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(54) Membrane fibre filtration apparatus

(57) In a filtration apparatus using a membrane consisting of a bundle of hollow fibres 3, two or more such membranes are collected and fixed with a cast-moulding material at one end, the membranes being closed at the other end, at least two seals 15 with a space between them are installed in a collecting and fixing portion 5 of the membranes or in a cylindrical cap member 4 connected to the collecting and fixing portion 5, a housing 1 is provided with an opening at its upper end for receiving the bundle of hollow fibres and a cover 2 for closing the upper end opening of the housing in liquid-tight manner is provided with two openings 13, 14 communicating with an inlet for liquid to be treated and an outlet for treated liquid in its bottom wall, in which the said collecting and fixing portion 5 or cylindrical cap member 4 is inserted into one of the two openings and held in that opening by a means for holding a bundle of hollow fibres; and a leakage opening 16 for leading any liquid leaking from the seals to the outside is formed on the side wall between at least two of the said seals 15.

The solution to be treated can be kept from leaking out of a mechanically sealed portion and any defect in the sealed portion can be detected from the outside by leading the leaked solution to the outside of the apparatus. This apparatus can be used for the manufacture of purified water free from bacteria, pyrogens and the like. Ultra-purified water of remarkably high purity can be obtained when it is used a a check filter in a process for manufacturing ultra-purified water.

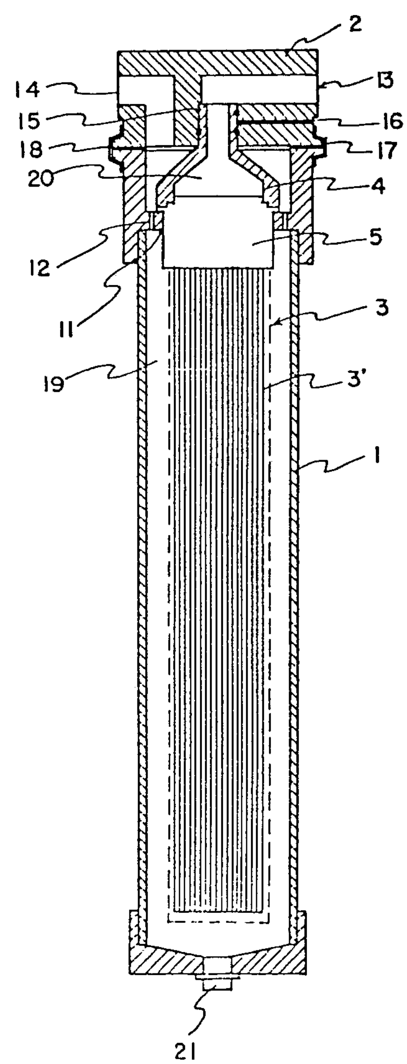

Fig-1

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Fig-1

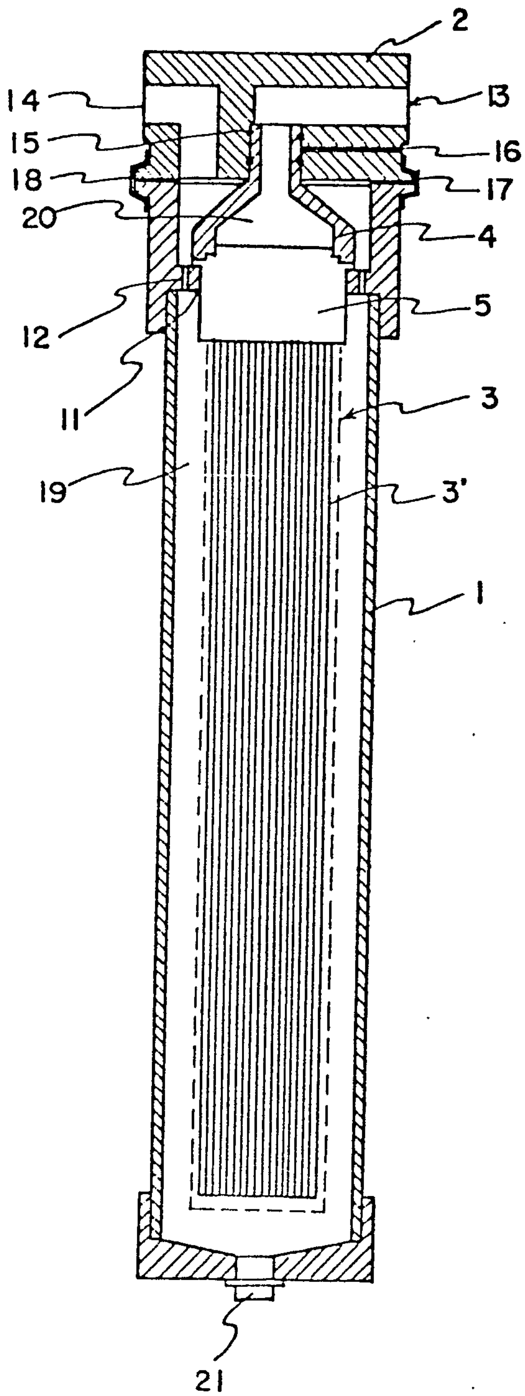

Fig-2

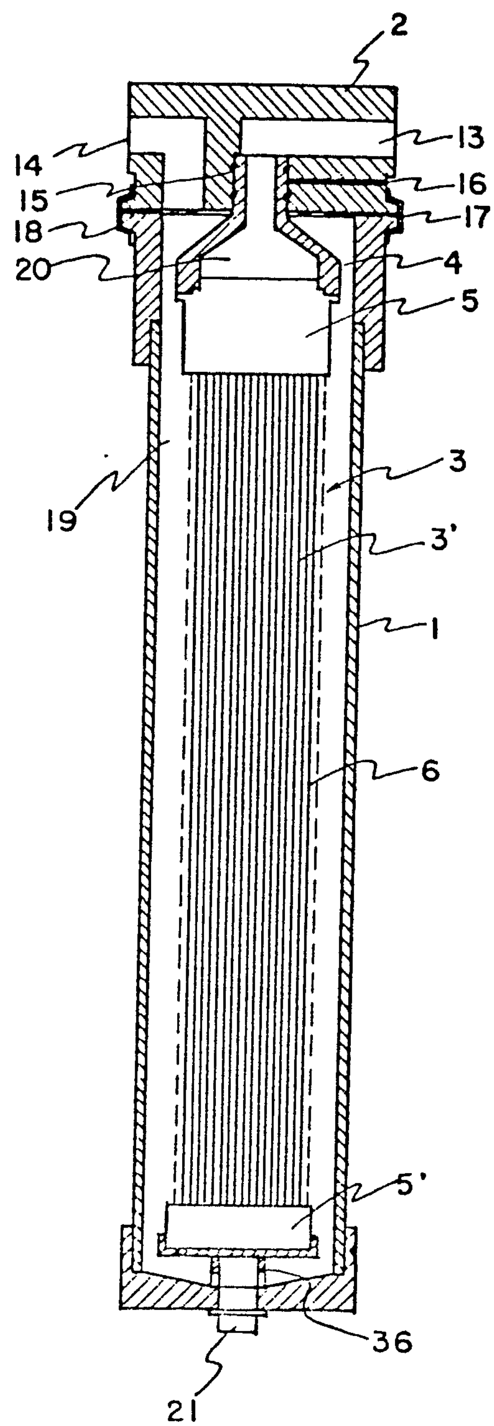

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Fig-3

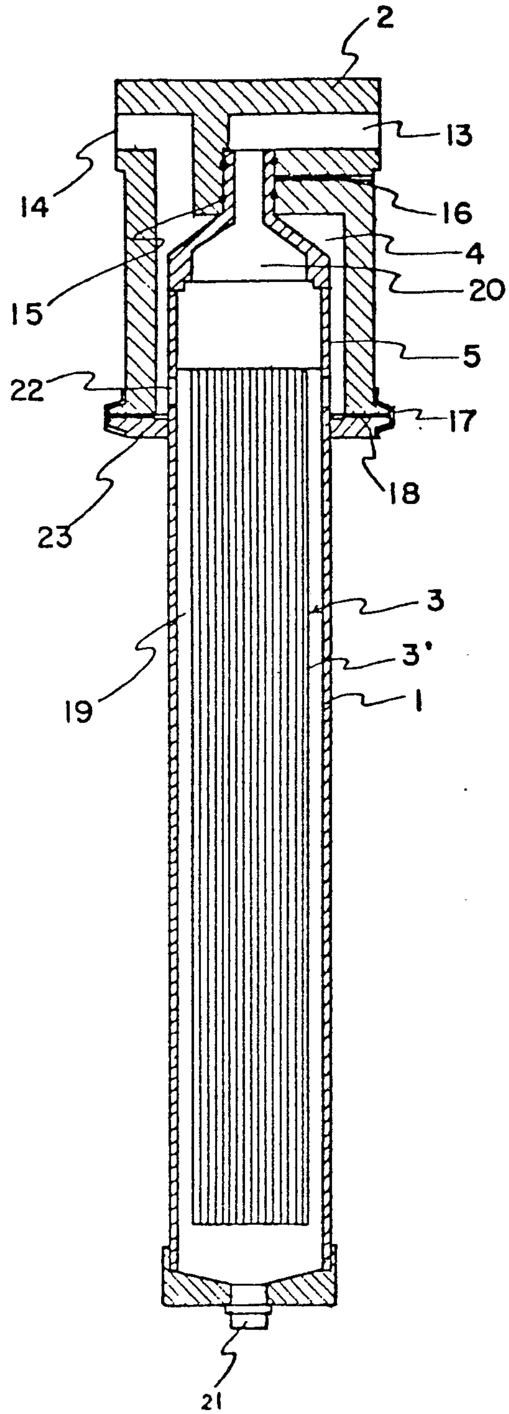


Fig-4

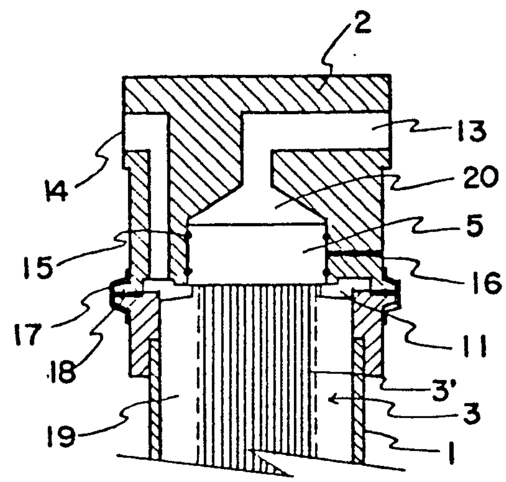


Fig-5

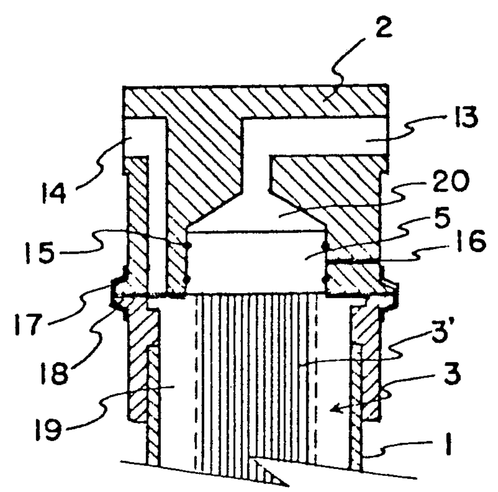


Fig-6

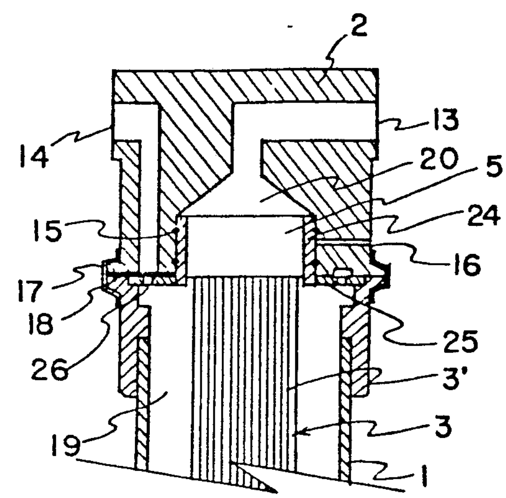


Fig-8

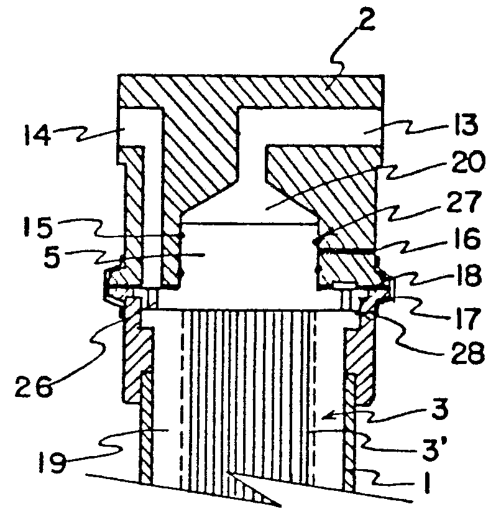


Fig-7

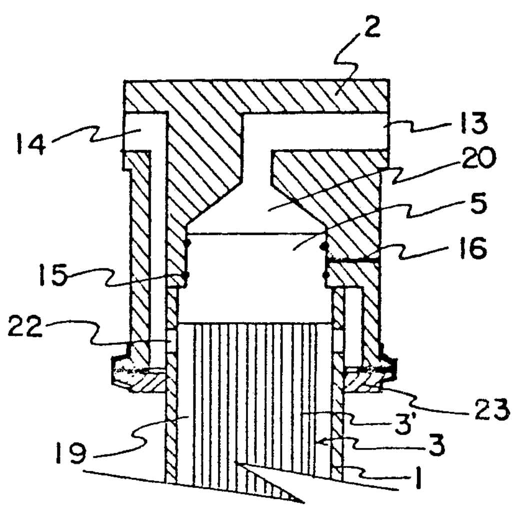


Fig-9

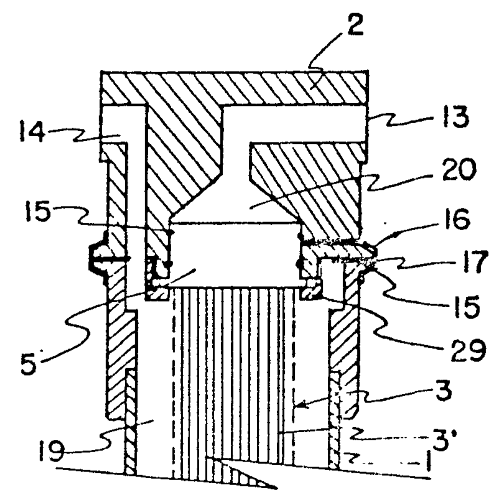


Fig-10

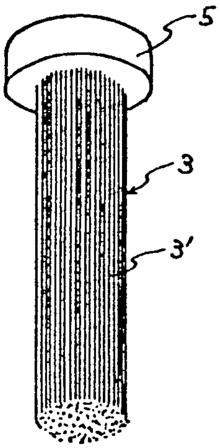


Fig-11

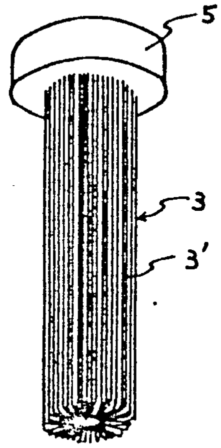


Fig-12

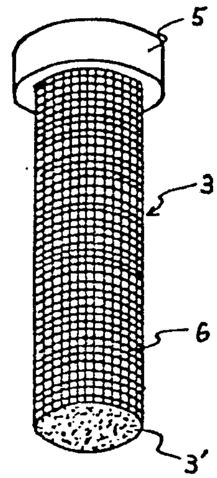


Fig-13

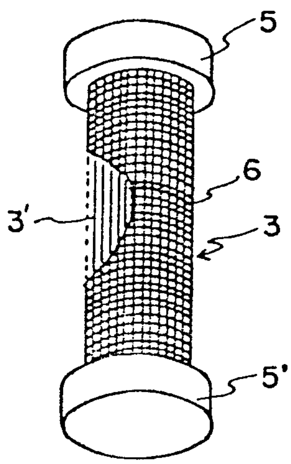


Fig-14

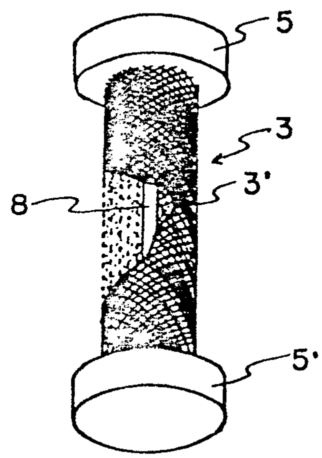


Fig-15

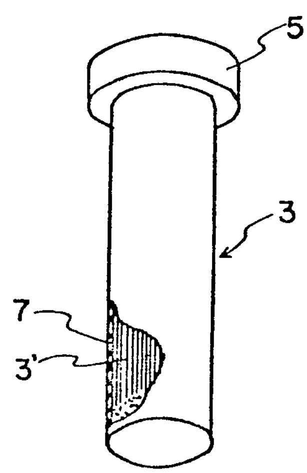


Fig-16

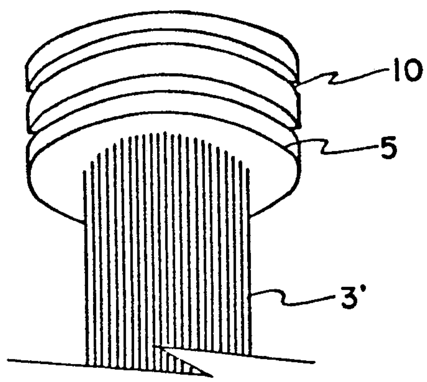
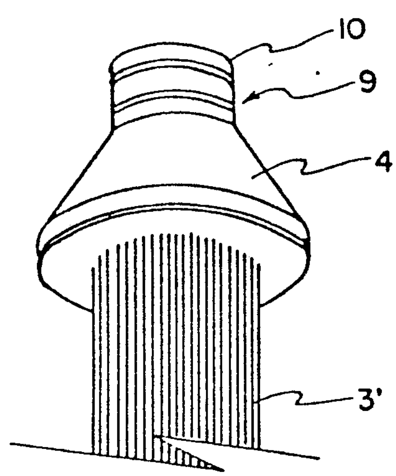


Fig-17



SPECIFICATION

Filtration apparatus

The present invention relates to filtration apparatus. More particularly, but not exclusively, the invention is concerned with an apparatus for purifying water in which undesirable components such as bacteria are removed from the untreated water. Such apparatus can be used for the concentration, purification and recovery of fruit juice, protein and saccharoid, the filtration of aqueous solutions and organic liquids or the treatment of industrial waste water.

Distillation and membrane filtration are known as methods of manufacturing purified water free of impurities such as bacteria and pyrogens. However, the distillation method has the disadvantage that the purity of the water is reduced by contamination resulting from splashes and bubbles and from dissolution of the materials of the apparatus by heating or other causes. In membrane filtration, although theoretically both bacteria and pyrogens would be removed almost entirely if a membrane that can reject them is used, the treated liquid (hereinafter referred to as a filtrate) is frequently found to be contaminated with bacteria and pyrogene, particularly in extended filtration. The following causes are postulated: (1) the membrane itself produces defects: (2) the membrane is incompletely fixed at one end by case-moulding materials; and (3) the liquid to be treated (hereinafter referred to as original liquid) leaks into the filtrate because the mechanical sealing materials, such as O-rings, used the apparatus do not form a complete seal. Since the amount of untreated liquid that leaks into the filtrate is generally very small, it is remarkably difficult to find the causes and routes to the contamination. Even if just one bacterium leaks into a filtrate, it immediately multiplies in and thereby contaminates it. In the production of purified water, leakage of original water into the filtrate must be strictly avoided. Although the leakage of original water into the filtrate rarely occurs from hollow fibres and the portions where they are collected and fixed, as a result of recent rapid advances in research on selectively permeable membranes, leakage of the original water into the filtrate from the mechanical sealing portions of the apparatus still presents an unsolved problem. In particular, although an inline filtration apparatus, where the inlet for original water and the outlet for filtrate are arranged in a straight line, is easily installed and operated, is compact, and has easily detachable bundles of hollow fibres, any leakage of original water from the outside into the filtrate, even from defects in the mechanical sealing portions, cannot be detected. In addition, even though it can be ascertained from a bacterial test of the filtrate that original water has leaked into it, leakage from mechanical sealing portions cannot at present be distinguished from leakage resulting from defects in the bundle of hollow fibres.

The present invention provides a filtration apparatus using a membrane consisting of a bundle of hollow fibres, in which two or more such membranes are collected and fixed with a cast-moulding material at one end, the membranes being closed at the other end, at least two seals with a space between them are installed in a collecting and fixing portion of the membranes or in a cylindrical cap member connected to the collecting and fixing portion, a housing is provided with an opening at its upper end for receiving the bundle of hollow fibres and a cover for closing the upper end opening of the housing in liquidl-tight manner is provided with two openings communicating with an inlet for liquid to be treated and an outlet for treated liquid in its bottom wall, in which the said collecting and fixing portion or cylindrical cap member is inserted into one of the two openings and held in that opening by a means for holding a bundle of hollow fibres; and a leakage opening for leading any liquid leaking from the seals to the outside is formed on the side wall between at least two of the said seals.

By using apparatus in accordance with the present invention it is possible to prevent leakage of the original water into the filtrate from mechanical sealing portions of the apparatus, so that a filtrate free from bacteria and pyrogens can be obtained over a long operating time. Any original water leaking from defects in the mechanical sealing portions does not flow into the filtrate, but such defects can be traced and identified by an operator from the outside of the apparatus. Apparatus of the invention can be rapidly and easily repaired by installing a pipe-line in which a bundle of hollow fibres pre-made in the form of module can rapidly be exchanged even by unskilled personnel. Examples of apparatus in accordance with the present invention will now be described with reference to the accompanying drawings in which:-

Figure 1 is a sectional view of an apparatus in which the upper portion of a bundle of hollow fibres provided with a tubular cap member is supported:

Figure 2 is a sectional view of an apparatus in which the lower portion of a bundle of hollow fibres provided with a tubular cap member is supported;

Figure 3 is a sectional view of an apparatus in which a bundle of hollow fibres provided with a tubular cap member forms, together with a housing, one body;

Figure 4 is a sectional view of another apparatus in which the upper portion of a bundle of hollow fibres is supported;

Figure 5 is a sectional view of another apparatus in which the lower portion of a bundle of hollow fibres is supported;

Figures 6 to *9* are sectional views of other apparatus in which the upper portions of a bundle of hollow fibres is supported;

Figures 10 to *12* and *15* are perspective views of a bundle of hollow fibres where the upper portion is supported;

Figures 13 and *14* are perspective views of a bundle of hollow fibres where the lower portion is supported; *Figure 16* is a perspective view showing a collecting and fixing portion of a bundle of hollow fibres, and *Figure 17* is a perspective view of a tubular cap member.

There are two types of apparatus according to the present invention: the "outside pressure" type, in which the original water is fed to the outside of hollow fibres, and the "inside pressure" type, in which the original water is fed to the inside of hollow fibres. Hereinafter, the description will be of an apparatus of the "outside pressure" type. As shown in Figures 1 to 9 an apparatus of the present invention is composed of a tubular housing 1 whose upper portion can be opened, a bundle of hollow fibres 3 inserted in housing 1 and a cover 2 mounted on the upper opening of housing 1. In an apparatus of the present invention, a collecting and fixing portion 5 of the bundle of hollow fibres 3 or a tubular cap 4 fixedly connected with the collecting and fixing portion 5, which is shown as a conical body with a head diameter smaller than that of portion 5, is held in an opening formed in member 2. There are two ways of keeping portion 5 or cap 4 inserted into said opening: the upper-portion-supporting type, in which the collecting and fixing portion 5 of the bundle of hollow fibres 3 is supported by engaging it with housing 1 or cover member 2, and the lower-portion-supporting type, in which the section of hollow fibres from portion 5 to a fixed portion 5′, which is fixed with a cast-moulding material so that the opening formed at the lower end of fibre bundle 3 is sealed, is supported by an independent member 6 and fixed portion 5′ is supported by a supporting member 36 projecting from the lower portion of housing 1. As shown in Figure 10, the upper end of this bundle of hollow fibres of the upper-portion-supporting type is collected and fixed with a cast-moulding material so that the upper end of each hollow fibre 3′ is open, the lower end opening of the membrane of hollow fibres is sealed closed with a cast-moulding material, and a bundle of hollow fibres, as shown in Figure 11, where the lower end of each hollow fibre 3′ is formed in a loop-like shape, and a cavity is formed within the bundle of hollow fibres if the lower ends of the hollow fibres formed in a loop-like shape are arranged in a ring. As a result the filtration efficiency is improved. There is also a type of bundle of hollow fibres, as shown in Figure 12, in which the lower end is sealed, housed in an independent net-like or porous cylindrical member 6 made of a plastics or a metallic material and a type of bundle of hollow fibres, as shown in Figure 15, in which the lower end is sealed, housed in a porous protecting cylinder 7. Cylinder 7, which effects the primary filtration, is made of ceramic or plastics material. The bundle of hollow fibres shown in Figure 11 can effectively contain a large amount of hollow fibres in a small volume. In addition, since the original water passes through the central portion of a bundle of hollow fibres, scales can be very effectively prevented from adhering to hollow fibres, so the life span of a membrane can be remarkably extended and the rate of flow of water can be increased.

There is also a bottom-supported type of bundle of hollow fibres shown in Figure 13, in which the upper and lower ends are fixed to an independent net-like or porous cylinder 6 with a cast-moulding material, a membrane of hollow fibres opens at the upper end and the lower-end opening is sealed with a cast-moulding material. The entire bundle is housed in the independent net-like or porous cylinder 6. As shown in Figure 14, the lower ends of a bundle of hollow fibres in a cast-moulding material to close them, and a membrane of the hollow fibres 3′ is collected, wound cross-wise around an independent core 8, and fixed at its upper end.

In addition, a conical tubular cap member 4 may be fixed to a collecting and fixing portion 5 of the bundle of hollow fibres. In Figures 16 and 17, two or more ring-like grooves 10 are formed on the collecting and fixing portion 5 or on the projecting portion 9 of a cap member 4 that is fixedly connected with portion 5, with space between them. O-rings are placed in the ring-like grooves 10. Usually, two such grooves are formed, but three or more ring-like grooves may be formed in order to make mechanical sealing more reliable.

Figure 1 shows a preferred embodiment of a filtration apparatus in which the bundle of hollow fibres 3 of the upper-portion-supported type is shown, and in which the conical cap member 4 is fixed to the collecting and fixing portion 5 with a cast-moulding material.

The cylindrical housing 1, which has an opening at its upper end, is provided with a flange 11 for supporting the collecting and fixing portion 5 inside it, flange 11 being provided with holes 12 or notches. The collecting and fixing portion 5 as shown in Figure 10, 11, 12 or 15 is placed in housing 1 so that it is supported by flange 11.

A cover member 2 mounted on the opening of housing 1 in a liquid-tight manner is provided with an opening communicating with an outlet 13 for the filtrate at the centre of the bottom wall and an opening communicating with an inlet for the original water 14 adjacent to the opening communicating with outlet 13. The openings communicating with outlets 13 and 14 are opened to each other in a straight line when the cover member 2 is turned through 90°. The opening communicating with outlet 13 is connected with a filtrate-exhausting pipe (not shown), and the opening communicating with the inlet 14 is connected with an original water-introducing pipe. If necessary, the inlet 14 and the outlet 13 may be formed vertically on the upper wall or side wall of the cover member 2. The protruding portion 9 of the conical cap member 4 is inserted into an opening communicating with the outlet 13, with the gap between the protruding portion 9 and the opening formed in cap member 4 sealed by two O-rings 15. If the inlet for the original water and the outlet for the filtrate are reversed, this apparatus can be used for filtration by inside pressure. In addition, an outlet 16 for leaked liquid is placed on the outside of the cover member 2 between two O-rings 15, which seals the said protruding portion 9, which is inserted into the cover member 2. A band coupling 17 connects the housing 1 with cover member 2 in a liquid-tight manner with a seal 18. Seal 18, O-ring 15, a chamber 19 for original water and a chamber 20 for filtrate form a liquid-tight structure with a wall membrane of hollow fibres betweem chambers 19 and 20. That is to say, original water is introduced into the chamber 19, which is outside the hollow fibres, through a conduit. The components that can permeate the hollow fibres pass through them and are collected in the filtrate chamber 20 via â passage formed inside the hollow fibres. They are then taken out through a filtrate-discharging conduit via cap member 4. The components that cannot permeate the hollow fibres are discharged through an exhaust port 21 formed at the bottom of housing 1.

Although there is a danger that the original water may leak into the filtrate side through the gap between the opening communicating with the filtrate-discharging conduit 13 and the protruding portion 9 of the cap 4, this gap is completely sealed by two O-rings. However, there is a danger of the original water leaking into the filtrate-chamber if the O-rings break and their sealing performance is spoiled. In an apparatus of the present invention, since the pressurized original water is under pressure on the outside of the apparatus form the outlet for leaked liquid 16 formed on the cover member 2 and communicating with the air, there is no possibility that original water could leak into filtrate-chamber 20. In addition, since the original water is flowing outside the apparatus from the outlet 16 for leaked liquid, the leak can be discovered by the operator or the measuring apparatus. Also a flat of similar seal can be used to seal the gap between the protruding portion and the opening formed on the cover member in addition to the O-ring. A flat seal can be used together with an O-ring. It is desirable to form an outlet for leaked liquid that opens to each of the spaces between seals, on the outside of the cover member when three seals are mounted on the conical cap member. The particular seal broken can be identified by forming outlets for the leaked liquid as described above. When the bundle of hollow fibres has deteriorated or become blocked in the manufacture of purified water, the original water is removed from the housing through the exhaust port 21 and then the band coupling 17 is removed to separate the cover member 2 from the housing 1, and the bundle of hollow fibres 3 is removed from the housing 1. Then, when the new bundle of hollow fibres has been fitted, the housing is re-connected with the cover member. Thus a bundle of hollow fibres can easily be exchanged. The apparatus described above, and shown in Figure 1, is used with the cover member arranged on the housing. However, it is often used turned upside down, depending on the place where it is located, in which case it is desirable that the exhaust port for original water remaining in the housing be installed in the piping for the original water.

Figure 2 shows an apparatus using a lower-end-supported bundle of hollow fibres 3 provided with conical cap member 4. A fixing portion 5', which fixes the lower end of the hollow fibres in a cast-moulding material, is placed on a supporting member 36 protruding from the lower portion of housing 1. A protruding portion 9 of the cap member 4 is held inserted into an opening communicating with a filtrate outlet 13, which is formed on the bottom of the cover member.

Figure 3 shows a bundle of hollow fibres 3 provided with a cap member 4 fixedly connected to a housing 1, which is provided with a openings 22 for introducing the original water at its upper end and a flange 23 for connecting the housing 1 with the cover member at a position below openings 22. Oringinal water, introduced into cover member through an inlet 14, is fed to the inside of the housing 1 through the upper openings 22. In this apparatus, the housing 1 containing a bundle of hollow fibres can be exchanged in its entirety when the hollow fibres deteriorate or become blocked.

Figure 4 illustrates an apparatus containing an upper-end-supported bundle of hollow fibres in which an O-ring is put in a ring-like groove 10 formed on the outside surface of the collecting and fixing portion 5 of the bundle 3 of hollow fibres. Figure 5 illustrates an equivalent apparatus containing a lower-end-supported bundle of hollow fibres. In Figures 4 and 5, the numbers mark the same parts as the numbers in Figures 1 and 2, and the description of them is omitted. Figures 6 to 8 show apparatus in which a housing 1 is united with a bundle of hollow fibres. Referring now to Figure 6, a bundle of hollow fibres 3 is collected and fixed in an intermediate ring 24 provided with an O-ring 15. The intermediate ring 24 is united with a ring-like plate 25 fixedly connected with housing 1. The ring-like plate 25 is provided with an opening 26 corresponding to an opening communicating with an inlet for original water 14 formed in the bottom wall of a cover member 2. The apparatus of Figure 7 corresponds to the apparatus of Figure 3, the same places being marked in the same manner, and the description of them is omitted. Figure 8 shows an apparatus containing a bundle of hollow fibres 3, in which the intermediate ring 24 is united with the ring-like plate 25 by means of a cast-moulding material for collecting and fixing a bundle of hollow fibres. The bundle of hollow fibres is fixedly connected with the upper end of the housing 1. Portion 5, which includes a protruding portion 27, is inserted into an opening formed in a cover member 2. A ring-like portion 28 closes the upper end opening of the cover member 2. Portion 28 is provided with an opening 26 for introducing original water into the housing 1 at a position corresponding to an opening communicating with the inlet for original water formed in the bottom wall of the cover member. Figure 9 shows an apparatus in which the cover member is provided with a screw and the portion 5 is fixed to cover member 2 by means of a nut 29. Various kinds of one-touch connectors can be applied instead of the above described nut.

When an apparatus of the present invention is used to manufacture purified water, it is desirable that the hollow fibres used can allow water to flow rapidly, for example at 1.5×10^3 m^3/m^3hr.kg/cm^2 or more, and to substantially prevent substances of 80 A or more from permeating, i.e. to reject ultrafiltration.

Although in general hollow fibres are characterized by water permeability per housing substantially higher that that of a flat membrane, it may be preferable to indicate water permeability in terms of the occupied volume K_V(m^3/m^3.hr.kg/cm^2) rather than the water-flux K_A (liter/m^2.hr.kg/cm^2, in respect to the area of a membrane of hollow fibres). If K_V is used instead of K_A, the outside diameter and/or the inside diameter of the hollow fibres becomes a very important factor. For example, when K_A is measured with respect to inside diameter, K_V is in inverse proportion to the square of the outside diameter and in proportion to the inside diameter. In addition, when K_A is measured with respect to the outside diameter, K_V is in inverse proportion to the outside diameter. The inside diameter of a membrane of hollow fibres used in an apparatus of the present invention is 250 to 1,500 μm, and preferably 300 to 1,000 μm; the outside diameter is 350 to 3,000 μm, and preferably 400 to 2,000 μm. At this time, a membrane of hollow fibres is superior in K_V and pressure resistance. In addition, the balance of the other performances is improved.

The water permeability of hollow fibres is stated against their occupied volume K_V and determined as follows, using a new bundle of membrane of hollow fibres whose membrane area is 200 cm^2 measured by the outside diameter, and containing hollow fibres 20 cm long.

Filtration: the water-flux ($m^3/hr.kg/cm^2$)K_A in a filtration process, in which pure water having a temperature of 25°C is filtered at a pressure of 1 kg/cm^2 using an outside pressure total filtration method, is measured.

Calculation of the water-flux

The occupied volume of the membranes of hollow fibres V is calculated by the following formula:

$V = (/4)Do^2 lf,$

where Do is the outside diameter of the membranes of the hollow fibres; *l* is the effective length of the membrane; *f* is the number of hollow fibres.

The water-flux K_V is calculated by dividing by V the water-flux K_A.

The water-flux of a membrane of hollow fibres K_V used in the manufacture of purified water is at least 1.5 $\times 10^3$ $m^3/m^3.hr.kg/cm^2$, preferably at least 2.5 $\times 10^3$ $m^3/m^3.hr.kg/cm^2$, and particularly 3.5 $\times 10^3$ $m^3/m^3hr.kg/cm^2$ or more.

K_V being large means that the required water permeability can be achieved by means of a more compact filtration apparatus. A membrane of hollow fibres having a K_V of 30 $\times 10^3 m^3/m^3.hr.kg/cm^2$ or more cannot be used in practice since only a small rejection coefficient R can be obtained under the present state of technology.

In addition, substances of 80 A or more do not substantially permeate through this membrane of hollow fibres. This holds good when the rejection coefficient R of colloidal silica, having an average particle diameter of 80 A, is measured under the following conditions and R is 95% or more.

A bundle of hollow fibres, of which the membrane area measured by the outside diameter is 200 cm^2, and which is 20 cm long, is used. The measuring solution is a 1% (by weight) aqueous solution of colloidal silica having an average particle diameter of 80 A.

The filtration conditions using the outside pressure total filtration method are a filtration pressure of 0.5kg/cm^2 and temperature of 25°C. Water is mostly removed from a bundle of hollow fibres prior to their use and also the inside of the wall of a membrane of hollow fibres is filled with a solution of colloidal silica. The filtration is started by applying pressure.

The original water is sampled directly before applying pressure and five 10-cc samples are taken from the initial flow of a filtrate obtained by applying pressure. These six samples are dried for 16 hours at 100°C and the concentration of solid fraction is measured.

R is calculated from the concentration C_D of solids contained in the original water and the largest concentration C_F max of solids contained in the five samples taken from the filtrate, as follows:

$R = (1 - C_F max/C_D) \times 100$

If a colloidal solution is used with this measuring method, even though a value for R of 97% is obtained, it does not mean that 3% of the particles with an average particle diameter of 80 A permeates through a bundle of hollow fibres. If R is 95% or more, it can be assumed that no particles having diameters of 80 A or more permeate through a bundle of hollow fibres.

Hollow fibres showing such rejection coefficients can substantially reject γ-globulin contained in bovine serum, which is globular protein having a molecular weight of 160,000. Further, they can completely reject not only all bacteria and viruses but also lipopolysaccharide which is a secretion of bacteria and called pyrogen.

In addition, it is preferable that such hollow fibres have a compaction index of 0.2 or less. The compaction index α is expressed by the following formula:

$\alpha = 1 - K_{V4}/K_{V1},$

where

K_{V1}: the flux ($m^3/m^3.hr.kg/cm^2$) of water at 100°C at a filtration pressure of 1 kg/cm^2 by the outside-pressure filtration method.

K_{V4}: the flux ($m^3/m^3.hr.kg/cm^2$) of water at 100°C at a filtration pressure of 4 kg/cm^2 by the outside-pressure filtration method.

A compaction index α of 0.2 or less, that is to say 0 to 0.2, means that the hollow fibres have superior pressure resistance, especially at high temperatures, and that the reduction in filtration speed is little. Accordingly, hollow fibres having α larger than 0.2 are undesirable.

In general, filtration is rarely carried out at 100°C but rather at 10 to 60°C. Consequently, it is thought that the value of α at 100°C has no meaning industrially. However, hollow fibres that are not compacted during short-time operation at 10 to 60°C, are classified into those that compact gradually, whereby the filtration speed is reduced over a lengthy operation, and those that are hardly compacted, whereby the flux is not reduced over a lengthy operation. The value of α for water at 100°C is useful in evaluating differences in compaction of hollow fibres quickly.

A membrane of hollow fibres with the above performance shows high water-flux and high pressure resistance as well as high heat resistance, although its rejection is of an ultrafiltration order.

Although the materials well known as materials for membranes of hollow fibres such as polysulphones, polyacrylonitriles, various celluloses, for example cellulose acetate, polyamides, polycarbonates and polyvinylalcohols can be used as materials for the hollow fibres, polysulphones are preferable since they are superior in heat resistance, acid-proofness, alkali-proofness and oxidizing resistance, and a mebrane can be regenerated by washing it, e.g. with oxidants, acids or alkalis and the like and can if desired be sterilized by heat sterilization or chemical sterilization, e.g. by formalin or chlorine.

Above all, a membrane of polysulphone hollow having slit-like fine gaps having an average width of 500 A or less on its inside surface, fine pores of an average diameter of 1,000 to 5,000 A at porosity of 10 to 80% in the outside surface, and an interior of fine porous structure, substantially rejecting substances having diameters of 80 A or more, and having a water-flux of 1.5 $m^3/m^3.hr.kg/cm^2$ or more, is preferably used. Such a membrane of hollow fibres is superior not only in water-flux but also in rejection of ultrafiltration. As a result it can substantially reject pyrogens. Further, its compaction index is 0.2 or less, so it is remarkably superior in pressure resistance and heat resistance.

Such a membrane of polysulphone hollow fibres has slit-like fine gaps of an average width of 500 A or less on its inside surface. "Slit-like fine gaps" are fine long gaps formed in the longitudinal direction of the fibres, and "average width" is the average value of short diameters of the fine gaps. The length of the fine gaps in the longitudinal direction of the fibres is at least three and preferably at least ten times the width of slit. It is desirable that the distribution density of the fine gaps in the inside surface of the membrane of polysulphone hollow fibres be uniform and as high as possible. In addition, if the width of the fine gaps is also as uniform as possible, the membrane of polysulphone hollow fibres has excellent rejection and pressure resistance. The average width of the fine gaps can be measured by means of a scanning electron microscope. Since the rejection becomes too great if the average width is larger than 500 A, such an average width is undesirable. An average width of 80 to 500 A, and in particular 100 to 200 A, gives a yet better balanced combination of water-flux and rejection. A membrane of polysulphone hollow fibres whose inside surface has a slit-like fine gap structure gives a water-flux remarkably larger than that of a membrane of polysulphone hollow fibres whose inside surface has a circular fine pore structure.

In addition, the membrane of polysulphone hollow fibres has fine pores with an average diameter of 1,000 to 5,000 A at a porosity of 10 to 50% on the outside surface. The average pore diameter described herein is expressed by the following formula:

$$\overline{D} = \sqrt{\frac{(D_i2)^2 + \cdots + (D_n)^2}{D_i^2 + \cdots + D_n^2}},$$

where

D: average pore diameter

D_i: measured diameter of the i-th fine pore

D_n: measured diameter of the n-th fine pore

In the case when the fine pores have circular shapes, D_i and D_n designate measured diameters while in the case when the fine pores are not circular, they designate the diameters of circles having the same areas as the fine pores.

If the average diameter of the pores formed in the outside surface of a membrane of polysulphone hollow fibres is less than 1,000 A, the water-flux becomes too low. An average pore diameter larger than 5,000 A is undesirable since pressure resistance is liable to be reduced. In addition, with outside pressure filtration, filtration cakes deposited on the surface of the membrane intrude into the inside of the membrane and accelerate the reduction of the water-flux and the recovery of the membrane cannot be made sufficient even by back washing or chemical washing. Consequently, outside-pressure filtration is undesirable. An average pore diameter of 1,500 to 3,500 A is best. Fine pores having diameters of 500 A or less are not included in the calculation of the average pore diameter. Although it is desirable that fine pores formed in the outside surface of a membrane of hollow fibres have a uniform diameter, they may be non-uniform. The porosity described herein designates the percentage ratio of the total area of fine pores formed in the outside surface of the membrane to the area of the outside surface. If porosity is less than 10%, water-flux is reduced. If the porosity is larger than 80%, surface strength is reduced, and the membrane is apt to be damaged when handled. If the porosity is 30 to 60%, the membrane shows a well-balanced combination of permeability and mechanical performances.

The inside of the membrane shows a fine porous structure. The fine porous structure described herein is a sponge structure such as a mesh structure, a honeycomb structure or a fine gap structure. Although the inside surface as well as the outside surface of a membrane and the inside of a membrane may include a finger-like structure of a macro-void structure, it is desirable that macro-voids having a size of 10 μm or more are not substantially contained in them. A membrane of uniform sponge structure, in which macro-voids having a size of 10 μm or more are not contained, is superior in pressure resistance, in particular compaction resistance in a long-time operation, and strength.

The above described hollow fibres show superior filtration performance especially in the outside-pressure filtration method. For example, every microorganism can be removed from tap water by carefully filtering it through the hollow fibres by the outside-pressure filtration method. In addition, pyrogenous substances, which are secretions of microorganisms, can also be completely removed from tap water, and pyrogenic pure water can be easily obtained. Further, the water-flux of the membrane is liable to be remarkably high in comparison with that of conventional membranes for rejecting pyrogens. It is because removal of pyrogens and high water-flux can be simultaneously attained by means of a simple system such as the outside pressure type filtration method that the membrane of hollow fibres contains comparatively large fine pores in its outside surface, a uniform sponge interior sructure and a skin layer of compact slit structure in the inside surface, whereby particles of submicron order or larger are caught in the outside surface and substances of submicron order or smaller including dissolved polymer are caught in the inside of the membrane or its inside surface. That is to say, since the outside surface and inside structure of the membrane serve as a prefilter, a water-flux remarkably larger than that attained by conventional hollow fibres can be attained.

Polysulphone hollow fibres of the above described structure can be manufactured as follows: the solution obtained by adding N,N′-dimethylformamide (hereinafter referred to as DMF) as a solvent and polyethylene glycol (hereinafter referred to as PEG) as an additive to polyarylsulphone is used as a spinning solution. At this time, it is desirable that a large amount of additive such as PEG is added so that the spinning solution may produce micro phase-separation in sensitive response to a slight change of temperature there or the introduction of a small amount of non-solvent such as moisture. In general, the spinning solution comprises polysulphone at a ratio of 12 to 25% by weight and PEG (molecular weight of 600) at a ratio of 20 to 45% by weight. The rest is DMF. Although the spinning solution of the above described composition is transparent at temperatures lower than a certain temperature, it produces whitening (phase separation) suddenly at temperatures higher than this certain temperature. Although in general the spinning solution having a phase-separation temperature of 10 to 70°C is used, in order to obtain such a spinning solution at first the mixture consisting of polysulphone, PEG and DMF is stirred at 70 to 130°C to produce whitened slurry and the resulting slurry is cooled to 0 to 70°C while stirred to obtain a uniform transparent solution.

The resulting spinning solution is then degassed and filtered. After lowering the temperature of the spinning solution to a temperature 9 to 20°C lower than the phase-separation temperature, it is subjected to a dry-wet spinning through a tube-in-orifice nozzle. It is desirable that the difference between the temperature of the spinning solution and the phase-separation temperature be less than 20°C when the spinning solution is discharged through a nozzle. The internal solidifying solution is discharged through a needle of the tube-in-orifice nozzle in order to obtain hollow fibres. The structure of the inside surface of the hollow fibres id dependent upon the composition of the internal solidifying solution. It is desirable that a solidifying solution which can solidify the inside surface rapidly, such as water, is used in order to obtain a membrane structure of ultrafiltration order. The spinning solution is introduced into a dry zone through the tube-in-orifice nozzle. The structure of the outside surface of the hollow fibres is dependent upon the atmosphere (temperature, vapour pressure of solvents or non-solvents) and the length of the dry zone. It is desirable that the vapour pressure of non-solvents (for example, water) in the dry zone be increased and the dry zone have such a length that the stay can be 0.1 seconds or more. In general, fresh humidified air is fed into the dry zone so that a humidity of 60% or more, preferably 90% or more, may be kept in the dry zone. The micro phase-separation is produced on the outside surface of the hollow fibres that were discharged through a nozzle by introducing moisture into them in the dry zone by controlling the atmosphere in and the length of the dry zone. The hollow fibres are then introduced into a solidifying solution where thay are subjected to a rapid solidifying action, whereby a micro phase-separation structure is fixed. After removing solvents and additives from the hollow fibres with water at room temperature or hot water, they are treated with an aqueous solution of a hydrophilic substance such as glycerin and dried.

The hollow fibres are made into a bundle to form an element. At this time, cast-moulding materials such as polyurethane, silicone and epoxy resin can be used as cast-moulding materials for collecting and fixing one end of a bundle of hollow fibres. Not only the hollow fibres but also the cast-moulding materials must be heat- and chemical-resistant, especially for applications where heat resistance and chemical resistance are required. It is desirable that imidazolic hardened epoxy resins be used for such uses. One end of a hollow fibre can be collected and fixed by filling the gap formed at the end portion of the hollow fibre with a liquid epoxy composition consisting of epoxy resin, a polyamine hardener in an amount having an amine equivalent of 25 to 70 mol % of the epoxy equivalent, and 0.5 to 10% by weight, based on epoxy resin of imidazolic hardeners in which the ratio of polyamine hardeners to imidazolic hardeners is from 100:50 to 100:1, fixing at 0 to 50°C and then curing at 60 to 150°C.

A housing and a cover for containing the bundle of hollow fibres are made of corrosion-proof metals such as stainless steel and resins. Usually, resins are used. Heat-resistant resins such as polypropylene, polytetrafluoroethylene, polyvinylidene fluoride, polyacetal, polycarbonate, polysulphone and poly-4-methyl-pentene-1 are preferable. Polysulphone is especially preferred due to its high heat resistance and modulus of bending elasticity. Non-heat-resisting resins such as poly(vinyl chloride), polystyrene and polyacrylonitrile may be used in apparatus operated at temperatures of 50°C or less.

In addition, industrial rubbers such as silicone rubber are used for seals.

The filtration pressure applied to the original water is 0.1 kg/cm^2 or more preferably 0.2-0.3 kg/cm^2. Although the water-flux increases with an increase of the upper limit of the filtration pressure, it goes without saying that the pressure must be selected so that hollow fibres are not broken. In general, it is 5 kg/cm^2 or less, preferably 3 kg/cm^2 or less. It is undesirable that the original water be continuously filtered at high pressure from the start since filter cakes compactly accumulate, and total filtration capacity is reduced. Accordingly, it is desirable that the filtration be carried out at lower pressures at the start and that the pressure be gradually increased as blocking occurs. When tap water is filtered, a highly pure water can be easily and very economically produced using the pressure of tap water and no auxiliary pump, by directly connecting an apparatus of the present invention with the waterworks.

It is better if the original water fed in an apparatus of the present invention for the manufacture of purified water, contains cakes (filter cakes having sizes of 80 A or more and accumulated on the surfaces of a membrane of hollow fibres) whose properties resemble those of non-compressible cakes. "Non-compressible cakes" are cakes whose shapes it is difficult to change when they are compressed by the filtration pressure. With these, water can easily permeate through a layer of cakes. For example, cakes of inorganic substances such as colloidal iron and silica, cross-linked polymer pieces such as ion-exchange resin pieces, and activated carbon are comparatively non-compressible. On the other hand, materials such as polysaccharides secreted from microorganisms, as well as denatured protein, are not good since they compress to form gel-like cakes and water can barely permeate a layer of these cakes. Even when non-compressible cakes are mixed with compressible cakes, they can be filtered out according to the present invention if the non-compressible cakes predominate. Excessively high concentrations of cakes are bad since it is necessary to frequently exhaust the concentrated slurry, back wash, and apply (for example) chemical washing on account of the rapid accumulation of cakes. "Original water" includes ultra-pure water, pure water, tap water, river water, industrial water and sea water. Ultra-pure water can be obtained if an apparatus of the present invention is used as a check filter in the manufacture of ultra-pure water. It is frequently desired to feed river water, industrial water and sea water to an apparatus of the present invention after it has been subjected to a preliminary treatment such as flocculating sedimentation, treatment by a sand filter or treatment by a cartridge filter or micron order.

The following Example, in which parts and percentages are by weight unless the contrary is indicated, illustrates the present invention.

Example

A mixture of 20 parts of polysulphone (Udel P-1700 manufactured by UCC), 36 parts of polyethylene glycol having a molecular weight of 600 (PEG 600 manufactured by Sanyo Kasei Co. Ltd.) and 44 parts of DMF is heated at 120°C while being stirred to obtain a slurry-like solution containing whitened phase-separation. The resulting slurry-like solution is cooled to 25°C while being stirred to obtain a uniform transparent solution. This solution produces whitened phase-separations at temperatures higher than 36°C.

The resulting uniform transparent solution is degassed by standing overnight and a spinning solution is obtained. This is subjected to a dry-wet spinning by means of a tube-in-orifice nozzle having 18 holes and an internal solidifying solution is injected. At this time, the temperature of the spinning solution is 31°C, the length of a dry zone is 10 cm, the temperature of the atmosphere in the dry zone is 25°C, the relative humidity of the atmosphere in the dry zone is 100% and the temperature of the water, which is the external solidifying solution, is 20°C. Then the resulting hollow fibres are washed with water, wound around a flat frame of 1.2 m, and subsequently immersed in water at 100°C for two hours to remove polyethylene glycol and simultaneously subjected to a heat treatment.

The membrane of hollow fibres thus obtained has an outside diameter of 750 μm and an inside diameter of 500 μm. It is found from the observation of the surfaces and the section of a membrane of hollow fibres by means of a scanning electron microscope (SEM) that micropores having an average diameter of 0.3 μm are formed in the outside surface of the membrane of hollow fibres at a porosity of 49%, slit-like gaps having an average width of 0.01 μm are formed in the inside surface of the membrane of hollow fibres, macrovoids of 10 μm or more are not formed at all in the inside and outside surfaces of the membrane of hollow fibres, nor in the inside of the membrane of hollow fibres, and the inside of the membrane of hollow fibres shows a uniform mesh-like sponge structure. The water-flux K_V of pure water at 25°C is 4.4×10^3 $m^3/m^3.hr.kg/cm^2$ which is an excellent value. In addition, the membrane of hollow fibres shows a rejection of 98% or more for an 0.1% aqueous solution of bovine serum alubumin and a rejection of 99% or more for an 0.1% aqueous solution of standard polyethylene oxide having a molecular weight of 300,000 (SE - 150 manufactured by Toyo Soda Co. Ltd.) Furthermore, the compaction index α measured by an outside pressure water-permeability measuring method at 100°C and an outside pressure of 1 kg/cm^2 as well as 4 kg/cm^2 is 0.15, which is an excellent value.

3,000 filaments of the hollow fibre are joined into a bundle. One end of the hollow fibres is sealed with a cast-moulding material to obtain a bundle of hollow fibres 50 cm long, as shown in Figure 10. The bundle of hollow fibres is installed in a housing to form an apparatus as shown in Figure 4. The assembled apparatus and a hose connected to an outlet for filtrate are sterilized, pyrogen is decomposed by immersing them in a 3% aqueous solution of hydrogen peroxide overnight and then the apparatus is connected to a water tap.

Tap water is directly filtered in accordance with an outside pressure total filtration method without any preliminary treatments. The filtration is continuously carried out for 32 days at a filtration pressure of 1 kg/cm^2. Filtrates sampled after one hour, one day, 3 days, 7 days, 14 days, 21 days, 32 days and 49 days, respectively, from the start of filtration are given the Limulus test. All samples show the result of −. For reference, the tap water itself is given the Limulus test. All of the results are ++. Accordingly pyrogen-free water can be easily obtained by means of a membrane of hollow fibres according to the present invention. The filtration speed is 2.3×10^3 m^3/m^3.hr on the average. That is to say, according to the present invention, a considerable amount of pyrogen-free water can be continuously obtained by means of a remarkably small module without any preliminary treatments and other systems such as pumps.

CLAIMS

1. A filtration apparatus using a membrane consisting of a bundle of hollow fibres, in which two or more such membranes are collected and fixed with a cast-moulding material at one end, the membranes being closed at the other end, at least two seals with a space between them are installed in a collecting and fixing portion of the membranes or in a cylindrical cap member connected to the collecting and fixing portion, a housing is provided with an opening at its upper end for receiving the bundle of hollow fibres and a cover for closing the upper end opening of the housing in liquid-tight manner is provided with two openings communicating with an inlet for liquid to be treated and an outlet for treated liquid in its bottom wall, in which the said collecting and fixing portion or cylindrical cap member is inserted into one of the two openings and held in that opening by a means for holding a bundle of hollow fibres; and a leakage opening for leading any liquid leaking from the seals to the outside is formed on the side wall between at least two of the said seals.

2. Apparatus as claimed in Claims 1, in which the bundle of hollow fibres has a structure in which two or more membranes of hollow fibres form loops at one end and the loops are arranged in a ring-like shape at the end.

3. Apparatus as claimed in Claim 1 or 2, in which the seals are spaced O-rings put in ring-shaped grooves formed in the said collecting and fixing portion or in the cylindrical cap member.

4. Apparatus as claimed in any preceding claim, in which the inlet for liquid to be treated and the outlet for treated liquid are symmetrically arranged in the side wall of the cover member.

5. Apparatus as claimed in any preceding claim, in which the collecting and fixing portion of the bundle of hollow fibres or the cylindrical cap member is inserted into an opening communicating with the outlet for treated liquid formed in the cover member.

6. Apparatus as claimed in any preceding claim, in which substances of 80 A or more do not substantially permeate the membrane of hollow fibres and the membrane shows a pure-water-permeating speed of 1.5×10^3 m^3/m^3.hr.kg/cm^2 or more.

7. Apparatus as set forth in Claim 6, in which the membrane of hollow fibres is made of polysulphone and has a structure such that slit-like fine gaps having an average width of 500 A or less are formed in the inside surface, fine pores having an average diameter of 1,000 to 5,000 A formed at a porosity of 10 to 80% in the outside surface, and the inside having a fine porous structure.

8. Apparatus as claimed in Claim 1 substantially as hereinbefore described with reference to any one of Figures 1 to 9 of the accompanying drawings, taken in conjunction with any of Figures 10 to 17 as appropriate.

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