COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

ARCO Chemical Technology Inc., Incorporated in Delaware, 3 Christina Centre Suite 902, 201 N Walnut Street, Delaware, 19801, UNITED STATES OF AMERICA, hereby apply for the grant of a standard patent for an invention entitled:

Recovery of Hydrogen Peroxide

which is described in the accompanying complete specification.

Details of basic application(s):

Basic Applic. No: Country: Application Date:
295,409 US 10 January 1989

The address for service is:

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this NINTH day of JANUARY 1990

ARCO Chemical Technology Inc.

By:

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 117201
S&F CODE: 58030

SO12388 09/01/90
5845/2
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Recovery of Hydrogen Peroxide
Megan G. Mayer, President
ARCO CHEMICAL TECHNOLOGY, INC.

of 3 Christina Centre, Suite 902, 201 North Walnut Street, Wilmington, DE 19801
USA

[full name of declarant(s)]

[full address of declarant(s) - not post office box]

I do solemnly and sincerely declare as follows:

1. I am/we are authorised by ARCO Chemical Technology Inc., the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in the United States of America on 10 January 1989 by Robert N. Cochran and Lawrence M. Candela.

3. Robert N. Cochran of 310 Carlyle Road, West Chester, Pennsylvania 19382 and Lawrence M. Candela, of 252 South 10th Street, Apt. 5, Philadelphia, Pennsylvania 19107 both in the United States of America [respectively], are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

   The said applicant is the assignee of the actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention(s) the subject of the application.

DECLARED at Delaware this 9th day of February 1990

Signature of Declarant

Megan G. Mayer,
President
ARCO Chemical Technology, Inc.
Delaware corporation, on behalf of the corporation.

LOIS A. McCRAVEY, ITINY FIEH
New South Wales 15655
My Commission Expires: March 17, 1991
The accompanying drawing illustrates in schematic form a suitable embodiment of the invention.

1. A process for the production of hydrogen peroxide which comprises reacting methyl benzyl alcohol with molecular oxygen in the liquid phase, and maintaining the concentration of water in the liquid phase below 4% by weight during the reaction.

4. In a process for the production of hydrogen peroxide wherein methyl benzyl alcohol contaminated with organic impurities which inhibit hydrogen peroxide formation is oxidized to form hydrogen peroxide, the improvement which comprises treating the contaminated methyl benzyl alcohol to remove the impurities or to convert the impurities to non-inhibiting materials, and thereafter reacting the treated methyl benzyl alcohol with molecular oxygen to form hydrogen peroxide.
The following statement is a full description of this invention, including the best method of performing it known to me/us.
Abstract of the Disclosure

Hydrogen peroxide is produced by liquid phase molecular oxygen oxidation of methyl benzyl alcohol, water concentration in the reaction mixture being maintained below 4% by weight, more preferably below 2% by weight, and most preferably below 1% by weight.
PRODUCTION OF HYDROGEN PEROXIDE

Background of the Invention

Field of the Invention

The present invention relates to the production of hydrogen peroxide by the oxidation of methyl benzyl alcohol.

Description of the Prior Art

Hydrogen peroxide is an important chemical of commerce which is produced in very large quantities for use in a number of industrial applications. The predominant process used commercially for the production of hydrogen peroxide involves the oxidation of anthrahydroquinone, extraction of hydrogen peroxide and reduction of the resulting anthraquinone to anthrahydroquinone which is reused. This process requires very high capital expenditures in that use of a working solvent with efficient recycle of various process components is a necessity.

Substantial efforts have been directed to processes which involve direct combination of hydrogen and oxygen but thus far such processes have not found widespread success.

Hydrogen peroxide has been formed by the oxidation of secondary alcohols. At one time the production of hydrogen peroxide by oxidation of isopropanol was practiced commercially. Other secondary alcohols which have been mentioned as possible starting materials for hydrogen,
-2-

peroxide production include methyl benzyl alcohol and cyclohexanol. See, for example, U.S. Patents 2,871,102-4 of Shell Development.

Hydrogen peroxide has also been formed by oxidation of very high boiling secondary alcohols such as diaryl methanol, the product hydrogen peroxide being stripped from the reaction mixture during oxidation; see U.S. Patent 4,303,632.

In certain commercial technologies, there are produced substantial quantities of various secondary alcohols. For example, in the coproduction of propylene oxide and styrene monomer by hydroperoxide epoxidation, methyl benzyl alcohol is formed and ultimately converted by dehydration to styrene monomer. See U.S. Patent 3,351,635.

The present invention provides a process where commercial streams containing methyl benzyl alcohol can be employed effectively and efficiently for hydrogen peroxide production.

**Summary of the Invention**

In accordance with the present invention there is provided an improved process for the production of hydrogen peroxide by oxidation of methyl benzyl alcohol. In particular, the process of this invention involves the production of hydrogen peroxide by molecular oxygen oxidation of methyl benzyl alcohol in the liquid phase wherein the concentration of water in the liquid reaction...
mixture is maintained below 4% by weight, preferably below 2% by weight, and most preferably below 1% by weight of the reaction mixture. Acetophenone is a coproduct.

**Brief Description of the Drawing**

The accompanying drawing illustrates in schematic form a suitable embodiment of the invention.

**Detailed Description of the Invention**

In accordance with the teachings of the prior art, the oxidation of secondary alcohols to produce hydrogen peroxide has been carried out either with water being added to the alcohol feed and/or under conditions of reflux whereby condensibles including water were returned to the reaction mixture and allowed to build up in concentration therein. See U.S. Patent 2,871,104 to Rust.

The surprising discovery has now been made, however, that, unlike other systems, in the oxidation of methyl benzyl alcohol to produce hydrogen peroxide and acetophenone, the presence of even low concentrations of water in the reaction mixture has a profound and adverse effect on the oxidation reaction. In fact, it has been found that the desired oxidation of methyl benzyl alcohol essentially ceases if the water content of the reaction mixture is permitted to rise to certain levels.

In accordance with the present invention, methyl benzyl alcohol is oxidized in the liquid phase with molecular oxygen at elevated temperatures and pressure with the
concentration of water in the reaction mixture maintained below 4% by weight, preferably below 2% by weight, and most preferably below 1% by weight. In this way high reaction rates and selectivities to hydrogen peroxide can be achieved.

In an especially preferred embodiment of the invention, hydrogen peroxide production can be integrated with the production of propylene oxide and styrene monomer by epoxidation with ethyl benzene hydroperoxide. In this embodiment, feed to the methyl benzyl alcohol oxidation comprises a methyl benzyl alcohol/acetophenone process stream from the propylene oxide and styrene monomer process as will be hereinafter described.

The oxidant which is used in the present invention is molecular oxygen. Air is a convenient source of the oxygen although pure oxygen, oxygen-enriched air, oxygen diluted with various inerts such as argon, carbon dioxide, and the like can also be used.

The conditions of temperature and pressure are such as to maintain the reaction mixture in the liquid phase. Elevated temperatures ranging from about 100-250°C, preferably 120-180°C are employed to achieve reasonable reaction rates.

It is important to provide substantial partial pressures of oxygen sufficient to maintain reasonable reaction rates. A preferred range is 15 to 250 psi partial
pressure of oxygen in the feed gases, with a broader useful range being 0.5 to 1000 psi.

Total pressure in the reaction zone should be sufficient to maintain the reaction mixture in the liquid phase. Generally, pressures in the range of 5 psig to 1000 psig are useful.

Metal contaminants and other materials which promote peroxide decomposition are to be avoided in the reaction zone. Known peroxide stabilizers such as pyrophosphates are useful and can be employed.

The oxidation of methyl benzyl alcohol to hydrogen peroxide and acetophenone is an exothermic reaction which requires removal of the heat of reaction. This can be accomplished, for example, by circulating a portion of the reaction mixture through indirect cooling means. Alternatively, the heat can be removed by boil-up and condensation of components of the reaction mixture.

Essential to practice of the invention is the maintaining of low water concentrations in the liquid reaction mixture, i.e. water concentration below 4 wt. %, preferably below 2 wt. % and most preferably below 1 wt. % water in the reaction mixture.

Water concentration can be controlled in a number of ways. In the first instance, the water content of the various feed materials is appropriately kept to a minimum. In batch or continuous systems, water can be removed as a
vapor from the reaction zone, for example, along with nitrogen, unreacted oxygen and various other components of the reaction mixture. Whereas in conventional systems this water is condensed and refluxed to the reaction zone, in practice of the present invention the water removed as vapor is not returned to the reaction zone thus preventing build up of substantial concentrations of water in the reaction mixture. In conjunction with these procedures, or as an alternative thereto, liquid reaction mixture can be removed, hydrogen peroxide and water can be separated therefrom, and the remaining components further processed or recycled.

The invention can be further described with reference to the attached drawing which illustrates in schematic form an especially preferred embodiment. Referring to the drawing, a process stream from a commercial process for propylene oxide/styrene monomer coproduction comprised mainly of methyl benzyl alcohol, acetophenone, and ethyl benzene in line 101 is combined with a methyl benzyl alcohol stream in line 102 from acetophenone hydrogenation and passed to distillation zone 103.

By conventional distillation ethyl benzene is separated overhead via line 104 for recycle to the propylene oxide/styrene monomer process. A higher boiling stream mainly comprised of methyl benzyl alcohol and acetophenone and containing small amounts of phenol and ethyl phenols is separated from distillation zone 103 through line 105.
A portion of the methyl benzyl alcohol and acetophenone stream passes via lines 106, 110 and 111 to dehydration zone 112. The remaining portion of this stream passes via line 107 to purification zone 108.

It has been found in accordance with the present invention, that certain compounds such as phenol and ethyl phenols which are usually present with methyl benzyl alcohol in commercial streams severely inhibit the molecular oxygen oxidation of methyl benzyl alcohol to hydrogen peroxide and acetophenone. Accordingly, the methyl benzyl alcohol and acetophenone stream from distillation zone 103 is first treated in purification zone 108 to remove materials which inhibit methyl benzyl alcohol oxidation or to convert these materials to non-inhibitive compounds.

Preferably, purification zone 108 comprises both distillation and caustic and/or ion exchange treatment. By distillation, ethyl phenols can be separated as high boiling material from methyl benzyl alcohol and acetophenone. Basic ion exchange resins such as poly(vinylpyridine) resins can be employed to separate the phenols as described, for example, in Sumitomo Japanese Patent Publication 39025 of 1981. Caustic treatment is effective to remove phenol.

From purification zone 108, the methyl benzyl alcohol/acetophenone stream passes via line 113 to oxidation zone 114 wherein the methyl benzyl alcohol is reacted with molecular oxygen to form hydrogen peroxide and acetophenone.
As shown, the molecular oxygen is provided by air introduced via line 115.

Conditions of temperature and pressure are maintained in zone 114 effective to maintain the reaction mixture in the liquid phase, and to maintain high reaction rate and selectivity to hydrogen peroxide and acetphenone. The water content of the reaction mixture is maintained below 4 wt. %, preferably below 2 wt % and most preferably below 1 wt. % by stripping water formed during the oxidation out of the reaction mixture with unreacted oxygen and inert gases via line 140.

Liquid reaction mixture which contains product hydrogen peroxide passes from 114 via line 116 and is pressurized for the recovery of the hydrogen peroxide. In an especially preferred practice as described in detail in copending application filed of even date herewith, ethyl benzene extraction is used in the separation of the oxidate mixture. The disclosure of said copending application is incorporated herein by reference.

The oxidate is admixed with ethyl benzene introduced via line 137 and with an ethyl benzene extraction mixture from back extraction extractor 124 via line 117. The mixture passes to tower extractor 119 and flows countercurrent to water which is introduced via line 120.

The organic phase comprised of ethyl benzene, methyl benzyl alcohol, and acetphenone passes via line 121 to
distillation zone 128. The aqueous hydrogen peroxide phase passes via line 122 to extractor 124 wherein small amounts of contained methyl benzyl alcohol and acetophenone are extracted with ethyl benzene introduced via line 123. The organic phase is removed via line 117 and recycled to admixture with oxidate from reactor 114.

The aqueous hydrogen peroxide phase passes via line 128 to purification zone 126 from which the final purified hydrogen peroxide is recovered via line 127.

In separation zone 129, ethyl benzene is separated overhead and can be recycled to admixture with oxidate from reactor 114 via lines 130 and 137.

Advantageously, the methyl benzyl alcohol and acetophenone stream passes via line 129 to integration with a commercial propylene oxide/styrene monomer process, as shown. The methyl benzyl alcohol and acetophenone pass via line 129 and are admixed with a comparable stream from separation zone 103 via lines 105, 106 and 110 and passed to dehydration zone 112 wherein methyl benzyl alcohol is dehydrated to styrene monomer. Dehydration effluent is transferred via line 131 to zone 132 wherein product styrene monomer is recovered and removed via line 133.

The remaining mixture of unconverted methyl benzyl alcohol and acetophenone is admixed with ethyl benzene introduced via line 137 and passed via line 134 to zone 135 wherein acetophenone is hydrogenated to methyl benzyl.
alcohol. The effluent stream from 135 is recycled via 102 to separation zone 103 and thus re-integrated into the process.

The following example illustrates practice of the invention. Unless otherwise stated, units are parts by weight per hour, and percentages are weight percent.

Example

Referring to the drawing, 1000 parts of a mixture comprised of 65% ethyl benzene, 25% methyl benzyl alcohol, and 6% acetophenone in line 101 is combined with 314.6 parts of a 92% ethyl benzene, 4% methyl benzyl alcohol, and 4% acetophenone stream from line 132 and passed to distillation zone 103. About 651 parts of ethyl benzene are recovered overhead and recycled via line 104 to the ethyl benzene oxidation of a propylene oxide/stryrene monomer process.

The bottom stream comprised of approximately 94% methyl benzyl alcohol, and 16% acetophenone and containing 1200 ppm phenol and 1600 ppm 2, 3, and 4 ethyl-phenols is divided into two streams, 20 parts passing via lines 106, 110 and 111 to dehydration zone 112, and 411 parts passing via line 107 to purification zone 108.

In zone 108, the oxidation inhibiting phenols are separated by distillation. Suitable conditions are an overhead pressure of 40 torr, overhead temperature of 110°C and bottom temperature of 135°C. About 208.5 parts of the bottoms, phenols-rich stream, comprised of approximately 84%
catalyst benzyl alcohol, and 16% acetophenone and containing
the predominance of the ethyl-phenol in sent via line 129, 130
and 111 to dehydration zone 112. About 469.5 parts of a
phenols-lean stream, comprised of approximately 04% methyl
denzy alcohol, and 16% acetophenone is sent via line 113 to
oxidation reactor 114.

Conditions in the oxidation reactor are 140°C and 100
psig; 66 parts of air are sparged into the reactor. Oxygen
partial pressure in the vent gas exiting via line 140 to 16
psia. Methyl benzyl alcohol conversion in the reactor is
30%, with H₂O₂ selectivity about 00%. About 217.5 parts of
liquid reaction mixture comprised of 95.4% methyl benzyl
alcohol, 9.6% acetophenone, 0.3% H₂O₂, and 0.7% H₂O are
removed via line 116, admixed with 170 parts pure ethanol
benzene from line 137 and 96 parts of an ethyl benzene
recycle stream in line 117 from the ethyl benzene back
extraction unit 114, comprised of 96.3% ethyl benzene, 1.2%
methyl benzyl alcohol, 0.1% H₂O, and 0.2% acetophenone. The
combined feed to the H₂O₂ extractor in line 118 to 440
parts, comprised of 81.5% ethyl benzene, 26.2% methyl benzyl
alcohol, 10.7% acetophenone, 2.6% H₂O₂ and 0.3% H₂O.

About 35 parts water is fed to the extractor via line
120. The heavier aqueous product from the extractor exits
via line 122; it is about 45 parts, comprised of
approximately 25.1% H₂O₂, 3% methyl benzyl alcohol, and 0.9%
acetophenone. The lighter organic product from the
extractor exits via lines 121 to the ethyl benzene separation zone 128. This stream is about 438 parts, comprised of about 52.6% ethyl benzene, 27.5% methyl benzyl alcohol, 19.1% acetophenone, 0.7% H₂O and 0.015% H₂O₂.

The organics in the aqueous product from the H₂O₂ extractor are recovered by back extraction with ethyl benzene in extractor 124. About 52.4 parts ethyl benzene are fed to 124 via line 123. The light organic product exits via line 117, and is sent back to be mixed with the organic feed to the H₂O₂ extractor 119. The heavy aqueous product exits via line 125 and is sent to H₂O₂ purification zone 126; it is about 43.4 parts, comprised of 26.6% H₂O₂ and 0.03% methyl benzyl alcohol, and 73.4% water.

Trace organics are separated in H₂O₂ purification section 131, and the peroxide product is concentrated, if desired, by evaporation of water (not shown).

The organic product from the H₂O₂ extractor is sent to ethyl benzene separation 128 via line 121. This stream is about 438 parts comprised of 52.6% ethyl benzene, 27.5% methyl benzyl alcohol, 0.7% H₂O, and 19.1% acetophenone.

The overhead ethyl benzene stream in amount of 230.6 parts is recovered in line 130, and recycled to H₂O₂ extraction 119 and ethyl benzene back extraction 124. About 3.1 parts water is also removed (not shown) in Unit 128. The bottoms stream 129 is about 204.5 parts, comprised of 59% methyl benzyl alcohol, and 41% acetophenone.
The combined streams in lines 110 and 129 in amount of 500 parts and comprised of 74% methyl benzyl alcohol, and 26% acetophenone is dehydrated in zone 112. About 95% conversion of methyl benzyl alcohol to styrene is experienced in 112, resulting in a product stream in line 131 of 500 parts comprised of 4% methyl benzyl alcohol, 26% acetophenone, 60% styrene, and 10% water. Styrene separation unit 132 separates 300 parts styrene in line 133 and 51 parts water (not shown). The other product exits line 134 and is 149 parts, comprised of 12% methyl benzyl alcohol, and 88% acetophenone. This is diluted with 163.5 parts ethyl benzene in line 137 and sent to acetophenone hydrogenation unit 135.

About 90% of the acetophenone fed to hydrogenation is converted by reaction with 2.1 parts hydrogen from line 136. The product stream in amount of 314.5 parts, is recycled back to propylene oxide/styrene monomer refining section 103, and is comprised of 52% ethyl benzene, 43% methyl benzyl alcohol, and 5% acetophenone.

The compound referred to throughout this specification as methyl benzyl alcohol is sometimes otherwise known as 1-phenyl ethanol, -phenyl ethanol or methyl phenyl carbinol.
WE CLAIM:  the invention are as follows:

1. A process for the production of hydrogen peroxide which comprises reacting methyl benzyl alcohol with molecular oxygen in the liquid phase, and maintaining the concentration of water in the liquid phase below 4% by weight during the reaction.

2. A process according to claim 1 wherein the concentration of water in the liquid phase is maintained below 2% by weight during the reaction.

3. A process according to claim 1 wherein the concentration of water in the liquid phase is maintained below 1% by weight during the reaction.

4. In a process for the production of hydrogen peroxide wherein methyl benzyl alcohol contaminated with organic impurities which inhibit hydrogen peroxide formation is oxidized to form hydrogen peroxide, the improvement which comprises treating the contaminated methyl benzyl alcohol to remove the impurities or to convert the impurities to non-inhibiting materials, and thereafter reacting the treated methyl benzyl alcohol with molecular oxygen to form hydrogen peroxide.

5. A process for the production of hydrogen peroxide by the oxidation of methyl benzyl alcohol, substantially as herein described with reference to Fig. 1.

6. A process for the production of hydrogen peroxide by the oxidation of methyl benzyl alcohol, substantially as herein described with reference to the Example and Fig. 1.

DATED this NINTH day of JANUARY 1990
ARCO Chemical Technology Inc.
Patent Attorneys for the Applicant
SPRUSON & FERGUSON
FIG-1

Diagram showing processes involving dehydration, separation, hydrogenation, and purification, with various chemical processes and flow paths indicated.