(12) PATENT **(11)** Application No. **AU 199921689 B2**
(19) AUSTRALIAN PATENT OFFICE **(10)** Patent No. **735787**

(54) Title
Method for preparing an aqueous hydrogen peroxide solution directly from hydrogen and oxygen and implementing device

(51)^7 International Patent Classification(s)
C01B 015/029

(21) Application No: **199921689** (22) Application Date: **1999.01.29**

(87) WIPO No: **WO99/41190**

(30) Priority Data

(31) Number	(32) Date	(33) Country
98/01524	**1998.02.10**	**FR**

(43) Publication Date : **1999.08.30**
(43) Publication Journal Date : **1999.11.04**
(44) Accepted Journal Date : **2001.07.12**

(71) Applicant(s)
Atofina

(72) Inventor(s)
Michel Devic; Lionel Delais

(74) Agent/Attorney
WATERMARK PATENT and TRADEMARK ATTORNEYS,Locked Bag 5,HAWTHORN VIC 3122

(56) Related Art
WO 96/05138
WO 92/04277
US 5169618

21689/99

PCT ORGANISATION MONDIALE DE LA PROPRIETE INTELLECTUELLE
Bureau international

DEMANDE INTERNATIONALE PUBLIEE EN VERTU DU TRAITE DE COOPERATION EN MATIERE DE BREVETS (PCT)

(51) Classification internationale des brevets 6 : **C01B 15/029**	**A1**	**(11) Numéro de publication internationale:** **WO 99/41190** **(43) Date de publication internationale:** 19 août 1999 (19.08.99)

(21) Numéro de la demande internationale: PCT/FR99/00186

(22) Date de dépôt international: 29 janvier 1999 (29.01.99)

(30) Données relatives à la priorité:
98/01524 10 février 1998 (10.02.98) FR

ATOFINA

(71) Déposant *(pour tous les Etats désignés sauf US)*: ~~ELF ATOCHEM S.A.~~ [FR/FR]; 4/8, cours Michelet, F-92800 Puteaux (FR).

(72) Inventeurs; et
(75) Inventeurs/Déposants *(US seulement)*: DEVIC, Michel [FR/FR]; 22, rue Georges Clémenceau, F-69110 Saint Foy Lès Lyon (FR). DELAIS, Lionel [FR/FR]; 44, rue Saint Lazare, F-60300 Senlis (FR).

(74) Mandataire: DANG, Doris; Elf Atochem S.A., Dépt. Propriété Industrielle, Cours Michelet, La Défense 10, F-92091 Paris la Défense Cedex (FR).

(81) Etats désignés: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, brevet ARIPO (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), brevet eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Publiée
Avec rapport de recherche internationale.

AUSTRALIAN PATENT OFFICE
92B15
10/8/00

IP AUSTRALIA
3 0 AUG 1999
RECEIVED

(54) Title: METHOD FOR PREPARING AN AQUEOUS HYDROGEN PEROXIDE SOLUTION DIRECTLY FROM HYDROGEN AND OXYGEN AND IMPLEMENTING DEVICE

(54) Titre: PROCEDE DE PREPARATION D'UNE SOLUTION AQUEUSE DE PEROXYDE D'HYDROGENE DIRECTEMENT A PARTIR D'HYDROGENE ET D'OXYGENE ET DISPOSITIF PERMETTANT SA MISE EN OEUVRE

(57) Abstract

The invention concerns a catalytic process and a device for preparing, in absolute safety, aqueous hydrogen peroxide solutions at high concentration levels directly from hydrogen and oxygen. More particularly, it concerns a method whereby hydrogen and oxygen are injected, into the aqueous medium in proportions corresponding to the flammability range of the hydrogen-oxygen mixture, and are present in proportions outside the flammability range in the continuous gas phase. The invention also concerns a device for implementing said method.

(57) Abrégé

La présente invention concerne un procédé catalytique ainsi qu'un dispositif pour préparer, en toute sécurité, des solutions aqueuses de péroxyde d'hydrogène à des concentrations élevées directement à partir d'hydrogène et d'oxygène. Plus particulièrement, elle a pour objet un procédé dans lequel l'hydrogène et l'oxygène sont injectés, dans le milieu aqueux, dans des proportions correspondant au domaine d'inflammabilité du mélange hydrogène-oxygène, et sont présents dans des proportions en dehors de la zone d'inflammabilité dans la phase gazeuse continue. L'invention a également pour objet un dispositif pour la mise en oeuvre du procédé.

Translation from French of PCT/FR99/00186

PROCESS FOR THE PREPARATION OF AN AQUEOUS HYDROGEN PEROXIDE SOLUTION DIRECTLY FROM HYDROGEN AND OXYGEN AND DEVICE ALLOWING ITS IMPLEMENTATION

The present invention relates to a catalytic process and to a device for preparing, in perfect safety, aqueous hydrogen peroxide solutions at high concentrations directly from hydrogen and oxygen. More particularly, a subject matter of the invention is a process in which hydrogen and oxygen are injected into the aqueous medium in proportions corresponding to the flammability range of the hydrogen-oxygen mixture and are present in proportions outside the flammability range in the continuous gas phase. Another subject matter of the invention is a device for the implementation of the process.

The hydrogen and oxygen gas mixture is known to be flammable, even explosive, when hydrogen is present at molar concentrations of between 4 and 94 % under standard conditions of temperature and pressure, that is to say when the ratio of the hydrogen molar concentration to the oxygen molar concentration is greater than 0.0416 (Encyclopédie des Gaz (Encyclopaedia of Gases), Air Liquide, page 909).

To avoid any risk of explosion or fire, it is recommended either to operate with a hydrogen/oxygen ratio below the lower flammability limit or to use an inert gas, such as nitrogen, argon, helium or neon (US 4 681 751, US 4 009 252, EP 0 787 681).

In point of fact, to obtain satisfactory results, it is necessary to work with a hydrogen/oxygen ratio within the flammability range. Thus, the document US 4 009 252 discloses a hydrogen/oxygen molar ratio between 1/20 and 1/1.5 and preferably between 1/10 and 1/2. Likewise, the document US 4 336 239 instructs the reader to operate in the presence of a hydrogen/oxygen molar ratio less than 0.2 and preferably between 1/15 and 1/12.

The term "direct synthesis of an aqueous hydrogen peroxide solution" is understood to denote the synthesis of hydrogen peroxide from hydrogen and oxygen in an aqueous medium that contains a catalyst.

The direct synthesis of an aqueous hydrogen peroxide solution, continuously or batchwise, in a stirred reactor has formed the subject of many studies. The reactor generally contains an aqueous region, occupied by the working solution and the catalyst, and a region, occupied by the gases, situated above the aqueous region. It is equipped with a stirring system, which makes it possible both to stir the aqueous region and to disperse the gases in the aqueous phase. The reactants, namely the hydrogen and the oxygen, as well as the inert gases are injected into the region of the gases.

The term "working solution" is understood to denote the aqueous medium, comprising water, acids and optionally decomposition inhibitors or stabilizers for hydrogen peroxide, in which the hydrogen peroxide is formed.

It has been observed that when the direct synthesis of an aqueous hydrogen peroxide solution is carried out in a stirred reactor as described above, the catalyst, thrown by the effect of the stirring on to the walls of the reactor and the shaft of the stirrer which are situated in the region of the gases, would be in direct contact with the reactants. During the synthesis, the catalyst particles in the region of the gases will dry out and will spontaneously bring about the ignition of the hydrogen-oxygen gas mixture if the molar concentration of the hydrogen is greater than 0.04.

This is why, in Example 1 of document US 4 279 883, which illustrates the direct continuous synthesis of an aqueous hydrogen peroxide solution in a stirred reactor, a gaseous mixture of hydrogen, oxygen and nitrogen is introduced continuously into the gaseous region of the reactor, so that the partial pressures of the hydrogen, oxygen and nitrogen in the gases collected at the outlet are maintained respectively at 5, 49 and 113 atmospheres, that is to say a hydrogen molar concentration of 3%. The industrial manufacture of an aqueous hydrogen peroxide solution under the safety conditions according to the document US 4 279 883 is economically out of the question, however, given the low concentration of the aqueous hydrogen peroxide solution obtained.

If this aqueous solution is to be useful, it requires an additional concentration stage.

The direct synthesis of an aqueous hydrogen peroxide solution can also be carried out in a tubular reactor composed of a long pipe (pipeline) filled with working solution in which the catalyst is suspended and into which gaseous oxygen and hydrogen are injected in the form of small bubbles in proportions above the lower flammability limit of the hydrogen-oxygen mixture (US 5 194 242). The safety of such a process is only assured provided that the gaseous reactants are maintained in the reactor in the form of small bubbles. According to the document US 5 641 467, the latter can only be obtained with a high rate of circulation of the working solution.

A catalytic process and a device have now been found which make it possible to prepare aqueous hydrogen peroxide solutions at high concentrations directly from hydrogen and oxygen in a stirred reactor, in perfect safety and economically.

This process is characterised in that:

- hydrogen and oxygen are injected separately, in the form of small bubbles, into the lower part of the aqueous reaction medium, which has been rendered acidic by the addition of an inorganic acid and which contains a catalyst in the dispersed state, with molar flow rates such that the ratio of the molar flow rate for hydrogen to that for oxygen is greater than 0.0416; and in that
- oxygen is introduced into the continuous gas phase and/or into the upper part of the aqueous reaction medium in an amount such that the molar ratio of hydrogen to oxygen in the continuous gas phase is less than 0.0416.

The term "small bubbles" is understood to denote bubbles with a mean diameter of less than 3 mm.

The injections of hydrogen and of oxygen in the form of small bubbles into the lower part of the aqueous reaction medium take place preferably at the bottom of the stirred reactor and are, for preference, next to each other so that the bubbles of H_2 and O_2 mix as quickly as possible.

As an inorganic acid, one could take, for example, sulphuric acid and orthophosphoric acid.

The aqueous reaction medium can additionally contain stabilizers for hydrogen peroxide such as, for example, phosphonates or tin, and decomposition inhibitors such as, for example, halides. Bromide is the inhibitor that is especially preferred and it is used to advantage in combination with bromine in the free state (Br_2).

According to the invention, the oxygen injected in the form of small bubbles into the lower part of the aqueous reaction medium, as well as the oxygen introduced into the continuous gas phase and/or into the upper part of the aqueous reaction medium, can additionally contain hydrogen in an amount such that the molar concentration ratio of hydrogen to oxygen is less than 0.0416.

According to the present invention, the operation can be carried out just as easily continuously as semi-continuously.

The oxygen feed in the form of small bubbles into the lower part of the aqueous reaction medium can be provided in whole or in part by the gaseous effluent at the outlet of the reactor.

It is also possible to use the gaseous effluent at the reactor outlet to feed the continuous gas phase and/or the upper part of the aqueous reaction medium. In this case, the composition of the gaseous effluent can be adjusted by addition of oxygen and optionally by removal of hydrogen, so that the molar concentration ratio of hydrogen to oxygen is less than 0.0416.

The catalyst generally used comprises at least one element chosen from the metals of Groups IB and VIII of the Periodic Table. Advantageously, gold, platinum, palladium and ruthenium are chosen. Use is preferably made of palladium, platinum or the palladium-platinum combination, or, better still, palladium or the palladium - platinum combination.

In the case of a palladium-platinum composite catalyst, the platinum preferably represents between 1 and 50% of the total weight of the metals and, better still, approximately 2%.

According to the invention, the catalyst can also be supported. The supports generally used are, for example, silica, alumina, silica-alumina combinations and titanium dioxide.

The supported or non-supported catalyst is generally suspended in the aqueous reaction medium. Use is preferably made of the supported catalyst and, even better, a supported catalyst containing between 0.2 and 2% by weight of metal or metals in relation to the support.

The temperature and the pressure prevailing inside the reactor are adjusted in order to optimise the selectivity of the reaction with respect to hydrogen and the productivity with regard to hydrogen peroxide.

The temperature is generally between 0 and 60°C and preferably between 5 and 30°C.

The pressure prevailing inside the reactor is generally above atmospheric pressure and preferably between 30 and 100 bar: advantageously, between 40 and 60 bar.

The ratio of the molar flow rate of hydrogen to that of oxygen injected into the lower part of the aqueous reaction medium can vary within wide limits. It is preferably between 0.05 and 5 and more particularly between 0.2 and 1. A molar ratio of about 0.3 is used advantageously.

When the operation is carried out semi-continuously, all of the working solution and all the catalyst are introduced into the reactor before the beginning of the direct synthesis and the hydrogen and the oxygen are introduced continuously.

It is also possible to feed the reactor continuously with the working solution, to which the catalyst has been added, and to introduce the hydrogen and the oxygen continuously. In this case, the solution containing the hydrogen peroxide formed is extracted continuously from the reactor.

The catalyst is subsequently separated, by filtration of the final solution containing the hydrogen peroxide formed under semi-continuous conditions or of the hydrogen peroxide solution extracted continuously from the reactor, then optionally reintroduced into the reactor.

When the reactor is equipped with a filter, the catalyst is held permanently in the reactor and the hydrogen peroxide solution is extracted and filtered simultaneously.

Another subject-matter of the invention is a device which makes it possible to manufacture, in perfect safety and economically, concentrated aqueous hydrogen peroxide solutions directly from hydrogen and oxygen. This device, which consists of a stirred reactor fed continuously or non-continuously with working solution, is characterised in that the reactor is equipped (i) with one or more inlet(s) for gaseous hydrogen, in the form of small bubbles, into the lower part of the aqueous reaction medium; (ii) with one or more inlet(s) for gaseous oxygen optionally containing hydrogen, in the form of small bubbles, into the lower part of the aqueous reaction medium, the inlet(s) for oxygen into the liquid phase being preferably adjacent to those for the hydrogen so that the bubbles of H_2 and O_2 mix rapidly; (iii) with a pressure regulator which makes it possible to keep the pressure prevailing inside the reactor constant by discharging excess unconsumed gaseous reactants; and (iv) with one or more inlet(s) for gaseous oxygen, optionally containing hydrogen, into the continuous gas phase and/or into the upper part of the aqueous reaction medium, which is/are controlled by an analyser of the gas flow exiting from the reactor so that the molar ratio of hydrogen to oxygen in the continuous gas phase is less than 0.0416.

The reactor is equipped with an outlet, which makes possible the continuous or semi-continuous extraction of the aqueous hydrogen peroxide solution. This outlet is optionally equipped with a filter, which makes it possible to separate the catalyst from the aqueous hydrogen peroxide solution.

According to the invention, the gas flow exiting from the reactor can be reinjected into the circuit feeding the lower part of the aqueous reaction medium with oxygen. This gas flow, after optional adjustment of the hydrogen content by addition of oxygen and optionally by removal of hydrogen, for example by using a membrane, can also be reinjected into the circuit feeding with oxygen the continuous gas phase and/or the upper part of the aqueous reaction medium. The hydrogen thus separated can be reinjected into the lower part of the aqueous reaction medium.

Preferably, at least one inlet for hydrogen and at least one inlet for oxygen, in the form of small bubbles into the lower part of the aqueous reaction medium, are situated at the bottom of the stirred reactor.

The reactor can be an autoclave of cylindrical, cylindro-conical or spherical shape, stirred by means of a vertical shaft equipped with one or more impellers or one or more turbines.

Generally, any reactor commonly used when a suspended catalyst is involved and which is capable of providing good heat exchange and of maintaining the gaseous reactants of the reaction in the form of a cloud of the greatest possible number of little bubbles may be suitable.

The stirring can also be provided by several independent impellers or turbines, each driven by a stirrer shaft which is attached to the bottom, or to the lid, or to the sides of the reactor. The turbine(s) situated in the upper part of the aqueous reaction medium may be of the "self-suction" type, that is to say that they suck the continuous gas phase of the reactor from the stirrer shaft, which is hollow, and then diffuse this gas phase into the aqueous reaction medium; or they may be of the "floppy" type.

The stirring can be supplemented by devices commonly used to render the stirring highly efficient, such as, for example, one or more baffles positioned vertically and/or radially.

Use is generally made of heat exchangers, such as tubular coils, bundles of vertical pipes, or else sets of radial vertical plates, or else wound spirals, in order to provide for the regulation of the temperature of the reaction medium. These exchangers are preferably situated inside the reactor. Use is advantageously made of a vertical tubular bundle or wound spirals or a bundle of vertical plates positioned radially.

The temperature of the mixture can also be regulated by using a jacketed reactor with circulation of water.

The reactor according to the invention is designed so that, if the stirring is accidentally halted, all the gas bubbles can rise and reach the continuous gas phase directly, solely under the influence of gravitational forces. The various devices installed inside the reactor in order to provide for the heat exchanges and/or the stirring must not form an obstacle to the rise of bubbles and must not result in the formation of pockets of gas inside the aqueous reaction medium.

The reactor can be composed of any material compatible with the reactants used. For example, use may be made of metals such as stainless steels (304L or 316L) or Hastelloy alloys, or else metals coated with chemically resistant polymers such as PVDF (polyvinyldifluoride), PTFE (polytetrafluoroethylene), PFA (copolymer of C_2F_4 and perfluorovinyl ether) or FEP (copolymer of C_2F_4 and C_3F_6).

The feeds of oxygen and of hydrogen, in the form of small bubbles, into the lower part of the aqueous reaction medium can be provided by pipes or plates made of sintered metal or else various types of nozzles which make it possible to eject gas at high speed and thus to bring about the formation of many small bubbles.

A device and a block diagram illustrating a specific embodiment of the process of the present invention are represented in the single Figure and are described below.

The device comprises a reactor stirred by means of a vertical shaft equipped with a self-suction turbine a and with a turbomixer b. On start-up:

- the reactor contains the catalyst suspended in the working solution, the combined mixture being brought to the reaction temperature,
- the oxygen introduced into the continuous gas phase at 3 originates from the flow 8, that is to say from non-recycled oxygen, and

- the hydrogen injected at the bottom of the reactor is fed via 2.

A pressure regulator i makes it possible to keep the pressure prevailing inside the reactor constant by discharging excess unconsumed gaseous reactants 9. Likewise, the temperature of the reaction medium is kept constant by virtue of the exchanger e.

The following are continuously introduced into the reactor: at 6, the working solution; at 2 and 4, hydrogen in the form of small bubbles; at 1, oxygen in the form of small bubbles; at 3, oxygen in an amount such that the molar concentration of hydrogen in the continuous gas phase is always less than 4%.

The feed system at 3 is controlled by the in-line analyser g of the gas flow 5 exiting from the reactor. The oxygen feed at 3 is provided by the flow 8 and by the flow 10; the latter originates from the gaseous effluent at the outlet of the reactor after removal of the hydrogen through a membrane s. The hydrogen thus removed provides for the partial hydrogen feed 4 into the lower part of the reaction medium.

The oxygen 1 injected into the lower part of the reaction medium originates entirely from the gaseous effluent at the outlet of the reactor and contains hydrogen.

All the gas flow rates are regulated using mass flow meters f. The flow rates for oxygen and for hydrogen injected into the lower part of the reaction medium are such that the ratio of the molar flow rate for hydrogen to that for oxygen is always greater than 0.0416.

The injection nozzles d makes it possible to inject the reactants in the form of small bubbles.

The pump h provides for the recycling of unconsumed hydrogen and unconsumed oxygen.

The aqueous solution containing the hydrogen peroxide formed is simultaneously separated from the catalyst using the filter c and extracted continuously, 7.

Other specific embodiments are given in the following examples.

EXPERIMENTAL PART

Preparation of the catalyst

The catalyst used contains 0.8% by weight of metallic palladium and 0.04% by weight of platinum, these being supported on a microporous silica. It is prepared by impregnating Aldrich Company silica (ref. 28 851-9), with the following characteristics:

Mean particle size = 5 to 15 μm
BET specific surface = 500 m^2/g
Pore volume: 0.75 cm^3/g
Mean pore diameter: 60 Å,

with an aqueous solution containing $PdCl_2$ and H_2PtCl_6, followed by drying and finally by heat treatment while flushing with hydrogen at 300°C for 3 hours.

The Reactor

The reactor is a jacketed, stainless steel autoclave with water circulation and a capacity of 100 cm^3, the internal walls of which are coated with PTFE (polytetrafluoroethylene). It is equipped with a stirrer comprising a vertical shaft with a turbine having six radial blades. The reactor is also equipped with two inlets made of PTFE capillary tubes situated at the bottom of the reactor, making it possible to inject hydrogen and oxygen, in the form of small bubbles, into the lower part of the aqueous reaction medium. It is furthermore equipped with an inlet situated in the lid of the autoclave which makes it possible to introduce oxygen so that the molar ratio of hydrogen to oxygen in the continuous gas phase is always less than 0.0416, that is to say outside the flammability range of the hydrogen-oxygen mixture.

The injection of the reactants into the aqueous medium and the injection of oxygen into the continuous gas phase are regulated using mass flow meters.

The pressure prevailing inside the reactor is kept constant by means of a venting device. The hydrogen and the oxygen constituting the gas flow exiting from the reactor are quantitatively determined in line by gas chromatography.

Preparation of an Aqueous Solution (I)

An aqueous solution is prepared by addition of 0.5 g of H_3PO_4, 2.5 g of H_2SO_4 and 50 mg of sodium bromide to 1000 cm^3 of distilled water and 5 mg of Br_2 in the form of 1% bromine water.

General Procedure

50 g of the aqueous solution (I) and 0.3 g of catalyst are introduced into the autoclave and then the aqueous reaction medium is brought to and maintained at the desired temperature. The inlet for oxygen into the continuous gas phase is subsequently opened. The pressure in the autoclave increases to the chosen value and it is then kept constant by means of the pressure regulator.

The hydrogen and the oxygen are subsequently injected into the aqueous reaction medium in the chosen proportions and then the hydrogen in the gas flow exiting from the pressure regulator is quantitatively determined every 10 minutes.

After the desired reaction time, the inlets for hydrogen and oxygen into the aqueous reaction medium are turned off and the injection of oxygen into the continuous gas phase is maintained until hydrogen has completely disappeared from the latter. The inlet for oxygen is then turned off, the reactor is then decompressed and, finally, the aqueous hydrogen peroxide solution is recovered.

The aqueous hydrogen peroxide solution recovered is subsequently weighed and then separated from the catalyst by filtration through a filter. The resulting solution is then quantitatively determined by iodometry, thus making it possible to determine the hydrogen peroxide concentration.

The consumption of hydrogen is measured by the difference between the amount injected and the amount that has exited from the reactor.

The selectivity of the direct synthesis of hydrogen peroxide with respect to hydrogen is defined as being the percentage of the number of moles of hydrogen peroxide formed to the number of moles of hydrogen consumed.

The operating conditions and the results obtained during various tests (Examples 1 to 10) are combined in Table I.

TABLE I

EXAMPLE	TEMPERATURE (°C)	DURATION (HOURS)	FLOW RATE FOR H_2 INJECTED INTO THE AQUEOUS MEDIUM Sl/h	FLOW RATE FOR O_2 INJECTED INTO THE AQUEOUS MEDIUM Sl/h	RATIO OF H_2/O_2 FLOW RATES, AQUEOUS MEDIUM	FLOW RATE FOR O_2 INJECTED INTO THE CONTINUOUS GAS PHASE Sl/h	RATIO OF H_2/O_2 FLOW RATES, INJECTED TOTAL	H_2O_2 CONCENTRATION OF THE SOLUTION %	SELECTIVITY WITH RESPECT TO H_2 %
1	20	3	4	0.1	40	95	0.042	15	60
2	20	3	4	1	4	95	0.041	17	69
3	20	3	4	2	2	94	0.041	18	72
4	20	3	4	3	1.3	93	0.041	17	75
5	20	3	4	4	1	92	0.041	17	77
6	20	3	4	6	0.67	90	0.041	15	81
7	20	3	4	8	0.5	88	0.041	13	82
8	12	5	2	0.01	200	48	0.041	15	41
9	12	5	2	9	0.2	39	0.041	7	88
10	12	5	2	2	1	46	0.041	13	88

Examples 11 to 13

A reactor is used, made of stainless steel of the 316 L type, cylindrical in shape, with an interior diameter of 98 mm, a height of 200 mm and a total capacity of 1500 cm^3. The internal walls of the reactor are coated with a layer of PTFE on millimetre thick.

Stirring is provided by a vertical shaft fitted with a floppy turbine in which the suction is directed towards the bottom. The floppy turbine is 45 mm in diameter, is situated in the middle of the reactor, and is equipped with eight blades.

An axial propeller, 30 mm in diameter and fitted with six tilted blades, is fixed to the end of the vertical shaft near the bottom of the reactor.

The reactor is also fitted with four vertical baffles and with a heat exchanger having a bundle of 8 vertical tubes in which water at 17°C circulates.

The hydrogen and the oxygen are injected into the liquid phase by means of two stainless steel nozzles; their inlets are adjacent and placed near the axial propeller.

The procedure used in the previous examples is repeated, apart from the fact that 700 g of aqueous solution (I) and 6 g of catalyst are used.

The operating conditions and the results obtained in the tests (examples 11 to 13) are collected in Table II.

"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

TABLE II

EXAMPLE	TEMPERATURE (°C)	DURATION (HOURS)	FLOW RATE FOR H_2 INJECTED INTO THE AQUEOUS MEDIUM Sl/h	FLOW RATE FOR O_2 INJECTED INTO THE AQUEOUS MEDIUM Sl/h	RATIO OF H_2/O_2 FLOW RATES, AQUEOUS MEDIUM	FLOW RATE FOR O_2 INJECTED INTO THE CONTINUOUS GAS PHASE Sl/h	RATIO OF H_2/O_2 FLOW RATES, INJECTED TOTAL	H_2O_2 CONCENTRATION OF THE SOLUTION %	SELECTIVITY WITH RESPECT TO H_2 %
11	21	3	120	300	0.4	2850	0.04	20.1	83
12	21	3	80	160	0.5	1760	0.04	15.3	84
13	20	3	80	188	0.42	1760	0.039	16.2	85

CLAIMS

1. Process for the preparation of an aqueous hydrogen peroxide solution in a stirred reactor directly from hydrogen and oxygen, characterised in that hydrogen and oxygen are injected in the form of small bubbles into the lower part of the aqueous reaction medium, which has been rendered acidic by the addition of an inorganic acid and which contains a catalyst in the dispersed state, with flow rates such that the ratio of the molar flow rate for hydrogen to that of oxygen is greater than 0.0416; and in that oxygen is introduced into the continuous gas phase and/or into the upper part of the aqueous reaction medium in an amount such that the molar ratio of hydrogen to oxygen in the continuous gas phase is less than 0.0416.

2. Process according to claim 1, characterised in that the injections of hydrogen and of oxygen in the form of small bubbles into the lower part of the aqueous reaction medium are situated at the bottom of the stirred reactor.

3. Process according to claim 1 or 2, characterised in that the inlets of hydrogen and of oxygen into the lower part of the aqueous reaction medium are adjacent.

4. Process according to any one of claims 1 to 3, characterised in that the reaction medium contains stabilizers for hydrogen peroxide.

5. Process according to any one of claims 1 to 4, characterised in that the reaction medium contains halides.

6. Process according to claim 5, characterised in that the halide is bromide.

7. Process according to claim 6, characterised in that the bromide is used in combination with bromine in the free state.

8. Process according to any one of claims 1 to 7, characterised in that the catalyst contains palladium.

9. Process according to claim 8, characterised in that the catalyst contains platinum.

10. Process according to claim 8 or 9, characterised in that the catalyst is supported.

11. Process according to claim 10, characterised in that the support is chosen from silica, alumina, and silica-alumina combinations.

12. Process according to any one of claims 1 to 11, characterised in that the oxygen introduced into the continuous gaseous phase and/or into the upper part of the aqueous reaction medium contains hydrogen.

13. Process according to any one of claims 1 to 12, characterised in that the oxygen injected in the form of small bubbles into the lower part of the aqueous reaction medium contains hydrogen.

14. Device for the preparation of an aqueous hydrogen peroxide solution directly from hydrogen and oxygen, comprising a stirred reactor fed continuously or non-continuously with working solution, characterised in that the reactor is equipped: with one or more inlet(s) for gaseous hydrogen, in the form of small bubbles, into the lower part of the aqueous reaction medium; with one or more inlet(s) for gaseous oxygen, optionally containing hydrogen, in the form of small bubbles, into the lower part of the aqueous reaction medium; with a pressure regulator which makes it possible to keep the pressure prevailing inside the reactor constant by discharging excess unconsumed gaseous reactants; and with

one or more inlet(s) for gaseous oxygen, optionally containing hydrogen, into the continuous gas phase and/or into the upper part of the aqueous reaction medium, which is/are controlled by an analyser of the gas flow exiting from the reactor so that the molar ratio of hydrogen to oxygen in the continuous gas phase is less than 0.0416.

15. Device according to claim 14, characterised in that the reactor is equipped with an outlet for the extraction of the aqueous hydrogen peroxide solution.

16. Device according to claim 14 or 15, characterised in that the gas flow exiting from the reactor is reinjected into the circuit feeding the lower part of the aqueous reaction medium with oxygen.

17. Device according to claim 14 or 15, characterised in that the gas flow exiting from the reactor, is reinjected, after optional adjustment by addition of oxygen and optionally by removal of hydrogen, into the circuit feeding with oxygen the continuous gas phase and/or the upper part of the aqueous reaction medium.

18. Device according to any one of claims 14 to 17, characterised in that at least one inlet for hydrogen and at least one inlet for oxygen, in the form of small bubbles, are situated at the bottom of the stirred reactor.

19. Device according to one of claims 14 to 18, characterised in that the inlets for oxygen and for hydrogen in the lower part of the aqueous reaction medium are adjacent.

20. Device according to any one of claims 14 to 19, characterised in that the stirring of the reactor is provided by one or more independent impellers or turbines.

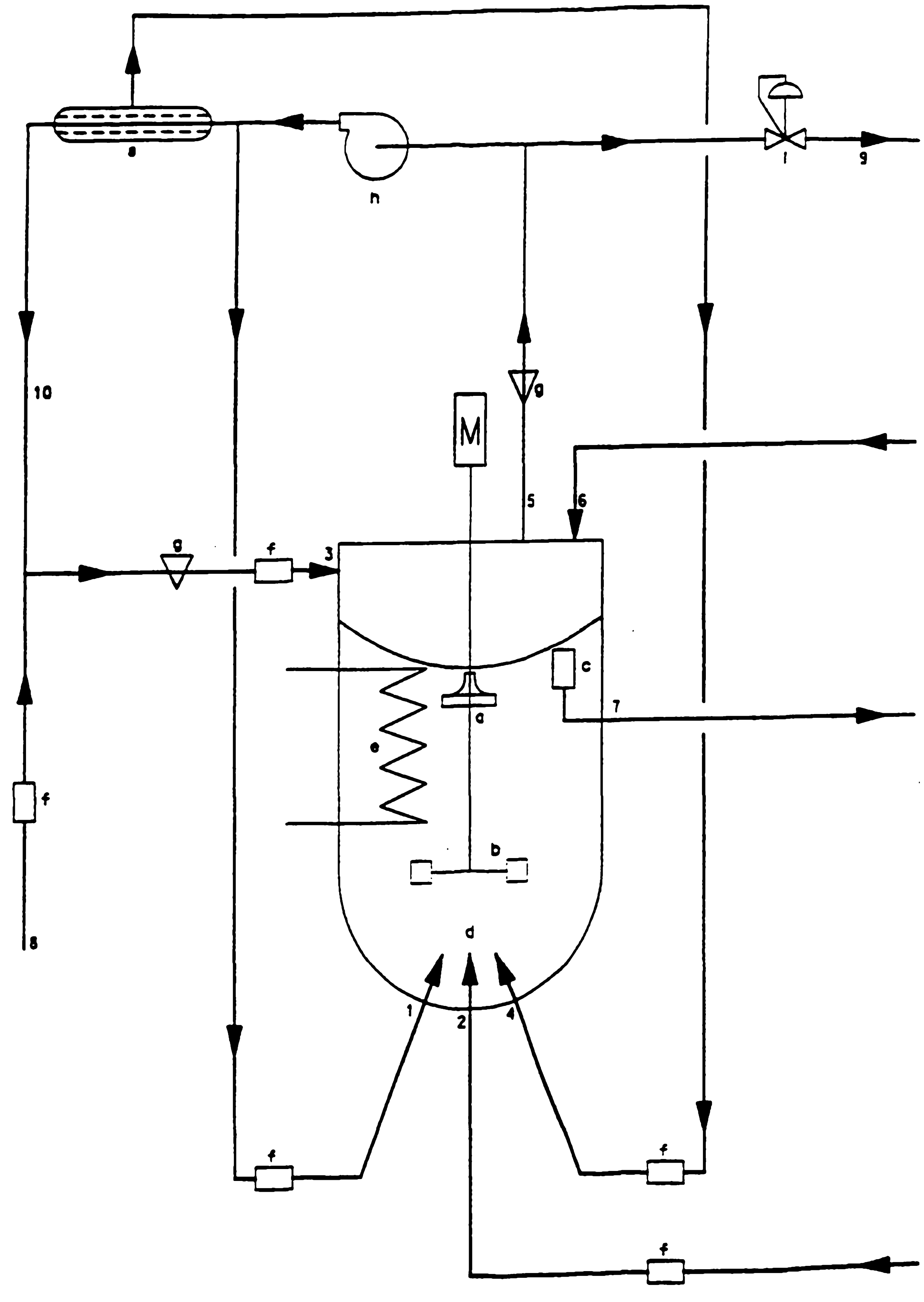
21. Device according to claim 20, characterised in that the turbines are floppy turbines.

22. Device according to claim 20, characterised in that the turbines are self-suction turbines.

23. Device according to any one of claims 14 to 22, characterised in that the stirred reactor is equipped with a heat exchanger.

24. Device according to claim 23, characterised in that the exchanger is a vertical tubular bundle or wound spirals or a bundle of vertical plates positioned radially.

25. Device according to any one of claims 14 to 24, characterised in that all the small bubbles in the aqueous reaction medium rise solely under the influence of gravity to the interface between the aqueous medium and the continuous gas phase when stirring is halted.


n
i
9
10
g
M
5
6
g
f
3
c
a
7
e
f
b
8
d
1
2
4
f
f
f