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(54) HOLLOW FIBRES AND METHODS OF MANUFACTURING SUCH FIBRES

(71) We, NIPPON ZEON CO LTD, a company organised and existing under the laws of Japan, of 2-6-1 Marunouchi, Chiyoda-ku, Tokyo, 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 hollow fibres, methods of manufacturing such fibres, and to uses of such fibres. More particularly, but not exclusively, the invention relates to hollow fibres having favourable selective permeability which is suitable for blood dialysis, ultrafiltration, reverse osmosis and the like.

Recently, semi-permeable hollow fibres have been used for blood dialysis, and for a fluid separator based on the principle of ultrafiltration, or reverse osmosis.

Such a hollow fibre should have a uniform shape, because when the hollow fibre is used, for example, for blood dialysis, the pressure in the interior of the hollow fibre is usually positive compared with the exterior of the hollow fibre. Thus if the hollow fibre is not uniform in wall thickness, there is a possibility of the hollow fibre being broken at the thinnest part. Also, it has been known that when the cross-section of the hollow fibre is substantially deformed from a true circle, blood is apt to coagulate in the hollow fibre.

When a hollow fibre is used for reverse osmosis, high pressures, of up to one hundred atmospheres, are applied to the outside of the hollow fibre. In this case, it is required that the cross-section of the hollow fibre should be close to true circle, and that the thickness of the wall of the hollow fibre should be uniform, otherwise, the hollow fibre is often squashed and becomes useless. When the cross-section of the hollow fibre is not uniform, the polarized concentration due to the non-uniform flow substantially reduces the permeability performance of the hollow fibre.

Accordingly, it is very important that the cross-section of the hollow fibre, particularly the inside diameter thereof, is uniform.

In the manufacture of the hollow fibre, a spinning solution (dope) is extruded from an annular slit of a double pipe orifice, to form a sheath solution, and simultaneously, a gaseous or liquid fluid is extruded from the inside pipe of the double pipe orifice to form a core fluid. In the manufacturing method in which a gaseous material (inert gas) is used as a core fluid, the resulting hollow fibre is apt to be squashed, because the direction of the running extruded filament after being spun is changed by a guide bar in the coagulation bath and washing bath. Thus, the running filament is pressed hard on the guide bar, and hence it is often deformed to be flattened, or squashed.

Such disadvantages are substantially reduced in the case of a melt spinning procedure. However, it is known that with this procedure it is very difficult to produce a hollow fibre having a favourable selective permeability.

So far, a wet spinning process has been considered to have a wide range of controllability to produce a hollow fibre having a variety of permeabilities. In the wet spinning process, spinning conditions such as dope concentration, and coagulation bath conditions can be widely changed. But, on the other hand, it is difficult to produce a hollow fibre of uniform shape, and the productivity is usually very low because of the very low speed of spinning.

In the method in which core liquid is extruded instead of gaseous core fluid, the deformation of the running filament at the guide bar is largely avoided. However, another problem may be developed, that is, a rapid coagulation of the sheath dope due to the instantaneous diffusion of the core liquid into the sheath dope immediately after being spun. In more detail, a thin skin layer is first formed on the inner interface of the spun sheath dope in contact with the core liquid, and another thin layer is formed on the outer surface of the spun-sheath dope by contact with the coagulation bath liquid when the running filament is introduced into the coagulation bath. These two layers set the dimensional shape of the hollow fibre, and subsequent coagulation between the two layers usually develops numerous macro-voids in the membrane of the hollow fibre. These voids serve to scatter light, and as a result the hollow fibre looks whitish. A desirable selective permeability cannot be obtained from such a hollow fibre, because the membrane has unfavourable macro-voids instead of desired micropores. Moreover, spinnability is very poor because of the rapid coagulation of the dope immediately after being spun. The hollow fibre obtained at an extremely low speed (up to 15 m/min, at best) had very poor mechanical properties. Also the skin layers formed on both inner and outer surface of the hollow fibre lowers the permeability.

A dry jet-wet spinning method, which means that the dope is extruded in the gaseous space, and it is then introduced into a coagulation liquid, is considered to be preferable for producing a hollow fibre having relative permeability. In this method, a spinning dope is extruded from an annular slit to form a sheath dope, and extruded sheath dope passes through a gaseous space before being introduced into a coagulation bath. The gaseous space may be occupied with inert gas or air, and it may contain the vapour of the solvent of the spinning dope.

The core liquid is preferably non-coagulative at least before the spun dope is introduced into a coagulation bath. For example, in the production of cellulose hollow fibres by the cuprammonium process, benzene, toluene, trichloroethylene, n-hexane or perchloroethylene, which are not miscible with water, are usually employed as a core liquid. In this procedure, the organic core liquid should be removed from the hollow fibre in the sequential process, which involves long, troublesome operations. Moreover, from the view-point of pollution, the use of a toxic organic solvent is not favourable.

Especially when the hollow fibre is used for medical therapy, such as blood dialysis, and for any process concerning foods, for example, concentration of juice, the above-mentioned toxic organic material should be completely washed out from the hollow fibre.

According to the present invention there is provided a method of manufacturing a hollow fibre, including the steps of extruding a spinning solution of high molecular weight compound from an annular slit into a coagulating bath spaced from said annular slit by at least 5 mm, and extruding an aqueous solution containing a water-soluble salt from an orifice encircled by said annular slit, the concentration of said water-soluble salt in said aqueous solution being sufficient to develop a phase separation between said spinning solution and said aqueous solution.

The invention will now be described by way of example with reference to the accompanying drawings, in which:

Fig. 1 is a graph showing the infra-red absorption spectrum of an acetone-soluble portion of the hollow fibre according to Example 20 of this invention;

Fig. 2 is a graph showing the infra-red absorption spectrum of an acetone-insoluble portion of the hollow fibre according to Example 20 of this invention;

Fig. 3 is a graph showing the infra-red absorption spectra of the inside portion and the outside portion of the hollow fibre according to Example 21 of this invention;

Fig. 4 is a graph showing the infra-red absorption spectrum of an intermediate portion of the hollow fibre according to Example 21 of this invention;

Fig. 5 is a graph showing the infra-red absorption spectrum of the inside portion of the hollow fibre according to Example 22 of this invention;

Fig. 6 is a graph showing the infra-red absorption spectrum of the outside portion of the hollow fibre according to Example 22 of this invention;

Fig. 7 is a graph showing the infra-red absorption spectrum of in intermediate portion of the hollow fibre according to Example 22 of this invention;

Fig. 8 is a graph showing the infra-red absorption spectrum of the inside portion of the hollow fibre according to Example 23 of this invention;

Fig. 9 is a graph showing the infra-red absorption spectrum of the outside portion of the hollow fibre according to Example 23 of this invention;

Fig. 10 is a graph showing the degree of swelling of the hollow fibre according to Example 25 of this invention;

Fig. 11 is a graph showing the degree of swelling of the hollow fibre according to Example 26 of this invention;

Fig. 12 is a graph showing the degree of swelling of the hollow fibre according to Example 27 of this invention;

Fig. 13 is a graph showing the degree of swelling of the hollow fibre according to Example 28 of this invention;

Fig. 14 is a graph showing the infra-red absorption spectra of the hollow fibre according to Example 29 of this invention;

Fig. 15 is a graph showing the degree of swelling of the hollow fibre according to Example 29 of this invention;

Fig. 16 is a graph showing the degree of hydrolysis of the hollow fibre according to Example 30 of this invention;

Fig. 17 is a cross-sectional view of the hollow fibre according to Example 53 of this invention; and

Fig. 18 is a cross-sectional view of a conventional hollow fibre.

First, a hollow fibre and a method of manufacturing the same, according to preferred embodiments of this invention will be described.

With embodiments of this invention, a hollow fibre having uniform shape and circular cross-section can be obtained with excellent spinnability and high productivity.

Also with embodiments of this invention, the membrane of a hollow fibre can be partially or totally hydrolyzed. In the case that the membrane is partially hydrolyzed, the degree of hydrolysis may vary from the inner wall surface of the membrane of the hollow fibre to the outer wall surface thereof.

Under certain conditions, it is even possible to produce a hollow fibre whose inner wall surface is perfectly hydrolyzed and outer wall surface is not hydrolyzed at all. Also with embodiments of this invention, it is possible to manufacture a hollow fibre which is very hydrophilic in the inner wall surface. Still further, with embodiments of this invention, a hollow fibre can be manufactured in which portions nearer to the inner wall surface in the membrane are more hydrophilic. Or a hollow fibre can be manufactured in which portions nearer to the inner wall surface in the membrane are more swellable or more able to absorb water.

For producing the hydrolyzed types of hollow fibre mentioned above, it is preferable that the high molecular weight compound (polymer) used contains a hydrolyzable group in the side chain of the polymer. The hydrolyzable groups are, for example, carboxylic esters, sulphonic esters, amides, and the like which can yield hydroxy group, carboxylic acid group, amino group, and sulphonic acid group etc. by hydrolysis.

A natural high molecular weight compound such as cellulose, a modified natural polymer such as cellulose derivatives, a synthetic polymer with or without a hydrolyzable side chain can be used. Or a blend of two or more of the above polymers can also be used.

The examples of cellulose derivatives are: Cellulose acetate, cellulose butyrate, cellulose propionate, cellulose acetate butyrate, and cellulose acetate propionate. The degree of acetylation is usually 30% to 65% for cellulose acetate.

For other carboxylic acid derivatives, the degree of esterification usually ranges from 30% to 65%.

Besides carboxylic ester of cellulose, esters of other acids such as nitric acid, sulphuric acid, and other derivatives can be used. For example, methyl cellulose (38% methoxy group), ethyl cellulose (46% ethoxy group), oxyethyl cellulose, benzyl cellulose, cyano ethyl cellulose, sulphuric cellulose, and phosphoric cellulose can be enumerated. As a natural polymer, for example, high-α-cellulose or cellulose pulp can be used.

A synthetic polymer used is any polymer which can dissolve in an organic solvent. Examples are polymers made of methyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, vinyl chloride, vinyl acetate, acrylic acid, methacrylic, acid, styrene, vinyl ether, α-methylstyrene, vinyl pyridine, butylacrylate, methylacrylate, ethylmethacrylate, methylvinylketone, and vinylidene chloride. Copolymers of two or more of the above described vinyl compounds may be used. Or polyesters such as polyethyleneterephthalate, polypeptide such as polyalanine and polybenzylglutamate and other polymers such as polyurethane, polyurea, polythioamide, and polypropyleneoxide may be used. The above mentioned synthetic high molecular compound may be atactic polymer, isotactic polymer, syndiotatic polymer or stereocomplex of them. As vinyl copolymers, acrylonitrile-methallyl sulphonic acid copolymer, vinylchloride-acrylonitrile copolymer, and acrylonitrile - diacetoneacrylamide copolymer are enumerated. Or graft polymer and block polymer may be used. As the above mentioned isotactic and syndiotactic polymers, isotactic polymethylmethacrylate and syndiotactic polymethylmethacrylate are enumerated, respectively.

As an example of a sterocomplex, the isotactic-syndiotactic complex of polymethyl methacrylate can be used.

Condensation polymer such as nylon, polyester and polysulphonic acid can be used.

In the preparation of the spinning solution (dope) any of the above described polymer is dissolved in an organic solvent. The organic solvent is preferably miscible with water.

A typical organic solvent dissolving cellulose derivatives may be dimethyl acetoamide, dimethyl formamide, dimethyl sulphoxide, tetramethylene sulphone, γ-butylo lactone, acetone, methyl-ethyl ketone, methyl acetate, methyl lactate, ethyl lactate, dioxane, tetrahydrofuran, methylene chloride, methyl cellosolve, methyl cellosolve acetate, nitromethane, nitropropane, furfural, glacial acetic acid, or a mixed solvent containing mainly these solvents. Such a mixed solvent may be nitromethane-methanol (8:2), nitropropane-ethanol (7:3), nitropropane-methanol (8:2), methylene chloride-ethanol (9:1), ethylene dichloride-ethanol (9:1), acetone-ethanol (9:1), acetone-water, acetone-triethylene glycol or the like. Typical combinations of a synthetic polymer and organic solvent which can dissolve the polymer are polyacrylonitrile-dimethyl acetoamide, polyacrylonitrile-dimethyl formamide, polyacrylonitrile-dimethylsulphoxide, polymethyl-methacrylate-acetone, polystyrene-tetrahydrofuran, polyvinylchoride-dimethyl-formamide or the like. In this case, polymer as described above, for example, polyacrylonitrile, and polymethyl methacrylate are not necessarily a homopolymer, and may be a copolymer with a major amount of acrylonitrile or methylmethacrylate units having other copolymerizable momomer units as a minor component. The most preferable organic solvent are water miscible from the viewpoint of de-solvating mechanism and pore-formation mechanism during coagulation in the membrane to form a selectively permeable membrane. It is required that the organic solvent must dissolve in water at least to a certain extent.

When the spun dope from the annular orifice is introduced into a water bath or water-containing bath, according to a conventional method, mutual diffusion between the solvent of the spinning dope and water occurs instantaneously. Thus, a thin layer is formed on the surface layer of the dope due to the strong coagulating effect of water. This first sets a dimensional shape of the membrane, then coagulation proceeds into the inside, replacing the solvent of the dope with water, and coagulation completes with the development of macro-voids which makes the resulting fibre whitish.

The unfavorable formation of macro-voids seriously reduces the spinnability, and the take-up speed of the spun filament is, at most 10 to 20 m/min. the mechanical strength of the resulting fibre thus obtained is very low and the fibre is brittle.

This inventor has found that very satisfactory results can be obtained by using special conditions. An aqueous solution containing water-soluble salt is used as a core-liquid in the production of hollow fibres. The spinning solution comprising a polymer, and an organic solvent is extruded from an annular slit to form a sheath dope, and simultaneously, the aqueous salt-containing core liquid is extruded into the interior portion of the spun-sheath-dope. The key to the successful result lies on the utilization of the principle of salting out-effect. In this case, the solvent of the dope and the core aqueous solution are essentially separated from each other into two phases by the effect of the salting-out phenomenon. Therefore, unfavourable mutual diffusion between core liquid and sheath dope is well-suppressed. This acts to reduce the formation of unfavourable macro-voids in the membrane of the hollow fibres. The spinnability is surprisingly improved and spinning velocity (take-up speed) can be 180 m/min, or more. The membrane of the hollow fibre formed is lustrous and rather transparent. The mechanical strength is also satisfactory. The hollow fibre thus obtained has very good selective permeability. The water soluble salt used for the core liquid may be an inorganic salt. Besides a neutral inorganic salt, a salt showing acidic or alkalic reaction in water may also be used. An inorganic salt may be used with acid or alkali reagent to adjust the pH of the core solution. Examples of the inorganic salt are: lithium salt such as lithium chloride, lithium bromide; sodium salt such as sodium chloride, sodium bromide, sodium sulphate, sodium sulphite, sodium nitrate, sodium chlorate, sodium carbonate, sodium dihydrogenphosphate, sodium hydrogenphosphate, sodium phosphate, sodium hydrogencarbonate, sodium nitrite and sodium thiocyanate; an ammonium salt such as ammonium chloride, ammomiun bromide, ammonium sulphate, ammonium nitrate, ammonium carbonate, and ammonium thiocyanate; a potassium salt, such as potassium chloride, potassium bromide, potassium sulphate, potassium hydrogen sulphate, potassium chlorate, potassium carbonate, potassium nitrite, potassium nitrate, potassium bicarbonate, potassium thiocyanate, potassium rhodanate and potassium sulphate; a magnesium salt such as magnesium chloride, magnesium bromide, magnesium bromate, magnesium sulphate, magnesium hydrogen sulphate, magnesium chlorate and magnesium nitrate; a calcium salt such as calcium chloride, calcium iodide, calcium hypophosphate, calcium nitrate, calcium nitrite, calcium phosphate, and calcium dihydrogen phosphate. Besides the abovedescribed salts cadium chloride, cadmium nitrate, zinc chloride, zinc sulphate and zinc nitrate may be used. The inorganic salt must be soluble in water, and the concentration of the salt is at least the minimum concentration which is enough to exhibit the salting-out effect which makes the core solution and the solvent of the sheath dope separate into two phases.

In addition to the inorganic salts, organic, salts may also be used. Examples of the organic salts are; organic carboxylic acid salt, alcoholate, phenolate, and organic sulphonic acid salt. A sodium salt, potassium salt, ammonium salt or calcium salt of the following acids can be used. The acids are citric acid, tartaric acid, formic acid, acetic acid, butyric acid, succinic acid, stearic acid, benzoic acid, propionic acid, oxalic acid, malonic acid, valeric acid, capronic acid, lauric acid, myristic acid, palmitic acid, stearic acid, acrylic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, glycolic acid, lactic acid, malic acid, pyruvic acid, acetoacetic acid, and levulinic acid. As example of the alcoholate, there are sodium methoxide and sodium ethoxide. As examples of the phenolate, there are sodium phenoxide and potassium phenoxide. And as examples of the organic sulphate acid salt, there are sodium benzensulphonate, sodium p-toluene-sulphonate, potassium P-toluene-sulphonate, ammonium benzensulphonate, sodium benzensulphonate and potassium benzensulphonate, and the like.

Examples, which are acidic in water are ammonium chloride or ammonium sulphate. And inorganic-salts which are alkaline in water are sodium carbonate, potassium carbonate, sodium hydrogen carbonate, sodium phosphate, sodium acetate, sodium phenoxide and potassium ethoxide. Two or more of the above salts may be used. Moreover, acidic or basic reagent can be added to adjust the pH of the aqueous salt solution.

To prepare the acidic or basic solution using a neutral salt, hydrochloric acid, sulphuric acid, phosphoric acid, acetic acid, or di-chloroacetic acid may be added to make the solution acidic, and ammonia, sodium hydroxide, potassium hydroxide, lithium hydroxide may be added to make the salt solution basic. The salt concentration in the core liquid must be, regardless the use of inorganic or organic salt, at least the minimum concentration which is enough to develop the phase separation between the core liquid and the solvent of the spinning solution.

Utilizing this salting-out effect, interfacial hydrolysis of the sheath material can be performed, that is, the hydrolysis reaction by acid or alkali in the interface between the core liquid and the sheath dope can be performed. The concentration of salt in the core solution may be arbitrarily determined within the range that develops the phase separation between the core and sheath solutions, and if desired, acid or alkali may be added to the core solution.

When the concentration of the salt is low, and is not enough to develop the phase separation between the core and sheath solutions, the spinnability becomes extremely poor and very low drafting can be achieved.

The minimum concentration of the salt depends on the kinds of the solvent for the dope, and on the kind of salt used in the core solution. Accordingly, it is difficult to specify the minimum concentration of the salt, but it generally ranges between 5% to 50%.

A small amount of organic material, for example, ethyl alcohol, may be contained in the aqueous core solution, if the organic material can be uniformly mixed with the aqueous core solution. Acidity and basicity of the core solution may be varied in accordance with the purpose for use of the hollow fibre. The kind of acidic or basic reagent, and pH used in the core solution depends on the degree of hydrolysis required, and also depends on the chemical behaviour of high molecular weight compounds used for the hollow fibre.

In an example of manufacturing the hollow fibre the spinning dope is extruded downward and substantially vertically from the annular slit of the nozzle, and the spun-filament is led into a coagulating bath, after the running filament passes through a gaseous space of at least 5 mm length. A hollow fibre having a uniform circular cross-section can be obtained. The outside and inside diameter in cross-section, and the thickness of the membrane of the resulting hollow fibre can be easily controlled by adjusting the spinning conditions.

Embodiments of methods of manufacturing a hollow fibre according to this invention may have the following advantages over the conventional methods.

(1) Spinnability in the production of the hollow fibre is excellent and the hollow fibre can be produced stably at a speed of 100 to 180 m/min, and the resulting hollow fibre has a uniform circular cross-section and a uniform wall thickness.

(2) Water can be used in the core liquid. So far, the use of water in the core liquid reduces the speed of spinning, and usually the take-up speed of the fibre is, at best 10 to 20 m/min, because of the rapid coagulation of the spun dope and the formation of macro-voids in the hollow fibre membrane.

Recently, hollow fibres have become widely used in various fields. Asepsis and innoxiousness are strictly required, particularly for medical and food uses. For example, a hollow fibre is now used for blood dialysis in medical therapy. A hollow fibre type ultra-filtration apparatus is also used for producing aseptic water, and for manufacturing processes concerning foods such as concentration of juice, and the removal of yeast in beer production. When other liquid, which has, if any, the slightest human toxity, is used as the core solution, this must be completely washed out from the hollow fibre for fulfilling the strict requirement on innoxiousness. This has been a very, difficult, and troublesome process. In the case of blood dialysis, blood may be directly contaminated with the liquid retained in the hollow fibre membrane. This contamination may be very serious for a patient. The hollow fibre made by some embodiments of this invention has no such a problem, because water and non-toxic inorganic salts are used as the core solution. Moreover, no recovery process of the core liquid is necessary, because the process does not bring any pollution problem.

(3) A favourable selective permeability can be given to the hollow fibre. The mechanism will be understood from the following explanation. As a example, consider an acetone solution of cellulose acetate (modified natural polymer) or of polymethyl methacrylate (synthetic polymer) is used as the spinning solution. The spinning dope is extruded from the annular slit of the nozzle to form the sheath solution, and simultaneously, for example, the aqueous calcium chloride solution (up to 48%) is extruded into the hollow portion of the spun-sheath dope to form the core solution, and the spun filament is led into a coagulation bath, desirably a water bath after passing through a gaseous space longer than 5 mm, for example, about 30 cm length. During the passage of the running dope-filament in the gaseous space, for example, in air, before being introduced into the coagulation bath, if no positive action is taken to evaporate the solvent of the running dope, the outer surface of the running dope filament is little changed from the inside part of the running dope filament. In such a case, extruded dope-filament can be led into a coagulation bath without forming a hard, dense skin layer on the outer surface of the filament.

Since the core solution contains a considerable amount of calcium chloride, the core solution and the dope are separated into two phases. This phenomenon is probably the key to excellent spinnability. Take-up speed of the fibre at the take-up roll can be up to 180 m/min. When the running dope-filament is led into the coagulation bath, mutual diffusion takes place between acetone in the dope-filament and water in the bath from the outer surface of the filament. The outer surface of the filament is rapidly coagulated by the strong coagulating action of water. Subsequently, the outer portion close to the surface of the dope-filament is then subjected to coagulation. The coagulated outer surface layer of the sheath dope sets the dimensional shape of the hollow fibre, then acetone in the dope is replaced with penetrating water to develop favourable micro-pores in the membrane of the hollow fibre. Now, consider the aqueous core solution. The core solution and acetone of the sheath dope is first substantially separated from each other by salting-out effect before being introduced into the coagulation bath. In the coagulation bath, the concentration of acetone in the sheath dope decreases as the water from the coagulation bath penetrates inside the sheath dope. This results in the disappearance of the phase separation, which allows the beginning of the mutual diffusion between the core and sheath solutions. This process produces very favourable micro-pores in the membrane of the resultant hollow fibre. Here, based on the principle of osmosis, water percolates into the hollow portion of the hollow fibre from outside so as to lower the concentration of salt in the aqueous core solution. As a result, the interior portion of the hollow fibre becomes positive in pressure which has an important role in maintaining a circular cross-section of the resulting hollow fibre. The hollow fibre does not deform at the guide bar where the direction changes.

The coagulation begins first from the outer surface of the sheath dope, and then the diffusion of water from the core liquid into the sheath dope starts a little later. When the concentration of acetone in the sheath dope is lowered, the sizes, of pores in the membrane are much smaller in the portions nearer to the inner surface of the hollow fibre. The reason is probably that when the diffusion of water starts from the core-side, the sheath dope has already become more dense, because some coagulation has already started from the outside.

The embodiments of method according to this invention can be applied to the dry jet-wet spinning process as well as the wet-spinning process. This method permits the production of a hollow fibre having very good selective permeability with a wide range of controllability of the permeability.

A selective permeable membrane having smaller pores can be manufactured by the dry jet-wet-spinning method than by the wet-spinning procedure.

While the extruded dope passes through the gaseous space, the solvent of the sheath dope can be evaporated to a certain extent by the employment of suitable conditions. The outer surface of the running dope filament then becomes more dense. In other words, the concentration of acetone is higher in the inner portion of the sheath dope. In this condition, the sizes of pores in the resulting hollow fibre membrane are larger in the portions nearer to the inner wall surface of the hollow fibre. The solvent may be evaporated from the running sheath dope in a spinning cell where a heated inert gas is flowing, so that the phase separation is no longer maintained between the core and sheath solutions. In such a case, water can penetrate into the sheath dope with the lowering of the acetone in the sheath part. The running filament is then led into the coagulating bath. Thus, a different type of selective permeability can be given to the hollow fibre.

With embodiments of this invention, ideal pores can be formed in the membrane of the hollow fibre by the following two principles during coagulation and washing. One is that the aqueous core solution containing salt moves towards the outside of the membrane with the disappearance of phase separation by diffusion and dialysis. Another is that water penetrates into the hollow portion through the membrane from outside so as to lower the concentration of salt in the core solution due to osmosis.

(4) The selective permeability of the hollow fibre can be widely controlled by embodiments of method according to this invention.

Conditions on the aqueous core solution, for example, the kind and concentration of salt can be widely changed in the range of the concentration which is enough to develop the phase separation between the core solution and the solvent of the spinning dope. The effect of salting-out phenomenon is different depending on the kind of salt, kind of cation or anion of the salt and also on the kind of organic solvent used in the spinning dope.

The behaviour of the mutual diffusion between the aqueous core solution and the solvent of the sheath dope is also different depending on the kinds and bulkiness of cation or anion. Thus, by selecting suitable conditions, the selective permeability of the resulting hollow fibre can be widely varied. The running distance of the extruded dope filament between the nozzle and the surface of the coagulation bath can be also varied. And, if desired, a positive action to evaporate the solvent from the running dope filament to a desired extent can be taken before being introduced into the coagulation bath. On the contrary, special action to prevent the evaporation of the solvent from the running filament can be taken, for example, by covering the running filament with a cylindrical hood.

If desired, inside the hood, the vapour of the solvent can be introduced to minimize the evaporation. Embodiments of method according to this invention may be applied to the dry-spinning method in which a positive action to dry the running filament is taken while the filament runs in the spinning cell. The hollow fibre thus produced is suitable for desalination and purification of water or concentration of juice on the basis of the principle of reverse osmosis.

(5) The membrane of the hollow fibre can be partially or totally hydrolyzed in a special way. As already described, the core solution contacts the sheath dope at the interface. Consider a case where the core solution is basic or acidic, and the sheath dope is made of acetone and cellulose acetate. The inner wall of the sheath dope can be hydrolyzed at the interface. During the phase separation, the alkali aqueous core solution cannot penetrate into the inside of the sheath dope, and the internal portion of the sheath dope cannot be allowed to react with alkali. Accordingly, it is possible to hydrolyze limitedly the inside wall of the membrane.

The membrane of the hollow fibre can be partially or totally hydrolyzed, depending on the manufacturing condition. When the alkali core solution is removed from the hollow portion of the cellulose acetate hollow fibre in such a condition that the inside wall of the membrane is limitedly hydrolyzed, then a thin layer of cellulose is regenerated around the inside wall of the membrane which functions as an active layer for selective permeability, but the major portion of the membrane still remains as cellulose acetate which acts as a substrate.

(6) A hollow fibre can be manufactured in which the degree of hydrolysis is higher in the portions nearer to the inner surface of the membrane of the hollow fibre. As already described, the alkali or acidic core solution contacts with the spinning solution at the interface. When the dope-filament is led into the coagulation bath, the phase separation disappears. Thus, alkali or acidic core solution begins to diffuse into the sheath dope. When the dope membrane contacts with water in the coagulation bath, water penetrates into the dope-membrane from outside due to osmosis, accompanying coagulation. The concentration of the alkali in the membrane is thus lower in the portions nearer to the outer surface of the membrane of the hollow fibre. Accordingly, hollow fibres can be obtained in which the degree of hydrolysis is lower in the portions nearer to the outer surface of the membrane. When cellulose acetate is used as the spinning solution, a hollow fibre in

which the inside wall of the membrane is made of regenerated cellulose, and the outside of the membrane is made of cellulose acetate can be obtained.

(7) A hollow fibre can be manufactured in which the membrane is more hydrophilic in the portions nearer to the inside wall. For example, consider that polyacrylonitrile solution in dimethyl formamide is used as the spinning dope. This is extruded as the sheath solution and the aqueous core solution containing sodium carbonate and sodium hydroxide is introduced in the interior portion of the sheath solution. The hydrolysis reaction occurs at the contact interface between the core and sheath solutions. A major part of dimethyl formamide is evaporated from the spun sheath dope while the spun-filament passes through a spinning cell. By evaporating the solvent, the phase separation disappears. The alkali aqueous solution thus gradually penetrates into the sheath membrane. When the filament is led into the coagulation bath, the dimethyl formamide retained in the membrane diffuses out into the water of the coagulation bath, and alkali moves outwards through the membrane, while water comes into the interior aqueous core portion through the membrane from the outside. As a result, the concentration of alkali in the outer portion of the membrane is greatly diluted. By employment of suitable conditions a hollow fibre can be manufactured in which the inner surface of the membrane is hydrolyzed to polyacrylic acid, the portions of the membrane close to the inner surface are partially hydrolyzed to a mixture of polyacrylic acid and polyacrylamide, the outside portions of the membrane close to the outer surface are also partially hydrolyzed to form a mixture of polyacrylamide and polyacrylonitrile, and the outer surface of the membrane still remains as polyacrylonitrile. In such a hollow fibre, the membrane is more hydrophilic in the portions nearer to its inner surface.

(8) A hollow fibre can be manufactured in which the membrane is more swellable in water in the portions nearer to the inner surface of the hollow fibre. This advantage has essentially the same characteristics as that described in the above item (7). The major constitution of the substance in the membrane varies in the direction of the thickness of the membrane, that is polyacrylonitrile, polyacrylonitrile-polyacrylamide, polyacrylamide-polyacrylic acid, polyacrylic acid in that order from the outer surface to the inner surface. Accordingly, it will be understood that the membrane is more swellable in water as it comes to nearer to the inner surface.

When polymethyl methacrylate is used as a starting material for the production of the hollow fibre, a hollow fibre can be manufactured in which the inner surface of the membrane or inside portions close to the inner surface is mainly polymethacrylic acid, and the content of polymethacrylic acid decreases in the direction towards the outer surface of the membrane, which remains as polymethyl methacrylate in unhydrolyzed form. This hollow fibre shows more swellability in the portions nearer to the inner surface. The total degree of hydrolysis and the degree of hydrolysis in the portions in the direction of the thickness of the membrane can be controlled by the selection of the manufacturing conditions. For example, the alkali core solution can be removed from the interior portion by cutting both ends of the fibre to a certain length, and then the cut-open hollow fibre obtained is subjected to washing. When an acidic aqueous coagulation bath, for example, containing acetic acid is used, the acetic acid penetrates into the membrane to neutralize the alkali in the membrane to form a buffer solution. In this case, only the inner surface or the portions close to the inner surface can be hydrolyzed.

In order to prevent the dissolution of the hydrolyzed parts in water, a small amount of a hydrophobic monomer may be incorporated by co-polymerization into the starting material. For example, a suitable amount of styrene may be copolymerized.

(9) A hollow fibre can be hydrolyzed without using a conventional hydrolysis process. As already described, the alkali or acidic aqueous solution is diffused outward through the membrane from the interior portion of the spun filament by dialysis. During its diffusion the material constituting the spun filament can be hydrolyzed. Accordingly, the conventional hydrolysis process is not required.

(10) A hollow fibre while is superior in anti-thrombus properties can be provided. Recently, a blood dialysis apparatus using hollow fibres has been widely used, since it has many advantages. However, it has a serious disadvantage that blood is apt to clot in the hollow fibres. Such a disadvantage has been considered inevitable, since blood flows through the very narrow hollow portion of the hollow fibre. A hollow fibre having the hydrophilic inner surface, exhibits a remarkable anti-thrombus property. The reason is not clear at present, but is presumably due to the hydrogel effect of the swollen wall or to the appearance of negative charges from carboxylic acid derived on the inner surface.

(11) A hollow fibre which is hydrophilic and has excellent mechanical properties can be provided. It has recently become known that a hydrophilic polymer is useful as a

biocompatible material and is superior in anti-thrombus properties.

For example. poly-hydroxyethyl acrylate (manufactured as Hydron, a trade name) is reported as an anti-thrombus material. However, a membrane made from Hydron is very weak in mechanical strength, and is therefore useless in practice. The membranes of polyacrylic acid or polymethacrylic acid absorb too much water, and are too weak in mechanical strength.

On the other hand, in the hollow fibre produced by embodiments of this invention, the hydrolyzed portions which are hydrophilic and inferior in mechanical strength are supported with adjoining less-hydrolyzed portions which are relatively hydrophobic and have good mechanical strength. Accordingly, the hollow fibre is, as a whole, superior in mechanical strength, and moreover has a good selective permeability. Although the molecular weight of the inner surface of the hollow fibre is more or less lowered by hydrolysis, high mechanical strength can be obtained by the outside portion of the membrane having the high molecular weight.

(12) A hollow fibre can be manufactured which maintains good selective permeability, even after the hollow fibre is dried. It is generally known that the selective permeability of a membrane is irreversibly lowered after being dried. For example, wet cellophane (Registered Trade Mark) produced by the viscose process which looks like a swollen gel has a remarkable selective permeability. However, when the cellophane is once dried, and then again wetted, the highly selective permeability of the gelled cellophane cannot be reproduced. The same can be said for the membrane of cuprophane produced by the cuprammonium process. Accordingly, the membrane of cuprophane for blood dialysis is plasticized with glycerin to prevent the reduction of the selective permeability during storage in the dry state. The reason why the selective permeability of the membrane is lowered after being dried seems that some structure develops, forming crystalline regions by the movement of molecular chains accompanying the relaxation of the super-structure which results in the collapse of micro-pores in the membrane.

The change or relaxation of the structure seems to be closely correlated with the swellability (or elongation) in the wet state, and with the shrinkage behaviour during drying. The greater change of the volume (shrinkage) during drying suggests a greater change of the structure or relaxation of the structure. The micro-pores of the membrane are collapsed by the relaxation of the structure. The cellulose membrane which has been most widely used for blood dialysis shows a great change in volume between wet and dry states, showing the big disadvantage of the cellulose membrane in view of the structural change or relaxation on drying.

Hollow fibres made by embodiments of the method according to this invention can overcome the above-described disadvantage of the conventional cellulosic hollow fibre. For example, in the hollow fibre made of cellulose acetate, the inner surface of the hollow fibre can be a regenerated cellulose having high selective permeability, and the major portion of the membrane which supports the inner surface is made of hydrophobic cellulose acetate. When the hollow fibre is once dried and again wetted, the change in the volume is controlled by the cellulose acetate substrate which constitutes the major portion of the membrane. Thus, the inner cellulose layer of the hollow fibre cannot make a big volume change, unlike the conventional cellulose. In other words, the structure of the membrane of the hollow fibre does not undergo a big change after being dried. This is probably the reason why the selective permeability can be maintained after being dried. The above-described fact is also true both for a hollow fibre made of polyacrylonitrile and polymethyl methacrylate, whose inner surface is hydrolyzed to polyacrylic acid and polymethacrylic acid respectively. The hydrolyzed inner portion is very hydrophilic in nature and has a high selective permeability. The disadvantage that the inner surface portion is weak in mechanical properties by itself can be overcome by being supported with a very hydrophobic, and strong un-hydrolyzed polymer substrate. Accordingly, the hollow fibre is, as a whole, good in mechanical strength and selective permeability. The hollow fibre blood dialyzer in the market is filled with formalin solution. Before being used for therapy, the formalin must be completely removed and this operation takes a long time and is troublesome.

However, hollow fibres for blood dialysis made by embodiments according to this invention can be stored and transported in the dry condition. This is very convenient and safe in handling.

(13) A hollow fibre having a nearly true-circular cross-section and uniform thickness of membrane can be manufactured. It is generally known in a dry jet-wet spinning process to produce conventional fibre such as the acrylic fibre, that the length of the running passage of the extruded dope-filament in a gaseous space from the nozzle

to the coagulation bath surface is very important to produce a uniform denier of the filament.

The shorter the length, the more uniform the filament produced. Particularly, when the filament is used for clothing, even a small variation of the denier of the filament develops un-evenness of the dyeing, and reduces the commercial value. Accordingly, the length of the passage of the running dope in the gaseous space is extremely important and it is generally recommended that the length should be less than 10 mm, preferably 5 mm.

On the other hand, the inventor has intensively investigated methods of manufacturing hollow fibres and found that to produce a hollow fibre having true circular cross-section and uniform thickness of the membrane, more than at least a certain length between the nozzle and coagulation bath surface is necessary, contrary to the common knowledge in this field. The length should be at least 5 mm and preferably longer than 10 mm. When the gaseous passage mentioned above is too short, the resulting hollow fibre often has un-even thickness, and poor controllability of the wall thickness is observed.

The thickness of the sheath dope will be averaged by the surface tension of the dope around the core solution during the drafting of the spun dope in the gaseous space. If the gaseous space is too short, the dwelling time of the dope filament in the gaseous space is too short to average the thickness of the sheath solution. This type of averaging effect of the sheath dope thickness can only be attained when the core solution is phase-separated from the sheath dope. But to attain satisfactory uniform thickness of the sheath dope, a distance longer than 5 mm is preferable, otherwise the unevenness of the sheath dope thickness is carried over into the final hollow fibre.

Since it is very difficult to position the inner orifice for the core liquid concentrically with the annular slit, the above described, averaging effect of the sheath dopes is very significant. When nozzle multi-holes are used, it is much more difficult, and almost impossible that all of the holes in the nozzle are concentrically positioned relative to the double pipe orifice.

Embodiments of method according to this invention can overcome difficulty by the employment of dry jet-wet spinning procedure with the gaseous space longer than 5 mm for the spun-running dope.

(14) While the extruded dope filament runs through the gaseous space of a certain length, the core aqueous solution containing salt, and the sheath solution have preferable influences on each other. As already described, these two solutions are phase-separated and a definite boundary layer exists in between. However, the boundary interface does not perfectly cut off the correlation between the two solutions, and they have subtle influences on each other. In more detail, a small amount of the solvent of the sheath solution penetrated into the core solution through the boundary interface, while a small amount of water diffuses into the sheath solution through the interface during the time that the spun-dope filament is running in the gaseous space. This gives a delicate shade of gellation to the sheath solution which contributes to the improvement of spinnability and also to the improvement of the permeability of the resultant hollow fibre.

(15) The coagulated filament maintains its true circularity in cross-section in the coagulation bath. The spun dope filament changes its running direction in the coagulation bath and washing water bath by guide bars in the production process. After passing the processes mentioned above, the hollow fibre is wound up on a take-up coil. During these processes, the running filament is strongly pressed on a guide bar several times, and the coagulating filament becomes flat or deformed. Surprisingly, in embodiments of the method according to this invention, the flattened or deformed filament easily recovers its circularity in cross-section. The reason is that water rapidly penetrated through the membrane into the core part so as to dilute the salt concentration due to osmosis, and the interior portion is always positively pressurized.

Next, the hollow fibre and the method of manufacturing the same, according to this invention, will be described in more detail with reference to examples and reference examples.

Reference Example 1

30 parts of cellulose acetate having a mean degree of polymerization of 150 and a degree of acetylation of 39.8% was dissolved into a mixed solvent of 60 parts of acetone and 10 parts of triethylene glycol to prepare a spinning solution.

The spinning solution was extruded into a gas medium by a constant feed pump from an annular slit. The slit has an external diameter of 2.0 mm and an internal diameter of 1.4 mm, and simultaneously water was extruded from an inner orifice positioned concentrically with the annular slit. The spinning solution extruded from the annular slit instantaneously became whitish and has very poor thread forming properties. The fibre obtained was very brittle and useless in practice. The reason was that mutual diffusion rapidly developed between the extruded sheath spinning solution and the water in the core liquid so that numerous unfavourable macro-voids developed in the membrane of the fibre. The take-up speed of the fibre was at most 13 m/min.

Reference Example 2

A ternary copolymer of acrylonitrile-methylacrylate-methallylsulphonic acid (93:3:4) having an intrinsic viscosity of 1.6 dl/g in dimethyl formamide at 30°C was dissolved in a dimethyl formamide to prepare a 30% spinning solution.

The spinning solution was extruded into a mixed coagulating bath of dimethyl formamide and water from an annular slit. The slit has an external diameter of 1.5 mm and an internal diameter of 1.0 mm, and simultaneously a 3% sodium phosphate aqueous solution was extruded from an inner orifice. A filament extruded from the orifice instantaneously became whitish and had remarkably poor thread-forming properties. The resulting hollow fibre was useless for practical use. The results were the same even when the conditions of the spinning operation were variously changed.

A similar result to that in this reference example was obtained when 28 parts of cellulose acetate having a mean degree of polymerization of 180 and a degree of acetylation of 40% was dissolved in a mixed solvent of 60 parts of acetone and 10 parts of triethylene glycol to prepare a spinning solution, and a 3% sodium chloride solution was used as a core solution.

Example 1

30 parts of cellulose acetate having a mean degree of polymerization of 150 and a degree of acetylation of 39.8% was dissolved in a mixed solvent of 60 parts of acetone and 10 parts of triethylene glycol to prepare a spinning solution.

The spinning solution (35° C) was extruded by a constant feed pump from an annular slit having an external diameter of 2.0 mm and an internal diameter of 1.4 mm, and simultaneously an aqueous solution containing 20% sodium chloride and 5% sodium hydroxide was extruded as a core solution. The extruded filament was passed through a spinning cell having a length of 1 m in which nitrogen at 70°C was counter-currently flowing at a rate of 1 m/sec, then it was introduced into a coagulating bath (water bath).

The spinnability in this example was excellent and the extruded dope had good thread-forming properties. Maximum take-up speed was 130 m/min. The fibre obtained was not whitish and was transparent. The fibre was sufficiently washed in a water bath at 20° C to remove the salt solution in the interior portion thereof and introduced into a glycerine bath for plasticization, and thereafter dried at 60° C in a constant length.

The resulting hollow fibre had a high tensile strength and had a dry strength of 2.2 g/d. The hollow fibre showed excellent permeabilities for urea, creatinine, sodium chloride and vitamin B_{12}.

The membrane of this hollow fibre was divided into two parts, one being nearer to the internal wall surface and the other being nearer to the external wall surface. According to the infra-red spectra for these two parts, it was found that the part nearer to the external wall surface showed an absorption spectrum similar to that for cellulose acetate, being a raw material, while the infra-red spectrum for the part nearer to the internal wall surface showed a remarkable decrease of carbonyl group and development of new peaks due to the formation of hydroxy group. In particular, the latter part gave an absorption spectrum similar to that for cellulose. These data indicated that cellulose was regenerated by hydrolysis of cellulose acetate at the part nearer to the internal wall surface, particularly at the internal wall surface. The hollow fibre after being dried had a permeability substantially the same as the permeability before being dried. The permeability was measured as clearance as follows using pseudo-blood dialysis:

	Clearance Before drying	After drying
Urea	152	153
Uric Acid	112	106
Vitamin B_{12}	22	24

The clearance C_L is defined as the following formula:

$$C_L = Q_B \frac{C_{Bi} - C_{Bo}}{C_{Bi}}$$

where Q_B stands for the pseudo-blood flow rate (ml/min) and C_{Bi} and C_{Bo} for the concentrations of ingredients at an inlet and an outlet of the pseudo-blood, respectively.

Example 2

28 parts of cellulose acetate having a mean degree of polymerization of 185 and a degree of acetylation of 40% was dissolved in a mixed solvent of 69 parts of acetone and 3 parts of water to prepare a spinning solution.

The spinning solution (38° C) was extruded as a sheath solution from an annular slit having an external diameter of 1.5 mm and an internal diameter of 1.0 mm, and simultaneously an aqueous solution containing 27% sodium chloride and 3% potassium hydroxide was extruded as a core solution. The extruded dope was passed through a spinning cell having a length of 2 m in which nitrogen at 90° C was counter-currently flowing at a rate of 1.2 m/sec. Then the filament was introduced into a coagulating bath of an aqueous solution containing 20% acetone. The fibre was subsequently washed by 1% acetic acid aqueous solution.

The spinnability in this example was excellent and the spun dope had excellent thread-forming properties. Thus a hollow fibre having an uniform circular cross-section was obtained in a very stable condition at a take-up speed 125 m/min. The fibre was sufficiently washed in a water bath at 20° C to remove the salt from the hollow portion thereof and then plasticized by glycerine and dried at 60° C in a constant length.

The hollow fibre obtained was strong and had a dry tensile strength of 1.8 g/d. It was found that the fibre showed very good permeability and ultra-filtration properties. The membrane of the fibre was divided into two parts, one being nearer to the internal wall surface and the other being nearer to the external wall surface. According to the infra-red spectra for these two parts, the latter part showed an absorption spectrum similar to that for cellulose acetate, while the former part showed a similar absorption spectrum to that for cellulose, which indicates that hydrolysis had taken place in the former part.

Example 3

28 parts of cellulose acetate having a mean degree of polymerization of 180 and a degree of acetylation of 39.8% was dissolved in a mixed solvent of 69 parts of acetone and 3 parts of ethanol to prepare a spinning solution.

The spinning solution (40° C) was extruded as a sheath solution, and simultaneously an aqueous solution containing 20% calcium chloride and 5% concentrated hydrochloric acid was extruded as a core solution. The spinnability was excellent and a fibre which was transparent was obtained at a take-up speed of 135 m/min. The spun filament was passed counter-currently through a nitrogen stream adjusted to 80° C which was flowing at a rate of 1.5 m/sec, and thereafter it was introduced into a mixed bath of water-calcium chloride (80:20). The fibre was then coagulated in a water bath and then sufficiently washed. After the core liquid had been moved, it was sufficiently washed and then plasticized by glycerine and dried at 20°C.

The resultant hollow fibre had a cross-section similar to true circle and a very high uniformity. The hollow fibre was strong and had excellent permeability and ultra-filtration properties.

Example 4

30 parts of cellulose acetate having a mean degree of polymerization of 150 and a degree of acetylation of 39.8% was dissolved in a mixed solvent of 60 parts of acetone and 10 parts of triethylene glycol to prepare a spinning solution.

The spinning solution was maintained at 38° C and was extruded as a sheath solution into a mixed bath at 30° C of water-acetone (80:20) by wet spinning. Simultaneously, an aqueous solution containing 30% calcium chloride and 5% concentrated hydrochloric acid was extruded as a core solution. Spun gelled fibre was subsequently washed in a water bath at 25° C and then plasticized by glycerine and dried at a constant length.

The resulting hollow fibre was substantially transparent and had a uniform cross-section close to a true circle and had excellent ultra-filtration properties.

The spectrometric examination of this fibre, showed that hydrolysis had taken place in a part nearer to the inner wall surface of the hollow fibre, where cellulose was regenerated.

Example 5

30 parts of cellulose acetate having a mean degree of polymerization of 170 and a degree of acetylation of 39.8% was dissolved in a mixed solvent of 60 parts of acetone and 10% of triethylene glycol to prepare a spinning solution.

The spinning solution was extruded by a constant feed pump from an annular slit having an external diameter of 2.0 mm and an internal diameter of 1.2 mm, and simultaneously an aqueous solution containing 20% ammonium chloride and 5% concentrated hydrochloric acid was extruded as a core solution in the usual manner. The extruded filament was passed through a spinning cell having a length of 3 m in which nitrogen at 60°C was flowing counter-currently at a rate of 1.5 m/sec, and then the filament was introduced into a water bath containing 10% acetone and subsequently introduced into another water bath at 30° C for removing the solvent.

The spinnability in this example was excellent and the dope extruded had good tread-forming properties without being broken. Take-up speed was 110 m/min. The resulting fibre was cut at a suitable interval of length and the core solution in the hollow portion thereof was removed. The cut fibre was further sufficiently washed and then introduced into a glycerine bath and dried at 40° C at a constant length.

The hollow fibre obtained was transparent and had a uniform cross-section close to a true circle. Both ultra-filtration and permeability of the fibre were excellent.

Example 6

28 parts of cellulose acetate having a mean degree of polymerization of 185 and a degree of acetylation of 40% was dissolved in a mixed solvent of 69 parts of acetone and 3 parts of water to prepare a spinning solution.

The spinning solution was extruded from an annular slit having an external diameter of 1.5 mm and an internal diameter of 1.0 mm, and simultaneously an aqueous solution containing 20% sodium chloride and 6% sodium hydroxide was introduced into the interior of the extruded dope. The spinning solution was maintained at 38° C and the extruded filament was passed through a spinning cell having a length of 2 m in which an inert gas at 90° C was flowing counter-currently at a rate 1.2 m/sec. The filament was thereafter introduced into a coagulating bath of an aqueous solution containing 20% acetone and then introduced into a water bath and allowed to stand therein, so that an alkaline aqueous core solution was dialyzed through the membrane by the principle of dialysis.

The spinnability in this example was excellent and the extruded dope had good thread-forming properties. Accordingly, a hollow fibre having a uniform cross-section of nearly a true circle was obtained very stably with a maximum take-up speed of 136 m/min. The fibre was plasticized by glycerine and dried at 60° C at a constant length.

The hollow fibre had a dry tensile strength of 1.2 g/d and had excellent dialysis and ultra-filtration performances.

According to the infra-red spectrum for the fibre obtained in this example, the membrane was converted to cellulose by total hydrolysis of the original cellulose acetate.

Example 7

The spinning solution prepared in Example 5 was wet-spun into a mixed acetone-water bath (82:18) containing 5% ammonium chloride. Simultaneously with the extrusion of the spinning solution, 20% ammonium chloride aqueous solution was extruded as a core solution. The resulting gelled filament was further introduced into a water bath to wash sufficiently and was dried in a constant length.

The spinnability in this example was very good. The resulting hollow fibre had very good ultra-filtration performances.

Example 8

The experimental conditions were the same except that an aqueous solution containing 18% potassium sulphate and 6% concentrated sulphuric acid was used as core solution and the temperature of the nitrogen was 90° C.

The spinnability was very good. The filament being passed through the spinning cell was dipped into the water bath for a substantial time for washing, whereby the core solution in the hollow fibre was replaced by the water by dialysis. The fibre was subsequently dried at a constant length.

The hollow fibre obtained was rather transparent and had a uniform cross-section close to a true circle and had an excellent reverse osmosis performance.

The result of analysis showed that hydrolysis of cellulose acetate was taken place up to about half of the membrane thickness from the inner wall surface of the hollow fibre.

Example 9

Tenite butylate (Reference 465E-22300-MH of Eastman Kodak Corp. and a kind of cellulose butylate) was dissolved in a mixed solvent of 70 parts of acetone and 30 parts of methylcellosolve acetate to prepare 24% spinning solution.

The spinning solution was extruded from an annular slit having an external diameter of 2.0 mm and an internal diameter of 1.4 mm, and simultaneously a 28% potassium acetate aqueous solution was extruded as a core liquid.

The spinnability in this example was very stable and the extruded dope filament had good tread-forming properties. A transparent and uniform hollow fibre could be manufactured.

The spun dope filament was passed through an atmosphere of dried inert gas at 90° C to vaporize a large amount of the solvent therefrom, and then introduced into a water bath to remove the remainder of the solvent completely. After being dried, the fibre was subject to heat treatment. The fibre obtained was excellent as a reverse osmosis membrane.

Moreover, additional spinning experiments were made in the same manner as mentioned above by the use of an aqueous core solution containing 20% sodium acetate and 5% sodium hydroxide, or an aqueous solution of 30% sodium acetate instead of the potassium acetate aqueous solution in this example. By these experiments, hollow fibres having good transparency, strength and ultra-filtration properties could be obtained. The spinnability was stable and excellent.

In these experiments, it was also found that hydrolysis was taken place at the inner wall surface of the hollow fibre to regenerate cellulose. The degree of hydrolysis in the membrane decreased in the portions of the membrane nearer to the external wall surface, which remained as the original cellulose butylate.

Example 10

Cellulose propionate having a mean degree of polymerization of 150 was dissolved in acetone to prepare a 29% spinning solution.

The spinning solution was extruded from the annular slit in the same manner as in Example 1, while a 25% sodium phenoxide aqueous solution was used as a core solution.

A transparent and uniform hollow fibre was obtained with a good spinnability. The fibre had a high tensile strength and an excellent ultra-filtration performance.

Example 11

22 parts of cellulose triacetate having a mean degree of polymerization of 360 and a degree of acetylation of 60.5% was dissolved in a mixed solvent consisting of methylene chloride and methanol (90:10) to prepare a spinning solution.

The spinning solution was extruded from an annular slit and simultaneously a 20% sodium phosphate aqueous solution was extruded from an inner orifice.

The hollow fibre of cellulose triacetate was obtained with very stable spinnability. This fibre was manufactured without any problems such as breakage, and had a transparent appearance.

After a large amount of the solvent was vaporized, the filament was introduced into a water-methanol bath (90:10) and further dipped in water for an appropriate time so that sodium phosphate in the hollow portion was removed through the membrane by dialysis, and then dried at 60° C at a constant length.

The hollow fibre obtained had an excellent performance as a reverse osmosis membrane. The result of analysis showed that hydrolysis occurred at the inner wall surface of the hollow fibre, and the inner wall surface was hydrolyzed to be substantially cellulose and a degree of hydrolysis in the membrane reduced nearer to the external wall surface.

Reference Example 3

Instead of the spinning solution used in Reference Example 1, 28 parts of acrylonitrile-methylacrylate copolymer (the former: the latter =94:6) having an intrinsic viscosity of 1.7 dl/g in dimethyl formamide at 30° C was dissolved in 72 parts of dimethyl acetoamide to prepare a spinning solution.

Experimental conditions were the same as those in Reference Example 1, except the spinning solution. The resulting hollow fibre became whitish and had extremely poor thread-forming properties. The take-up speed was at best 13 m/min. The fibre was very brittle and practically useless.

Reference Example 4

Instead of the spinning solution used in Reference Example 2, a commerical polymethylmethacrylate plate was used for preparing a spinning solution, thus 28 parts of polymethylmethacrylate resin was dissolved in 72 parts of acetone.

The spinning solution was extruded in the same manner as described in Reference Example 2, and a 3% sodium acetate or 3% sodium chloride aqueous solution was extruded as a core solution.

The hollow fibre obtained, however, became whitish instantaneously and was very brittle as in Reference Example 2. The extruded dope had very poor thread-forming properties with a maximum take-up speed of 16 m/min.

Example 12

Instead of the spinning solution used in Example 1, 28 parts of acrylonitrile-vinyl acetate copolymer (the former: the latter=94:6) having an intrinsic viscosity of 169 dl/g in dimethyl formamide at 30° C was dissolved in 72 parts of dimethylacetoamide to prepare a spinning solution.

The spinning solution was maintained at 55° C and extruded as a sheath solution as described in Example 1; and simultaneously an aqueous solution containing 20% potassium chloride and 3% potassium hydroxide was extruded as a core solution. The extruded filament was introduced through the spinning cell in which nitrogen was flowing at 120° C.

Subsequent processes were carried out as the same manner as described in Example 1. The hollow fibre formed had a high degree of transparency, good tenacity and showed good permeability. The spinnability and other processability were excellent with a maximum take-up speed of 132 m/min.

With the infra-red spectrum, absorption spectra of carboxylate and amide were observed for the inner wall surface of the hollow portion of the fibre, and nitrile groups were converted to amide and some of them were further hydrolyzed to carboxylic acid. On the other hand, the near region of the external wall surface of the hollow fibre remained as the original acrylonitrile-vinyl acetate copolymer.

Example 13

Instead of the spinning solution used in Example 2, 28 parts of acrylonitrile-methallyl sulphonic acid copolymer (the former: the latter=97:3) having an intrinsic viscosity of 1.8 dl/g in dimethylformamide at 30° C was dissolved in 72 parts of dimethylformamide to prepare a spinning solution.

The spinning solution was maintained at 120° C and extruded from the annular slit in the same manner as described in Example 2, and simultaneously aqueous solution containing 10% sodium phosphate and 15% potassium hydroxide was extruded from the inner orifice. The spun dope filament was passed through the spinning cell, in which an inert gas was flowing at 120°C, and then introduced into the coagulating bath as in Example 2. But in this Example, a water bath at 20° C was used. A fibre having a substantially uniform cross-section of true circle was obtained with very good spinnability. The fibre was then dippped in water so that the alkaline salt solution in the hollow portion was removed by dialysis, and then washed in the water bath at 20° C. The fibre was plasticized by glycerine and dried at 80° C at a constant length, whereby a strong hollow fibre having a dry tensile strength of 2.9 g/d and superior dialysis and ultra-filtration performances could be manufactured.

According to the detailed examination of this fibre, the inner wall surface of the hollow fibre was almost hydrolyzed to carboxylate, which was observed by its absorption spectrum. After being treated with acetic acid, the absorption spectrum was changed to that of carboxylic acid and an absorption spectrum of nitrile groups was scarcely observed. Absorption spectra of carboxylic acid and amide were observed at the parts nearer to the inner wall surface and also an absorption spectrum of nitrile group was slightly observed. These data showed that hydrolysis largely occurred at the parts nearer to the inner wall surface. The amount of nitrile group increased and the amount of carboxylic acid decreased, respectively in the portions of the membrane nearer to the external wall surface, indicating that the degree of hydrolysis was decreased towards the external wall surface, which substantially remained as the original material. When a blood dialyzer using the hollow fibre obtained in this example was used for dialysis therapy, no blood coagulation was observed.

Example 14

Instead of the spinning solution used in Example 3, 26 parts of the crushed commerical polymethyl-methacrylate plate was dissolved in 74 parts of acetone to prepare a spinning solution.

The spinning solution was extruded, and simultaneously an aqueous solution containing 20% potassium carbonate and 5% potassium hydroxide was extruded in the same manner as described in Example 3, which resulted in a transparent fibre with a stable spinning property. The extruded dope filament was passed through the same spinning cell, in which nitrogen was flowing at 70° C, and then introduced into the water bath. The fibre obtained was cut in predetermined lengths and the core liquid was removed therefrom. The fibre was then washed by 2% acetic solution and subsequently washed by water and plasticized with glycerine before being dried at 30° C.

A hollow fibre having a cross-section close to a true circle and a very high uniformity could be obtained. The fibre had a dry tensile strength of 1.8 g/d and good ultra-filtration and dialysis performance.

In the hollow fibre obtained in this example the inner wall surface was almost hydrolyzed so that ester groups were changed to carboxylic acid, and the hydrolyzed parts were relatively limited to the inner wall surface and the parts nearer thereto, while the parts nearer to the external wall surface were still substantially polymethylmethacrylate. Practical blood dialysis by the use of a dialyzer with the hollow fibre obtained in this example showed almost no blood coagulation and good anti-thrombus properties.

Example 15

23 parts of polymethylmethacrylate having a molecular weight of about 48,000 was dissolved in 77 parts of acetone to prepare a spinning solution.

The spinning solution was maintained at 38 C° and then was extruded from an annular slit, and simultaneously an aqueous solution containing 25% calcium chloride and 5% sodium hydroxide was extruded as a core solution. The extruded filament was introduced into a mixed solvent of water-acetone (90:10) after being passed through a gaseous space of 30 cm in length. The coagulated filament was subsequently washed with water at 30° C containing acetic acid. The resulting hollow fibre was wound up and then cut at regulat intervals of length to remove the salt solution from the hollow portion. The fibre was further washed by a 1% acetic acid aqueous solution and washed with water and plasticized by glycerine before being dried. The inner wall surface of this fibre was hydrolyzed to polymethacryl acid while the parts nearer to the external surface remained as the original polymethylmethacrylate.

A blood dialyzer with the hollow fibre

showed a good ability to remove urea and a good anti-thrombus properties.

Example 16

Instead of the spinning solution used in Example 13. 28 parts of copolymer of acrylonitrile and 2-acrylamide-2-methylpropyl sulphonic acid (the former: the latter=97:3) having an intrinsic viscosity of 1.6 dl/g in dimethylformamide at 30° C was dissolved in 72 parts of dimethyl acetoamide to prepare a spinning solution.

The spinning solution was extruded in the same manner as described in Example 13, and simultaneously an aqueous solution containing 10% calcium chloride, 3% hydrogen peroxide and 20% potassium hydroxide was extruded as a core solution. The filament was introduced into a mixed solvent of dimethyl acetoamide-water after being passed through a space 30 cm in length and subsequently washed with a 2% acetic acid aqueous solution and then wound up around a take-up roll. The wound hollow fibre was cut to remove the salt aqueous solution from the hollow portion. The fibre was further washed with water and treated with glycerine before being dried at 80° C.

In the hollow fibre obtained in this example, nitrile groups which had existed at the inner wall surface were hydrolyzed to carboxylic acids while the parts nearer to the external wall surface remained as the original copolymer.

The hollow fibre was transparent and had a uniform cross-section close to a true circle. The fibre also had very good ultra-filtration and dialysis properties.

Example 17

A spinning operation and apparatus used were the same as those described in Example 16, except that a 20% potassium acetate aqueous solution was used as a core liquid. A fibre was spun and subject to washing, plasticizing and drying processes in the same manner as in Example 16.

The spinnability was very good and stable. The resulting fibre was transparent and had a uniform cross-section close to a true circle and showed a very good reverse osmosis performance.

Example 18

Instead of the spinning solution prepared in Example 9, polyvinyl chloride having an intrinsic viscosity of 2.0 dl/g in cyclohexanone at 30° C was dissolved in tetrahydrofuran to prepare a 22% spinning solution.

A hollow fibre was manufactured in the same manner as described in Example 13. The extruded filament had excellent spinnability and thread-forming properties. The fibre obtained was rather transparent and uniform in shape and was found to be very suitable for an ultra-filtration membrane.

Example 19

Instead of the spinning solution prepared in Example 13, poly-γ-benzylglutamate manufactured by the N-carboxylic acid anhydride method was dissolved in dimethylsulfoxide to prepare a 29% spinning solution.

A hollow fibre was manufactured by the use of this spinning solution in the same manner as described in Example 13. Other experimental conditions were the same as described in Example 13. The fibre obtained was transparent and uniform. It also had excellent ultra-filtration performance and satisfactory spinnability.

Example 20

The hollow fibre obtained in Example 2 was dipped into acetone and was allowed to stand for one hour. A greater part of this fibre was dissolved in acetone, however, the part nearer to the inner wall surface was not dissolved in acetone. Infra-red spectra of the acetone-soluble part and the acetone insoluble part are in Fig. 1 and Fig. 2 respectively. The acetone-insoluble part was dissolved in dimethylsulphoxide containing 10% paraformaldehyde and from this solution a membrane was prepared. As understood from these figures, no carbonyl group is found and the hydroxyl group increased at the inner wall surface of the hollow fibre which was hydrolyzed to cellulose, while the soluble part gave the infra-red spectrum similar to that of cellulose acetate.

Example 21

The hollow fibre obtained in Example 13 was cut in a spiral way with a razor. The spiral-cut fibre was bonded on a flat plate in such a manner that the inner side was directed upward, and then sliced by a microtome from the surface to obtain a very thin membrane. A thin membrane of the inner wall surface was thus obtained. On the other hand, another spiral-cut fibre was bonded on a flat plate in a such a manner that the outer side was directed upward, and then sliced by the microtome from the surface to obtain a thin membrane of the outer wall surface. The infra-red spectra for both thin membranes are shown in Fig. 3.

From Fig. 3, it will be understood that the outer surface part is similar to the original polyacrylonitrile from the absorption spectrum, while the peak of carbonyl group is developed and the peak of nitrile group disappears at the inner surface showing the formation of sodium salt of polyacrylic acid.

An infra-red spectrum for the intermediate part of the hollow fibre membrane is shown in Fig. 4. Fig. 4 shows that nitrile groups can be observed although the amount of them is significantly decreased, and absorption spectrum for amide groups can be found, indicating that a part of amide groups was hydrolyzed to acrylamide.

Example 22

The hollow fibre obtained in Example 14 was razor-cut in a spiral way in the same manner as described in Example 21 to obtain a thin membrane of the parts nearer to the inner wall surface and the outer wall surface. Infra-red spectra for these two parts are shown in Fig. 5 and Fig. 6, respectively.

Fig. 5 indicates that free carboxylic acids exists in the form of polymethacrylic acid at the part nearer to the inner wall surface, while the part nearer to the outer wall surface gave an infra-red spectrum similar to that of polymethylmethacrylate.

An infra-red spectrum for the intermediate portion of the hollow fibre membrane is shown in Fig. 7, which indicates that the intermediate portion was partly hydrolyzed to carboxylic acid, since both of an absorption of free carboxylic acid and of methyl ester of carboxylic acid can be observed.

Example 23

Polymethylacrylate having a molecular weight of about 30,000 was dissolved in acetone to prepare a 24.5% spinning solution for manufacturing a hollow fibre. An aqueous solution containing 20% sodium phosphate and 6% sodium hydroxide was used as a core solution. The spinning was carried out with very stable spinnability. The extruded dope-filament was introduced downward through a space of 30 cm length of air and then introduced into an aqueous solution containing 10% phosphoric acid and then washed by water. The fibre was subsequently cut at regular intervals of length to remove the salt aqueous core solution from the hollow portion and then washed by 1% acetic acid aqueous solution before being washed with water and dried at room temperature.

From this hollow fibre, two thin membranes of the inner and outer wall surface parts were sliced respectively in the same way as described in Example 21. Infra-red spectra for these two parts are shown in Fig. 8 and Fig. 9. An absorption of methyl ester of carboxylic acid is found at the outer wall surface part according to Fig. 9. This means that the outer wall was not hydrolyzed. Moreover, absorption of free carboxylic acids is found and absorption of methyl ester disappears at the inner surface according to Fig. 8. This shows that the inner wall was hydrolyzed.

Example 24

The hollow fibres obtained in Example 2 were dyed by a direct-dye (Pontamine Fast Heliotrope β) by which cellulose is dyed. However, cellulose acetate is not dyed. After being dyed, the fibres were sufficiently washed with water. The cross-sections of the fibre were observed through a microscope. The inner wall surface of the fibre obtained in Example 2 was dyed while the other part thereof was hardly dyed. This shows that only the part near to the inner wall surface was hydrolyzed to cellulose.

On the other hand, when the fibre obtained in Example 6 was dyed in the same way as mentioned above, the part nearer to the inner wall surface was deeply dyed, while the degree of dyeing became smaller as the parts in the membrane approach the outer wall surface. This shows that the degree of hydrolysis increased as the parts approach the inner wall surface. In order to confirm this, the fibre membrane was divided into three parts, namely, a part nearer to the inner wall surface, an intermediate part and a part nearer to the outer wall surface, by the use of the method described in Example 21. The absorption ratio of carbamyl group to methylene group,

$$D_{Co}(1740\ \mathrm{cm}^{-1})/D_{CH_2}\ (2870\ \mathrm{cm}^{-1})$$

was measured based upon infra-red spectra of the above three parts. The absorption ratio was nearly zero for the part nearer to inner wall surface, 4.70 for the part nearer to the outer wall surface and 1.76 for the intermediate part. According to these results, it was confirmed that hydrolysis was predominantly performed nearer to the inner wall surface.

The same absorption ratio was measured for the parts nearer to the inner and outer wall surfaces of the fibre obtained in Example 2. The ratio was 0.23 and 5.10 respectively. This shows that the inner wall surface was almost hydrolyzed, while the part nearer to the outer wall surface was not substantially hydrolyzed. The absorption ratio measured for original cellulose acetate for reference was 5.50.

Example 25

The hollow fibre obtained from cellulose acetate in Example 6 was sliced and divided into five sections in the range from the inner wall surface to the outer wall surface by the use of the method described in Example 21. Thus five thin membranes were obtained.

The degree of swelling of these five membranes in water was measured. It was shown that the first membrane, located the nearest to the inner wall surface, was most swollen in water and the degree of swelling decreased as the membrane approaches the outer wall surface. The degree of swelling represented as S was calculated from the following formula:

$$S=\frac{W_s-W_d}{W_0}+100$$

where W_0 stand for the weight of a sample before being measured, W_s for the weight of the sample when swollen with water, and Wd for a weight of the sample when completely dried after being swollen. The result is shown in Fig. 10.

Example 26

The hollow fibre obtained from polymethyl methacrylate in Example 15 was sliced and divided into five sections in the range from the inner wall surface to the outer wall surface by the use of the method described in Example 21.

The degree of swelling in water of these five sections was measured, and the results are shown in Fig. 11. As apparent from Fig. 11, the amount of absorbed water at the parts nearer to the inner wall surface are greater than the parts near to the outer wall.

Example 27

The hollow fibre obtained from acrylonitrile polymer in Example 13 was sufficiently washed by acetic acid and then divided into six sections in the range from the inner wall surface to the outer wall surface by the use of the method described in Example 21. The degree of swelling in water of these sections was measured. The results are shown in Fig. 12, which indicates that the degree of swelling at the first section which was located the nearest to the inner wall surface was greatest. The degree of swelling decreased as the location of the sections approaches the outer wall of the hollow fibre membrane.

Example 28

The hollow fibre obtained from polymethyl acrylate in Example 23 was sliced to form thin membranes and divided into four sections in the range from the inner wall surface to the outer wall surface by the use of the method described in Example 21. It was shown that the part nearest to the inner wall surface was extremely swollen. The degree of swelling is shown in Fig. 13. It will be understood also in this Example that the degree of swelling in water is greater as the sections approach the inner wall surface.

Example 29

The hollow fibre obtained in Example 11 was divided into six sections in the range from the inner wall surface to the outer wall surface by the use of the method described in Example 21. Fig. 14 shows infra-red spectra for the first section nearest to the inner wall surface, the third section corresponding to the intermediate part and the sixth section corresponding to the outer wall surface. These spectra show that the amount of hydroxyl groups are greatest in the first section, intermediate in the third section, and least in the sixth section nearest to the outer wall surface. Degrees of swelling in water of these sections are shown in Fig. 15, which indicates that the degree of swelling increased as the sections approach the inner wall surface.

Example 30

The hollow fibre of polymethylmethacrylate obtained in Example 26 was divided into five sections. A calculation was made based upon a quantitative analysis of how much polymethyl methacrylate was converted to carboxylic acid by the hydrolysis. The results are shown in Fig. 16.

Example 31

A 20% sodium chloride aqueous solution was introduced from the inner orifice as a core solution in Example 1. The other conditions were the same as those in Example 1. The spinnability was excellent and the filament could be wound up on a take-up roll with a maximum speed of 180 m/min. The fibre thus obtained had a tensile dry strength of 2.1 g/d and was very uniform. The fibre was further hydrolyzed to regenerate cellulose. The regenerated fibre showed a superior dialysis performance in a dialysis experiment for a solution containing urea, creatinine, sodium chloride and vitamin B_{12}.

Example 32

Experimental conditions were the same as in Example 2, except that a 30% sodium chloride aqueous solution was used as a core solution. The spinnability was excellent, and uniform hollow fibre having a cross-section of nearly a true circle was obtained with a take-up speed of 175 m/min. The fibre had a dry strength of 2.0 g/d.

Example 33

Experimental conditions were the same as in Example 3, except that a 25% calcium chloride aqueous solution was used as a core solution. The spinnability was surprisingly excellent, and an uniform fibre having a dry-strength of 1.9 g/d and a nearly true circular cross-section was obtained with a take-up speed of 189 m/min.

Example 34

In Example 4, the spinning solution was extruded into a mixed bath at 30° C of water-acetone (75:25), and simultaneously a 35% calcium chloride aqueous solution was extruded from the inner orifice. The spinnability was satisfactory and a uniform hollow fibre was obtained.

Example 35

Experimental conditions were the same as in Example 5, except that a 26% ammonium chloride aqueous solution was used as a core liquid. The spinnability was superior and the thread-forming properties were very good. The fibre was obtained with a take-up speed of 191 m/min. The resultant fibre was then washed with water and hydrolyzed in an alkaline aqueous bath to regenerate cellulose, and thereafter was introduced into a glycerine bath before being dried at 40° at a constant length. The hollow fibre thus obtained showed similar characteristics to those described in Example 5.

Example 36

The spinning solution prepared in Example 5 was wet spun using a 20% ammonium chloride aqueous solution as a core solution in the same manner as described in Example 7. On this occasion, a mixed bath of acetone-water (77:23) containing 5% ammonium chloride was used as a coagulating bath. The spinnability was good and the hollow fibre was very uniform in cross-section.

Example 37

A spinning was carried out by the use of the spinning solution and the apparatus used in Example 35, and a 18% potassium chloride aqueous solution was extruded as a core solution. Nitrogen at 90° C was flowing in the spinning cell.

The spinnability was excellent and was very stable. The dope-filament passed through the spinning cell, and was then sufficiently washed in the water bath. The take-up speed was 168 m/min.

A hollow fibre obtained in this example had good transparency and a uniform cross-section similar to a true circle. The fibre also had very good reverse osmosis properties.

Example 38

A spinning operation was carried out in the same way as described in Example 9, except that a 28% ammonium acetate aqueous solution was used as a core liquid. The spinnability and other processability were excellent and a very uniform hollow fibre having a circular cross-section was obtained with a take-up speed of 192 m/min.

Thus fibre obtained showed the same good characteristics as in Example 9.

Moreover, another spinning operation was carried out by the use of an aqueous solution containing 35% potassium acetate or 30% sodium acetate instead of the above ammonium acetate aqueous solution. A strong uniform hollow fibre having good transparency and a superior reverse osmosis performance could be obtained stably with a take-up speed of 176 m/min.

Example 39

A spinning operation was carried out in the same way as described in Example 11, except that a 20% calcium chloride aqueous solution was used as a core solution. A hollow fibre having good reverse somosis performance was obtained with a maximum take-up speed of 246 m/min. The fibre was uniform in cross-section which was close to a true circle.

Example 40

22 parts of Cotton Linter having a mean degree of polymerization of 900 to 1000 and containing 98% α-cellulose was dissolved in 78 parts of dimethyl sulphoxide containing 20% paraformaldehyde and then non-soluble substances were filtered. The prepared transparent solution was used as a spinning solution.

The spinning solution was extruded by a constant feed pump from an annular slit having an external diameter of 2.0 mm and an internal diameter of 1.2 mm, and simultaneously a 25% ammonium chloride aqueous solution was extruded from an inner orifice as a core solution. The temperature of the spinning solution was 50° C.

The filament was introduced into a coagulating bath of dimethyl sulphoxide-water (1:1) at 40° C after being passed through a gaseous space of length 2 cm and then sufficiently washed in a water bath at 30° C before being dried at 60° C at a constant length.

The resulting hollow fibre was transparent in appearance, and had a cross-section similar to a true circle. The spinnability was excellent, and the filament could be wound up on the roll with a take-up speed of 172 m/min. The fibre was found to be suitable for a blood dialysis.

Example 41

Cellulose comprising high α-structure and having a mean degree of polymerization of 560 was dissolved into dimethyl sulphoxide containing 30% paraformaldehyde to prepare a 26% spinning solution.

The spinning solution was maintained at 120° C and extruded into a spinning cell from an annular slit in the same manner as described in Example 1. A 23% calcium chloride aqueous solution was extruded as a core solution and a spinning cell of a length of 2.5 m with co-current gas flow at 180° C was used. The filament was sufficiently washed by introducing into a water bath at 30° C.

The hollow fibre obtained had a cross-section similar to a true circle and a superior dialysis property. The fibre was also strong and had a dry-strength of 2.9 g/d. The take-up speed in this example was 212 m/min.

Example 42

When a spinning was carried out in the same manner as described in Example 12 using a 20% sodium chloride aqueous solution as a core liquid, maximum take-up speed was 280 m/min. The spinnability was excellent and the extruded dope had very good thread-forming properties. The fibres obtained had transparency with high strength of 20 g/d and good selective permeability.

Example 43

A spinning was carried out in the same manner as described in Example 13, except that a 30% sodium chloride aqueous solution was used as a core solution and an aqueous solution containing 30% dimethyl formamide was used as a coagulating bath.

The spinnability was excellent and the extruded dope had very good thread-forming properties. The fibre obtained had a cross-section of substantially uniform true circle. The maximum take-up speed was 287 m/min. The fibre was then washed in a water bath at 20° C and plasticized with glycerine before being dried at 80° C at a constant length. A hollow fibre having a dry-strength of 2.8 g/d and superior dialysis properties and ultra-filtration properties could be manufactured.

Example 44

A spinning operation was carried out in the same way as described in Example 14, except that a 25% calcium chloride aqueous solution was used as a core solution. The extruded dope-filament was subsequently passed through the spinning cell. The fibre was then washed by water and plasticized by glycerine before being dried at 30° C. The maximum take up speed was 297 m/min. The hollow fibre obtained had a cross-section similar to a true circle and a very high uniformity. The fibre was strong and had a dry-strength of 2.4 g/d. Ultra-filtration properties and dialysis properties of the fibre were good.

Example 45

23 parts of polymethyl methacrylate having a molecular weight of about 48,000 was dissolved into 77 parts of acetone to prepare a spinning solution.

A hollow fibre was manufactured by the use of the above-spinning solution in the same way as described in Example 4. The hollow fibre obtained was rather transparent and had a uniform cross-section similar to a true circle and had very good ultra-filtration properties.

Example 46

Using the spinning solution used in Example 16 and a 26% ammonium chloride aqueous core solution a hollow fibre was produced in the usual manner using the equipment in Example 35. The extruded dope-filament was passed through the same spinning cell in which nitrogen was flowing at 160° C, and the filament was then introduced into a water bath containing 10% dimethyl formamide. The solvent retained in the filament was removed in a water bath at 30° C. The extruded dope had good spinnability and very good thread forming properties. After being washed in water as mentioned above, the fibre was introduced into a glycerine bath and then dried at 40° C at a constant length. The maximum take-up speed was 246 m/min.

The hollow fibre obtained was transparent and had a cross-section similar to a true circle, and a good uniformity in shape. The fibre had very good ultra-filtration and dialysis properties.

Example 47

Instead of extruding the spinning solution prepared in Example 46 into the nitrogen, the spinning solution was wet-spun into a mixed bath of dimethyl formamide-water (70:30) containing 10% ammonium chloride in the usual manner with a 26% ammonium chloride aqueous core solution.

The gelled fibre was introduced into a water bath to be sufficiently washed and then dried at a constant length.

The spinnability was good and stable. The fibre also had a superior ultra-filtration properties.

Example 48

When a spinning was carried out by the use of the same spinning solution and apparatus as those in Example 46, 18% potassium chloride aqueous solution was extruded as a core solution. The extruded filament was passed through the spinning cell in which nitrogen was flowing at 190° C and then washed in a water bath before being dried at a constant length.

The spinnability was very good and stable. The take-up speed was 170 m/min.

The fibre had a high transparency, and a uniform cross-section similar to a true circle and good reverse osmosis properties.

Example 49

Polyvinyl chloride having an intrinsic viscosity of 2.0 dl/g in dimethylformamide at 30° C was dissolved into dimethylformamide to prepare a 22% spinning solution.

A hollow fibre manufacture from this spinning solution in the same way as described in Example 38 had a high degree of transparency and uniformity, and was very good as an ultra-filtration membrane. Spinnability and other processability were excellent, and the maximum take-up speed was 290 m/min.

Moreover, a 35% potassium acetate aqueous solution or a 30% sodium acetate aqueous solution was used as a core solution instead of an ammonium acetate aqueous solution to perform another spinning experiment. Also in this case, a hollow fibre having the same good properties could be obtained with excellent spinnability.

Example 50

A spinning was carried out in the same way as described in Example 10 using the spinning solution prepared in Example 19. The resultant hollow fibre showed the same characteristics as those in Example 10.

Example 51

Acrylonitrile-methyl acrylate copolymer having an intrinsic viscosity of 1.69 dl/g in dimethyl formamide at 30° C was dissolved into dimethyl formamide to prepare a 24% spinning solution.

The spinning solution was extruded from an annular slit into a stream of an inert gas atmosphere, and simultaneously a 20% calcium chloride aqueous solution was extruded from an inner orifice. The extruded dope-filament was passed through a gaseous space having a length of 8 mm from the annular slit and the instantaneously introduced into a coagulating bath at 50° C of dimethyl acetoamide-water (55:45). The fibre was subsequently washed in a water bath at 20° C and further dried at 60° C at a constant length. The maximum take up speed in this example was 256 m/min.

The hollow fibre obtained had a cross-section similar to a true circle and a very good dialysis property.

Example 52

Polymethyl methacrylate having a mean molecular weight of 36,000 was dissolved into acetone to prepare a 20% spinning solution.

The spinning solution was extruded from the annular slit as described in Example 51, and simultaneously a 18% sodium chloride aqueous solution was extruded from the inner orifice. The extruded dope filament was passed through a space having a length of 1 cm and then introduced into a coagulating bath of an acetone-water mixed solvent to coagulate, and subsequently was washed with water before being dried. The take up speed was 143 m/min. A rather transparent and strong hollow fibre was obtained. The fibre was found to have very good dialysis properties.

Example 53

A commercial cellulose diacetate having a degree of polymerization of 151 supplied by Eastman Kodak Corp. was dissolved into acetone to prepare a spinning solution.

The spinning solution was maintained at 30° C and was extruded from an annular slit vertically downward at a rate of 1.7 ml/min, and simultaneously an aqueous solution containing 23% calcium chloride was extruded as a core liquid from the orifice encircled by the annular slit.

The spinnability was very good. The resultant fibre had a beautiful appearance. The extruded dope filament was introduced into a water bath at 30° C, the surface of the bath being 30 cm below from the nozzle. In the water bath, the fibre was run about 3 m substantially in the horizontal direction. The course of the running filament was changed by a guide bar. The fibre was then wound up on a take-up roll. Even when the take-up speed was raised progressively to 160 m/min, the fibre could be wound up very stably without any breaking of the filament.

The more the take-up speed increases, the more strongly is the spun filament pressed on the guide bar in changing the running direction in the water bath. As a result, the filament was deformed to be flat, however, it recovered to the original cross-section of a true circle while running in the water bath. The cross-section of the hollow fibre wound up on the take-up roller at a speed of 130 m/min had uniform thickness and was true-circular as shown in Fig. 17.

Reference Example 5

A spinning operation was the same as that in Example 53 except that a distance between the nozzle surface and the liquid surface of the coagulating bath (water bath) was 4 mm. In this case, the maximum winding-up speed was 103 m/min. The cross-section of the hollow fibre wound up at such a speed was not uniform as shown in Fig. 18.

Example 54

The spinning conditions were the same as those in Example 53 except the distance between the nozzle surface and the coagulation bath surface was variously changed. The cross-sections of the resultant fibres were observed. These results are shown in the following table, which indicates that a deformation of the resulting fibre becomes greater when the distance between the nozzle surface and the coagulating bath surface becomes less than 5 mm.

Distance between nozzle surface and coagulating bath surface	Maximum winding-up speed (m/min)	Shape of cross-section (Uniformity of membrane thickness)	Degree of flatness
2 mm	60	bad	rather flat
4 mm	80	,,	flat
6 mm	102	fairly good	almost true circle
20 mm	150	good	true circle
50 mm	160	,,	,,
100 mm	162	,,	,,
150 mm	160	,,	,,
200 mm	170	,,	,,
250 mm	170	,,	,,
300 mm	170	,,	,,
500 mm	180	,,	,,
1 m	260	,,	,,
2 m	300*	,,	,,
3 m	500	,,	,,
7 m	560*	,,	,,

* The solvent was positively vaporized by supply of hot air.

Example 55

Copolymer of acrylonitrile-methyl acrylate (94:6) having an intrinsic viscosity of 1.7 dl/g in dimethyl formamide at 20° C was dissolved into dimethyl acetoamide to prepare a 26% spinning solution.

The spinning solution was extruded from the annular slit vertically downward as described in Example 53, and simultaneously a 23% sodium chloride aqueous solution as a core liquid was extruded into the hollow portion of the spun dope-filament. The filament was introduced into a water bath after passing through a space having a length of 20 cm. In the water bath, the filament was run substantially in the horizontal direction after the running course was changed by a guide bar, and was wound up on a take-up roll at a speed of 80 m/min. The maximum winding-up speed was 186 m/min.

The hollow fibre obtained was lustrous and transparent, and had a good tenacity. The cross-section of the fibre was uniform and maintained a true-circular shape.

Reference Example 6

Spinning conditions were the same as those in Example 55 except that a running distance of a spun dope filament from the nozzle to the coagulating bath surface (water bath) was 3 mm. On this occasion, the maximum winding-up speed was 86 m/min. In this example, the fibre was wound up at a speed of 80 m/min in order to equalize the experimental conditions to those of Example 55. The cross-section of the fibre thus obtained was observed. The result was that the extent to which a truely circular cross-section was maintained was inferior to that obtained in Example 55. Some deformation and flatness were observed and the thickness of the membrane was not uniform.

Example 56

Spinning conditions were the same as those in Example 55 while the distance between the nozzle and the coagulating bath surface was variously changed. The maximum winding-up speed and the cross-section of a resultant hollow fibre were observed. These results are shown in the following table.

Distance between nozzle surface and coagulating bath surface	Maximum winding-up speed (m/min)	Shape of cross-section (Uniformity of membrane thickness)	Degree of flatness
2 mm	40	bad	flat
4 mm	42	"	"
6 mm	102	good	almost true circle
10 cm	120	"	true circle
30 cm	128	"	"
50 cm	130	"	"
120 cm	130	"	"
200 cm	135	"	"

Example 57

Chips of a commerical polymethylmethacrylate were dissolved into acetone to prepare a spinning solution. Spinning conditions were the same as those in Examples 53 and 55 except that a 21% ammonium chloride aqueous solution was used as a core liquid.

The extruded dope filament was introduced into a water bath after being passed through gaseous space having a vertical length of 43 cm substantially vertically downward and then wound up on a wind-up roll as described in Example 53.

The hollow fibre obtained had an almost uniform cross-section close to a true circle. The distance between the nozzle and the coagulating bath surface was changed and the maximum wind-up speed and the cross-section of the fibre were observed.

It was found that the maximum wind-up speed was more than 90 m/min in all cases when the running distance of the dope filament before being introduced into the coagulation bath was more than 5 mm, while it was abruptly decreased and became 40 m/min or less when the running distance of the filament was less than 5 mm. The cross-section of the hollow fibre obtained was not uniform when the running distance was less than 5 mm. The cross-section become flat and deformed because the maintenance of a true circle was poor.

Example 58

Spinning conditions were the same as those in Example 53 except that a dimethyl formamide solution of polyvinyl chloride was used as a spinning solution. The space running distance of the spun dope filament was also 30 cm as in Example 53.

On this occasion, the extruded dope had a good spinning property. The fibre obtained was rather transparent, beautiful and lustrous. The maximum wind-up speed was 180 m/min and the cross-section of the fibre was close to a true circle and uniform in thickness.

The distance between the nozzle surface and the coagulating bath surface was variously changed and the spinnability and the cross-section of the fibre were observed. It was found that the spinnability abruptly became poor when the running distance became less than 5 mm, and that the maximum wind-up speed became nearly 60 m/min. In this case, the thickness of the membrane of the fibre was uneven and was not uniform. This fibre had a poor maintenance of a true circle and showed a non-uniform flat cross-section.

WHAT WE CLAIM IS:—

1. A method of manufacturing a hollow fibre, including the steps of extruding a spinning solution of high molecular weight compound from an annular slit into a coagulating bath spaced from said annular slit by at least 5 mm, and extruding an aqueous solution containing a water-soluble salt from an orifice encircled by said annular slit, the concentration of said water-soluble salt in said aqueous solution being sufficient to develop a phase separation between said spinning solution and said aqueous solution.

2. A method according to claim 1 wherein said aqueous solution is acidic or alkaline.

3. A method according to claim 2 wherein said water-soluble salt gives acidity or alkalinity in water.

4. A method according to claim 1 wherein acid or base is added to said aqueous solution containing said water-soluble salt.

5. A method according to claim 1 wherein said water-soluble salt is an inorganic salt including at least one of a lithium salt, a sodium salt, an ammonium salt, a potassium salt, a magnesium salt, a calcium salt, a cadmium salt and a zinc salt.

6. A method according to claim 1 wherein said water-soluble salt is an organic salt including at least one of an organic carboxylic acid salt, an alcoholate, a phenolate, and an organic sulphonic acid salt.

7. A method according to any one of the preceding claims wherein the concentration

of said water-soluble salt is 5 to 50% by weight.

8. A method according to claim 1 wherein said high molecular weight compound is cellulose or a cellulose derivative.

9. A method according to claim 1 wherein said high molecular weight compound is a synthetic high molecular weight compound which is at least one of vinyl polymer, vinyl copolymer, polyester, polypeptide, polyurethane, polyurea, polythioamide and polypropylene oxide.

10. A method according to any one of the preceding claims wherein said high molecular weight compound is hydrolyzable.

11. A method according to any one of claims 1 to 9 wherein said high molecular weight compound has a hydrolyzable side chain.

12. A method according to claim 10 wherein at least one of a hydroxyl group, a carboxyl group, an amino group, an imid group, and a sulphonic group is yielded by hydrolysis of said high molecular weight compound.

13. A method according to any one of the preceding claims wherein said high molecular weight compound is dissolved into an organic solvent miscible with water, to form said spinning solution.

14. A method according to any one of the preceding claims wherein said spinning solution is downwardly extruded substantially in the vertical direction into said coagulating bath.

15. A method according to claim 14 wherein said coagulating bath is spaced from said annular slit by more than 10 mm.

16. A method according to any one of the preceding claims wherein said coagulating bath is a water bath or a water-containing bath.

17. A method according to any one of the preceding claims wherein at least part of the solvent of said spinning solution is evaporated between said annular slit and said coagulating bath.

18. A method according to claim 2 wherein said acid or alkali in said aqueous solution occupying the hollow portion of said hollow fibre is dialysed through the membrane of said hollow fibre, whereby said water-soluble salt in said aqueous solution is removed from the hollow portion of said hollow fibre.

19. A method according to claim 2 wherein said aqueous solution occupying the hollow portion of said hollow fibre is removed by cutting said hollow fibre, and said hollow fibre is then neutralized.

20. A method according to claim 2 wherein said acid or alkali occupying the hollow portion of said hollow fibre is neutralized from outside by dipping said hollow fibre into an alkaline or acidic solution.

21. A hollow fibre manufactured by a method according to any one of the preceding claims.

22. A hollow fibre according to claim 21 wherein the inner portion closer to the internal wall of the membrane of said hollow fibre and the outer portion closer to the external wall thereof are different from each other in the degree of hydrolysis.

23. A hollow fibre according to claim 22 wherein the outer surface of the membrane of said hollow fibre is not hydrolyzed.

24. A hollow-fibre according to claim 22 wherein portions of the membrane of said hollow fibre nearer to the inner surface swell more in water than do the portions nearer to the outer surface.

25. A hollow fibre according to claim 22 wherein portions of the membrane of said hollow fibre nearer to the inner surface are more hydrophilic than portions nearer to the outer surface.

26. Use of a hollow fibre according to any one of claims 21 to 25 wherein the membrane of said hollow fibre is used as a selectively permeable membrane.

27. Use of a hollow fibre according to any one of claims 21 to 25 wherein the membrane of said hollow fibre is used for purification of or dialysis of blood, ultrafiltration or reverse osmosis.

28. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 1.

29. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 2.

30. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 3.

31. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 4.

32. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 5.

33. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 6.

34. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 7.

35. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 8.

36. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 9.

37. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 10.

38. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 11.

39. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 12.

40. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 13.

41. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore desctibed with reference to Example 14.

42. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 15.

43. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 16.

44. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 17.

45. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 18.

46. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 19.

47. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 23.

48. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 31.

49. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 32.

50. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 33.

51. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 34.

52. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 35.

53. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 36.

54. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 37.

55. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 38.

56. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 39.

57. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 40.

58. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 41.

59. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 42.

60. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 43.

61. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 44.

62. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 45.

63. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 46.

64. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 47.

65. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 48.

66. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 49.

67. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 50.

68. A method of manufacturing a hollow fibre, the method being substantially as

hereinbefore described with reference to Example 51.

69. A method of manufacturing a hollow fibre, the method being substantially as herebefore described with reference to Example 52.

70. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 53.

71. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 55.

72. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 57.

73. A method of manufacturing a hollow fibre, the method being substantially as hereinbefore described with reference to Example 58.

74. A hollow fibre made by a method according to any one of claims 28 to 73.

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1566581 COMPLETE SPECIFICATION

9 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG.1

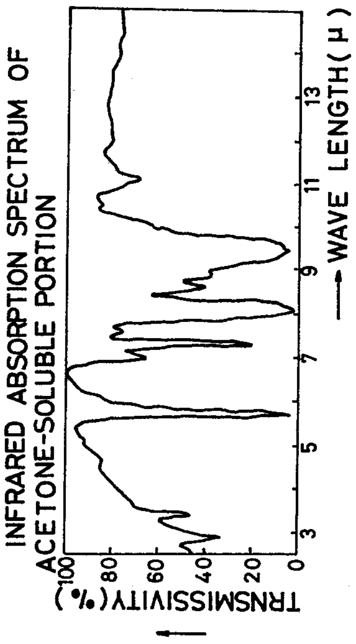

INFRARED ABSORPTION SPECTRUM OF ACETONE-SOLUBLE PORTION

FIG.2

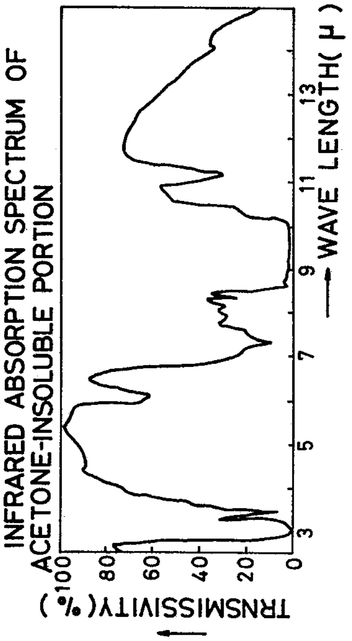
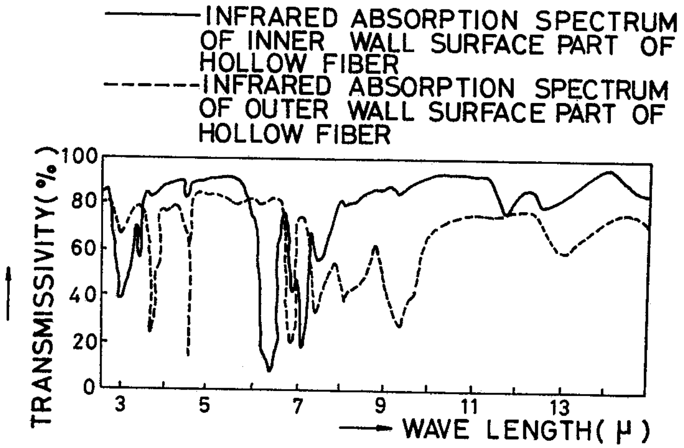

INFRARED ABSORPTION SPECTRUM OF ACETONE-INSOLUBLE PORTION

FIG.3


INFRARED ABSORPTION SPECTRUM OF INNER WALL SURFACE PART OF HOLLOW FIBER
INFRARED ABSORPTION SPECTRUM OF OUTER WALL SURFACE PART OF HOLLOW FIBER
TRANSMISSIVITY(%)
100
80
60
40
20
0
3
5
7
9
11
13
WAVE LENGTH(μ)

1566581 COMPLETE SPECIFICATION

9 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 3

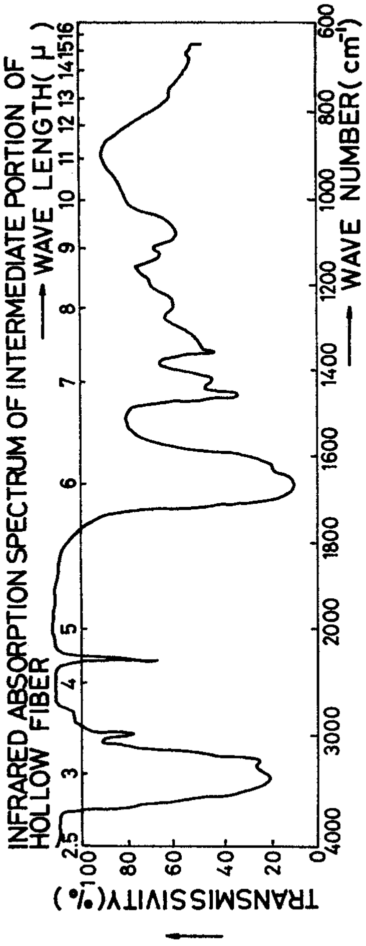

INFRARED ABSORPTION SPECTRUM OF INTERMEDIATE PORTION OF HOLLOW FIBER

FIG.4

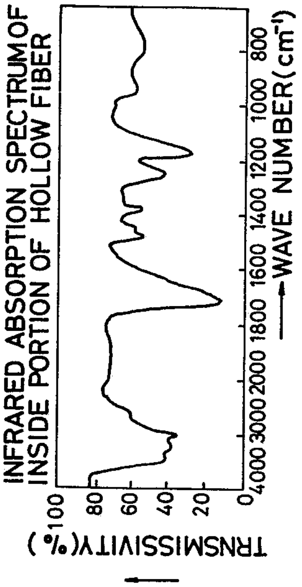

INFRARED ABSORPTION SPECTRUM OF INSIDE PORTION OF HOLLOW FIBER

FIG.5

1566581 COMPLETE SPECIFICATION

9 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 4

FIG.6

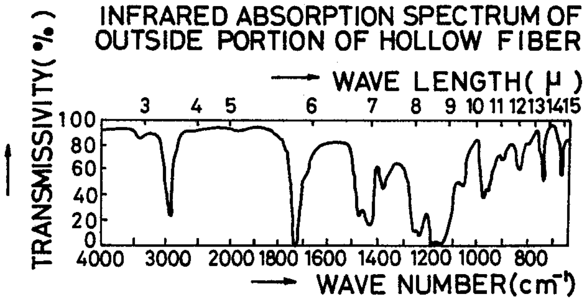

INFRARED ABSORPTION SPECTRUM OF OUTSIDE PORTION OF HOLLOW FIBER

FIG.7

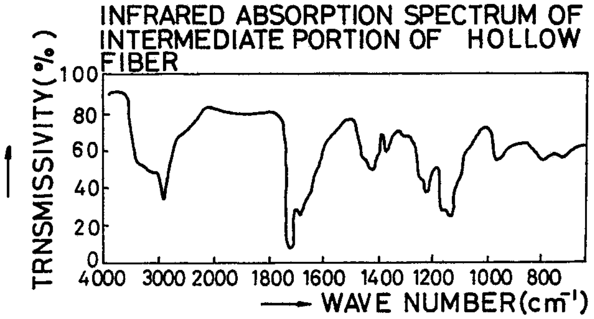

INFRARED ABSORPTION SPECTRUM OF INTERMEDIATE PORTION OF HOLLOW FIBER

FIG.8

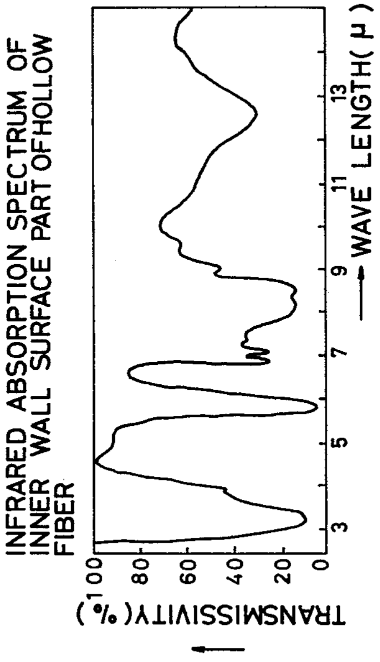

INFRARED ABSORPTION SPECTRUM OF INNER WALL SURFACE PART OF HOLLOW FIBER

FIG.9

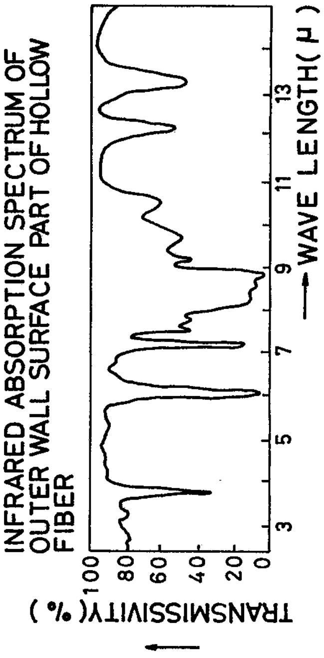

INFRARED ABSORPTION SPECTRUM OF OUTER WALL SURFACE PART OF HOLLOW FIBER

FIG.10

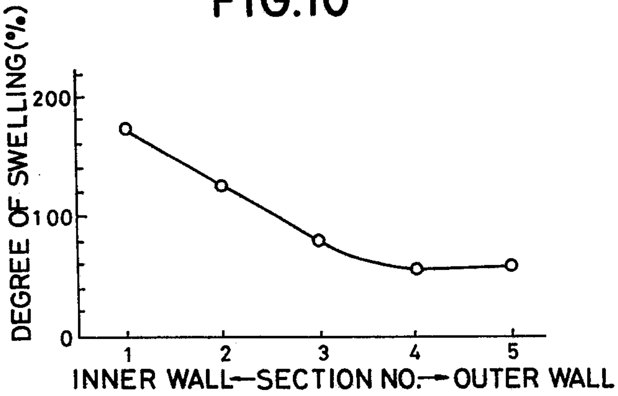

DEGREE OF SWELLING(%)
200
100
0
1
2
3
4
5
INNER WALL—SECTION NO.→OUTER WALL

FIG.11

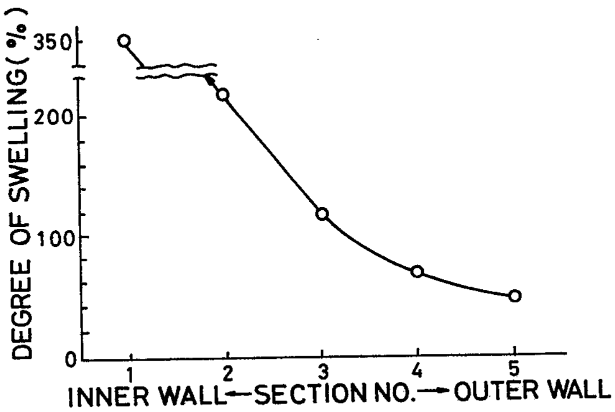

DEGREE OF SWELLING(%)
350
200
100
0
1
2
3
4
5
INNER WALL←SECTION NO.→OUTER WALL

FIG.12

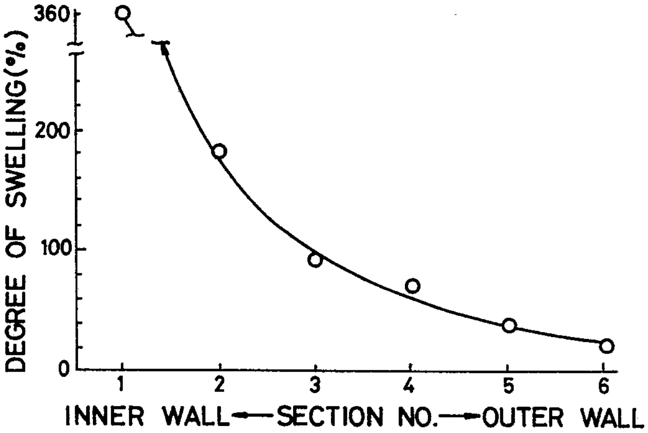

360
200
100
0
DEGREE OF SWELLING(%)
1
2
3
4
5
6
INNER WALL←SECTION NO.→OUTER WALL

FIG.13

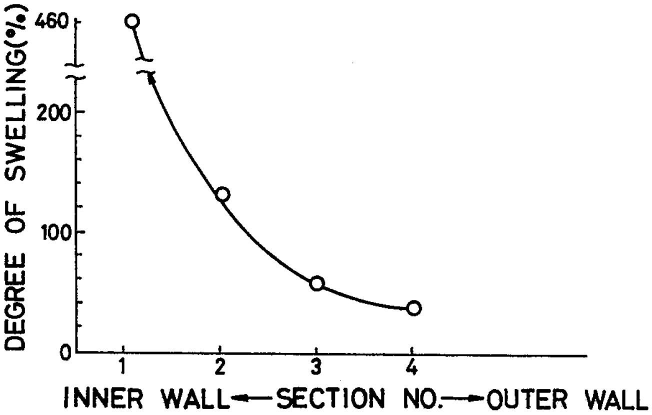

460
200
100
0
DEGREE OF SWELLING(%)
1
2
3
4
INNER WALL←SECTION NO.→OUTER WALL

FIG.14

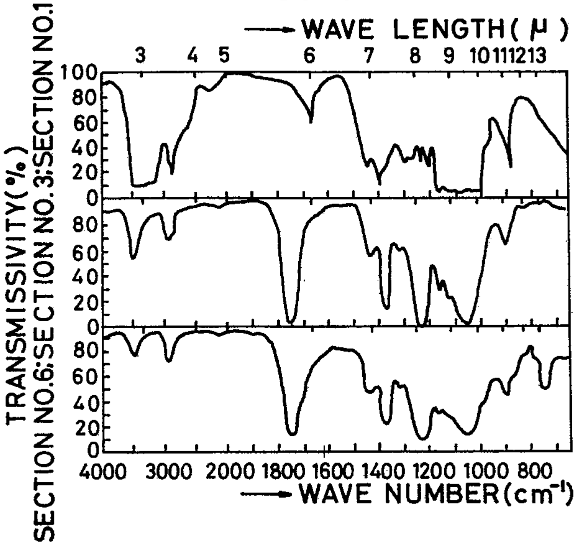

WAVE LENGTH(μ)
3
4
5
6
7
8
9
10
11
12
13
TRANSMISSIVITY(%)
SECTION NO.6; SECTION NO.3; SECTION NO.1
100
80
60
40
20
0
4000
3000
2000
1800
1600
1400
1200
1000
800
WAVE NUMBER(cm^{-1})

FIG.15

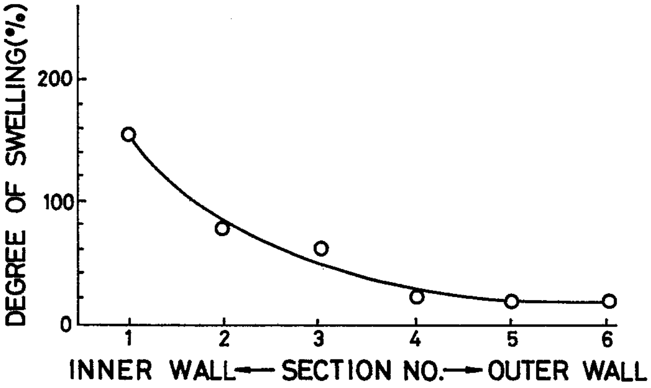

DEGREE OF SWELLING(%)
200
100
0
1
2
3
4
5
6
INNER WALL ← SECTION NO. → OUTER WALL

FIG.16

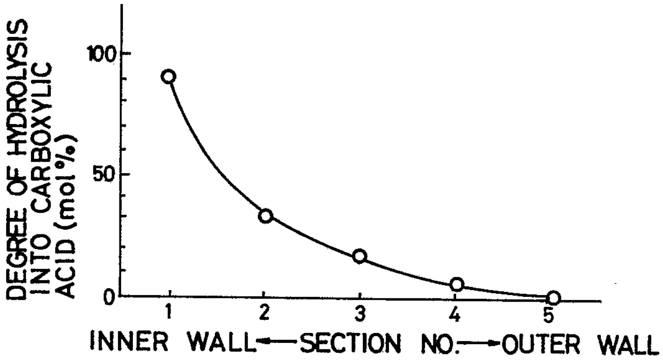


FIG.17

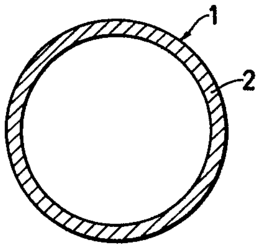


FIG.18