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Hydrogen Peroxide

Peroxo Compounds, Inorganic and Peroxy Compounds, Organic are separate keywords.

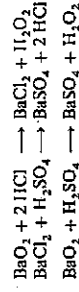
GUSTAAF GOOR, WOLFGANG KUNKEL (Chaps. 1-7), OTTO WEBER (Chap. 8), Degussa AG, Hanau, Federal Republic of Germany

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1. Introduction and Historical Aspects

The industrial production of hydrogen peroxide passed through three phases, starting with wet chemical processes, followed by electrochemical processes, and then by organic autoxidation processes. Almost all hydrogen peroxide is now produced by organic autoxidation (AO) processes, primarily the anthraquinone process.

Wet Chemical Processes. In 1818, L. J. THENARD [9] obtained hydrogen peroxide for the first time by reacting barium peroxide [1302-29-6] with nitric acid. This process was improved by using hydrochloric acid to release hydrogen peroxide. The water-soluble barium chloride which is formed simultaneously, was precipitated with sulfuric acid.



With this reaction, THENARD established the foundation for the commercial manufacture of aqueous hydrogen peroxide solutions based on wet chemical processes, which began around 1880.

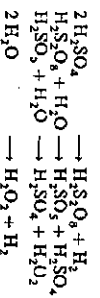
Industrial plants using the barium peroxide process were still operating until the middle of this century. Around 1900, approximately 10 000 t/a of barium peroxide was processed by this technology, yielding ca. 2000 t of hydrogen peroxide per year. Sales opportunities for the co-product barium sulfate (BaSO_4 , blanc fixe) had a decisive effect on the profitability of the process.

The 3% aqueous hydrogen peroxide solutions manufactured by the barium peroxide solu-

cess had only a limited market because of their high production cost, low hydrogen peroxide content, and unsatisfactory stability due to impurities.

Electrochemical Processes. The introduction of electrochemical processes eliminated the disadvantages of the barium peroxide process.

In 1853, MENDINGER discovered the formation of hydrogen peroxide during electrolysis of aqueous sulfuric acid [10]. In 1878, BERTHELOT showed that peroxodisulfuric acid [3345-49-3] is formed during this electrolysis and then hydrolyzed by water to give sulfuric acid and hydrogen peroxide via peroxomonosulfuric acid [12788-01-1] [11]:



In 1905, following the work of ELIAS and SCHÖNHERR [12], G. TEICHNER developed an electrolytic process at the Konsortium für Elektrochemische Industrie. The first hydrogen peroxide plant based on this new technology went on stream in 1908 at the Österreichische Chemische Werke in Weissenstein. The *Weissenstein process* was followed in 1910 by the *Münchener process* developed by A. PIETZSCH and G. ADOLPH at the Elektrochemische Werke, München, and then in 1924 by the *Riedel-Loewenstein process* developed by L. LOEWENSTEIN and first used by RIEDEL DE HAEN. In these processes, an ammonium sulfate solution was electrolyzed instead of free sulfuric acid, and the resulting ammonium peroxodisulfate (Riedel-Loewenstein) or potassium peroxodisulfate made from it (Pietzsch-Adolph) was hydrolyzed. After introduction of these processes, production (calculated as 100% hydrogen peroxide) increased steadily and, in 1950, reached approximately $(30-35) \times 10^3$ t annually [13].

Organic Autoxidation Processes. The decisive breakthrough in industrial production of hydrogen peroxide, which enabled the construction of modern large-scale plants, came with the development of organic autoxidation processes, especially the anthraquinone process.

In 1901, MANCHOT discovered that hydroquinones (or hydrazobenzenes) react quantitatively with oxygen to form quinones (or azobenzenes) and hydrogen peroxide [14]. In

1932, WALTON and FILSON in the United States went back to this work and proposed a cyclic process for the manufacture of hydrogen peroxide based on azobenzene—hydrazobenzene [15].

PLEIDERER of I. G. Farbenindustrie AG, Ludwigshafen (BASF), subsequently developed a process for the alkaline autoxidation of hydrazobenzene in which sodium peroxide is obtained instead of free hydrogen peroxide [16]. This process was used on an industrial scale by Kymmene AB in Kuusankoski (Finland) under BASF license (see Section 4.4.3).

The azobenzene process showed two major technical drawbacks: hydrogenation of azobenzene was performed with sodium amalgam whereas oxidation of hydrazobenzene proceeded satisfactorily only in alkaline solution. PLEIDERER and RIEDEL overcame these problems by using alkylated anthraquinones instead of azobenzene. Between 1935 and 1945, BASF developed the Riedel-Pleiderer process (generally referred to as the anthraquinone or AO process) in a pilot plant with a monthly output of 30 t. At the end of World War II, this work was stopped in Germany because of Allied Control Commission Regulations, but it formed the basis for all present production processes. In 1953, Du Pont of Memphis, Tennessee, commissioned the first hydrogen peroxide production plant based on the AO process. Several other companies began to produce hydrogen peroxide by this process, and production capacity increased greatly. In 1987, it was estimated to be 10^6 t (calculated as 100% H_2O_2) per year [17].

Another organic autoxidation process, the 2-propanol process, used by Shell in Norco (United States) between 1957 and 1980, made only a limited contribution to the increase of hydrogen peroxide production with an annual production capacity of about 15 000 t.

2. Physical Properties

Hydrogen peroxide [7722-84-1, *M*, 34.016, is a clear, colorless liquid which is miscible with water in all proportions. Hydrogen peroxide and highly concentrated aqueous solutions (>65 wt%) are soluble in a variety of organic solvents such as carboxylic esters.

Hydrogen peroxide and water do not form an azeotropic mixture and, in theory, can be sepa-

Table 1. Physical properties of hydrogen peroxide and water

Property	Value	
	H ₂ O ₂	H ₂ O
<i>mp.</i> , °C	-0.43	0
<i>bp</i> (101.3 kPa), °C	150.2	100
Heat of melting, J/g	368	334
Heat of vaporization, J g ⁻¹ K ⁻¹		
At 25°C	1519	2443
At <i>bp</i>	1387	2238
Specific heat, J g ⁻¹ K ⁻¹		
Liquid (25°C)	2.629	4.182
Gas (25°C)	1.352	1.865
Relative density, g/cm ³		
0°C	1.4700	0.9998
20°C	1.4500	0.9980
25°C	1.4425	0.9971
Viscosity, mPa·s		
0°C	1.819	1.792
20°C	1.249	1.002
Critical temperature, °C	457	374.2
Critical pressure, MPa	20.99	21.44
Refractive index <i>n</i> _D ²⁰	1.4084	1.3330

Table 2. Physical properties of aqueous hydrogen peroxide solutions

Property	H ₂ O ₂ concentration, wt%		
	35	50	90
Relative density, g/cm ³			
0°C	1.1441	1.2110	1.3071
20°C	1.1312	1.1953	1.2886
25°C	1.1282	1.1914	1.2839
Viscosity, mPa·s			
0°C	1.82	1.87	1.93
20°C	1.11	1.17	1.23
Refractive index			
<i>n</i> _D ²⁰	1.3563	1.3672	1.3827
<i>mp.</i> , °C	-33	-52.2	-40.3
<i>bp</i> (101.3 kPa), °C	107.9	113.8	125.5
H ₂ O ₂ partial pressure (30°C), kPa	0.05	0.11	0.17
			0.29

rated completely by distillation. In practice, 100 wt% hydrogen peroxide is obtained by fractional crystallization of highly concentrated (ca. 90 wt%) aqueous solutions. Pure 100 wt% hydrogen peroxide is of scientific interest only and is not produced on an industrial scale.

Data pertaining to molecular structure (obtained by neutron diffraction of solid H₂O₂) are as follows [18]:

Bond length, O—O	0.1453 ± 0.0007 nm
Bond length, O—H	0.0998 ± 0.0005 nm
Bond angle, O—O—H	102.7 ± 0.3°
Azimuthal angle	90.2 ± 0.6°

Physical constants of hydrogen peroxide and water are compared in Table 1. Physical constants of some aqueous hydrogen peroxide solutions in commercially available concentrations are listed in Table 2.

The vapor pressure and partial pressure of aqueous hydrogen peroxide solutions are shown as a function of temperature in Figures 1 and 2, respectively. Figure 3 shows the vapor-liquid equilibrium curve for aqueous hydrogen peroxide solutions [19].

The solid-liquid phase diagram (Figure 4) shows eutectic points for the mixtures ice-H₂O·2H₂O at 45.2 wt% hydrogen peroxide and for solid H₂O₂-H₂O₂·2H₂O at 61.2 wt% hydrogen peroxide with a congruent melting point for the compound H₂O₂·2H₂O between them.

Heat of formation and of decomposition of hydrogen peroxide are

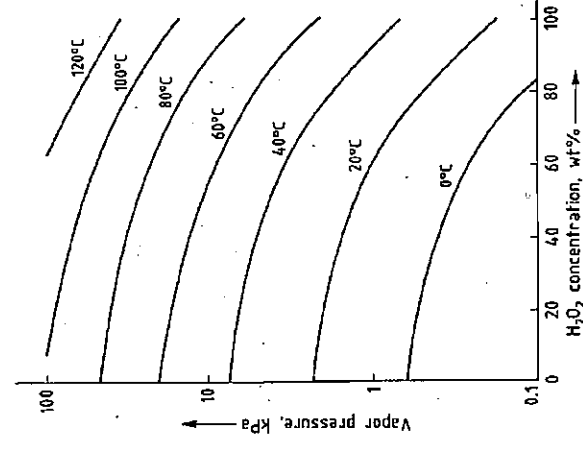
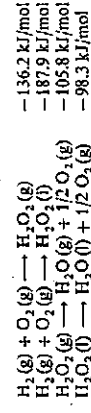


Figure 1. Vapor pressure of aqueous hydrogen peroxide solutions

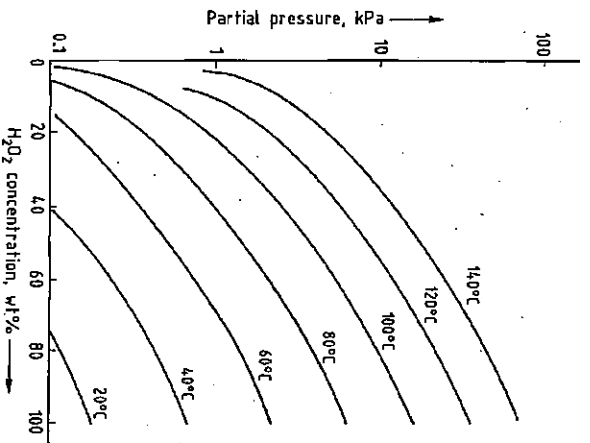


Figure 2. Partial pressure of hydrogen peroxide over aqueous hydrogen peroxide solutions

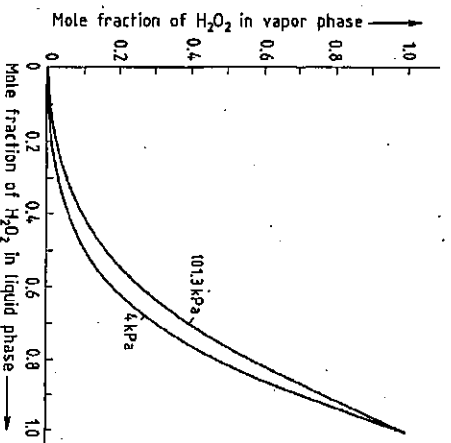


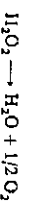
Figure 3. Vapor-liquid equilibrium curve for water-hydrogen peroxide

3. Chemical Properties

Dissociation. Hydrogen peroxide is weakly acidic in aqueous solution, with a dissociation constant of 1.78×10^{-12} (pK 11.75) at 20°C. As a weak acid, hydrogen peroxide forms salts with various metals.

Oxidation and Reduction. Hydrogen peroxide can behave both as an oxidizing and as a reducing agent (Tables 3 and 4). Systems with a redox potential $E_0 < -1.80$ V at pH 0 cannot be oxidized by hydrogen peroxide; systems with a redox potential $E_0 > -0.66$ V at this pH cannot be reduced by hydrogen peroxide [6], [20].

Decomposition of hydrogen peroxide occurs with disproportionation



and is extremely important in handling hydrogen peroxide during storage and in the laboratory. This reaction is highly exothermic (see Chap. 2) and takes place in the presence of small amounts of catalyst even in aqueous solution. In the ab-

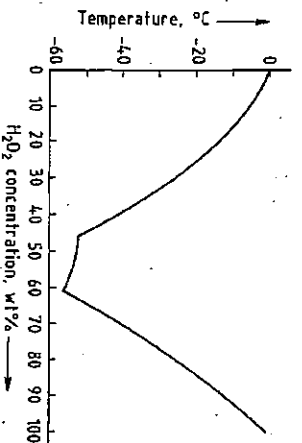


Figure 4. Freezing point curve for water-hydrogen peroxide

Table 3. Hydrogen peroxide as an oxidizing agent [20]

Redox reaction	Standard potential E_0 , V*
pH 0	
$\text{HOOH} + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{HOH}$	+1.80
$\text{HSO}_3^- + \text{HOH} \longrightarrow \text{SO}_3^{2-} + 3\text{H}^+ + 2\text{e}^-$	-0.17
$\text{NO}_2^- + \text{HOH} \longrightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-$	-0.94
$2\text{Cl}^- + \text{Cl}_2 + 2\text{e}^-$	-1.36
$2\text{Br}^- + \text{Br}_2 + 2\text{e}^-$	-1.07
$2\text{I}^- + \text{I}_2 + 2\text{e}^-$	-0.54
pH 14	
$\text{HOOH} + 2\text{e}^- \longrightarrow 2\text{OH}^-$	+0.87
$\text{Mn}(\text{OH})_2 + 2\text{OH}^-$	
$\text{MnO}(\text{OH})_2 + \text{HOH} + 2\text{e}^-$	+0.05

* Standard potential of redox reactions measured against a hydrogen electrode (25°C, 100 kPa).

Table 4. Hydrogen peroxide as a reducing agent [20]

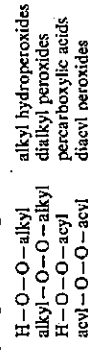
Redox reaction	Standard potential E_0 , V*
pH 0	
$\text{HOOH} \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$	-0.66
$5\text{e}^- + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{HOH}$	+1.51
$1\text{e}^- + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$	+1.61
pH 14	
$\text{HOOH} + 2\text{OH}^- \rightarrow 2\text{HOH} + \text{O}_2 + 2\text{e}^-$	+0.08
$1\text{e}^- + \text{ClO}_2 \rightarrow \text{ClO}_2^-$	+1.16
$2\text{e}^- + \text{ClO}^- + \text{HOH} \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89

* Standard potential of redox reactions measured against a hydrogen electrode (25 °C, 100 kPa).

sence of catalyst, it occurs only in the gas phase at high temperature.

Decomposition can be catalyzed both homogeneously by dissolved ions (especially of the heavy metals iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver.

Substitution. The hydrogen atoms of hydroperoxide can be substituted by alkyl and acyl groups, leading to the formation of



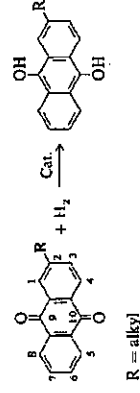
Hydrogen peroxide forms peroxohydrates with a number of compounds. Addition compounds with sodium carbonate (sodium carbonateperoxyhydrate [15630-89-4]) and with urea (urea peroxohydrate [124-43-6]) are industrially important. For a detailed description of peroxo compounds see → Peroxo Compounds, Inorganic; → Peroxy Compounds, Organic.

4. Production

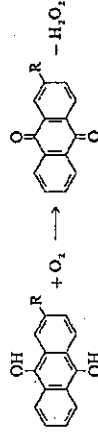
4.1. Anthraquinone Process (AO Process)

4.1.1. Principles

In the AO process, 2-alkyl-9,10-anthraquinones react with hydrogen in the presence of a catalyst to form the corresponding hydroquinones.



After the catalyst is removed (otherwise, the hydrogen peroxide would decompose), the hydroquinones are oxidized to quinones with oxygen (usually air) with simultaneous quantitative formation of hydrogen peroxide:



Hydrogen peroxide is extracted with water, and the quinones are returned to the hydrogenator to complete the loop.

The AO process, therefore, leads to the net formation of hydrogen peroxide from gaseous hydrogen and oxygen.

Solvents. Anthraquinones must be dissolved in a suitable solvent for hydrogenation, oxidation, and extraction (the so-called working solution).

Although a number of individual solvents have been proposed (e.g., aromatic alcohols or their esters [21]), solvent mixtures are almost always used because the quinones and hydroquinones formed during the synthesis loop have different solubilities. Quinones dissolve readily in nonpolar, aromatic solvents (quinone solvents). Hydroquinones dissolve well in polar solvents, especially alcohols and esters (hydroquinone solvents). Proposed solvents or solvent mixtures are

Quinone solvents

Benzene [22]
tert-Butylbenzene [23]
tert-Butyltoluene [24]
 Trimethyl benzene [25]
 Polyalkylated benzenes [26]
 Methylisophthalene [27]

Hydroquinone solvents

Alkyl phosphates [28]
 Alkyl phosphonates [29]
 Nonyl alcohols [27]
 Alkylcyclohexanol esters [30]
N,N-Dialkyl carbonamides [31]
 Tetraalkyl ureas [32]
N-Alkyl-2-pyrrolidones [33]

Solvent mixtures

- Polalkylated benzenes and alkyl phosphates [26]
- Polalkylated benzenes and tetraalkyl ureas [32]
- Trimehyl benzenes and alkylcyclohexanol esters [25]
- Methylphenylalene and nonyl alcohols [27]

The following criteria must be fulfilled when choosing solvents and preparing solvent mixtures:

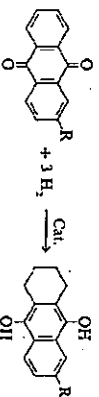
- 1) good solubility of both quinone and hydroquinone
- 2) good stability in the hydrogenator and oxidizer
- 3) low solubility in water and aqueous hydrogen peroxide solutions
- 4) sufficiently higher density than water to ensure separation of the two phases during extraction
- 5) low volatility, i.e., high boiling point and flash point
- 6) high distribution coefficient for hydrogen peroxide in the solvent-water system
- 7) low toxicity

Quinones. Criteria similar to those used for selecting solvents also apply to the quinone or quinone mixture, which is used as the working compound:

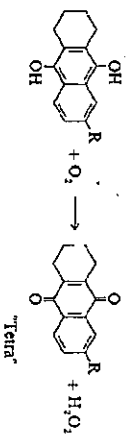
- 1) good solubility of the quinone form
- 2) good solubility of the hydroquinone form
- 3) good resistance to oxidation
- 4) good availability

The choice of quinone, depends mainly on the properties, especially the solubility, of the products formed in the AO process. Examples of working compounds proposed in the patent literature are 2-ethylanthraquinone [84-51-5] [34], 2-*tert*-butylanthraquinone [84-47-9] [35], eutectic mixtures of alkylanthraquinones [36], and mixtures of 2-amylanthraquinones [37].

The formation of degradation products and their ability to be regenerated to active quinones also play a role in the decision. In addition to hydroquinone formation, a number of secondary reactions occur during the hydrogenation step; of these, hydrogenation of the anthraquinone ring system is particularly important. One ring of the anthraquinone molecule, preferably the one that is not substituted by an alkyl group, is hydrogenated.



2-Alkyl-5,6,7,8-tetrahydro-9,10-dihydroxyanthracene is formed, which is also oxidized by oxygen to regenerate the 2-alkyl-5,6,7,8-tetrahydroanthraquinone (known as "tetra"), with simultaneous quantitative formation of hydrogen peroxide.



Although "tetra" is more readily hydrogenated than 2-alkylanthraquinone, the resulting "tetra" hydroquinone is much more difficult to oxidize than the readily oxidizable anthrahydroquinone.

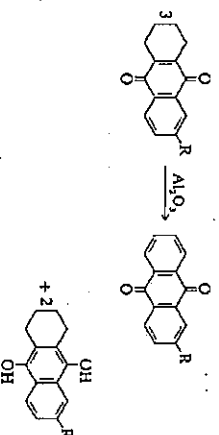
The formation of "tetra" in the synthesis loop depends on process conditions and has led to two methods for carrying out this process—the "anthra" system and the "all-tetra" system.

Anthra System. The slower oxidation rate of the "tetra" hydroquinone causes difficulties in the oxidizer. Actions have, therefore, been proposed which suppress the formation of "tetra" or to dehydrogenate it to anthraquinone.

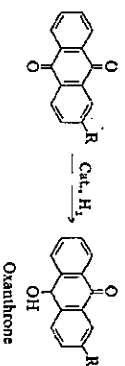
When the "tetra" content of the working solution is kept low (i.e., if 2-alkylanthrahydroquinone is formed almost exclusively during hydrogenation), the process is referred to as the "anthra" system.

"Tetra" formation is suppressed by using selective catalysts [38], special solvents [39], special working compounds [40], and mild hydrogenation conditions [41] (e.g., the use of olefins has been recommended for the steady dehydrogenation of "tetra" [42]).

"Tetra" can be dehydrogenated in the presence of active aluminum oxide:



When the "anthra" system is used, tautomeric 2-alkyl-10-hydroxy-9-anthrone (oxanthrone) is also formed during hydrogenation [13], [43]:



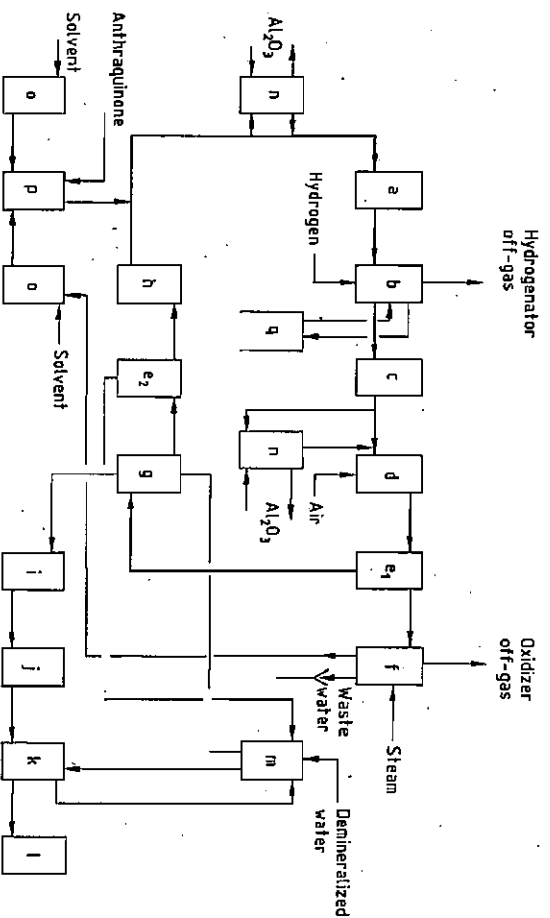


Figure 5. Production of hydrogen peroxide by the anthraquinone (AO) process.
 a) Storage tank for working solution or hydrogenator feed tank; b) Hydrogenator; c) Safety filtration; d) Oxidizer;
 e) Separator; f) Activated carbon adsorber; g) Extraction; h) Drying; i) Prepurification; j) Crude product storage tank;
 k) Hydrogen peroxide concentration; l) Hydrogen peroxide storage tank; m) Demineralized water feed tank; n) Regenera-
 tion and purification; o) Solvent storage tank; p) Working solution make up tank; q) Catalyst regeneration

Hydrogenation. From the storage tank or hydrogenation feed tank (a), the working solution enters the hydrogenator (b) where it is hydrogenated in the presence of a suspended, supported, or fixed-bed catalyst.

If a suspended catalyst (e.g., palladium black or Raney nickel) or a supported catalyst (e.g., palladium) is used, the hydrogenation step includes a main filtration stage which retains the catalyst and allows it to be returned to the hydrogenator. The heat of reaction released during hydrogenation can be removed (1) before hydrogenation (by cooling the oxidized working solution), (2) during hydrogenation (by cooling the reactor) or (3) after hydrogenation (by cooling the hydrogenated working solution).

Oxidation. Before the hydrogenated working solution that contains hydroquinone can be fed to the oxidation step, it must pass through a safety filtration stage (c). This is particularly important because the hydrogenation catalysts used in the AO process (palladium and Raney nickel) also catalyze the decomposition of hydrogen peroxide. Even a small amount of these catalysts in the oxidation and extraction steps would

lead to considerable loss of hydrogen peroxide and serious disturbances.

During the oxidation step (d), the hydrogenated working solution is gassed with air. Dissolved hydroquinones are oxidized to quinones, and hydrogen peroxide is formed.

After the working solution has been separated (e), air from the oxidation step passes over activated carbon adsorbers (f), and adsorbed solvent is recovered from them. Several adsorbers are usually loaded and regenerated alternately, for example, with steam.

Extraction and Recovery of the Working Solution. The oxidized working solution is then treated with water to extract hydrogen peroxide (g).

The working solution leaving the extraction unit must be adjusted to a specific water content before being returned to the hydrogenation step. Free water taken up by the working solution during extraction is separated (e₂) and the water content is adjusted to the desired level in the drier (h).

To purify the working solution and regenerate the quinone decomposition products into ac-

tive quinones, some or all of the working solution is passed through a regeneration step (n).

Hydrogen Peroxide Concentration. Crude aqueous hydrogen peroxide from the extraction stage (H_2O_2 concentration 15–35 wt%) is fed into the crude product storage tank (i) via a purification unit (i).

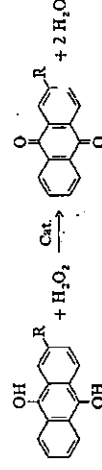
From the crude product storage tank, aqueous hydrogen peroxide goes to the concentration unit (2) where it is distilled. Here, hydrogen peroxide is freed from most of its impurities and concentrated to the commercial concentration of 50–70 wt%; it is then collected in a storage container (1).

Water vapor produced during distillation is condensed and fed into the water storage tank (m).

Auxiliary Processes. A number of additional processes are required to maintain the AO operation. For example, to maintain hydrogenation activity, part of the catalyst is removed, regenerated in the catalyst regeneration area (q), and returned to the hydrogenator. To compensate for quinone and solvent losses, working solution is periodically made up with anthraquinone and solvent (o, p).

4.1.2.1. Hydrogenation

The hydrogenation step is the most important step of modern AO processes. Quinone de-



The solutions are passed through the precontact column (Fig. 6, a) and collected in the hydrogenator feed tank (b). The working solu-

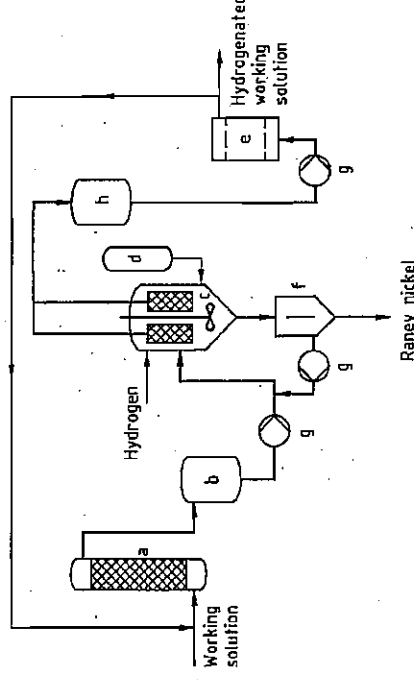


Figure 6. BASF hydrogenation step