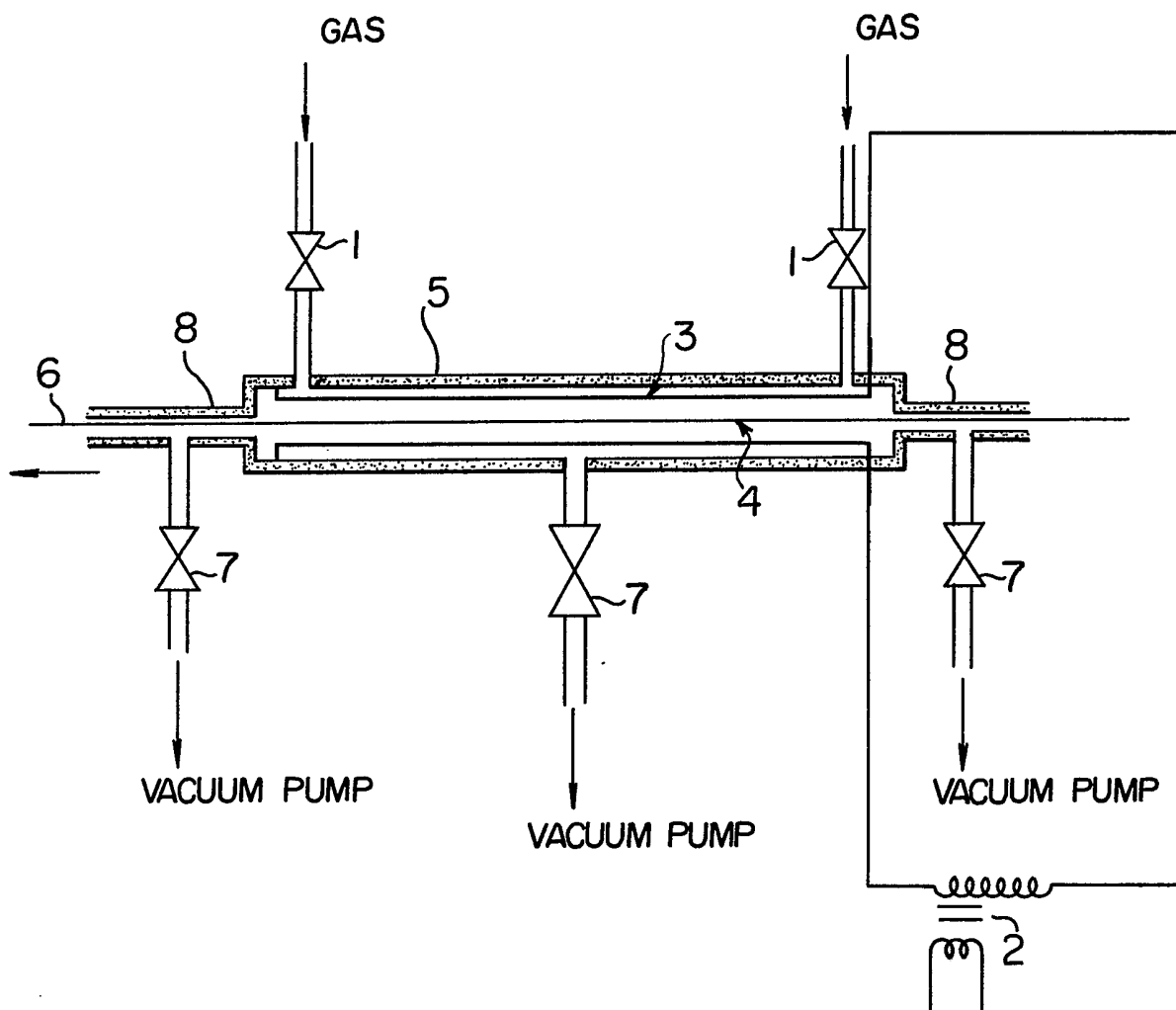


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(54) **Hollow fiber membrane for separating gases and process for producing the same**

(57) A membrane for separating gases is obtained by exposing a porous hollow fiber consisting of polysulphone, polyacrylonitrile, or a copolymer containing 40% by mole or more of acrylonitrile and showing a bubble point of 0.01 kg/cm² or higher and having an air permeating velocity of 1 liter/m²/hour or more under an elevated pressure of 1 kg/cm² to a plasma consisting of a gaseous organic compound, an inorganic gas or a mixture of said gaseous organic compound and inorganic gas at room temperature at 0.01 Torr to 10 Torr either directly or after coating a solution of a polymeric substance on the outer surface of said fiber and drying it.

Figure

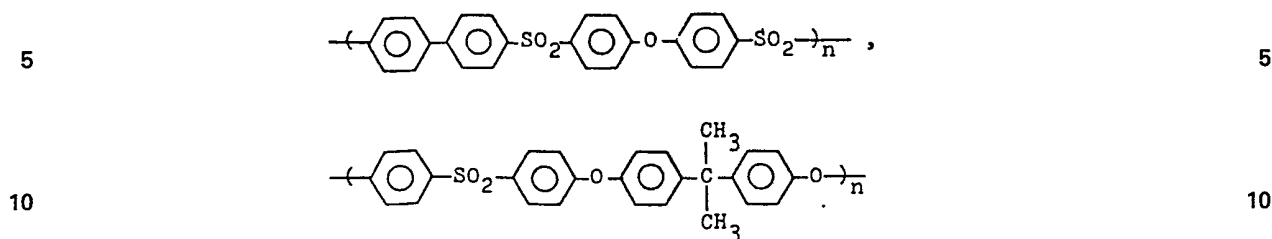


SPECIFICATION

Hollow fiber membrane for separating gases and process for producing the same

- 5 This invention relates to a hollow fiber membrane for separating gases which consists of an acrylonitrile type polymer or polysulfone and has an excellent gas-separating function, and to a process for producing said membrane. More particularly, this invention relates to a novel hollow fiber membrane for separating gases which consists of an acrylonitrile type polymer or polysulfone and has a high mechanical strength, excellent heat and chemical resistances and high performances with regard to selective permeability to
- 10 gases and amount of gas permeation, and to a process for producing said membrane. 10
- As hollow fiber membrane for separating gases actually in use industrially, the Prism membrane constituted of composite polysulfone membrane mentioned in Chemical and Engineering News, May 19 (1980), p. 57 is the substantially only one, which should be said to be quite rare as compared with the extensive practical utilization of cellulose triacetate type hollow fiber membrane (mentioned in, for example,
- 15 Japanese Patent Publication No. 14,215/69), polyamide type hollow fiber membrane (mentioned in, for example, Japanese Patent Publication No. 21,885/71) and others in the reverse osmosis. 15
- Although a few attempts have hitherto been made for producing a hollow fiber membrane from acrylonitrile type polymers (for example, Japanese Patent Application Kokai (Laid-Open) Nos. 6,552 and 18,771/74), they are all nothing more than providing a membrane for ultrafiltration and there is yet known no
- 20 attempt of producing a hollow fiber membrane for separating gases. 20
- In other words, the attempt of producing a high performance hollow fiber membrane for separating gases from acrylonitrile type polymers has scarcely succeeded up to today.
- Polysulfone is a thermoplastic resin readily available, readily moldable and quite stable chemically, mechanically and thermally. For this reason, a number of attempts have been made for producing a
- 25 semi-permeable membrane by the use of polysulfone. However, all these attempts are nothing more than providing a membrane for ultrafiltration or a support of composite membrane, and no attempts have been made for producing a semi-permeable membrane for directly separating gases. 25
- Very many examinations have been conducted for separating gases by the use of polymer membrane, of which examples are too many to enumerate in literature. Further, very many studies have been conducted
- 30 also on the dissolution and diffusion of gases into various polymer membranes, as mentioned in detail in, for example, the review of Nakagawa (Plastics, Vol. 24, No. 12, p. 9). 30
- Nevertheless, a polymer membrane which shows an excellent selective permeability, i.e. separation coefficient, to a special gas and shows a large amount of permeation to a special gas to be let pass through itself on an industrial scale is scarcely known as has been mentioned above. This is only for the reason that
- 35 production of such a membrane is accompanied by a difficulty in the stage of practical application. 35
- Further, it has long been known that the amount of permeation of a gas to be let pass through a polymer membrane is proportional to the area of polymer membrane and the pressure difference between both sides of polymer membrane and inversely proportional to the thickness of polymer membrane used. Therefore, in the industrial production, it is usual to take a measure of giving the membrane a form of hollow fiber in order
- 40 to increase the membrane area per unit volume of apparatus and on the other hand making the membrane quality uneven in order to increase the amount of permeation. However, such a measure has gained an actual success only quite rarely. 40
- From some time past, the present inventors have conducted earnest studies for producing a semi-permeable membrane by irradiating various polymeric substances with plasma and thereby modifying
- 45 only its surface. As the result, there has been found a surprising and important fact that when a porous hollow fiber of acrylonitrile type polymer or polysulfone is irradiated with plasma a very thin and dense crosslinked layer of 1 μ or less is formed on its surface, when this hollow fiber membrane irradiated with plasma is used for reverse osmosis or ultrafiltration it shows a high water permeability and has an enough ability to separate a solute, particularly sodium chloride, from water, and its performances are superior to
- 50 those of cellulose acetate and commercial synthetic polymer membranes. This technique has already been proposed as Japanese Patent Application Kokai (Laid-Open) No. 66,382/79. 50
- Thereafter, with the aim of overcoming the faults in the process for producing hollow fiber membrane for separating gases, the inventors conducted a study also on the plasma irradiation of porous hollow fibers of various polymeric substances. As the result, it was found that a hollow fiber membrane of high
- 55 performances for separating gases can be obtained from porous hollow fiber of acrylonitrile type polymer or polysulfone by specifying the performances of hollow fiber to be irradiated with plasma and the conditions of plasma irradiation. 55
- Thus, the object of this invention consists in providing a novel hollow fiber membrane for separating gases having high performances with regard to selective permeability to gas and amount of gas permeation and a process for producing said membrane characterized by exposing a porous hollow fiber of acrylonitrile
- 60 type polymer or polysulfone to a plasma consisting of a gaseous organic compound or an inorganic gas or a mixture of gaseous organic compound and inorganic gas either directly or after coating the outer surface of said hollow fiber with a solution of a polymeric substance and drying it, and forming a dense crosslinked layer on said surface. 60
- 65 The polysulfone used in the process of this invention preferably has $-\text{SO}_2-$ and aromatic ring as recurring 65

units in main chain and has a high glass transition temperature, and its structure is represented by, for example, the following formulas:



As examples of the commercial polysulfone usable in the process of this invention, Polysulphone (manufactured by UCC Co.), Ucadel (manufactured by UCC Co.), Arylon (manufactured by Uniroyal Co.), Polyethersulfon (manufactured by ICI Co.) and the like can be referred to. 15

The acrylonitrile type polymer used in the process of this invention can be obtained by the well known process. As comonomer constituting a copolymer together with acrylonitrile, well known ones copolymerizable with acrylonitrile can be referred to. Examples of nonionic monomer include acrylamide, diacetoneacrylamide, N-vinyl-2-pyrrolidone, hydroxyethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, vinyl acetate and the like. Acrylonitrile readily forms a copolymer also with ionic monomers. Examples of anionic monomer include acrylic acid, ethylenesulfonic acid, methacrylic acid, methallylsulfonic acid, sulfopropyl methacrylate, vinylbenzenesulfonic acid, and their metallic salts. Examples of cationic monomer include tertiary amines such as 2-vinyl- and 4-vinyl-pyridines, dimethylaminoethyl methacrylate and the like, and quaternary ammonium salts obtained by alkylating 25 them. Acrylonitrile copolymers used herein are copolymers of one or more of these comonomers.

In these copolymers the components of copolymer may be varied arbitrarily. However, if the amount of acrylonitrile in copolymer becomes less than 40% by mole, the mechanical properties of the membrane formed from the copolymer become worse remarkably. Accordingly, the copolymer particularly preferably contains acrylonitrile in an amount of 70 - 95% by mole. 30

The porous hollow fiber used in the process of this invention is not particularly limited in process for its production. However, a porous hollow fiber obtained by a spinning process comprising a step of extruding the polymer solution from usual circular nozzle, a step of evaporating the solvent, a step of coagulation, a step of stretching etc. is particularly suitable. A general process for producing the porous hollow fiber is as follows. Thus, first of all, polyacrylonitrile, an acrylonitrile type polymer or polysulfone is dissolved into a solvent so that the concentration of the polymer comes to 5 - 30% by weight. As the solvent, polar organic solvents such as dimethylacetamide, dimethylformamide, dimethyl sulfoxide, hexamethylphosphoric triamide and the like are preferable. It is also allowable to use a solvent mixture prepared by adding a non-solvent miscible with water in any proportion to said solvents for the purpose of controlling the dissolved state of polymer. In a strict sense, said non-solvent and its amount added should be selected from the viewpoint of solubility parameter depending on what the polymer used is. However, as examples of preferable non-solvent, there can be referred to methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, t-butyl alcohol, ethylene glycol, various polyethylene glycols, glycerine, propylene glycol, 1,4-butanediol, ethanolamine, diethylenetriamine, dipropylene glycol, formamide, formic acid, propionic acid, butyric acid, acetone, diacetone alcohol, acetonitrile, dioxane, tetrahydrofuran, γ -butyrolactone, ethylene cyanhydrin, ethylene chlorohydrin and the like. 45

In the case of polyacrylonitrile or acrylonitrile type copolymers, it is also possible to use a concentrated aqueous solution of inorganic salt such as sodium thiocyanate, zinc chloride and the like as an inorganic solvent.

The step for spinning the porous hollow fiber from the solution of acrylonitrile type polymer or polysulfone thus prepared is preferably carried out according to a step which comprises spinning the fiber by the usual wet spinning process with a nozzle for hollow fiber, partially evaporating the solvent while keeping an appropriate space distance, then coagulating the spun fiber in water or water-organic solvent mixture as a non-solvent and winding up it. Stretching may also be carried out optionally. 50

As the nozzle for hollow fiber, the so-called double-tube nozzle is usually employed. Water may be passed through the inner tube as a coagulating solution, or the inner tube may be filled with an inorganic gas. As the coagulating solution in the inner tube, a solvent mixture of water and organic solvent may be used without any trouble, so far as it is a non-solvent. 55

The starting porous hollow fiber used in this invention must satisfy the following performances in a dry state, regardless of the material from which it is made and the process by which it is made. Thus, it must have a bubble point of 0.01 kg/cm² or more and an air permeation rate of 1 liter/m²/hour or more under an elevated pressure of 1.0 kg/cm². Those having a bubble point of 1.0 kg/cm² or more are particularly preferable. As used herein, the term "bubble point" has the following meaning: in a system comprising water and air which are separated from each other by a membrane, a pressure at which the air begins to enter the water through the membrane when pressure on the air is slowly increased. 60

For producing a porous hollow fiber satisfying these performances, various conditions such as 65

concentration of polymer, temperature of doping solution, temperature of atmosphere, a time period for evaporating the solvent, space distance, composition of coagulating bath, temperature of coagulating bath, stretch ratio, and so on must be controlled. More particularly, it is preferable to select a polymer concentration of 5 - 30% by weight, a doping solution temperature of 5 - 100°C, an evaporation time of 0 - 60 seconds, an atmosphere temperature ranging from 5°C to the boiling point of solvent, a space distance of 0 - 1,000 mm, a coagulating bath temperature of 0 - 50°C and a stretch ratio falling in the range of 1 - 5.

So far as the starting hollow fiber has no defect, it can be used for the plasma irradiation of this invention if it satisfies the above-mentioned conditions. However, the essential point of this invention consists in controlling the performances of the final product as a membrane for separating gases by changing the conditions of plasma irradiation. As a rule, a hollow fiber of dry state is used in the plasma irradiation.

Hereunder, the method of plasma irradiation for controlling the gas-separating performances which is the essential point of this invention will be mentioned in more detail.

It is well known that, in the permeative separation of gases, the dissolution or adsorption of gas into the surface layer of polymer membrane constitutes the first step and subsequently the diffusion process of the gas dissolved therein through the pores of porous hollow fiber constitutes the second step as have been mentioned above.

Accordingly, it can be expected that, if a thin film of a polymeric substance promoting the dissolution or adsorption of gas or, in other words, a thin film of a polymeric substance exhibiting a high solubility or a high adsorbability to a particular gas is formed on the surface layer part of porous hollow fiber, separation and concentration of the gas will be practicable easily.

From such a point of view, the inventors treated a porous hollow fiber of acrylonitrile type polymer or polysulfone with a plasma of gaseous organic compound and/or inorganic gas and succeeded in forming a thin film of a crosslinked polymer having a skeleton resembling that of said organic compound in the surface layer of said hollow fiber. Based on this success, this invention was accomplished.

Accordingly, it is considered that this invention is applicable not only to acrylonitrile type polymers and polysulfones but also to all the elementary materials from which porous hollow fiber can be produced, such as polyamide and the like.

The outlined view of one example of the plasma-irradiating apparatus used in the process of this invention is shown in the drawing, wherein 1 and 7 are cocks; 2 is neon transformer; 3 and 4 are electrodes; 5 is reaction vessel; 6 is hollow fiber as a sample; and 8 is preliminary vacuum chamber.

As used in this invention, the term "plasma" means a plasma formed by glow discharge, corona discharge or the like. For example, a plasma by glow discharge is generated by introducing an organic compound in gaseous state, an inorganic gas or in the state of gaseous mixture consisting of organic compound and inorganic gas into the evacuated vessel 5 shown in the drawing so that the pressure in said vessel comes to 0.01 - 10 Torr and applying an alternating current voltage or direct current voltage of 0.5 - 50 kilovolts between electrodes 3 and 4 by means of neon transformer 2.

In the case of industrial production, it is preferable to provide a preliminary vacuum chamber 8 composed of capillary tubes. It is also possible to form a plasma by generating a corona discharge in the atmospheric air or in the atmosphere of inorganic gas. In this case, the production of membrane is more easy to practice industrially. Plasma treatment is preferably carried out at room temperature e.g. 15°-25°C.

As the gaseous organic compound used in the process of this invention, any gaseous materials can be used so far as they have an ability to form a non-volatile film in the atmosphere of plasma. Examples of said gaseous organic compound include saturated hydrocarbons and their halides such as methane, ethane, propane, cyclohexane, methyl chloride and the like; unsaturated hydrocarbons and their halides such as ethylene, propylene, 4-methyl-pentene-1, butadiene, isoprene, vinyl chloride, tetrafluoroethylene and the like; aromatic hydrocarbons such as benzene, toluene and the like; vinyl compounds such as acrylonitrile, acrylic acid, methyl methacrylate, glycidyl methacrylate, sulfopropyl methacrylate, vinyl acetate, allyl alcohol, allylamine, 4-(or 2-)vinylpyridine, vinyl alkyl ethers, acrylamides and the like; alcohols such as methanol, ethanol and the like; esters such as ethyl acetate and the like; ethers such as diethyl ether, methyl ethyl ether and the like; ketones such as acetone, methyl ethyl ketone and the like; carboxylic acids such as acetic acid and the like; amines such as diethylamine, ethylenediamine and the like; heterocyclic compounds such as ethyleneimine, pyridine, 4-ethylpyridine, 2,6-dimethylpyridine, ethylene oxide, N-methylpyrrolidone and the like; siloxanes such as dimethyl siloxane and the like; silane compounds such as tetramethylsilane and the like; and mixtures thereof. Among them, those suitable for the practice of this invention are unsaturated organic compounds having double bond such as acrylonitrile, acrylic acid, 4-(or 2-)vinylpyridine, allylamine, vinyl acetate, allyl alcohol, glycidyl methacrylate, sulfopropyl methacrylate, vinyl alkyl ethers, acrylamides, tetrafluoroethylene and the like; saturated organic compounds such as methane, ethane, propane and the like; silane compounds such as tetramethylsilane and the like; and cyclic organic compounds having hetero atom (for example, nitrogen, oxygen or the like) such as pyridine, 4-ethylpyridine, 2,6-dimethylpyridine, ethylene oxide, N-methylpyrrolidone, ethyleneimine and the like.

As used herein, the term "inorganic gas" means helium, argon, nitrogen, oxygen, carbon monoxide, carbon dioxide, ammonia or the like.

These plasmas are quite poor in the property of passing through materials, so that they are suitable for modifying only the surface of porous hollow fiber of acrylonitrile type polymer or polysulfone to give it a semi-permeability to gases. The action of plasma on polymeric substances may generally be considered as

comprising crosslinking, polymerization, etching and closure of pores.

The gas-separating characteristics of the hollow fiber membrane for separating gases obtainable by the process of this invention are determined by controlling various factors, among which time period of irradiation and dosage of irradiation are important. By varying them, the extent of surface crosslinkage, the velocity of polymerization, the amount of etching and the extent of pore closure can be controlled and a membrane having arbitrary gas-separating characteristics can be obtained.

Further, the kind of organic compound to be formed into plasma also exercises a determinative effect on the gas-separating characteristics of the membrane of this invention. When separation or concentration of gases is discussed, the solubility and adsorbability of gas into the crosslinked polymer obtainable by the plasma polymerization of the organic compound introduced into the reaction system in this invention or the co-crosslinked product between said organic compound and hollow fiber of acrylonitrile type polymer or polysulfone are important factors. According to this invention, these factors can easily be controlled by appropriately selecting the kind of organic compound to be formed into plasma.

In other words, when it is intended to pass only a particular gas, such a passage can be realized by selecting the organic compound introduced into the system so that it gives a plasma polymer into which said gas can dissolve easily or be adsorbed easily. Though the plasma polymer herein referred to is greatly different from the organic compound used in the chemical structure, there is no great difference between them in the fundamental elementary constitution and functional group structure, so that the design of membrane necessary to the separation and concentration of particular gas can be practised by the aid of the existing data. For example, the values of gas permeability constants of various polymer membranes mentioned in "Zairyo to Suibun Handbook" (Handbook of Materials and Moisture), edit. by Kobunshi Gakkai, publ. by Kyoritsu Shuppan (1968) are suitable for this purpose.

For example, for the permeation of oxygen gas, silane compounds, siloxanes such as dimethyl siloxane and the like, hydrocarbons such as 4-methylpentene-1, butadiene, isoprene and the like, esters, ethers, carboxylic acids and the like are preferable; for the permeation of nitrogen gas, halogenated hydrocarbons such as vinyl chloride, methyl chloride and the like, hydrocarbons such as butadiene, isoprene and the like, and nitrogen-containing compounds such as diethylamine, ethylenediamine and the like are preferable; for the permeation of helium gas, acrylonitrile, vinyl acetate, acetic acid, hydrocarbons such as ethylene, propylene and the like, and halogenated hydrocarbons are preferable; for the permeation of hydrogen or hydrocarbons such as methane, ethylene and the like, various hydrocarbons are preferable; and the permeation of carbon dioxide or sulfurous acid gas, siloxanes and hydrocarbons such as butadiene, isoprene, ethylene, 4-methylpentene-1 and the like are preferable.

As has been mentioned above, the characteristic feature of the production process of this invention consists in that only the vicinity of the surface of porous hollow fiber made of acrylonitrile type polymer or polysulfone is crosslinked or its pores are closed to produce a dense layer by utilizing the small ability of plasma to pass through materials, and further in that a thin film having a new chemical structure not found in substrate is formed in the vicinity of surface of said hollow fiber by causing a plasma polymerization of organic compound, and in that a crosslinked dense layer having a thickness of 1 μ or less can easily be formed on the outer surface of hollow fiber according to this new technique. Accordingly, unlike the casting process, this technique is by no means accompanied by difficulty in forming the active skin layer.

On the other hand, if the hollow fiber to be irradiated with plasma in the process of this invention is previously coated with a solution of polymeric substance and dried and then irradiated with plasma, the process of this invention can be practised more effectively. As the polymeric substance used therefor, anything may be used without particular restriction so far as it can form a thin film from a state of solution on the outer surface of porous hollow fiber of acrylonitrile type polymer or polysulfone. The polymeric substance is not limited in molecular weight, too. That is to say, it may be a liquid oligomer, and it also includes substances non-volatile at ordinary temperature under a pressure of 0.01 Torr, of course.

Examples of said polymeric substance include polyethylene, polypropylene, polyisoprene, polybutadiene, polychloroprene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyacrylic esters, polymethacrylic esters, polyethylene terephthalate, polybutylene terephthalate, nylon-6, nylon-6.6, polyacetal, cellulose esters, polysulfone, polyphenylene oxide, copolymers and blends containing them as main component, and the like, though they are not limitative.

If a thin film of polymeric substance is formed on a porous hollow fiber of acrylonitrile type polymer or polysulfone by merely coating a solution of the polymeric substance thereon, it is quite difficult to form a thin film having a small and uniform thickness and showing a sufficient amount of gas permeation in the separation and concentration of gases. However, if an irradiation with plasma is used in combination as in this invention, formation of thin film and its uniformization become easier owing to the etching action and pore-closing action of plasma. The concentration of the solution of polymeric substance is not particularly limited, and a concentration capable of forming a thin film of 0.1 - 10 μ on the porous hollow fiber is enough for the purpose.

As has been mentioned above, according to the process of this invention, a novel hollow fiber membrane for separating gases having a high mechanical strength, being excellent in heat and chemical resistances, retaining a high pressure resistance and having high performances with regard to selective permeability to gas and amount of gas permeation can be obtained from a porous hollow fiber of acrylonitrile type polymer or polysulfone. Further, since the solubility and adsorbability of gases into the vicinity of surface can be

varied in a wide range by the plasma irradiation of the porous hollow fiber of acrylonitrile type polymer or polysulfone of this invention, the scope of application of the gas-separating membrane of this invention becomes very wide.

Accordingly, the hollow fiber membrane obtained by the plasma irradiation of this invention can be applied quite effectively to the separation and concentration of hydrogen, nitrogen, oxygen, helium, argon, neon, carbon dioxide, carbon monoxide, hydrogen sulfide, sulfuric acid gas, nitrogen dioxide, methane, ethane, propane, ethylene, propylene, butylene and other low molecular weight gaseous compounds, as well as to separation of a gas from gas-liquid mixture and to other objects.

In general, the method of forming a semi-permeable membrane into a hollow fiber and thereby increasing the packing quantity of the membrane per unit space is a technique well known in the field of reverse osmosis. However, the forming of such hollow fiber requires a high technique, so that its successful case is quite rare.

This invention has made it possible for the first time by combining conventional wet spinning with plasma irradiation, so that it should be said to be just epoch-making.

This invention will be illustrated more concretely with reference to the following examples which are presented in no limitative way.

Example 1

A doping solution was prepared by dissolving 25 parts of a copolymer ($[\eta] = 1.40$, in dimethylformamide at 25°C) consisting of 89% by mole of acrylonitrile and 11% by mole of vinyl acetate into a solvent mixture consisting of 67.3 parts of dimethylformamide and 7.7 parts of formamide.

Then, the doping solution was spun by extruding it from usual double tube nozzle by the wet process to obtain a porous hollow fiber having an outer diameter of 440 μ , an inner diameter of 160 μ , an air permeation velocity of 15.2 liters/m²/hour (LMH) in a dry state under an elevated pressure of 1.0 kg/cm², a bubble point of 18.0 kg/cm² and a hole size increasing from the outer side toward the inner side as observed by means of electron microscope.

It was continuously passed through an evacuated vessel shown in the drawing while winding it up at one side at a constant speed, and irradiated with tetramethylsilane-oxygen plasma (volume ratio 50/50). Thus, first of all, this gaseous mixture was introduced from cock 1, and cocks 1 and 7 were regulated so as to give a pressure in system of 0.1 Torr. Thereafter, an alternating current voltage of 1.45 KV was applied between electrodes 3 and 4 by means of neon transformer 2, and irradiation with plasma was carried out for 20 minutes. (The winding device was operated so that the residence time of membrane in the plasma zone became 20 minutes.)

The membrane thus obtained was cut into 40 cm pieces, and 20 pieces were bundled and bent into U-form. After running the open end through the hole provided at the center of flange and bonding it with epoxy resin, the whole was set on the pressure vessel of an air-separating test apparatus conventionally used in laboratory to perform an air permeation test at room temperature under an elevated pressure of 10 kg/cm².

In the permeation test, the amount of permeating gas flow was measured by withdrawing it from the central cavity to the outside of system, and its composition ratio was analyzed, in order to evaluate the gas permeating performances.

In this experiment, the amount of permeation of the permeating gas was found to be 422 LMH and the oxygen concentration in the gas after permeation was found to be 39% by volume, demonstrating that the plasma-irradiated membrane obtained in this example was excellent in selective permeability and amount of permeation.

Example 2

A doping solution was prepared by dissolving 27 parts of a copolymer ($[\eta] = 1.46$, in dimethylformamide at 25°C) consisting of 90% by mole of acrylonitrile and 10% by mole of methyl acrylate into a solvent mixture consisting of 58 parts of dimethylformamide and 15 parts of dioxane.

Then this doping solution was spun by extruding it from conventional double tube nozzle by the wet process to obtain a porous hollow fiber having an outer diameter of 350 μ , an inner diameter of 100 μ , an air permeation velocity of 37.0 LMH in a dry state under an elevated pressure of 1.0 kg/cm², a bubble point of 17.4 kg/cm² and a hole size increasing from the outer side toward the inner side as observed by means of electron microscope.

It was continuously passed through an evacuated vessel shown in the drawing and irradiated with tetrafluoroethylene plasma for 2 minutes in the same manner as in Example 1 under a pressure of 0.10 - 0.14 Torr by applying an alternating current voltage of 1.40 KV between electrodes 3 and 4.

The membrane thus obtained was cut into 40 cm pieces, 20 pieces were bundled, and a permeation test to natural gas containing 0.76% by mole of helium was carried out with the same apparatus as in Example 1 at room temperature under an elevated pressure of 10 kg/cm².

In this experiment, the amount of permeation of the permeating gas was found to be 295 LMH and the concentration of helium in the gas after permeation was found to be 3.50% by mole.

In another run, a sample only subjected to drying and not irradiated with plasma was similarly tested. The amount of permeation of natural gas was 135 LMH, and the helium was not concentrated.

Example 3

The porous hollow fiber obtained in Example 1 was continuously introduced into a bath consisting of an acetone solution containing 3% by weight of ethyl cellulose to coat the solution on the surface of said hollow fiber, after which the acetone was evaporated off with a hot air flow of 50°C.

5 Then it was continuously passed through an evacuated vessel shown in the drawing and irradiated with oxygen plasma for 20 minutes in the same manner as in Example 1 under a pressure of 0.1 Torr by applying an alternating current voltage of 1.40 KV between electrodes 3 and 4. 5

The membrane thus obtained was subjected to an air permeation test just in the same manner as in Example 1.

10 In this experiment, the amount of permeation of the permeating gas was found to be 285 LMH and the oxygen concentration in the gas after permeation was 43% by volume. 10

In another run, a sample not irradiated with plasma (only coated with ethyl cellulose and then dried) was similarly tested. As the result, the amount of permeation of gas was as small as 42 LMH, and oxygen was not concentrated.

15 *Example 4* 15

A yarn which had been spun by the same process as in Example 1 was continuously passed through an evacuated vessel shown in the drawing and irradiated with helium plasma. The irradiation was carried out under the following conditions: pressure in system 0.1 Torr, applied voltage 1.1 KV, time period of irradiation 20 2 minutes. The membrane thus obtained was set on a pressure vessel by the same method as in Example 1, and a permeation test to a gaseous mixture of methane and hydrogen (methane/hydrogen = 1/1) was performed at room temperature under an elevated pressure of 5 kg/cm². 20

In this experiment, the amount of permeation of the permeating gas was found to be 83 LMH, and the proportion of methane in the gas after permeation was 13%. In another run, a membrane not irradiated with plasma was similarly tested to find that the amount of permeation was 30 LMH and the proportion of methane in the gas after permeation was 42%. 25

Example 5

A doping solution was prepared by dissolving 22% by weight of commercial polysulfone P-1700 (manufactured by UCC Co.) into a solvent mixture consisting of 75% by weight of dimethylformamide and 3% by weight of formamide. 30

Then this doping solution was spun by extruding it by the wet process from conventional double tube nozzle to obtain a porous hollow fiber having an outer diameter of 190 μ, an inner diameter of 45 μ, an air permeation velocity of 12.3 liters/m²/hour (LMH) in a dry state under an elevated pressure of 1.0 kg/cm², a bubble point of 18.0 kg/cm² and a hole size increasing from the outer side toward the inner side as measured by means of electron microscope. 35

It was continuously passed through an evacuated vessel shown in the drawing and irradiated with tetramethylsilane-oxygen plasma (volume ratio 50/50). The conditions of irradiation were the same as in Example 1.

40 By the same method as in Example 1, its performances for gas permeation were measured. As the result, the amount of permeation of the permeating gas was 230 LMH and the oxygen concentration in the gas after permeation was 37% by volume, demonstrating that the plasma-irradiated membrane obtained in this example had excellent selective permeability and amount of permeation. 40

45 *Example 6* 45

A doping solution was prepared by dissolving 23% by weight of commercial polysulfone P-1700 (manufactured by UCC Co.) into a solvent consisting of 77% by weight of dimethylformamide.

Then this doping solution was spun by extruding it through conventional double tube nozzle by the wet process to obtain a porous hollow fiber having an outer diameter of 180 μ, an inner diameter of 43 μ, an air permeation velocity of 8.5 LMH in a dry state under an elevated pressure of 1.0 kg/cm², a bubble point of 20.0 kg/cm² and a hole size increasing from the outer side toward the inner side as observed by means of electron microscope. 50

It was continuously passed through an evacuated vessel shown in the drawing and irradiated with tetrafluoroethylene plasma for 2 minutes in the same manner as in Example 1 under a pressure of 0.10 - 0.14 Torr by applying an alternating current voltage of 1.40 KV between electrodes 3 and 4. 55

The membrane thus obtained was cut into 40 cm pieces, 20 pieces were bundled, and a permeation test to natural gas containing 0.76% by mole of helium was performed at room temperature under an elevated pressure of 10 kg/cm² with the same apparatus as in Example 1.

In this experiment, the amount of permeation of the permeating gas was 193 LMH and the concentration of helium in the gas after permeation was 2.80% by mole. 60

In another run, a sample not irradiated with plasma (a sample only dried) was similarly tested. As the result, the amount of permeation of natural gas was 118 LMH and helium was not concentrated.

Example 7

The porous hollow fiber obtained in Example 5 was continuously introduced into a bath consisting of an acetone solution containing 3% by weight of ethyl cellulose to coat the solution on the surface of said hollow fiber, after which the acetone was evaporated off with hot air flow of 50°C.

- 5 Then it was continuously passed through an evacuated vessel shown in the drawing and irradiated with oxygen plasma for 20 minutes in the same manner as in Example 1 under a pressure of 0.1 Torr by applying an alternating current voltage of 1.40 KV between electrodes 3 and 4. 5

The membrane thus obtained was subjected to an air permeation test just in the same manner as in Example 1.

- 10 In this experiment, the amount of permeation of the permeating gas was found to be 216 LMH and the concentration of oxygen in the gas after permeation was found to be 40% by volume. 10

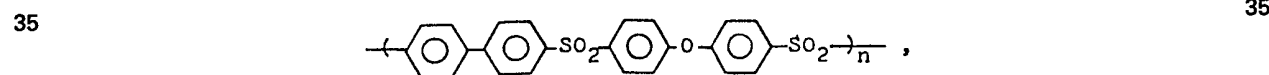
In another run, a sample not irradiated with plasma (a sample only coated with ethyl cellulose and dried) was similarly tested. As the result, the amount of permeation of the gas was as small as 35 LMH and oxygen was not concentrated.

- 15 CLAIMS 15

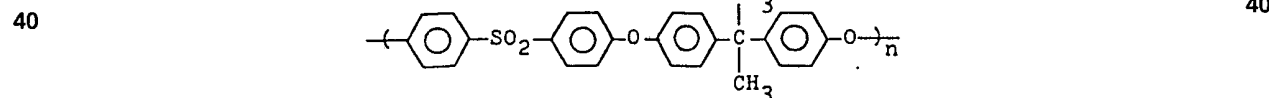
1. A process for producing a membrane for separating gases which comprises exposing a porous hollow fiber consisting of polyacrylonitrile or a copolymer containing 40% by mole or more of acrylonitrile or a polysulphone, showing a bubble point of 0.01 kg/cm² or higher and having an air permeating velocity of 1 liter/m²/hour or more under an elevated pressure of 1 kg/cm² to a plasma consisting of a gaseous organic compound, an inorganic gas or a mixture of said gaseous organic compound and inorganic gas at 0.01 Torr to 10 Torr either directly or after coating a solution of a polymeric substance on the outer surface of the fiber and drying it. 20

- 25 2. A process according to claim 1 wherein said copolymers containing 40% by mole or more acrylonitrile are those comprising acrylonitrile and one or more components selected from nonionic monomer including acrylamide, diacetoneacrylamide, N-vinyl-2-pyrrolidone, hydroxyethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and vinyl acetate; anionic monomer including acrylic acid, ethylenesulfonic acid, methacrylic acid, methallylsulfonic acid, sulfopropyl methacrylate, vinylbenzenesulfonic acid, and their metallic salts; and cationic monomer including tertiary amines such as 2-vinyl and 4-vinyl pyridines, dimethylaminoethyl methacrylate, and quaternary ammonium salts obtained by alkylating the tertiary amines. 30

3. A process according to claim 1 wherein said polysulfone is one represented by the following formulae:



or



- 45 4. A process according to any one of the preceding claims wherein the plasma is generated by flow discharge. 45

5. A process according to any one of the preceding claims wherein said gaseous organic compounds are selected from unsaturated organic compounds having double bond such as acrylonitrile, acrylic acid, 4-(or 2-)vinylpyridine, allyloamine, vinyl acetate, allyl alcohol, glycidyl methacrylate, sulfopropyl methacrylate, vinyl alkyl ethers, acrylamides, tetrafluoroethylene and the like; saturated organic compounds such as methane, ethane, propane and the like; silane compounds such as tetramethylsilane and the like; and cyclic organic compounds having at least one hetero atom (for example, nitrogen, oxygen or the like) such as pyridine, 4-ethylpyridine, 2,6-dimethylpyridine, ethylene oxide, N-methylpyrrolidone, ethyleneimine and the like. 50

- 55 6. A process according to any one of the preceding claims wherein said inorganic gases are selected from helium, argon, nitrogen, oxygen, carbon monoxide, carbon dioxide and ammonia. 55

7. A process according to any one of the preceding claims wherein said polymeric substance is selected from polyethylene, polypropylene, polyisoprene, polybutadiene, polychloroprene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyacrylic esters, polymethacrylic esters, polyethylene terephthalate, polybutylene terephthalate, nylon-6, nylon-6.6, polyacetal, cellulose esters, polysulfone, polyphenylene oxide, their copolymers and blends containing them as main component. 60

8. A process for producing a membrane for separating gases according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

9. A process for separating gases which comprises bringing a mixture of at least two gases or a gas/liquid mixture into contact with a membrane obtained by a process according to any one of the 65

preceding claims or a membrane according to claim 11.

10. A process according to claim 9 substantially as hereinbefore described with reference to any one of the Examples.

11. A hollow fiber membrane for separating gases comprising an acrylonitrile type polymer or
5 comprising a polysulfone.

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