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# *Applications of Hydrogen Peroxide and Derivatives*

**Craig W. Jones**

*Formerly of Solvay Interlox R&D, Widnes, UK*

**RS•C**

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## Applications of Hydrogen Peroxide and Derivatives

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# *Preface*

Hydrogen peroxide, as well as being an incredibly simple inorganic compound, is also a beautifully versatile one. Over the last decade it has had somewhat of a rebirth in both industrial and academic circles. The rather glib explanation for such a renaissance is due to regulatory forces causing the chemical industry to reduce, and in some instances eliminate, environmental pollution. However, such a reason does a great disservice to hydrogen peroxide. Whilst it is true that environmental agencies and legislation have caused a major shift in emphasis during the latter half of the century and polarised our efforts on so called 'green chemistry', by far the most overriding reason why hydrogen peroxide is now more popular is due to the fact that the chemical industry has learnt to employ the chemical in a safer, more efficient, and innovative manner. In addition, hydrogen peroxide and its derivatives can not only be employed for their traditional bleaching applications or for the manufacture of pharmaceutical and fine chemicals, but also have uses in a diverse array of industries. Precious metal extraction from the associated ores, treatment of effluent, delicing of farmed salmon, and pulp and paper bleaching are but a few areas where hydrogen peroxide has had a profound effect on the quality of all our lives.

The aim of this book is to allow those unfamiliar with the versatility of hydrogen peroxide and its derivatives to walk into their laboratories and to look for possible applications in their own areas of expertise where hydrogen peroxide can perhaps help increase a yield, purify a compound, or afford a more environmentally benign route to be devised. The author would also like to encourage educationalists to attempt to introduce courses on hydrogen peroxide on an academic and practical level to not only undergraduates but to those of school age studying the sciences. The introduction of topics like this coupled with an understanding of catalytic routes to industrially important chemicals will hopefully encourage future scientists to think in terms of relatively benign synthetic methodologies rather than being constrained by the chemistries of the 19th century synthetic chemist.

This book has been organised such that each chapter can be read as a stand-alone monograph in its own right. However, the author would encourage those readers unfamiliar with the use of hydrogen peroxide to read Chapter 1, which includes an important section on its safe use. In this book I have aimed to present a description of the preparation, properties and applications of hydrogen peroxide, and its derivatives. The number of different peroxygen systems, and their structural diversity, makes it difficult to gain a thorough under-

standing of the subject by studying individual peroxygen systems. I have, therefore, tried to emphasize general features of the properties of the peroxide bond by reference to the activation of hydrogen peroxide throughout the book.

Chapter 1 puts hydrogen peroxide in its historical context with particular emphasis on the preparation of hydrogen peroxide from the acidification of barium peroxide to the integrated generation of hydrogen peroxide. The chapter concludes with a practical approach to employing hydrogen peroxide and its derivatives in a safe manner. The activation of hydrogen peroxide is discussed in Chapter 2, and this is intended to provide a firm basis for the understanding of the chemistry of hydrogen peroxide. Chapter 3 is intended to illustrate the application of activated hydrogen peroxide towards the oxidation of important organic functions such as olefinic compounds to epoxides, diols or diol cleavage to aldehydes, ketones or carboxylic acids. Other functional group oxidation includes organonitrogen, organosulfur, ketones, alcohols, and alkyl side chains of arenes. Chapter 4 briefly describes to the reader the application of heterogeneous systems for the activation of hydrogen peroxide. It is this area of hydrogen peroxide chemistry which is likely to become of pivotal importance in relation to 'integrated pollution control' programmes. Chapter 5 summarizes the use of hydrogen peroxide for the clean up of environmental pollutants. Fenton's chemistry is discussed in this respect together with other advanced oxidation processes for the generation of hydroxyl radical. The final chapter of the book looks at the impact hydrogen peroxide has had on several industries, from the preparation of chemical pulp to the purification of industrially important chemicals.

I hope everyone who turns the pages of this book finds something which helps them in their deliverance for the sake of humankind, or discovers the rich tapestry of chemistries, and industries, that have been founded on the simple peroxygen bond.

In writing this book I have been fortunate to have had the expert guidance, and encouragement from my colleagues at the Solvay Interlox R&D department based in Widnes in the UK. It is also with deep sadness that when this book is finally published the department at Widnes will no longer be in existence. It is to all those people that I say a special thank you to and dedicate this book to them, especially Bill Sanderson, Phil Wyborne, Sharon Wilson, Colin McDonagh and Gwenda McIntyre, because without their learning, understanding and good humour, this book could never have come to fruition. I would thank all those workers in the field of peroxygen technology, some of whom I have had the privilege to meet professionally, and many I have not met. It is their work which is referenced and discussed within these pages. It is their selfless dedication to the ongoing understanding of materials containing peroxygen bonds that has breathed new life into a wonderfully diverse chapter of science. My wife Helen deserves a special mention as she has typed a large proportion of this manuscript, and was a constant source of advice, encouragement, and practical assistance during its preparation.

*To Helen, and the memory of Solvay Interlox R&D, Widnes*



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## CHAPTER 1

# *Introduction to the Preparation and Properties of Hydrogen Peroxide*

## 1 Introduction

The following chapter will discuss the preparation of hydrogen peroxide, historically, the present day and future vistas for its *in situ* preparation. A brief introduction to the physical properties of hydrogen peroxide will also be made for the sake of completeness. Finally, the chapter will conclude with a practical approach to the safe handling of peroxygen species, destruction of residual peroxygens, and the toxicological and occupational health considerations required when handling hydrogen peroxide.

## 2 Industrial Manufacture of Hydrogen Peroxide

The industrial manufacture of hydrogen peroxide can be traced back to its isolation in 1818 by L. J. Thenard.<sup>1</sup> Thenard reacted barium peroxide with nitric acid to produce a low concentration of aqueous hydrogen peroxide; the process can, however, be significantly improved by the use of hydrochloric acid. The hydrogen peroxide is formed in conjunction with barium chloride, both of which are soluble in water. The barium chloride is subsequently removed by precipitation with sulfuric acid (Figure 1.1).

Hence, Thenard gave birth to the first commercial manufacture of aqueous hydrogen peroxide, although it took over sixty years before Thenard's wet chemical process was employed in a commercial capacity.<sup>2</sup> The industrial production of hydrogen peroxide using the above route was still operating until the middle of the 20th century. At the turn of the 19th century, approximately 10 000 metric tonnes per annum of barium peroxide were converted to about 2000 metric tonnes of hydrogen peroxide. Thenard's process has, however, some major drawbacks which quenched the expectant explosion of its use in an aqueous form. Firstly, only three percent *m/m* aqueous hydrogen peroxide solutions were manufactured using the barium peroxide

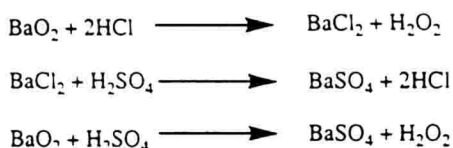


Figure 1.1 *Thenard's route to aqueous hydrogen peroxide.*

process, and hence only a limited market was afforded because production costs were prohibitively high. Further, due to the high levels of impurities present in the isolated hydrogen peroxide, subsequent stability was poor.

The disadvantages of the process discovered by Thenard were largely alleviated by the discovery in 1853 by Meidinger that hydrogen peroxide could be formed electrolytically from aqueous sulfuric acid.<sup>3</sup> Berthelot later showed that peroxodisulfuric acid was the intermediate formed,<sup>4</sup> which was subsequently hydrolysed to hydrogen peroxide, and sulfuric acid (Figure 1.2).

The first hydrogen peroxide plant to go on-stream based on the electrochemical process was in 1908 at the Österreichische Chemische Werke in Weissenstein. The Weissenstein process was adapted in 1910 to afford the Müncher process developed by Pietzsch and Adolph at the Elektrochemische Werke, Munich. In 1924, Reidel and Lowenstein used ammonium sulfate under the conditions of electrolysis instead of sulfuric acid, and the resulting ammonium peroxodisulfate (Reidel–Lowenstein process) or potassium peroxodisulfate (Pietzsch–Adolph process) was hydrolysed to hydrogen peroxide. As a result of this process, production of hydrogen peroxide as 100% *m/m* rose to approximately 35 000 metric tonnes per annum.<sup>5</sup>

In 1901, Manchot made a decisive breakthrough in the industrial preparation of hydrogen peroxide. Manchot observed that autoxidizable compounds like hydroquinones or hydrazobenzenes react quantitatively under alkaline conditions to form peroxides.<sup>6</sup> In 1932, Walton and Filson proposed to produce hydrogen peroxide via alternating oxidation and reduction of hydrazobenzenes.<sup>7</sup> Subsequently, Pfeleiderer developed a process for the alkaline autoxidation of hydrazobenzenes in which sodium peroxide was obtained, and sodium amalgam was used to reduce the azobenzene.<sup>8</sup> A commercial plant based on this technology was operated by Kymmene AB in Kuisankoski, Finland.

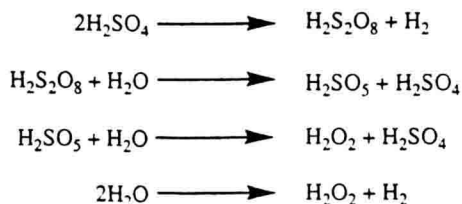
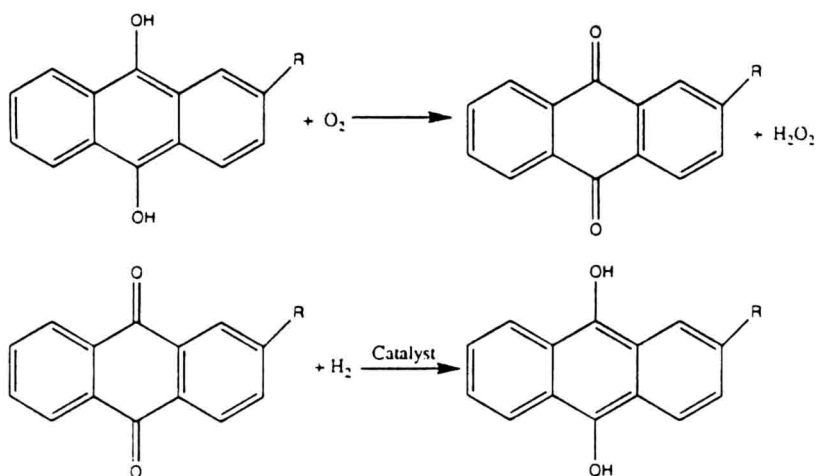


Figure 1.2 *Electrochemical manufacture of aqueous hydrogen peroxide.*

The major drawbacks associated with the azobenzene process, i.e. hydrogenation of azobenzene with sodium amalgam, and oxidation of hydrazobenzene in alkaline solution, were ultimately resolved by Riedl. Riedl employed polynuclear hydroquinones. Based on Reidl and Pfeleiderer's work, BASF developed, between 1935 and 1945, the anthroquinone process (often referred to as the AO process) in a pilot plant with a monthly production of 30 metric tonnes. Two large plants were then constructed at Heidebreck and Waldenberg, each having a capacity of 2000 metric tonnes per annum. Both plants were partially complete when construction was halted at the end of World War Two. In 1953, E.I. Dupont de Nemours commissioned the first hydrogen peroxide plant using the AO process, and consequently the production capacity of hydrogen peroxide was greatly increased. In 1996, world capacity stood at  $1.3 \times 10^6$  metric tonnes as 100% *m/m* hydrogen peroxide.<sup>9</sup>

The underlying chemistry of the AO process is outlined in Figure 1.3 and a typical autoxidation plant schematic is summarized in Figure 1.4.

The features of all AO processes remain basically the same, and can be described as follows. A 2-alkylanthraquinone is dissolved in a suitable solvent or solvent mixture which is catalytically hydrogenated to the corresponding 2-alkylanthrahydroquinone. The 2-alkylanthraquinone solution is commonly referred to as the reaction carrier, hydrogen carrier or working material. The 2-alkylanthraquinone-solvent mixture is called the working solution. Carriers employed industrially include 2-*tert*-amylanthraquinone, 2-*iso-sec*-amylanthraquinone and 2-ethylanthraquinone. The working solution containing the carrier product alkylanthrahydroquinone is separated from the hydrogenation catalyst, and aerated with an oxygen-containing gas, nominally compressed air, to reform the alkylanthraquinone, and simultaneously forming hydrogen peroxide. The hydrogen peroxide is then extracted from the oxidized working solution using demineralized water, and the aqueous extract is then purified



**Figure 1.3** Anthrahydroquinone autoxidation process for the manufacture of aqueous hydrogen peroxide.

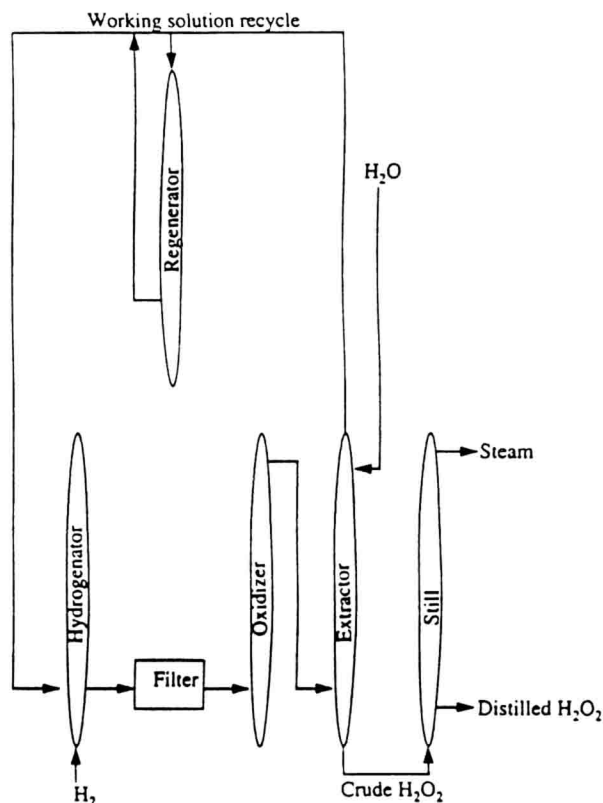
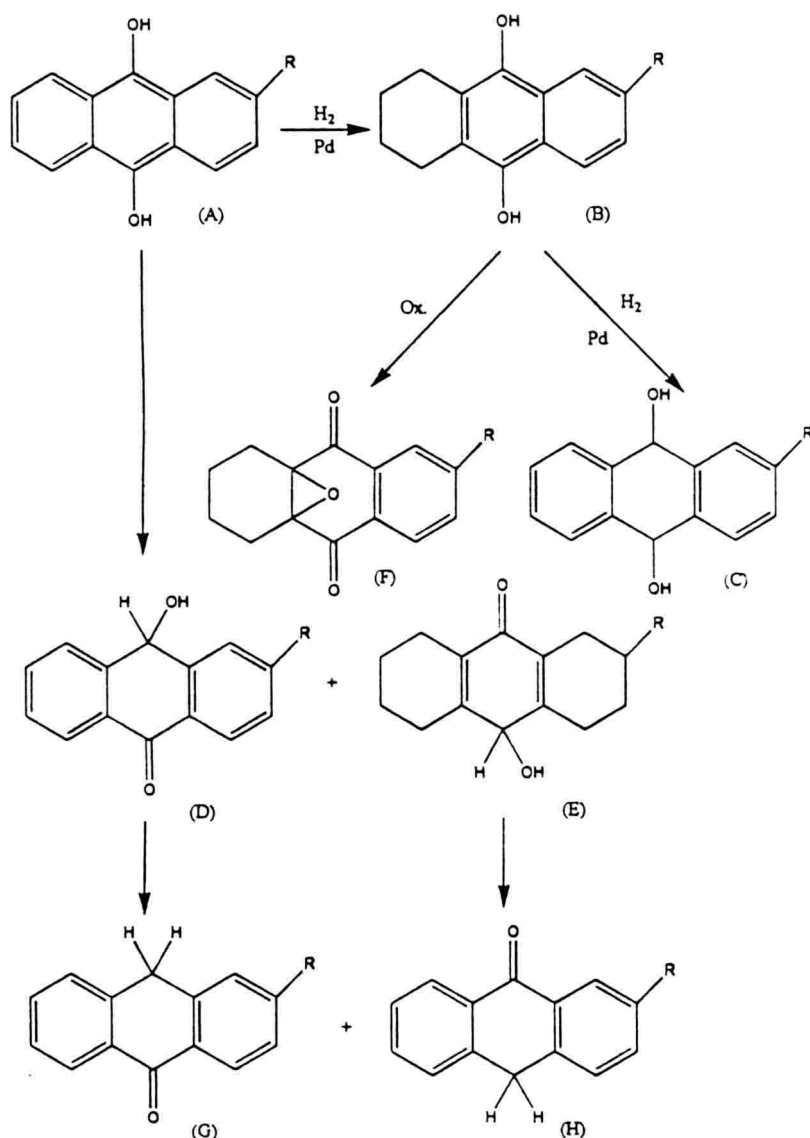


Figure 1.4 Schematic diagram of the AO process.

and concentrated by fractionation to the desired strength. The AO process, therefore, leads to the net formation of hydrogen peroxide from gaseous hydrogen and oxygen.

The choice of the quinone must be carefully made to ensure that the following criteria are optimized: good solubility of the quinone form, good solubility of the hydroquinone form, good resistance to non-specific oxidation and easy availability. The formation of degradation products, and their ability to be regenerated to active quinones also plays a rôle in the decision. A number of by-products can be formed during the hydrogenation step, and these are summarized in Figure 1.5. The process when first engaged, contains in the working solution only the 2-alkylanthraquinone species. The 2-alkylanthraquinone forms a complex with the hydrogenation catalyst, which is usually a palladium metal. The complex then reacts with hydrogen to form a species now containing the metal and the 2-alkylhydroanthraquinone. The 2-alkylhydroanthraquinone is subject to a number of secondary reactions which are continuously taking place during each process cycle.

The 2-alkylhydroanthraquinone (A) when in contact with the catalyst will undergo a small amount of catalytic reduction (B) on the ring, initially on the unsubstituted ring, yielding a tetrahydroalkylanthrahydroquinone. Unfortu-

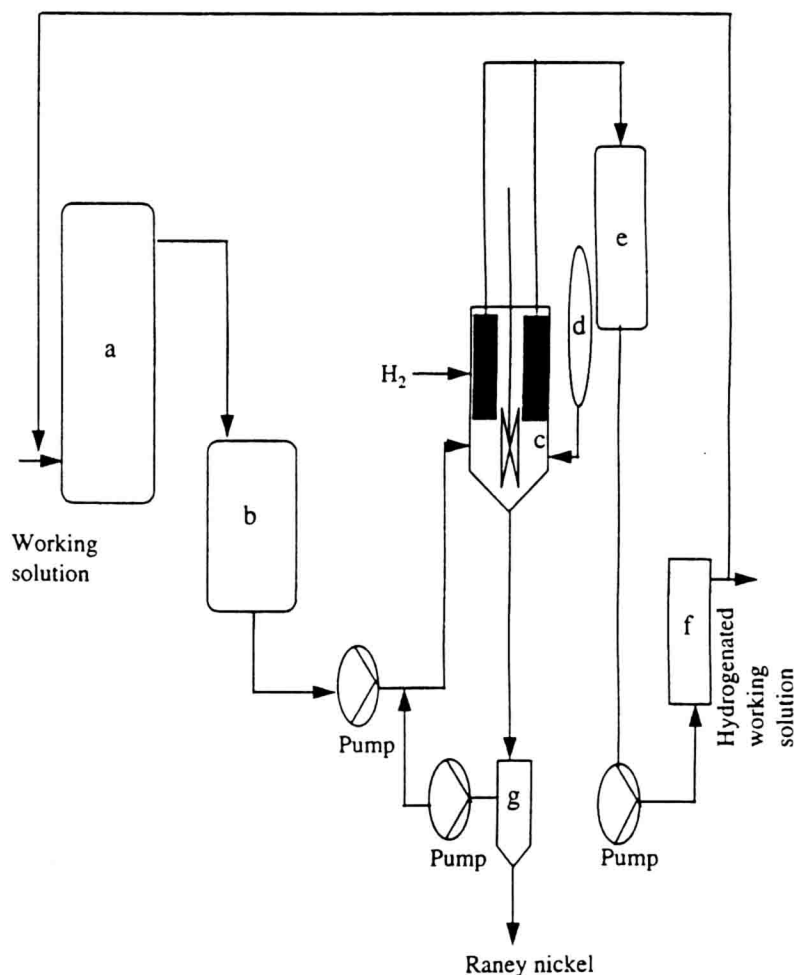


**Figure 1.5** Secondary reactions taking place in the presence of 2-alkylanthrahydroquinones.

nately, once the octa-product (C) is formed, it remains until purged owing to its very low rate of oxidation. Tautomerism of the 2-alkylhydroanthraquinone yields hydroxyanthrones (D, E) which can be further reduced to the anthrones (G, H). The epoxide (F) formed from the alkylhydroanthraquinone does not participate in the formation of hydrogen peroxide, and leads to a loss of active quinone. Measures have, therefore, been suggested for regenerating the tetrahydro compound from the epoxide.<sup>10</sup>

A number of additional processes are also required to maintain the AO process. For example, in order for the hydrogenation phase to run efficiently,

part of the catalyst load is removed, regenerated and returned to the hydrogenator. The hydrogenation step is possibly the most important feature of the modern AO process. Quinone decomposition products that cannot be regenerated into active quinones are always formed during the hydrogenation phase. Therefore a tremendous amount of effort has been invested in the development of new hydrogenation catalysts and hydrogenator designs which have, in some cases, deviated dramatically from the BASF principle. The hydrogenation step in the BASF plant (Figure 1.6) employs a Raney nickel catalyst at a slight excess of pressure. However, because Raney nickel is sensitive to oxygen, the working solution from the extraction, drying and purification steps cannot be fed directly into the hydrogenator. The working solution at this stage still contains residual hydrogen peroxide, and has to be decomposed over a supported Ni-Ag catalyst



a = pre-contact column; b = feed tank to hydrogenator; c = reactor; d = catalyst feed tank; e = oxidizer feed tank; f = safety filter; g = catalyst removal tank.

Figure 1.6 BASF hydrogenator.



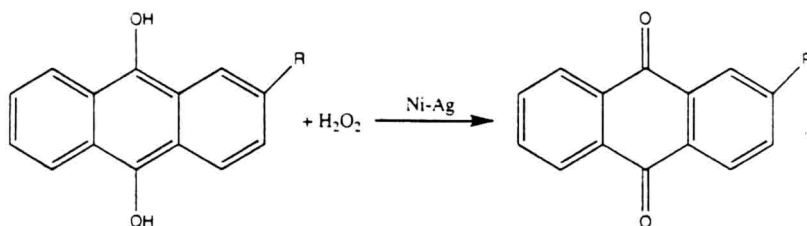


Figure 1.7 Destruction of residual hydrogen peroxide in the BASF process.

(Figure 1.7), together with a small amount of hydrogenated working solution (which also contains 2-alkylhydroanthraquinone). Such a step removes the hydrogen peroxide completely, thus extending the life of the Raney nickel catalyst.

The problem with Raney nickel as the hydrogenation catalyst is that it has a limited selectivity, i.e. the ratio of hydroquinone formation to the tetrahydro compound is low. BASF have largely alleviated this problem via pre-treatment of the catalyst with ammonium formate.<sup>11</sup> The pyrophoric properties of Raney nickel also require more stringent safety procedures when handling the material. Despite the drawbacks of Raney nickel, the catalyst is still used in some AO plants. The majority of AO plants worldwide prefer, however, to employ palladium hydrogenation catalysts because of their higher selectivity, their greater stability towards hydrogen peroxide residues and the simplified handling procedures in comparison to the Raney nickel systems. Degussa have employed palladium black as the hydrogenation catalyst in the majority of their plants.<sup>12</sup> The main advantages of the Degussa hydrogenation stage are: near-quantitative conversion of hydrogen, easy exchange of palladium black, the catalyst is non-pyrophoric and the palladium black is easily re-activated. Laporte chemicals made a significant breakthrough in the operation of the hydrogenation phase by employing supported palladium, which has a particle size diameter of 0.06–0.15 mm.<sup>13</sup> The supported palladium catalyst allows for easier filtration, and recirculation of the catalyst back to the hydrogenator. Laporte, at the same time, also employed a new design for running the hydrogenation phase.<sup>14</sup> Figure 1.8 illustrates the Laporte design.

The Laporte hydrogenator contains a series of tubes which dip just below the surface of the liquid. Hydrogen is then fed into the bottom of each tube, and small gas bubbles are formed. A counter current flow is set up due to the density difference between the solutions in the tube and the reactor. The palladium catalyst suspension is drawn into the tubes by a continuous movement of the working solution.

The problem with all three methods thus far discussed is the fact that the hydrogenator catalyst has to be removed prior to the formation of hydrogen peroxide. If the catalyst is not removed, then catastrophic dismutation of the hydrogen peroxide can occur. In response to the problem, FMC developed a mixed-bed hydrogenation process. The bed is impregnated with palladium, and hence the problem associated with catalyst removal is alleviated.<sup>15</sup>