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(54) SEMIPERMEABLE MEMBRANES AND
METHOD FOR PRODUCING SAME

(71) We, ASAHI KASEI KOUYO KABUSHIKI KAISHA, a Japanese Body Corporate, of 2-6 Dojima-hama 1-chome (formerly 25-1, Dojimahamadori-1-chome), Kitaku, Osaka, Japan do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to semipermeable membranes for ultrafiltration and microfiltration. More particularly it relates to preparation of semipermeable membranes containing a gradient type porous layer (or region) wherein the specific property of molecular weight fractionation of the semipermeable membranes i.e. the size of pores of mesh structure of the semipermeable membranes is freely convertible, and also to semipermeable membranes having a characteristic structure, obtained by said preparation.

A method for separation which uses a semipermeable membrane can be carried out with much lower energy cost and easiness of operation as compared with other separation methods such as evaporation method, ion-exchange membrane method, adsorption method and the like, and hence it has recently come into actual utilization for the purpose of the improvement of separation steps and waste water treatment in wide application fields such as food industry, pharmaceutical industry, electronics industry, paint industry, mechanical industry, chemical industry and the like. The substances to be treated in these application fields include various kinds of materials from low molecular weight substances to high molecular weight substances e.g. salts, proteins, viruses, colloids, emulsions, polymer lattices, and several kinds of semipermeable membranes have already been sold on market with the object of carrying out separation efficiently depending upon the materials to be separated. However, fractions of molecular weight separable by a semipermeable membrane, i.e. pore sizes are determined depending upon the composition of membrane-forming solution, coagulation condition, condition of heat treatment after coagulation, etc., and thus it is the present status of art that the variable range of pore sizes of semipermeable membrane of the same raw material is extremely narrow when the membrane-forming property and the strength of membrane are taken into consideration. Accordingly, semipermeable membranes of the same raw material used for membrane have limited utilization fields, and semipermeable membranes of various kinds of membrane raw materials must be prepared depending upon the materials to be separated. Further, there are membranes which are not useful in a certain relationship between membrane raw material and material to be separated, or in case where a membrane must be replaced by a membrane of other raw material on account of the difference of only molecular weight of a material to be separated even though other compositions are same, it may be often necessary to control substances to be separated, to the useful condition suitable for membrane raw material. Such a limitation not only makes separation operation complicated, but also produces a limitation to the useful amount of the membrane of same raw material, resulting in increase of price of the membrane on this account. Furthermore the necessity of change of the method of use depending upon the raw material also increases separation cost. As above-explained, infeasibility of optional change in pore sizes of semipermeable membrane of same raw material has been a serious factor hindering the popularization of membrane separation method having the above-mentioned superior characteristic features.

In order to overcome the drawback of the narrow variable range of pore sizes in

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semipermeable membrane, we have been earnestly endeavoring with the aim of enlarging the variable range of pore sizes, and as a result have developed an art capable of changing the pore sizes of raw material in a wide range and yet optionally, and have prepared a semipermeable membrane according to the art, and also have made it possible to treat 5 various kinds of substances to be treated, with a semipermeable membrane of same membrane raw material and to provide a membrane raw material most suitable to substances to be treated.

At the present time, the membrane having a porous layer of reticulate structure which becomes denser as it approaches the membrane surface, namely the membrane which has a 10 nearly uniform pore size in the places equidistant from the membrane surface, and wherein the pore size on the membrane surface is minimum and pore sizes become greater continuously toward the inside of the membrane, has been known as an ultrafiltration membrane or microfiltration membrane having superior filtration characteristic properties. Since such a porous layer has been called a gradient type porous layer, such a porous layer 15 will be referred to herein also that way.

Further, such a gradient type porous layer is not present alone. A membrane having, in succession to the gradient type porous layer, a reticulate layer which has uniformly pore sizes equal to or greater than the maximum pore size of the gradient porous layer, or in 20 which its minimum pore size is equal to the maximum pore size of the gradient type porous layer, has been known as an improved membrane possessing good permeability in spite of its high membrane strength. The size of mesh of the reticulate layer existing in succession to the gradient type porous layer is generally in the range of 500Å - 1μ, and it has been also known that if voids having a major axis in the direction perpendicular to the membrane surface and also having a large size are introduced in the reticulate layer, better 25 permeability can be attained. Even in case of any of the above mentioned shapes of membranes, it has been regarded that practical forming is impossible unless the gradient type porous layer has a thickness of at least 3μ, most preferably a thickness of 10μ or more. Further, as for the maximum value of membrane thickness of the gradient type porous 30 layer, there is no particular regulation, but it has been regarded to be generally 100μ or less, more usually 50μ or less, because there is a physical limitation in making uniform the size of pores existing equidistantly from the membrane surface.

As for methods for producing semipermeable membrane having such a gradient type porous layer, there are various kinds of reports. So long as polymers have semipermeable 35 membrane-forming capability by way of wet process, any of them are useful. For example, such polymers as acrylonitrile polymers, acetylcellulose, aromatic polyamides, polybenzimidazole, polyvinyl chloride, polypiperadine, polysulfone, polymethyl methacrylate, 40 regenerated cellulose, etc. can be employed for producing the semipermeable membranes.

Any of these polymers are dissolved in a suitable solvent to prepare a membrane-forming solution, and coagulated in a suitable coagulant into a membrane. For a coagulant, water or 45 these containing water as a principal component are preferably used, but any materials which do not dissolve the polymer but are soluble in and dissolve the solvent for the polymer, are generally useful.

The semipermeable membranes having a gradient type porous layer include naturally 45 those of any of film form, tubular form and hollow fiber form, and a film form semipermeable membrane can be prepared by casting a membrane-forming solution on a glass plate or the like in a thin membrane form, introducing it together with the glass plate into a coagulating bath to effect coagulation thereof, followed by washing. It can be prepared also by extruding membrane-forming solution from a slit-form T die into a coagulation bath.

Further, various production methods of hollow fiber form semipermeable membranes 50 have so far been disclosed. For example, the official gazette of Japanese application laid-open No. 90684/1974 shows a hollow fiber form semipermeable membrane of acrylonitrile polymer having a large water permeability as well as a production method thereof, and describes that it has a structure in which there is a reticulate porous layer in succession to the gradient type porous layer and containing large voids of 10μ or more in 55 diameter.

According to the present invention there is provided a semipermeable membrane having, on either one or both of the surfaces of the membrane, a gradient type porous layer wherein the average size of pores contained in the layer becomes smaller as the pores approach the 60 surface(s) of the membrane.

and having, on the surface(s) of said gradient type porous layer, a number of concave portions having a size larger than that of pores of the outermost surface of said gradient type porous layer and a depth smaller than the thickness of said gradient type porous layer.

The present invention is described in more detail below with reference to the 65 accompanying drawings, in which:

Figure 1 shows schematically the cross-sectional structure of a film form semi-permeable membrane having a gradient type porous layer.

Figure 2 shows schematically the cross-sectional structure of film form semi-permeable membrane of the present invention.

5 Figure 3 shows schematically the cross-sectional structure of one type of hollow fiber form semipermeable membrane of the present invention.

Figure 4 shows schematically the cross-sectional structure of another type of hollow fiber form semipermeable membrane of the present invention.

10 Figure 5 shows a cross-section of a ring form orifice nozzle for producing hollow fiber form semipermeable membranes.

Figure 6 shows schematically an apparatus for spinning hollow fiber form semipermeable membranes.

15 Figure 7 shows a cross-section of an apparatus for measuring the amount of permeated water of hollow fiber form semipermeable membranes.

Figure 8 shows a cross-section of an apparatus for measuring an amount of permeated water of film form semipermeable membrane.

20 Figure 9 shows a cross-section of an inside pressure type module for hollow fiber form semipermeable membranes.

As is apparent from the foregoing, it is now known that a semipermeable membrane having a gradient type porous layer 1 as shown by a schematical cross-section in Figure 1 is a semipermeable membrane having a superior permeability, but the semipermeable membrane of the present invention has a large number of concave portions 2 on its surface as shown by a schematical cross-section in Figure 2. The size of the concave portions is in the range smaller than the thickness of the gradient type porous layer and larger than the pore size of the gradient type porous layer which is present on the inner surface of the concave portion. It can take any value within this range.

25 As evident from the production method hereinafter described, the gradient type porous layer of the semipermeable membrane of the present invention is essentially not different from the one shown in Figure 1, resulting in the exposure of pores of large pore size on the surface of the concave portion, and the deeper the depth of the concave portion, the greater the pore size on the surface of the concave portion.

30 Accordingly, even in case of a semipermeable membrane obtained from the same raw material and having the same gradient type porous layer, it is possible to vary the molecular weight of filtration limit enabling to permeate through this semipermeable membrane, by 35 varying the size of the concave portions.

Figure 3 shows schematically the cross-sectional structure of the hollow fiber of the 40 present invention. It has the gradient type porous layers both on the inside 3 and outside 4, and also concave portions both on the inside 5 and outside 6. Figure 4 shows schematically the cross-section of another type of the hollow fiber of the present invention. Numerals 3 and 4 show its inside and outside gradient type porous layers, respectively, and 5 and 6 show its inside and outside surface concave portions, respectively. Numeral 7 shows voids having a large pore size. These voids are large voids in the reticulate porous layer arranged in succession to the above-mentioned gradient type porous layer and having nothing to do with the formation of concave portions of the surface.

45 The present invention also provides a method for the production of the membranes of the invention which comprises dispersing in a solution of a semipermeable membrane-forming polymer and a solvent therefor, a liquid having a solubility not more than 5, based on said solvent, to form a homogenous liquid dispersion, passing said dispersion through a shaping nozzle into a coagulating liquid which is soluble in and also dissolves said solvent but does not dissolve said dispersed liquid, and then removing said dispersed liquid from the 50 resulting semipermeable membrane shape.

55 In this production method the solubility of the dispersed liquid in the solvent is 5 parts by weight or less based on 100 parts by weight of the solvent, preferably zero. If the solubility of the dispersed liquid is larger, the solubility of the polymer is reduced and the viscosity of the solution is increased to make the membrane-making impossible.

60 The present invention also a method for the production of the membranes of the invention which comprises dispersing in a solution of a semipermeable membrane-forming polymer and a solvent therefor, a liquid having a solubility not more than 5, based on said solvent, to form a homogenous liquid dispersion, passing said dispersion through a shaping 65 nozzle into a coagulating liquid which is soluble in and also dissolves said solvent but does not dissolve said dispersed liquid, and then removing said dispersed liquid from the resulting semipermeable membrane shape.

In this production method the solubility of the dispersed liquid in the solvent is 5 parts by weight or less based on 100 parts by weight of the solvent, preferably zero. If the solubility of the dispersed liquid is larger, the solubility of the polymer is reduced and the viscosity of

the solution is increased to make the membrane-making impossible.

Thus, it becomes impossible to vary the amount of the liquid added, to a large extent. However, the increase or decrease of the amount of the liquid added is related with the size of dispersed particles, which results in determining the size of voids free of the liquid and the size of the concave portions on the surface(s) of the gradient type porous layer, and hence the broadness of the range in which the amount of the liquid added is varied is important.

Since the amount of the liquid added varies depending on the composition of the membrane-making solution and the kind of liquid, its range cannot be univocally specified.

10 However, it is possible to use the liquid varying the amount optionally in the range wherein the dispersed phase is not reversed into a continuous phase, preferably in an amount of 80% or smaller of the amount of the liquid added in which the phase reversion occurs. For homogeneously dispersing the liquid, mechanical stirring is carried out, but it is effective to add an auxiliary agent for dispersion such as surfactant, etc., if necessary.

15 As for the kind of liquid, it is possible to employ those having an extremely small solubility in the solvent for the polymer, selected from among those generally widely employed, which are water-insoluble, have a comparatively high viscosity and have a low vapor pressure, concretely for example, in case where water is employed as coagulating bath, liquid paraffin, chlorinated paraffin, various kinds of vegetable oils such as olive oil, linseed oil, etc., various kinds of organic compounds for heat medium such as silicone oil, hydrogenated triphenyl, diethyldiphenyl, etc., various kinds of mineral oils such as insulating oil, spindle oil, etc., or the like.

20 If membrane-making is carried out employing a conventional combination of polymer, solvent and coagulating bath, from which combination a semipermeable membrane having a gradient type porous layer can be prepared, and also employing a solution containing a dispersed liquid satisfying the above-mentioned conditions, then coagulation is carried out to give a membrane, unaffected by the presence of the dispersed liquid, since the liquid does not dissolve in the coagulating bath. Thus, a membrane having all the same gradient type porous layer as that in case of the absence of the dispersed liquid is formed, and the liquid particles are enclosed in the texture of the membrane or embedded in and protruded from the surface of the membrane to give a membrane having a gradient type porous layer wherein the particles are fixed. Thus, when the liquid particles are removed, there is formed a semipermeable membrane having a gradient type porous layer entirely same as conventional ones except that the membrane is lacking its tissue at the inside voids and has concave portions on the surface of the membrane, formed by the dispersed liquid. Namely, the semipermeable membrane of the present invention as shown in Figures 2 - 4 and as mentioned above is obtained. In addition, in Figures 3 and 4, numeral 5' shows inside voids formed by the dispersed liquid, the voids being not related with the size of molecule of filtration limit, but contributing to the improvement in permeability, and having been filled with the dispersed liquid prior to its removal.

25 Next, a general method for preparing a semipermeable membrane in the form of hollow fiber will be mentioned below.

30 The above-mentioned liquid is uniformly dispersed in a solution having an appropriate concentration in the range of 2 - 40% by weight, preferably 5 - 30% by weight, followed by 35 filtration and defoaming. As shown in Figure 6, employing a nozzle 8 having a ring form orifice as shown in Figure 5, the solution is sent and extruded through a gear pump 9, while a coagulating liquid, through a gear pump 10. The resulting extrudate is passed through a coagulating bath 11 and taken up on a coil 12.

40 When the dispersed liquid is removed by extraction, after the take-up, there is obtained a semipermeable membrane in the form of hollow fiber, having a gradient type porous layer on both the inner and outer surfaces thereof and a reticulate porous layer between said surfaces. Further, when a non-coagulating liquid is sent through the gear pump 10, a semipermeable membrane in the form of hollow fiber, having a gradient type porous layer on the outer surface alone, is obtained.

45 55 When a semipermeable membrane in the form of film or tube is prepared, this is effected by replacing the nozzle by a T-die or a circular slit.

50 Semipermeable membranes are generally heat-treated for stabilizing the performance, and when the semipermeable membrane of the present invention is heat-treated in the state where the dispersed liquid is still contained in the gradient type porous layer and the 55 reticulate porous layer, it shows only a smaller change in the shape than the membrane containing no liquid, and hence it can be heat-treated at a higher temperature to provide a product having a superior heat-stability for practical use. Further, since the semipermeable membrane of the present invention has concave portions on the surface, the flow on the surface of the membrane forms a turbulent flow, which hinders the formation of concentration-polarization layer and prevents the adhesion of deposits onto the surface of

the membrane. Thus it is possible to carry out a stabilized separating operation over a long period of time. Furthermore, in case of usual semipermeable membranes, when they are used at high temperatures or under dry condition, the whole of membrane tends to shrink in many cases to lose the performance as a membrane, whereas, in case of the semi-permeable membrane of the present invention, even when it is used at high temperatures or under dry condition, the voids left behind after the dispersed liquid present in the gradient type porous layer and the reticulate porous layer has been removed, plays a role of a buffer function against the membrane shrinkage and thus the influence of the above-mentioned conditions upon the surface of the gradient type porous layer having a separating function is smaller. Thus, it is possible to maintain the water-permeability which might have been lost in case of membranes of conventional structure. As mentioned above, the semipermeable membrane of the present invention has a structure which could have never been found in the past ones, and hence has superior specific characteristic based upon this structure, and also has a great advantage that various kinds of semipermeable membranes having various values of filtration limit can be prepared from the same raw material.

Further, it is also possible to preserve a semipermeable membrane wherein the liquid dispersant is still maintained dispersed therein, in the form as it is, after coagulation and well it to consumers. Such a membrane is heat-treated by the consumers and thereafter subjected to removal of the dispersed liquid to be used as semipermeable membrane. Thus such a membrane still maintaining the dispersed is also a very useful product.

The present invention will be further illustrated by way of Examples. In advance of this illustration, however, parameters employed for expressing the characteristic properties of the semipermeable membrane will be collectively explained below.

25 *Water-permeability (mg/cm².min.atm):*

In case of hollow fiber semipermeable membrane, a given number of hollow fiber semipermeable membranes whose inner and outer diameters have been measured in advance, are collectively adhered at one side ends thereof as shown in Figure 7, and an amount of distilled water permeated per unit time is measured under a pressure difference of one atmosphere between the injecting inlet and the flowing-out exit. In Figure 7, numeral 13 means a bundle of hollow fibers; 14, a part where the ends of the bundle of hollow fibers are adhered; and 15, an injecting inlet for a testing liquid.

Next, the area of the inner wall surface of the hollow fibers is sought by calculation to regard the resulting value as the effective area of membrane. The above-mentioned amount of distilled water permeated is divided by this effective area of membrane to give a water-permeability in terms of a value per unit area. On the other hand, in case of semipermeable membrane in the form of film, measurement is carried out employing a permeating cell as shown in Figure 8, under a pressure difference of one atmosphere. In Figure 8, numeral 16 means a stirrer; 17, a semipermeable membrane in the form of film; and 18, a porous plate.

30 *Pore size*

Since the pore size is very small, it cannot be directly measured. Thus, values obtained according to the following two methods have been made a measure for the pore size:

35 As for the pore size of ultrafiltration field, aqueous solutions of various kinds of spherical proteins having different sizes are filtered and the resulting filtrates are analyzed, whereby the least molecular weight completely (100%) uncapable of passing through the semipermeable membrane, as the molecular weight of filtration limit, was regarded as the measure for the pore size. A list of spherical proteins employed is shown in Table 1.

Table 1

Spherical proteins for measuring pore sizes

	Molecular weight	
5		5
	Thyroglobulin (cattle)	669,000
	Urease	480,000
	Fibrinogen	300,000
10	Catalase	250,000
	γ -Globulin	160,000
	β -Globulin	90,000
	Hemoglobin	68,000
	Egg albumin	45,000
15	α -Chymotrypsin	24,500
	Cytochrome	13,000
	Insulin	5,700
	Bacitracin	1,400

20 As for the pore size of microfiltration field, in the measurement apparatus shown in Figure 7, air in place of water is sent into the bundle of hollow fibers immersed in water, and the pressure under which air begins to show leakage (bubble point pressure) was regarded as the measure for the pore size. 20

25 *Example 1* 25
 A copolymer (having an intrinsic viscosity of 1.3 as measured in N,N-dimethylformamide) consisting of 90 mol % of acrylonitrile and 10 mol % of methyl acrylate was dissolved in 65% nitric acid maintained at -5°C to give a polymer solution having a concentration of 15% by weight. Thereafter a liquid paraffin (solubility: 1 or less) 30 containing 3% by weight of a surfactant, Nonian P 208 (trade name of product manufactured by Nihon Yushi Co., Japan) as an auxiliary agent for dispersion was added to the abovementioned polymer solution in proportions as shown in Table 2, followed by stirring to give a homogenous dispersion. Thereafter this dispersion, while being maintained at -5°C , was subjected to defoaming with stirring under reduced pressure and subsequently 35 defoaming while being allowed to stand, followed by spinning with the apparatus shown in Figure 6. 35

The spinning conditions were as follows: 40
 There was employed a ring form orifice-nozzle for spinning, containing a capillary having an outer diameter of 0.8 mm at the central portion, and a dispersion-extruding nozzle having an inner diameter varied in the range of 1.5 - 2.5 mm. The dispersion was sent to the nozzle at a rate of 13 - 44 ml/min. by means of a gear pump 9, while water was supplied to the central portion of the nozzle at a rate of 5.0 ml/min. by means of a gear pump 10. A coagulating bath 11 filled with water and having a total length of 10 m was employed, and the take-up speed was made 10 m/min. During the spinning, flowing-out of liquid paraffin 45 into the coagulating bath was almost not observed. 45

The resulting hollow fibers obtained by the spinning were sufficiently washed with water, followed by heat-treatment with hot water at 60°C for 30 minutes, treatment with dioxane to remove by extraction, the liquid paraffin dispersed in the hollow fiber, and immersing in water. 50

50 These hollow fibers had a cross-sectional structure as shown in Figure 4. 50
 The hollow fibers thus obtained were fixed into an apparatus as shown in Figure 7 to measure the water-permeability, the molecular weight of filtration limit, bubble point pressure, etc. These values together with other values are shown in Table 2. In this Table, the average sizes of pores in the gradient type porous layer and the reticulate porous layer 55 mean average values of the sizes of pores indicated by numerals 5 and 5' in Figure 4, as measured by means of a microscope. 55

As seen from the data of Table 2, by varying the amount of liquid paraffin added, the pore sizes of the hollow fiber semipermeable membrane are varied over a broad range from the ultrafiltration field to the microfiltration field. Further the water-permeabilities are also 60 high and the strengths are sufficient for practical uses. 60

TABLE 2
Performances of hollow fiber semipermeable membranes of acrylonitrile polymer

Example 2

Diacetylcellulose was dissolved in dimethylsulfoxide at 25°C in a concentration of 20% by weight, and a chlorinated paraffin (percentage chlorination: 40%, solubility: 1 or less) was uniformly dispersed in the polymer solution obtained above, in an amount of 10% by

5 weight based thereon, followed by coagulation in water maintained at 20°C in the same manner as in Example 1, to give a material of hollow fiber structure containing the chlorinated paraffin. This material was heat-treated with warm water at 40°C for 10 minutes, followed by extracting the chlorinated paraffin present in the material with carbon tetrachloride and immersing in water, to give a hollow fiber semipermeable membrane.

10 Its water permeability and molecular weight of filtration limit were 0.50 mfl/cm².min.atm and 160,000, respectively.

The cross-section of this hollow fiber had a structure as depicted in a model manner in Figure 3, and voids as seen in Example 1 were absent.

15 Example 3

The material of hollow fiber structure containing liquid paraffin, prepared in Example 1, was dried by hot air at 60°C, and the liquid paraffin was extracted with dioxane.

15 The resulting hollow fiber semipermeable membrane was dried by air, followed by immersing in water for one hour and measurement of water permeability. The results are 20 shown in Table 4.

TABLE 4

25	Amount of liquid paraffin added (wt. % based on polymer solution)	Amount of water permeated (m ³ /cm ² .min.atm)	Percentage retention of amount of water permeated (%) (based on amount of water permeated shown in Table 2)	25
30	0	0.05	1	30
	10	1.8	20	
	20	5.1	19	
	30	17	22	
35	40	25	24	35
	50	41	27	

As shown in Table 4, the hollow fiber semipermeable membranes of the present invention prepared by adding liquid paraffin had water-permeabilities even after dried, and their amounts of water permeated were 19 - 27% of those in wet state. This is due to the specific structure of the hollow fiber semipermeable membrane of the present invention.

Example 4

45 The membrane-making solution containing 15% by weight of liquid paraffin, employed in Example 1, was cast on a glass plate so as to give a thickness of 0.3 mm, and then immersed in water at 20°C, together with the glass plate to coagulate it, followed by extracting the liquid paraffin in the resulting semipermeable membrane with tetrahydrofuran and immersing in water. The amount of water permeated and the molecular weight of

50 filtration limit of the flat film semipermeable membrane were 18 m³/cm².min.atm and 160,000, respectively. The cross-section of this flat film semipermeable membrane had a structure as shown in Figure 2, wherein a gradient type porous layer having concave portions on the surface was present on one side.

Example 5

55 A hollow fiber was prepared in the same manner as in Example 1 except that the system of Example 1 but having added no liquid paraffin was employed and the temperature of the coagulating bath was made 40°C. The water-permeability and the molecular weight of filtration limit of the hollow fiber thus obtained were 5.4 m³/cm².min.atm and 24,500, respectively.

60 This hollow fiber and that of Example 1 prepared by adding 5% by weight of liquid paraffin were cut to a length of 30 cm, respectively, and 100 ends of the cut material were bundled to prepare a module as shown in Figure 9.

The exit pressure of the module was fixed to 1 kg/cm², and 1% aqueous solution of dextran T-110 (trade name of a dextran having a weight average molecular weight of 65 110,000, manufactured by Pharmacia Fine Chemicals Co., Sweden) maintained at 20°C was

fed at a linear velocity of 1 m/sec to measure the change of the amount of water passed, with time. The results are shown in Table 5.

As apparent from Table 5, since the module of the hollow fiber of the present invention has specific concave portions on the surface of the hollow fiber, it is possible to maintain a separating performance stabilized over a long time. 5

TABLE 5

Module 10 added system (Present Hour	Hollow fiber of liquid paraffin- system (Comparison) invention	Hollow fiber of 40°C coagulation	10
15 0	4.1 $\ell/\text{min.module}$	3.2 $\ell/\text{min.module}$	15
1	4.0	3.0	
3	3.9	2.7	
6	3.9	2.4	
12	3.8	2.1	
20 24	3.8	1.7	20

WHAT WE CLAIM IS:

- 25 1. A semipermeable membrane having, on either one or both of the surfaces of the membrane, a gradient type porous layer wherein the average size of pores contained in the layer becomes smaller as the pores approach the surface(s) of the membrane, and having, on the surface(s) of said gradient type porous layer, a number of concave portions having a size larger than that of pores of the outermost surface of said gradient type porous layer and a depth smaller than the thickness of said gradient type porous layer. 25
- 30 2. A semipermeable membrane according to Claim 1 wherein said membrane has a film form. 30
- 35 3. A semipermeable membrane according to Claim 1 wherein said membrane has a tubular form. 35
- 40 4. A semipermeable membrane according to Claim 1 wherein said membrane has a hollow fiber form. 40
- 45 5. A semipermeable membrane according to any one of claims 1 to 4 wherein said membrane has a number of voids in a reticulate porous layer in the central part. 45
- 50 6. A semipermeable membrane according to any one of claims 1 to 4 wherein said membrane consists of said gradient-type porous layer or layers. 50
- 55 7. A semipermeable membrane according to any one of claims 1 to 4 wherein said membrane has a reticulate layer in the central part. 55
- 60 8. A semipermeable membrane according to any one of claims 1 to 4 wherein said membrane is formed from a high molecular weight polymer composed mainly of acrylonitrile units. 60
- 65 9. A method for producing semipermeable membranes which comprises dispersing in a solution of a semipermeable membrane-forming polymer and a solvent therefor, a liquid having a solubility not more than 5, based on said solvent, to form a homogenous liquid dispersion, passing said dispersion through a shaping nozzle into a coagulating liquid which is soluble in and also dissolves said solvent but does not dissolve said dispersed liquid, and then removing said dispersed liquid from the resulting semipermeable membrane shape. 65
- 70 10. A method according to claim 9 wherein said coagulating liquid is applied to both of the surfaces of said membrane forming solution as it is formed into a semipermeable membrane in the form of a film, tube or hollow fiber. 70
- 75 11. A method according to claim 9 wherein said coagulating liquid is applied only onto 65

either one of the surfaces of said membrane-forming solution as it is formed into a semipermeable membrane in the form of film, tube or hollow fiber, and a non-coagulating liquid is applied onto the other surface.

5 12. A semipermeable membrane according to claim 1 substantially as described herein 5 with reference to Figure 2, figure 3 or Figure 4 of the accompanying drawings.

13. A method according to claim 9 substantially as described in any one of the Examples or with reference to Figure 5 or Figure 6 of the accompanying drawings.

10 14. A semipermeable membrane obtained by a method according to any one of claims 9, 10, 11 or 13.

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FIG. 1

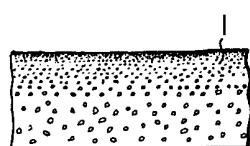


FIG. 2

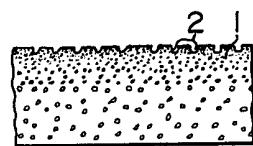


FIG. 3

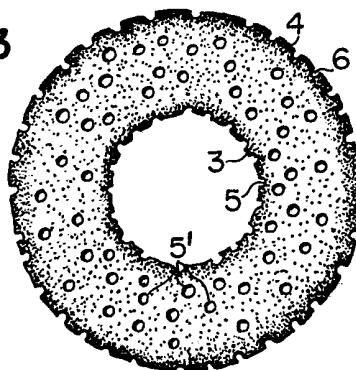


FIG. 4

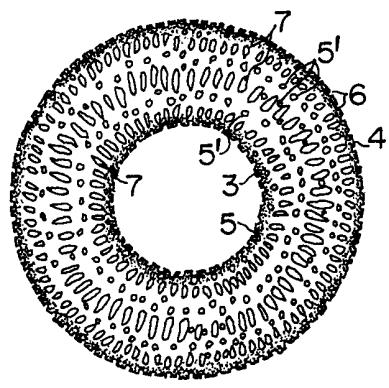
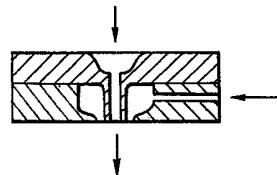


FIG. 5



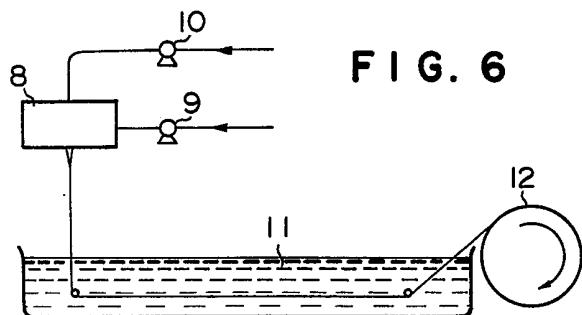


FIG. 6



FIG. 7

FIG. 8

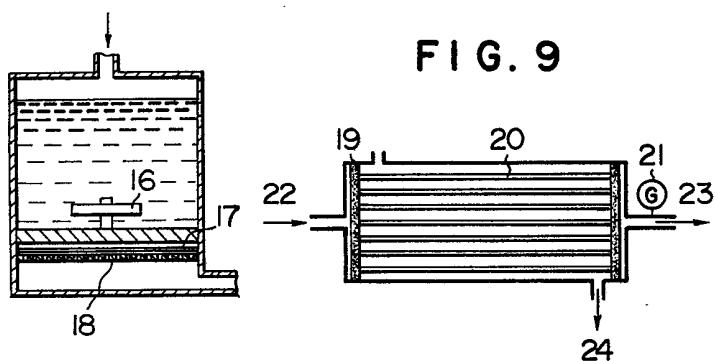


FIG. 9