marketing Reporter, midyear issues.

             (B)   Communication with industry.

The following table lists unit shipment values for H_2O_2 (100% basis), based on total shipments (including interplant transfers) and total shipment values.

	Unit Shipment Values	
	Cents per Pound	Cents per Kilogram
1956	47.85	105.5
1957	47.50	104.7
1958	46.55	102.7
1959	46.70	101.6
1960	44.15	97.4
1961	44.40	97.8
1962	45.35	100.0
1963	41.60	91.8
1964	39.10	86.2
1965	37.40	82.4
1966	35.90	79.1
1967	35.00	77.2
1968	34.20	75.3
1969	32.35	71.3
1970	29.80	65.7
1971	27.80	61.3
1972	27.45	60.6
1973	26.25	57.9
1974	27.35	60.3
1975	31.25	68.9
1976	34.35	75.7
1977p	38.25	84.3

See MANUAL OF CURRENT INDICATORS - SUPPLEMENTAL DATA
for additional information.

SOURCE: Current Industrial Reports, Series M28A, U.S. Department of Commerce, Bureau of the Census.

peroxyde d'hydrogène

C'est au chimiste français Louis-Jacques Thenard que l'on doit la découverte en 1818 de « l'eau oxygénée ». Il fallut attendre le début du 20e siècle pour voir apparaître ses premières applications dans la désinfection des plaies et le blanchiment du papier et des textiles. La nature, elle, avait depuis longtemps mis a profit les étonnantes propriétés du peroxyde d'hydrogène : un petit coléoptère, le bien nomme Brachinus crepitans (L), n'utilise-t-il pas des projections d'un melange « explosif » de H_2O_2 et d'hydroquinone généré par ses glandes anales pour éloigner ses ennemis ?

Developpee progressivement entre les deux guerres la production industrielle de peroxyde d'hydrogene a d'abord fait appel a la methode de Thenard (hydrolyse du peroxyde de baryum) qui ne conduisait qu'à des solutions tres diluees en H_2O_2. La mise au point en Allemagne, aux USA et en France, du procede electrolytique devait permettre d'atteindre des concentrations de l'ordre de 30 %. Mais, c'est a partir de l'invention, pendant la seconde guerre mondiale dans les laboratoires de l'I.G. Farben, du procede de fabrication a partir d'anthraquinone que l'industrie du peroxyde d'hydrogene devait recevoir une impulsion decisive. Cette technique est aujourd'hui universellement utilisee. Elle fait intervenir une alkylanthraquinone (tres generalement l'éthyl-2 anthraquinone, mais aussi l'amyl-2 anthraquinone dans le cas du procede Mitsubishi) et comporte 3 etapes :
— hydrogenation de l'ethyl-2 anthraquinone en hydroquinone correspondante par H_2 en presence d'un catalyseur (ex : Pd/Al_2O_3);
— oxydation par l'air de l'hydroquinone en un melange d'hydroxy-hydroperoxydes;
— decomposition de ces hydroperoxydes en H_2O_2 et quinone de depart.

La solution reactive est recyclee et subit des transformations chimiques complexes avec apparition d'autres especes notamment de derives du type 4H-anthraquinone (I) dont l'efficacite est egale, voire superieure, a celle de l'anthraquinone de depart dans le process mais aussi de derives epoxydes (IV) et polyhydroxyles inactifs. Le peroxyde d'hydrogene est extrait avec un solvant approprie puis concentre par distillation. La taille minimum d'une unite industrielle se situe aux alentours de 20 000 t/an, la plus grande unite mondiale, celle d'Oxysynthese (joint-venture L'Air Liquide-ATOCHEM) à Jarrie atteint 90 000 t/an.

Signalons que Du Pont de Nemours a annonce la decouverte d'un nouveau procede de fabrication d'H_2O_2 « par synthese directe » à partir d'hydrogene et d'oxygene gazeux. Le systeme catalytique est constitue d'une solution aqueuse acide contenant des ions halogenures (Br de preference) servant de milieu de suspension a du Pd depose sur charbon a une concentration d'environ 2 %. La reaction s'effectue a basse temperature (0-25 °C) et a des pressions moyennes (29 à 170 bar). Les concentrations d'H_2O_2 obtenues sont de l'ordre de 15 %. Selon Du Pont ce
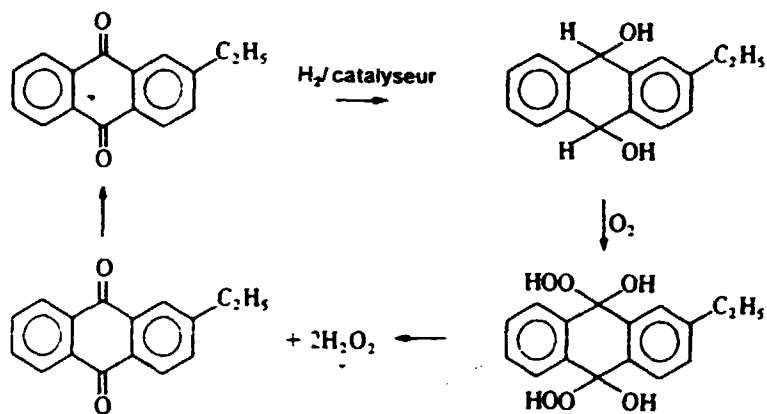
Le procédé H_2O_2 à l'éthylanthraquinone (d'après °)
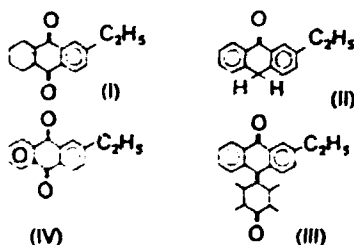
Sous-produits se formant dans la solution.

procédé permettrait de réduire de 50 % le coût d'investissement des unités d'H_2O_2 par rapport à la technique classique passant par l'auto-oxydation d'anthraquinones et l'extraction avec des solvants.

Reste à savoir dans quelle mesure cette nouvelle méthode remet en cause toute l'économie des procédés existants. Autant qu'on puisse en juger par le brevet Du Pont (USP n° 4681751) le procédé qui fournit de l'eau oxygénée relativement diluée s'appliquerait plutôt à des productions décentralisées d'H_2O_2 situées à proximité des gros utilisateurs (fabrications de pâte à papier essentiellement).

Concernant ses avantages en matière de sécurité il faut souligner que, si l'élimination des solvants supprime les risques d'incendie, l'emploi d'un mélange gazeux d'hydrogène et d'oxygène entraîne des risques d'explosion évidents.

L'oxydant écologique par excellence

L'utilisation du peroxyde d'hydrogène dans l'industrie de la pâte à papier est en pleine expansion au Canada et dans l'Est des États-Unis. En remplaçant le chlore dans le blanchiment de la pâte le H_2O_2 permet non seulement de supprimer des rejets d'effluents chlorés mais aussi de produire un papier de qualité supérieure. C'est le principal débouché du peroxyde d'hydrogène sur le marché nord-américain dont il absorbe environ 20 % de la production. Situation quelque peu différente en Europe où la détergence, c'est-à-dire la production de perborates et autres persels pour utilisation dans les détergents, constitue, avec 40 % du marché, la principale utilisation du H_2O_2...

Au delà des emplois dans la chimie, l'industrie papetière, les détergents, l'époxydation d'huiles de soja pour la stabilisation du PVC, la fabrication de l'hydrazine (carburants — fusées, pesticides), l'électronique, de nombreuses applications nouvelles de l'eau oxygénée sont envisagées à l'horizon 90 : assainissement et désodorisation d'effluents gazeux ou liquides, régénération des sols et des nappes phréatiques, époxydation du caoutchouc naturel, production d'eau potable (en association avec l'ozone pour remplacer le chlore), obtention de produits diététiques fibreux à faible valeur calorique à partir de sous-produits agricoles. Plusieurs de ces marchés présentent un potentiel de développement considérable.

Plus généralement le peroxyde d'hydrogène apparaît de plus en plus comme l'oxydant écologique par excellence, sans résidu ni pollution, d'où l'intérêt croissant que lui portent les chimistes. Pour répondre à une demande dont la croissance mondiale se situe aux alentours de 5 % par an, avec des pointes à 10 % environ en Amérique du Nord, les grands producteurs (Interox, Laporte, Degussa, Oxysynthèse, Du Pont) ont investi massivement dans des unités nouvelles portant la capacité mondiale à plus de 1,2 Mt.

D. Savostinnoff

Bibliographie : J.-P. Schirmann, S.Y. Delavarenne, Hydrogen Peroxide in Organic Chemistry" ; EDI

EAU OXYGÉNÉE à 100 %

PAYS A ÉCONOMIE
PLANIFIÉE
63 – 68

AMÉRIQUE DU NORD
289 – 341

EUROPE DE L'OUEST
614 – 614

JAPON
167 –
167

AUTRES PAYS
D'ASIE ET OCÉANIE
79 – 104

AFRIQUE
0 – 5
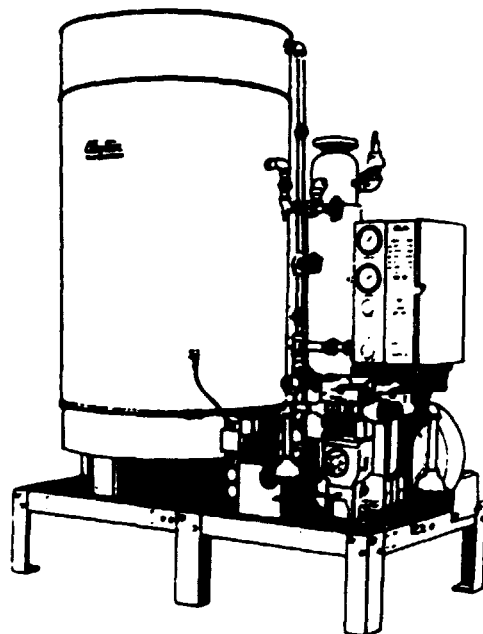
AMÉRIQUE
CENT. - DU SUD
25 – 35
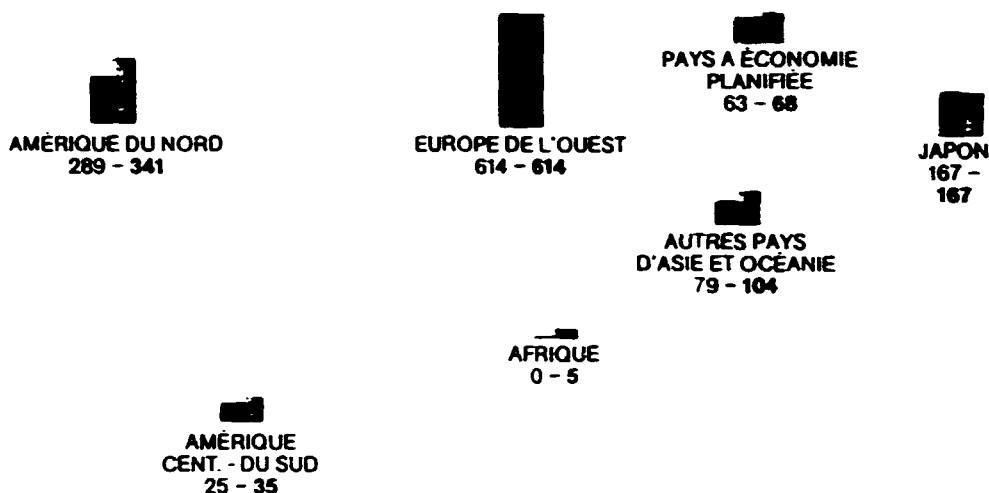
Capacité en 1000 tm/an ● à fin 1988
● en projet

EAU OXYGÉNÉE à 100 %

PAYS À ÉCONOMIE
PLANIFIÉE :
5,10 %

AMÉRIQUE DU
NORD : 23,40 %

ASIE ET
OCÉANIE :
19,90 %

(1)

PAYS À ÉCONOMIE
PLANIFIÉE :
5,10 %

AMÉRIQUE DU
NORD : 25,60 %

ASIE ET
OCÉANIE :
28,30 %

(2)
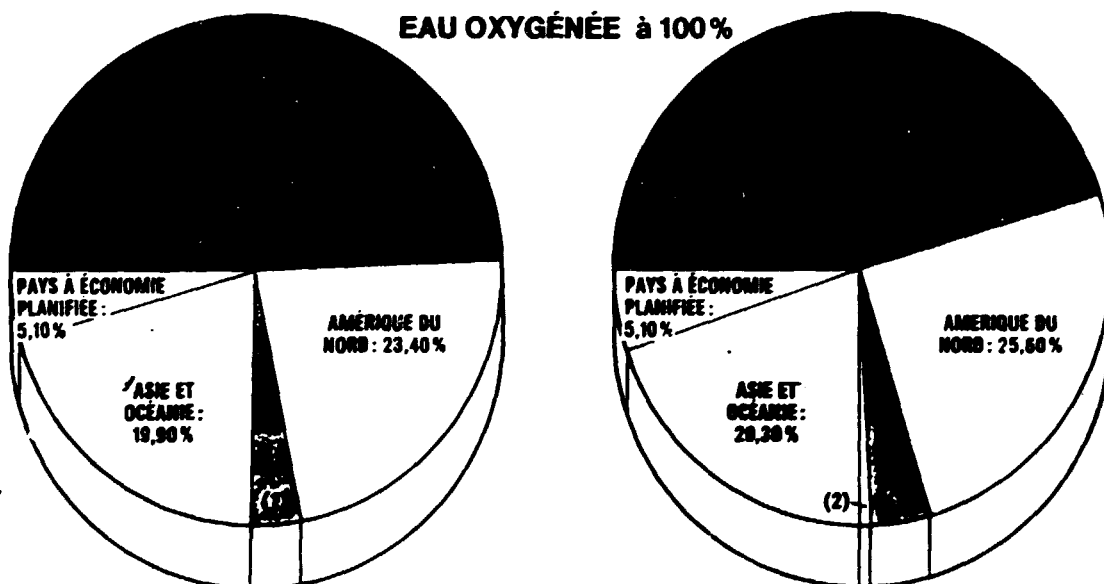
(1) AMÉRIQUE CENTRALE ET DU SUD : 2,00 %

(1) AMÉRIQUE CENTRALE ET DU SUD : 2,60 %
(2) AFRIQUE : 0,40 %

*Répartition des capacités par zones géographiques
en 1000 tm/an : 1237 à fin 1988.*

*Répartition dans les proches années compte-tenu des projets
actuellement annoncés, en 1000 tm/an : 1334.*

JIS

JAPANESE INDUSTRIAL STANDARD

Hydrogen Peroxide

JIS K 1463-1971

JAPANESE INDUSTRIAL STANDARD

Hydrogen Peroxide

H_2O_2 Mol. wt. = 34.01

1. Scope

This standard specifies hydrogen peroxide intended for industrial use.

2. Grade

Hydrogen peroxide shall be classified into three grades as follows.

    60 % hydrogen peroxide

    50 % hydrogen peroxide

    35 % hydrogen peroxide

3. Quality Requirements

Hydrogen peroxide shall conform to the quality requirements given in the following table when tested by the procedures prescribed in 5.

Table

	60% hydrogen peroxide	50% hydrogen peroxide	35% hydrogen peroxide
Hydrogen peroxide %	60.0 min.	50.0 min.	35.0 min.
Evaporation residue %	0.10 max.	0.10 max.	0.10 max.
Free acid (as H_2SO_4) %	0.05 max.	0.05 max.	0.05 max.
Stability %	97.0 min.	97.0 min.	97.0 min.

Remark: The values specified indicate the guaranteed figures when the chemicals are received by the consumer.

Reference Standards:

JIS K 0050	General Considerations for Chemical Analysis
JIS K 8005	Primary Standard Substances for Volumetric Determination
JIS K 8102	Ethyl Alcohol (95 v/v %)
JIS K 8247	Potassium Permanganate
JIS K 8576	Sodium Hydroxide
JIS K 8852	Bromothynol Blue
JIS K 8896	Methyl Red
JIS K 8951	Sulfuric Acid
JIS R 3503	Glass Apparatus for Chemical Analysis

Indian Standard

SPECIFICATION FOR
HYDROGEN PEROXIDE

UDC

491 (0.75) (54)