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Shindo et al.

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[54] **GAS TRANSFER PROCESS WITH HOLLOW FIBER MEMBRANE**

[75] Inventors: **Mizuo Shindo; Takashi Yamamoto,** both of Ootake; **Kensuke Kamada,** Chiba, all of Japan

[73] Assignee: **Mitsubishi Rayon Co., Ltd.,** Tokyo, Japan

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**[3] **B01D 13/00;** B01D 53/22

[52] **U.S. Cl.** **55/16;** 55/158; 210/321.3; 422/48

[58] **Field of Search** ..... 55/16, 158, 159; 210/321 B; 422/44, 48

[56] **References Cited**

U.S. PATENT DOCUMENTS

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1536681	12/1978	United Kingdom	55/159

Primary Examiner—Robert H. Spitzer

Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

A process which comprises allowing a liquid to contact with the inside of a microporous hollow fiber and a fluid to contact with the outside, thereby allowing the gaseous components contained in both fluids to transfer between said liquid and said fluid. For use in the process, the inner diameter of the hollow fiber should be 50 to 5,000μ and the wall membrane should have an average micropore diameter of 0.01 to 0.5μ, a porosity of 10 vol.-% or more, a micropore surface area of 5 m^2/g or more, and an oxygen permeability of 10^{-6} $cm^3(STP)\cdot cm/cm^2\cdot sec\cdot cmHg$ or more. In cases where the liquid is water or a liquid substance with aqueous medium, the process can be used effectively in artificial lung units or the like by using a hollow fiber of a polyolefin or a fluorinated polyolefin.

4 Claims, 1 Drawing Figure

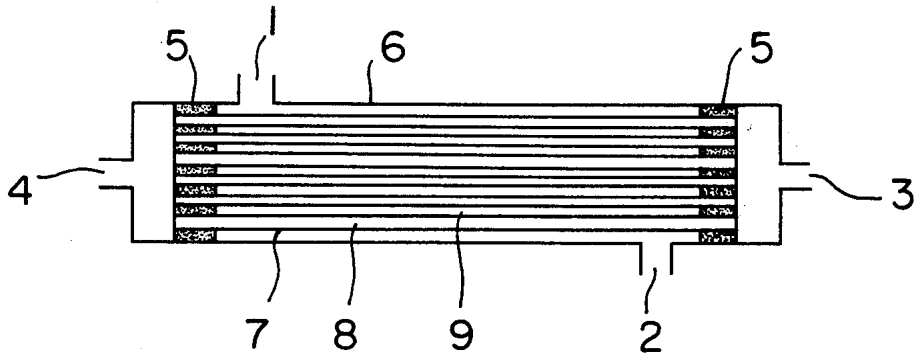


FIG. 1

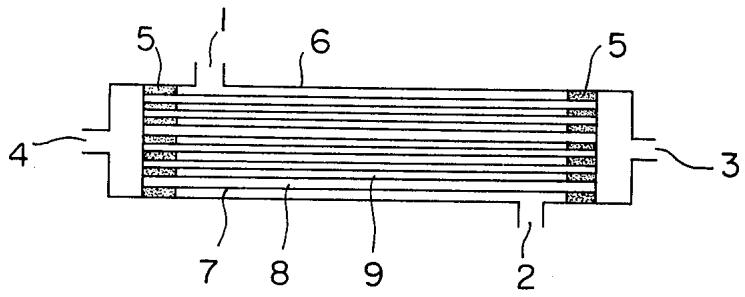
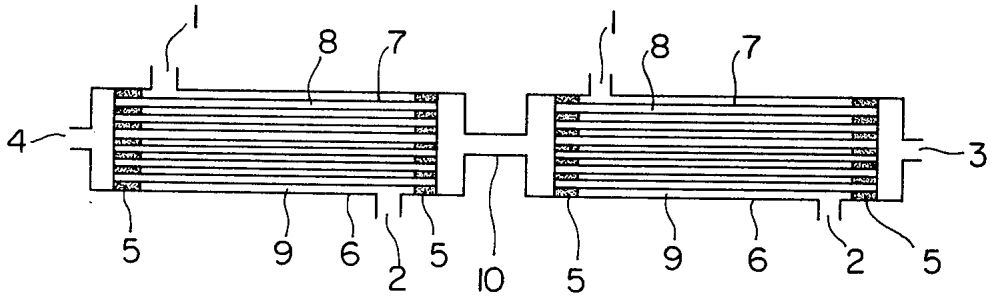


FIG. 2



GAS TRANSFER PROCESS WITH HOLLOW FIBER MEMBRANE

This invention relates to a gas transfer process which comprises contacting a liquid substance with a fluid comprising a gas or a liquid through a separatory membrane of high gas permeability of hollow fibers to allow gaseous substances contained in the fluid to be supplied to or absorbed by said liquid substance or to allow gaseous substances contained in the liquid substance to be discharged into the fluid or to effect simultaneously such supply and discharge. This invention relates also to a device for carrying out such a process, construction materials therefor, and applications of such a process.

For the purpose of supplying or separating specific gaseous components by contacting a fluid with a liquid substance so that the gaseous substances contained in the fluid are chemically or physically absorbed in the liquid substance or, conversely, the gaseous substances contained in the liquid substance are released into the fluid, or these gaseous substances are exchanged between the fluid and the liquid substance, there have been widely used in industries such equipments and methods as bubbling tower, packed tower, plate tower, spray tower, wetted wall tower, bubble cap tower, rotating disks, aeration tank, etc. These systems have merits and demerits and are properly used in accordance with the purpose of use. A disadvantage common to these systems is the small gas-liquid contact surface area per unit volume of the equipment and, hence, it is difficult to make the small equipment and to effect the gas-liquid contact with high efficiency. Moreover, these methods are excluded from some uses where it is necessary to avoid the direct contact between the gas and the liquid.

On the contrary, the gas transfer process with a separatory membrane can eliminate the difficulties mentioned above and provide new uses. An example of using a separatory membrane has been disclosed in British Pat. No. 1,536,681, wherein a silicone tube is used as the gas permeable membrane and water containing gases such as oxygen dissolved therein is passed along the outer surface of the tube while passing a carrier gas through the tube, whereby the gases dissolved in the water is effectively removed. This tubular membrane, however, has disadvantages in that it is insufficient in gas permeability and because of the difficulty in enlarging the contact surface owing to the tubular form of the device, it is difficult to treat efficiently a large volume of substances.

Among typical means for supplying a gas to a liquid substance through a gas permeable separatory membrane, there has been known an artifical lung unit. In conventional artificial lung units of the membrane type, use was made of mainly a film-type membrane of silicone resin which has a comparatively high permeability. In order to increase the membrane area per unit volume of the device, an artificial lung unit comprising a membrane formed of capillary tubes has been disclosed in U.S. Pat. No. 2,972,349. According to the description in said patent, the shaping of said capillary tube membrane required a pains-taking procedure of immersing cores of fine pins in a polymer solution to form a polymer film on the surface of each pin and thereafter extracting the pins, leaving behind a capillary tube membrane. Among various polymer materials cited as suitable, choice was made of silicone rubber in examples of embodiments of the process. It is presumable that in the prior art at that time, the object of investigation was non-porous membranes and silicone rubber was selected because of a higher gas permeability.

On the other hand, with the progress in membrane technology in later years, various porous hollow fiber membranes have been developed and the structures and manufacturing methods of hydrophobic polymers have been disclosed in U.S. Pat. No. 4,020,230 for polyethylene and in U.S. Pat. No. 4,055,696 for polypropylene. When the order of magnitude of oxygen permeability is compared in terms of $cm^3(STP)\cdot cm/sec\cdot cm^2\cdot cmHg$, that of silicone rubber is 10^{-8}, whereas that of polyethylene and polypropylene hollow fibers is as large as 10^{-6}. However, these patents have scarcely disclosed about the gas transfer between fluids.

The present inventors advanced extensive studies on the gas transfer process utilizing these microporous hollow fibers and, as a result, found that in an artificial lung model experiment in which a liquid simultating human blood had been fed into the lumen of hollow fibers, the liquid-phase resistance to transfer of oxygen at the inside of the hollow fibers was extraordinarily large and it is necessary for the construction of a useful artificial lung unit to increase the oxygen permeability of the hollow fiber membrane to an order of magnitude of at least 10^{-6}. This finding was a starting point to accomplish the present invention.

The objects of this invention are to provide a process for the gas transfer between fluids utilizing microporous hollow fibers, particularly an effective process in the application to artificial lung units; a device and materials thereof for use in said process; and the method of manufacturing such a device.

This invention provides a process which comprises using a microporous wall membrane of a microporous hollow fiber as contacting wall membrane and placing a liquid inside the hollow fiber and a fluid outside, thereby allowing the gaseous components to transfer to the inside or outside of the hollow fiber by utilizing transmembrane pressure difference of said gaseous component between the inside and the outside of the hollow fiber. For this purpose, said porous hollow fiber membrane should have

(i) an average micropore diameter in the range of from 0.01 to 0.5μ,
(ii) an internal diameter of the hollow fiber in the range of from 50 to 5,000μ,
(iii) a porosity of the membrane of 10% by volume or more,
(iv) a micropore surface area of the membrane of 5 m^2/g or more, and
(v) an oxygen permeability of the membrane of 1×10^{-6} $cm^3(STP)\cdot cm/cm^2\cdot sec\cdot cmHg$ or more.

The invention is described below in detail.

The method of this invention is a method of gas transfer through a separatory membrane. Therefore, attention must be paid to the fact that the phase of a substance which moves through the membrane is fundamentally different from that in the dialysis or ultrafiltration using a conventional hollow fiber membrane. In the method of this invention, the substance passing through the membrane is in the gas phase even if the fluids contacting through the membrane are liquids. Accordingly, in such a case, the substances moving through the membrane are gaseous components dissolved in a liquid and components which are comparatively volatile. Also, the membrane itself should have such properties that it

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ditions. Non-porous films of common polymers may be said to be substantially gas permeable and liquid impermeable membranes. However, even a silicone film which is highly permeable to gases has a gas permeabil-

not useful for the method of this invention. If the porosity is small, even though the surface area is quite large, the film has pores of small average diameter and it is

ride. Particularly preferred liquids are water and aqueous liquids (liquids with water as medium). The aqueous liquids include aqueous solutions, aqueous dispersions, aqueous colloidal solutions, fluids containing acidic or alkaline compounds, various salts, gaseous substances or organic compounds which are dissolved or dispersed in aqueous media, and body fluids. Other liquids such as alcohols, esters, hydrocarbons, blood and the like may also be used. In the case of liquids having a small contact angle with the material of hollow fibers, difficulties may often be encountered in the operation of the method of this invention such as clogging of micro-

These microporous hydrophobic hollow fibers have a large contact angle against water, being mostly 90° or more. The homopolymers are inherently hydrophobic or difficulty wettable with water and the microporous hollow fibers of these materials function excellently especially when the liquid flowing inside the hollow fibers is water or an aqueous liquid. For instance, when it is intended to render a gas to be absorbed by water or an aqueous liquid, it is not always necessary to keep the flowing gas pressure higher than the pressure in liquid flow channel which is separated by the wall membrane

In FIG. **1**, **1** is a fluid inlet, **2** a fluid exit or inlet, **3** a liquid inlet, **4** a liquid exit, **5** an adhesive, **6** a pressure vessel, **7** a microporous hollow fiber, **8** a liquid channel inside the microporous hollow fiber, and **9** a fluid channel.

The liquid being subjected to gas removal or gas feed treatment is introduced via the liquid inlet **3**. While passing through the lumen of the microporous hollow fiber, the liquid is released of a gaseous component or fed with a gas or subjected to exchange of gaseous components through the microporous wall of the hollow fiber, and finally discharged from the exit **4**. On the other hand, a gas or a fluid containing a gas is introduced via the fluid inlet **1** into the device, passes through the fluid channel **9** outside the microporous hollow fiber **7** in the pressure vessel **6**, and is discharged from the fluid exit **2**.

When the feeding and releasing of gases are carried out simultaneously, the fluid exit **2** serves as the exit for the residual gas in the fluid introduced from the inlet **1** and the fluid containing a gaseous substance released from the liquid. When it is intended only to feed a gas to a liquid, the fluid exit **2** is not necessarily kept fully open but can be partially or completely closed to increase the pressure in the fluid channel for the purpose of feeding the gas more positively and efficiently.

When it is intended only to release the gaseous components from a liquid, a gas is frequently used as the outside fluid. In this case, the fluid inlet **1** serves as the inlet for a carrier gas employed to carry away the released gases. The fluid exit **2** can be connected to either an outside atmosphere at atmospheric pressure or an outside atmosphere under a reduced pressure to promote the release of gaseous components by applying a negative pressure to the fluid channel against the liquid channel.

FIG. **2** is a front sectional view of an example of the device according to this invention to carry out separately the feeding of a gas and the release of a gas by arranging two hollow fiber modules in series. In FIG. **2**, **1** is a fluid inlet or exit, **2** a fluid exit or inlet, **3** a liquid inlet, **4** a liquid exit, **5** an adhesive, **6** a pressure vessel, **7** a microporous hollow fiber, **8** a liquid channel inside the

outside the hollow fiber an absorbent solution for the gaseous components.

The gas-liquid contact device according to this invention has the following characteristic features and the invention can provide an excellent practicable gas transfer process useful in not only industrial fields but also medical treatment devices, e.g. artificial lung.

1. The separatory membrane is microporous and yet has a large gas permeability.

2. Since the microporous membrane is in the form of hollow fiber and its lumen serves as a liquid channel, the surface area of contact with a gas per unit volume of liquid is large.

3. Since the lumen of the hollow fiber is the liquid channel, it is feasible by proper selection of the lumen diameter to reduce the liquid phase resistance by increasing the linear velocity of liquid flow, thereby to increase the efficiency of gas-liquid contact.

4. Particularly when the liquid is water or a liquid with aqueous medium, clogging of the microporous membrane can be minimized by selecting the material of separatory membrane from the inherently hydrophobic polymers such as polyolefins and fluoro polymers; hence, the pressure difference between the liquid channel and the fluid channel can be selected from a wide range.

5. Particularly when the liquid flowing inside or outside the hollow fiber is water or a liquid with aqueous medium and the material of separatory membrane is selected from inherently hydrophobic polymers such as polyolefins and fluoro polymers, it is possible to use a gas absorptive liquid as the liquid flowing either side of the separatory membrane, because there is no fear of intermixing of liquids, thus rendering the gas transfer more efficient.

6. The device is excellent in gas-liquid contact efficiency and can be reduced in size or made compact.

7. The device is low in operational cost and manufacturing cost.

The invention is further illustrated below with reference to Examples.

The gas permeability, surface area and porosity cited in the forgoing description and the following Examples

diameter, having a concentric double tube structure of an annular slit width of 1.5 mm, the extrusion cross-sectional area having been 1.34 cm^2: introduction of air: self-suction; spinning temperature: 205° C.; extrusion rate: 10 g/min.; extrusion linear velocity: 8.27 cm/min.; take-up speed: 500 m/min.; spinning draft: 6046; spinning cylinder: 30 cm in length. The resulting undrawn hollow fiber was then heat treated to increase the crystal orientation by passing over a heated roller at 140° C. while maintaining the fiber length unchanged, the time of contact with the heated roller having been 60 seconds. The heat treated fiber was drawn by 20% between two rollers at room temperature to form a great number of crazes in the hollow fiber wall. The fiber was then hot drawn in 4 steps by passing through 4 slit heaters at 130° C. each disposed between rollers of

refresh the aqueous sodium carbonate solution. After the device had been operated continuously for 24 hours under the above conditions, the removal of hydrogen sulfide in the first module was 80%, indicating that the decline in purifying ability was very little.

EXAMPLE 3

In a manner similar to that in Reference Example, polyvinylidene fluoride having a melt index of 13 g/10 min. (230° C.) was melt spun to obtain a microporous hollow fiber having an outer diameter of 360μ, inner diameter of 300μ, porosity of 32%, surface area of 36 m^2/g, GPR of $2.4\times10^{-5}cm^3(STP)\cdot cm/cm^2\cdot sec\cdot cmHg$, and average pore diameter of 0.036μ. By using the microporous polyvinylidene fluoride hollow fibers ob-

(i) an average micropore diameter in the range of from 0.01 to 0.5μ,

(ii) an internal diameter of the hollow fiber in the range of from 50 to 5,000μ,

(iii) a porosity of the membrane of 10% by volume or more,

(iv) a micropore surface area of the membrane of 5 m^2/g or more, and

(v) an oxygen permeability of the membrane of 1×10^{-6} $cm^3(STP)\cdot cm/cm^2\cdot sec\cdot cmHg$ or more,

and wherein the microporous hollow fiber is polypropylene.

2. A gas transfer process according to claim 1, wherein the liquid inside the hollow fibers is water or a liquid substance with aqueous medium; and the fluid outside the hollow fibers is a gaseous substance or a liquid substance with aqueous medium.

3. A gas transfer process according to claim 1, wherein the liquid inside the hollow fiber is water or a liquid substance with aqueous medium; and the fluid outside the hollow fiber is a gas.

4. A gas transfer process according to claim 1, wherein the liquid inside the hollow fiber is a blood.

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