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MEMBRANE CARD AND METHOD FOR THE PRODUCTION AND USE THEREOF

Field of the Invention

The present invention relates to the field of the separation of particles of various sizes from a liquid (gaseous) medium. More particularly, it relates to processes for making membranes, membrane packages, separation elements, separation units and separation systems to separate out such particles from liquid (gaseous) media, methods for quality control of such membranes, and more efficient systems for the separation of particles from liquid (gaseous) media.

Background of the Invention

The twenty first century may be remembered as a period of uncontrolled climatic change that results in numerous adverse effects on the human population. One of the adverse effects is the occurrence of severe droughts in areas of the world that have not experienced such droughts in the past. This is believed to result in a tremendous demand for additional fresh potable water. Unquestionably, fresh potable water is the most important compound on earth, for without water all life ceases.

There is vast prior art on the separation of unwanted particles from raw, untreated water to produce fresh potable water. Filtration systems are used to remove particles of various sizes from raw water resulting in treated water containing dissolved salts, primarily sodium chloride. Special systems are used for the desalination of seawater or demineralization of brackish water. For example, reverse osmosis or hyperfiltration membrane separation systems remove particles such as dissolved salts in the 1 to 10 Angstrom unit range and include chemical compounds of about 180 to 15,000 molecular weights, nanofiltration systems remove particles in the 10 to 100 Angstrom unit range, ultrafiltration systems remove particles in the 30 to 1100 Angstrom unit range that include macromolecules of molecular weight of 10,000 to 250,000, and microfiltration systems remove particles in the 500 Angstroms to 20,000 (0.05 to 2 μm) Angstroms (see, for example, U.S. Patent No. 6,540,915).

These membrane separation systems typically use spiral wound type membrane packages or modules, which have low pressure loss and can be manufactured at a relatively low cost. In general, the spiral wound type membrane package is formed from spiral wound type separation



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membranes that include nanofiltration membranes, ultrafiltration membranes or microfiltration membranes (see, for example, U.S. Patent No. 6,565,747).

The specific type of desalination system used depends on the nature and amount of impurities in the water. For example, impurities in particulate form and in solution may both need to be removed from the water. The object is to purify the water so that it contains sufficiently low amounts of suspended particles, suspended microbes and dissolved salts to meet the quality requirements for drinking water, production of food and drink, agricultural irrigation and other industrial uses (see, for example, U.S. Patent No. 6,793,824).

Other processes for the purification of water besides reverse osmosis include filtration and distillation. In conventional particle filtration processes, impurities in particulate form greater than about 10 μm , such as suspended inorganic particles, are removed using porous constructions such as knitted webs, woven or non-woven fabrics. In cases where very small particles must be filtered, polymer membranes are used which are semi-permeable or microporous, that is, the membranes have very small holes etched through the membrane.

In addition to the vast prior art for desalination of seawater or demineralization of brackish water for coping with water shortage, separation systems are known for preparing ultrapure water for the electronic industry and the medicinal field, recycling of waste water and separation, purifying and concentrating liquid (gaseous) media in the fields of food, medicine and fine chemicals production (see U.S. Patent No. 6,565,747).

In general, separation systems are used to separate out unwanted and wanted particles from liquid (gaseous) media. Particles to be removed by separation processes include suspended solids, dissolved solids, pollutants, salts, biological material, emulsified oil, and similar particles removed from liquid (gaseous) media such as water, blood, oil, and the like.

Thin-film perfluoroacyl-modified cellulose acetate membranes laminated on a porous substrate can be used in seawater desalination, ultrafiltration, microfiltration, and hemodialysis, but preferably are used in gas separation (see U.S. Patent No. 4,549,012).

One prior art process for making membranes used for ultrafiltration and microfiltration includes the steps of extrusion, controlled thermo stretching and cooling. Examples of materials used in such membranes include microporous polytetrafluoroethylene, polypropylene and polyethylene (see U.S. Patent No. 6,540,915).

Various separation membranes are installed in ultrafiltration and microfiltration units, which are, in turn, placed in systems that are used to selectively filter out particles including chemical compounds of various sizes and molecular weights. This is achieved by manipulating the pore sizes of these membranes to the desired size range depending on the required type of separation.

An ultrafiltration system is known where increased filtration efficiency is achieved due to back-flushing of membranes with the aid of a hydraulic accumulator using a vibrating interrupter (see USSR Certificate of Invention No. 1667912 of August 7, 1991, Bulletin No. 29, protected by copyright. However, such system has the disadvantage of being complicated in design and resulting in high filtering costs.

Another prior art liquid (gaseous) medium filtration system is disclosed and claimed in Russian Federation Patent No. 2144422 of January 20, 2000, Bulletin No. 2. This liquid (gaseous) medium filtration system includes a filter, a hydraulic accumulator for back-flushing of the filter, pipes for the source, processed and unprocessed liquid (gaseous) media with regulating valves, a source water pump, an electric valve of back-flushing and a timer. This system reportedly has the advantage of extended filter life due to reverse-flow flushing of the processed water, the flushing proceeds without turning-off the system; the flushing step is implemented by equipment that is reported to be simple to manufacture and operate. However, this filtration system has the disadvantage that the operating pump produces extra pressure in the filter during the flushing step that reduces the differential pressure across the system resulting in a decrease in the system's efficiency. Flushing is realized according to a previously specified timing diagram that neither takes into account the composition of the source water, i.e., the concentration of suspended particles, the type of contaminants, etc., nor the possible variations that occur during the filtration process. This may result either in excessive consumption of processed liquid (gaseous) medium for back flushing, or in a rapid reduction of filter permeability because of too much time between flushings.

In the near future, predictions indicate there will be a critical need for water purification and separation systems of increased efficiency. There is also a need for systems for the separation of a wide variety of particles from liquid (gaseous) media other than water and for processes for producing improved porous membranes, membrane packages, and separation elements for such separation systems.

Brief Description of the Drawings

Further features and advantages will become apparent from the following and more particular description of various embodiments of the invention, as illustrated in the accompanying drawings in which:

FIG. 1 is a simplified block flow diagram of one embodiment of the process of the present invention for producing a separation element useful in a separation unit;

FIG. 2A is a left perspective view of a typical cassette and bath used for the etching step of cut strips of polymeric film of the process shown in FIG. 1;

FIG. 2B is a side cross-sectional view of the internals of the cassette shown in FIG. 2A;

FIG. 3 is a simplified block flow diagram of another embodiment of the process of the present invention for the manufacture of a membrane element useful in a separation unit;

FIG. 4 is a left perspective view of a typical spiral wound separation element;

FIG. 5A is a left perspective view of a collection tube of the separation elements shown in FIGS. 4 and 6D;

FIG. 5B is a left perspective view of a membrane card that includes a porous track membrane laminated to a porous substrate of the separation element shown in FIG. 6D;

FIG. 5C is a left perspective view of a drain of the separation elements shown in FIGS. 4 and 6D;

FIG. 5D is a left perspective view of a turbulizer of the separation elements shown in FIGS. 4 and 6D.

FIG. 6A is a left perspective view after the first step of one embodiment of the process of the present invention for producing a separation element in which four membrane cards are installed on a collection tube of the type shown in FIG. 5A;

FIG. 6B is a left perspective view after the second step of said embodiment of the process of the present invention for producing a separation element in which four sheets of a drain are joined between each of the membrane cards to form four tongue-shaped membrane packages;

FIG. 6C is a left perspective view after the third step of said embodiment of the process of the present invention for producing a separation element in which four sheets of a turbulizer are joined between each of the tongue-shaped membrane packages;

FIG. 6D is a left perspective view of the final separation element produced in accordance with one embodiment of the present invention;

FIG. 7 is a schematic representation of a preferred embodiment of testing equipment for determining the maximum pore sizes of porous track membranes in accordance with another embodiment of the present invention;

FIG. 8 is a process flow diagram of a preferred embodiment of the separation system of still another embodiment of the present invention; and

FIG. 9 is a typical separation system containing a separation element of one embodiment of the present invention.

Detailed Description of Various Embodiments of the Present Invention

The following definitions are used herein:

A “liquid (gaseous) medium” is a gas or liquid that can range from air, water, blood, hydrocarbons, and other liquid (gaseous) media that in their unprocessed state contain particles that are separated by processes and systems that include those of the present invention.

A “collection tube” is a perforated tube used to collect processed liquid (gaseous) media.

A “membrane card” is either a porous membrane or a porous track membrane laminated to a porous substrate using an adhesive which membrane as laminated has the parameters specified.

A “membrane package” is a combination of two projections of two different membrane cards with one or more sheets of a drain interspersed between each of the porous substrate surfaces of the projections.

A “porous membrane” is a thin pliable sheet or layer of a polymeric material containing pores to separate or filter out particles from liquid (gaseous) media.

A “porous track membrane” is a tracked film chemically etched to produce pores of a specified diameter along the tracks.

A “separation system” is a combination of at least one separation unit, pumps, valves, pipes or lines, and other equipment for the separation of particles from liquid (gaseous) media.

A “separation unit” is a unit in which one or more separation elements are installed in working position to carry out the separation or filtration of a particle from a liquid (gaseous) medium.

A "separation element" is one or more membrane packages attached to a liquid (gaseous) medium collection tube with one or more turbulizers placed between each of the membrane packages.

A "tracked film" is a polymeric film exposed to a bombardment of heavy ions to produce tracks serving as etching sites to produce pores.

A "particle" is any substance that has a finite size ranging from about 0.01 to about 1.5 μm that can be separated from a liquid (gaseous) medium using a porous membrane having an appropriate pore diameter ranging from about 0.01 to about 1.5 μm .

1. A Process For Producing a Membrane Card and a Separation Element Useful In the Separation of Particles From a Liquid (Gaseous) Medium

FIG. 1 shows a block diagram showing one embodiment of the process of the present invention in which a backed or supported porous track membrane, i.e., a membrane card, is produced and combined with a turbulizer to form a separation element useful in the separation or filtration of particles from a liquid (gaseous) medium.

Block 10 represents the step of acquiring a polymeric film usually acquired in continuous rolls of varying widths, typically about 600 millimeters (mm) in width, and thicknesses, typically about 10 μm . One embodiment of the present invention is not limited to a specific type of polymeric film so long as the film is capable of being rendered porous. Typical examples of polymeric materials that have been found to be etched to a desired porosity include polyamides, fluoropolymers, polystyrene, polyacrylonitrile, cellulose acetate, polysulfone, and polyolefins, such as polypropylene, polyethylene, and copolymers thereof.

In a preferred embodiment of the present invention, the polymeric film is a fluoropolymeric film, and still more preferably a polyvinylidene fluoride (PVDF) film. While polyvinylidene fluoride (PVDF) film is preferred, other fluoropolymer films can be used including, but not limited to those of polychlorotrifluoroethylene (PCTFE), copolymer of chlorotrifluoroethylene with ethylene (ECTFE), polytetrafluoroethylene (PTFE), copolymers of tetrafluoroethylene and perfluoroalkoxyethylene (PFA), copolymers of tetrafluoroethylene and hexafluoropropylene (FEP), terpolymers of tetrafluoroethylene, hexafluoropropylene and perfluoroalkoxyethylene (EPE), copolymers of tetrafluoroethylene with ethylene (ETFE), polyvinyl fluoride (PVF), and any combinations of the these fluoropolymeric resins.

Block 20 represents the exposing step in which the polymeric film is bombarded by heavy ions to provide a film with a predetermined track density. Track density is the number of tracks per unit of area on the surface of the polymeric film as left by heavy ions, i.e., high-energy charged particles, traveling on a path of trajectory from a cyclotron or other particle accelerator. Each of the tracks left by these charged particles is capable of being acted upon by a suitable etchant.

Typical examples of suitable heavy ions for this purpose include but are not limited to the following: argon, krypton, xenon, bismuth and a combination of these heavy ions. Preferably, the track density is in a range of about 10^7 cm^{-2} to about 10^9 cm^{-2} (See U. S. Patent No. 5,449,917 and Russian Federation Patent No. 2233196 published on July 27, 2004, the relevant discussion of the exposing step is incorporated herein by reference). In addition see E. U. Apel, "Measurements of the Diameter of Selectively Etchable Tracks Produced in Polymer by Heavy Ions" (Nuclear Tracks, Vol. 6, Nos. 2-3, pages 115-118, 1982).

The etching step of block 30 is the next major step in one embodiment of the present invention. In this step, the tracked film is placed in or passed through an etching solution to etch the film with pores that correspond to the track density. The etching step results in a polymeric film having a pore for substantially every track left by a charged particle on the surface of the film. In the resulting porous membrane there is a substantially one to one correspondence between the pore density of pores through the membrane and the track density of high-energy particle tracks. A film having a width of about 600 mm, thickness of about $10 \text{ }\mu\text{m}$, and a length of about 1 to about 20 m with a track density of about 10^7 tracks per cm^2 , e.g., 10^7 cm^{-2} , results in a pore density of 10^7 cm^{-2} with pores having a size of about $1 \text{ }\mu\text{m}$. Similarly, the same size of film with a track density of about 10^9 cm^{-2} results in a pore density of 10^9 cm^{-2} with pores having a size of about $0.01 \text{ }\mu\text{m}$. By varying the track density between these lower and upper ranges, the pore density can be controlled. By varying the etching time, the pore size can be controlled within a range of about 0.01 and about $1.5 \text{ }\mu\text{m}$. Preferably, an alkaline solution is used for etching if the polymeric film is made from a fluoropolymeric resin.

It has been demonstrated by experimentation that the preferred alkaline solution is an alkaline solution of potassium permanganate for etching PVDF films. The etching of PVDF film is preferably carried out at temperatures ranging from about 100 to about 150°C . One method for raising the temperature of the alkaline solution to more than 100°C is to add salts of an alkali

metal, preferably sodium chloride, in sufficient concentrations to achieve the desired rise in etching temperature.

Another variable in the preferred etching process is to pass the alkaline solution in contact with the PVDF film under conditions to maintain turbulent flow. This is accomplished by circulating the etching solution over the PVDF film at a Reynolds Number from about 100 to about 500. At such flow rates, the temperature gradient of the solution in contact with the film is substantially reduced to zero and the rate of etching is substantially the same on all tracks of the film surface. Accordingly, these flow rates result in a narrowing of the range of pore size distribution on the finished porous track membrane.

While the etching step is carried out for a period ranging from about 1 to about 24 hours, the recommended optimal period for an alkaline solution of potassium permanganate is shorter, i.e., about 3 to 9 hours are recommended. The exact etching time depends on the required diameter of pores and the thickness of the film.

It has been found with longer etching periods that manganese dioxide is formed as a result of the etching reaction and settles on the film surface. The manganese dioxide deposition hinders the access of the etching solution to the reaction zone and results in reduced reaction velocity. By circulating the etching solution in the etching bath under turbulent conditions as indicated above, the settling manganese dioxide reaction products are at least partially washed off the film surface and the reaction velocity remains approximately constant during the entire etching step.

By controlling the process conditions of temperature, flow rate and time as described above, it has been found that the etching step takes place without any substantial overheating. Etching without substantial overheating is defined as no overheating or if overheating of the etching solution does occur it does not exceed 1°C. These conditions can be expressed in the following equation:

$$N \leq Q \cdot C_s \cdot \Delta T$$

Where:	N	Is the power of the preheater, W;
	Q	is the flow rate of the etching solution, m ³ /s;
	C _s	is the specific heat of the solution, J/(m ³ ·K);
	ΔT	is the overheating of the solution, K.

If ΔT is maintained at no more than 1°C or 1°K , $N \leq Q \cdot C_s$.

The intervals of time and temperature are determined by the following factors. Preferably the etching is not carried out at a temperature below 100°C because the etching time increases considerably and results in low process efficiency. On the other hand, it is difficult to provide a temperature above 120°C using the proposed method of addition of an alkali metal salt. If the etching time is not more than about 1 hour, no pores are formed on the membrane. If the etching time is longer than the specified range of 24 hours, there is no further increase of any favorable effect. In addition, high porosity membranes will lose their mechanical properties upon being subjected to etching times outside the desired range.

The result of maintaining these optimum process conditions is a high quality of semi-permeable membranes, i.e., porous membranes. One of the characteristics of the porous membranes produced by the process of this embodiment of the present invention is that the resulting porous membranes maintain the same maximum pore size throughout their useful life in a separation system, i.e., usually an average of about 6 months before the membranes must be replaced.

Block 35 represents the step of acquiring the porous substrate that protects the porous track membrane from breaking throughout the useful life of the membrane in a separation system. Preferably the porous substrate is impregnated with an epoxy adhesive so that it has the desired strength to withstand the rigorous forces on the resulting membrane card during its use in a separation system.

The lamination step of block 40 is the last major step required in the production of a membrane card suitable for being formed into a separation element for use in a separation system. It has been found that a porous track membrane produced in accordance with the above process conditions of the present invention can be laminated to a porous substrate even though fluoropolymeric films in the absence of such conditions are known to have poor adhesion. It has also been found that it is critical to apply a suitable adhesive under the optimum conditions to obtain good adhesion between the porous substrate and the porous track membrane. The type of porous substrate is not critical and can include woven, non-woven or bonded papers, fabrics and screens that are permeable to water vapor. Examples of suitable substrate material are those constructed from fibers of organic and inorganic polymers stable to moisture such as polyesters, fiberglass, and polyolefins, such as polyethylene and polypropylene, etc.

One embodiment of the lamination step to achieve optimum adhesion of the substrate to the porous track membrane to produce the membrane card is to spray the adhesive onto one surface of the porous substrate at a concentration of about 1 to about 30 g/m² and then to overlay the porous substrate onto the porous track membrane to laminate.

Another embodiment of the lamination step represented by block 45 is to apply the adhesive to one surface of the porous substrate at a concentration in a range of about 1550 to about 31000 drops of adhesive per square meter before overlaying the porous substrate onto the porous track membrane and laminating.

The type of adhesion that has been found to be the most effective is to spray one surface of, for example, a polyester porous substrate with a polyester adhesive and adhering the porous substrate to the PVDF porous track membrane obtained from the above etching step. One suitable polyester adhesive is Super 77 adhesive made by 3M Corporation. Alternatively, the porous substrate is bonded to the PVDF porous track membrane by applying an adhesive transfer tape to one porous substrate surface and bonding that surface to the PVDF porous track membrane. A suitable adhesive is #924 Adhesive Transfer Tape made by 3M Corporation.

In one embodiment of the present process, the tracked polymeric film is cut into a number of separate sections of a finite length prior to the etching step of block 30. By cutting the tracked film into manageable lengths, the etching step can be carried out in a batch type operation using a cassette 200 as shown in FIG. 2A. Lengths of the tracked film that are in the range of about 1 to about 20 m are preferred for the cassette 200.

FIGS. 2A and 2B show an etching unit 200 including a cassette 200 and a bath 220 shown in phantom. The cassette 210 includes a frame 215, a first turning support 225 mounted on a first lateral support 227 on frame 215, a second turning support 235 mounted on a second lateral support 237 on frame 215, and a number of equally spaced fixed upper horizontal supports 255 and lower horizontal supports 265. The frame 215 has an upper member 250 upon which upper horizontal supports 255 are mounted and a lower member 260 upon which the lower horizontal supports 265 are mounted.

During the film loading step of the etching operation cassette 210 is removed from bath 220. The right end of the first length 262 of a polymeric tracked film is fixed on a fixed upper horizontal support 255 by a first clip 254. The free left end of the first length 262 is fed under a lower horizontal support 265 and then over an upper horizontal support 255 until the free left end

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is at turning support 225. The left end is then attached to turning support 225 by a second clip 256 to fix the first length 262 of the film firmly in place on the supports. Similarly, the left end of a second length 267 of the film is fixed on a fixed upper horizontal support 255 by a third clip 257. The free right end of the second length 267 is fed under a lower horizontal support 265 and then over an upper horizontal support 255 until the free end is at turning support 235. The right end is then attached to turning support 235 by a fourth clip 258 to fix the second length 267 of the film firmly in place. Preferably all of the clips are made from titanium.

At this point in the etching process, the turning supports 225 and 235 are rotated counterclockwise and clockwise, respectively to place the first and second lengths 262 and 267 under a sufficient degree of preliminary or controlled stretching. The stretching compensates for the tendency for the film lengths to expand when they are placed in the etching bath at etching solution temperatures of no less than 100°C. Although only two lengths of film are shown fixed into position on the supports, up to four lengths can easily be accommodated by one cassette.

During the etching operation, etching solution is poured into the bath 220 and the cassette 210 is lowered into the bath 220. The cassette 210 is raised and lowered to increase the rate of the etching reaction.

The following examples demonstrate the method of using the etching unit 200. In each of the examples below, a solution, containing 20 mass % of KMnO_4 , 13 mass % of NaOH , and a salt of an alkali metal in a concentration of 200 g/l to achieve a concentration of complete saturation at the boiling temperature, was poured into the etching bath 220. A pump and an electric heater were switched on and the etching solution was circulated as it was brought to the working temperature. When the solution reached the necessary temperature, the cassette 210 containing the fluoropolymeric film that had been exposed to a bombardment of heavy charged particles, was immersed into the bath 220 and was subjected to chemical etching for a period of 3 to 9 hours. The heating of all surfaces of the tracked film was uniform as a result of the continuous circulation of the etching solution within the etching bath. As indicated above, the exact temperature and the time of etching vary for different types of film.

Example 1

A polyvinylidene fluoride film having a thickness of 13 μm thick and first exposed to a bombardment of accelerated Kr ions to have a track density of $1 \cdot 10^8 \text{ cm}^{-2}$ was etched in an etching solution containing 20 mass % of KMnO_4 , 13 mass % of NaOH and 20 mass % of NaCl

at 110°C for 5 hours. The etching solution circulated inside the etching bath at a flow rate of 1 m³/h to provide $N_{Re} = 200$ for this example. The porous track membrane that was produced in this example had an effective pore diameter of 0.3 μm .

Example 2

For comparison, a similar example was performed in which the same tracked PVDF film was etched in a bath containing 20 mass % of KMnO_4 and 13 mass % of NaOH at 100°C for 6 hours to produce a porous track membrane with an effective pore diameter of 0.17 μm . This diameter was smaller by a factor of 1.8 as compared to the porous track membrane produced at temperatures above 100°C.

Example 3

Another PVDF film having a thickness of 25 μm thick and first exposed to a bombardment of accelerated Kr ions to have a track density of $5 \cdot 10^7 \text{ cm}^{-2}$ was etched in an etching solution containing 20 mass % of KMnO_4 , 13 mass % of NaOH and 20 mass % of NaCl at 105°C for 8 hours. The etching solution circulated inside the etching bath at the same flow rate to provide the same N_{Re} as in Example 1. The porous track membrane that was produced in this example had an effective pore diameter of 0.4 μm .

Example 4

For comparison, a similar example was performed in which the same tracked PVDF film was etched in a bath containing 20 mass % of KMnO_4 and 13 mass % of NaOH at 100°C for 8 hours to produce a porous track membrane with an effective pore diameter of 0.1 μm . This diameter was smaller by a factor of 4 as compared to the porous track membrane produced at temperatures above 100°C.

Therefore, it has been found that by strictly controlling the temperature of the process above 100°C, the time to produce a given maximum pore size is one fourth of the time required when the temperature is maintained at 100°C.

The backed porous track membrane is cut into membrane cards of the desired size in block 40 for combining with the drain represented by block 80 and the turbulizer represented by block 90 to form the separation element represented by block 95 for use in a separation system of the type described below.

FIG. 3 shows another embodiment of producing a membrane card in which a continuous roll of tracked polymeric film represented by block 310 is passed to block 320 for exposure to a

bombardment by heavy ions as described above. From block 320, the continuous roll of tracked film is passed to block 330 to be subjected to a suitable etching solution as described above. However, in the case of a continuous roll, a continuous etching unit (not shown) is contemplated that includes introducing fresh etching solution at the tracked film inlet end of the etching unit and removing the spent etching solution at the tracked film outlet end.

A continuous roll of porous substrate from block 340 is sprayed with a layer of adhesive on the upper surface of the porous substrate in block 350. The roll of etched tracked film is laminated to the roll of porous substrate and is cut into membrane cards of the desired lengths in block 360. The membrane cards are then combined with the drain in block 380 and the turbulizer in block 390 to form the separation membrane element of block 395.

2. A Process For Producing a Separation Unit Useful In the Separation Of Particles From a Liquid (Gaseous) Medium

FIG. 4A shows a typical spiral wound separation element 400 suitable for a separation unit. The process for manufacture of a membrane package 400 starts with a liquid (gaseous) medium collection tube 401 upon which are spirally wound two sheets of porous track membrane 402 or a single sheet of porous track membrane 402 that is folded in half. The porous track membrane 402 is laminated to porous substrate 403 in accordance with the process of one embodiment of the present invention described above. Alternatively, two pieces of porous substrate 403 formed from a spun-bonded polypropylene fiber or the like are used between the two halves of the porous track membrane 402. In this alternative, a sheet of a drain 404 is interspersed between each of the porous substrates 403 as shown to assure the draining of the processed liquid (gaseous) medium to the perforations of the collection tube 401. A first sheet of a turbulizer 405 is then placed as the top or upper surface 408 of the resulting spirally wound element 410. A second sheet of turbulizer 405 is placed as the bottom or lower surface 412 of element 410. The result of this orientation is to have a portion of bottom surface 412 in direct contact with and attached to tube 401 using techniques that are well known in the art.

In the last step of the process of this embodiment of the present invention, one or more separation elements 400 are installed in a separation unit of the type shown in FIG. 9. The turbulizer 405 is made from a porous gauze-like material. The drain 404 is also made from a porous gauze-like material. The porous gauze-like material can be gauze made from cotton or from polymer fabric such as a polyester cloth.

FIGS. 5A-5D show the individual components that are combined to produce the separation element shown in FIG. 6D. FIG. 5A shows the collection tube 510 having a series of equally spaced upper perforations 520 along the upper portion 522 of tube 510 and lower perforations 525 along the lower portion 530 of tube 510. FIG. 5B shows the membrane card 540 having porous track membrane 545 laminated to the porous substrate 550, preferably in accordance with the process of one embodiment of the present invention described above. FIG. 5C shows the draining cloth or gauze 560. FIG. 5D shows the turbulizer 570 that is preferably made from a more porous gauze than that used in the draining cloth 560. A protector 575 on the lower edge of the turbulizer 570 provides a tab for gluing turbulizer 570 to the membrane card 540 as described below. The protector 575 prevents the possibility of the porous track membrane 545 breaking at the point of contact between the porous track membrane 545 and the turbulizer 570 during the manufacture of the separation element as well as during the filtering or separation operation itself. The use of protectors for this purpose is known in the art.

FIGS. 6A-6D show the three essential steps in producing the preferred embodiment of separation element 600 shown in FIG. 6D. The separation element 600 is produced by first attaching four membrane cards 540 around the circumference of a collection tube 510 as shown in FIG. 6A so that the porous substrate 550 is toward the collection tube 510 and the porous track membrane 545 faces outward from the collection tube 510. Each membrane card 540 is bent along a bending line 607 so that it has a first projection 605 on one side of the membrane card 540 and a second projection 610 on its other side. The central section 615 between the first projection 605 and second projection 610 of the membrane card 540 is joined to a portion of the collection tube 510 by a suitable adhesive as described in detail below. The first projection 605 of a first membrane card 540 is positioned along the upper portion 522 of the collection tube 510 so that the bending line 607 is parallel to one side of the row of the equally spaced upper perforations 520. The second projection 610 of the second membrane card 540 is positioned along the upper portion 522 of tube 510 so that the bending line 607 is also parallel to the other side of the row of equally spaced perforations 520. In a similar manner, the first projection 605 of the third membrane card 540 is positioned along the lower portion 530 of the collection tube 510 adjacent one side of the row of lower perforations 525 and the second projection 610 of the fourth membrane card 540 is positioned along the lower portion 530 of the collection tube 510 adjacent the other side of lower perforations 525. Four separate sheets of the drain 560 are

interspersed between the porous substrate 550 side of each of the first projections 605 and the second projections 610.

Each of the porous substrates 550 is pressed around the perimeter to form a glue joint 630 as shown in FIG. 6B. Glue is applied to each of the glue joints 630 and the glue is drifted along the glue joint 630 and around the perimeter of the porous substrate 550 surface of the membrane card 540 that includes the central section 615. The first projection 605 and second projection 610, as well as the central section 615 and the collection tube 510 are then pressed together. Glue is then applied to the protector 575 of each turbulizer 570 and each of the protectors is pressed to the central section 615 of the membrane card 540. The type of glue used for these operations is preferably not the same as that used to glue the porous substrate 550 to the porous track membrane 545. The resulting separation elements from the steps shown in FIGS. 6A-6C are rolled in the final step by a suitable rolling machine to produce separation units 600 as shown in FIG. 6D.

The preferred length of separation unit 400 and separation unit 600 was established by the formula:

$$L=3/\sqrt{2k_2/k_1},$$

where: L is length of the membrane package, meters (m)

k_1 is the drain parameter, $m^3/hr \cdot MPa$;

k_2 is the membrane card parameter, $m^3/hr \cdot MPa \cdot m^2$.

The membrane elements of the present invention are considered attached in working position to the collection tube when at least a portion of the drain is in liquid (gaseous) medium communication with the perforations of the collection tube 510. In the embodiment shown in FIG. 6D, the upper drain 635 and the lower drain 640 are centered directly over the row of upper perforations 520 and lower perforations 525 to insure that when the separation element is installed in a separation system, the processed liquid (gaseous) medium passes through the membrane card 540 and drain 635 to the interior of the collection tube 510 and leaves through the liquid (gaseous) medium outlet as described below in connection with FIG. 8.

3. A Method for the Determination of the Maximum Pore Size of a Porous Membrane

One embodiment of the present invention is to control of the structural properties of porous membranes of the type obtained by the processes described above. Such membranes have

widespread uses in the chemical, medical, electronic and other industries where it is critical that all the membranes have a given maximum pore size that has been accurately determined.

A prior art method of studying porous materials is based on a comparison of the maximum flow rate during the evaporation of liquid from the surface of the porous membrane with the flow rate at the available hydrostatic pressure differences. This prior art method allows for calculation of the average radius of capillaries and the measurements obtained using this method are indirect. Measurement error depends upon the state of a porous body. When large pores are present in the porous membranes, the error will be too high. This method does not allow for accurate determination of the exact size of the maximum pore diameters (see USSR Certificate of Invention No. 524110, IPC: G01N11/00 published on 08/05/1976, Bulletin No. 29).

A method of determining the maximum size of a pore using the bubble method is described in GOST R 50516-93, "Polymer Membranes. A Method of Determination of the Point of a Bubble for Plane Membranes." In the bubble method, a thin porous membrane is steeped in liquid until it is saturated and then is clamped into a cell. The cell is filled with liquid so as the surface of liquid fully covers the surface of the porous membrane. Gas is fed into the cell under the membrane while continuously measuring the gas pressure. The maximum pore size is calculated based on the pressure at which the first bubble of gas passes through the membrane. The method is simple and effective, but its practical usage is restricted by the strength of membranes. Specifically, in determining the maximum pore size of membranes having pore sizes from 0.05 to 0.5 μm , the pressure difference on the membrane leads to stresses that destroy the membrane. The use of a substrate distorts the measurement results. This method is not practically applicable as a method for determining the maximum pore size of the track membranes of the present invention as it leads to their destruction during the test.

The objective of this embodiment of the present invention is to increase the efficiency of the maximum pore size measurements without causing the destruction of the membranes. Another objective of this embodiment is to increase the range of membrane thickness on which it is possible to make these measurements.

These objectives are achieved by installing a preliminarily liquid-impregnated porous track membrane into a cell, filling the cell with liquid, supplying gas to the cell and measuring its pressure. The cell with the membrane is placed into a vessel. The cell and the vessel are

hydraulically connected with each other. A non-destructive pressure difference is applied to the membrane as the liquid is pumped out of the vessel. Gas in the form of a vapor having the same composition as the liquid in the cell is fed into the vessel. The vapor pressure in the vessel is constantly measured. The pressure at which the pressure difference disappears over the membrane is recorded. Once this pressure is recorded, a determination is made of the value of the liquid surface tension force. Using this data, the value of the maximum membrane pore size is calculated using Laplace's formula. Because the pressure difference on the membrane is minimized by pumping the liquid out of the membrane as the pressure difference is applied, the integrity of the method is realized and any losses of membranes as a result of breakage during the test are minimized.

Specifically, the calculations for determining the maximum pore diameter of the membranes are as follows: Pressurization of the vessel with the cell by the same liquid vapor leads to vapor condensation on the membrane surface. In so doing, the temperature increases. The heat supplied from the vapor to the liquid-impregnated membrane surface occurs by condensation. The heat discharged from the membrane to the liquid occurs by heat conductivity. The boundary conditions are determined by the following equation:

$$Bi = a \cdot d/l$$

Where: Bi is the criterion of boundary similarity (criterion Bi_o);

a is the coefficient of convective heat transfer;

l is the coefficient of heat conductivity; and

d is the typical size (diameter of the cell).

As Bi tends to infinity (practically at $Bi > 100$), the membrane surface temperature will be equal to the vapor temperature over the membrane (see "Theoretical Foundations of Heat Engineering-Heat. Technical Experiment," a reference book under the editorship of V.A. Grigoriev and V.M. Zorin, Book 2. Moscow, Energoatomizdat Publishing House, 1988, pp. 197-198). Criterion Bi equals 1000 for a cell of diameter 50 mm using liquid Freon 12. The temperature of the liquid-impregnated membrane surface can be determined based on the vapor pressure over the membrane. The surface tension value reduces as a result of liquid heating because the vapor breakthrough occurs under the membrane. Therefore, the pressure difference on the membrane disappears.

The method excludes a visual examination of the membrane thereby increasing the accuracy in determination of the maximum pore size of the membrane by the bubble test method. This method can be used to determine the maximum pore diameter of a membrane without destroying the membrane during the pore diameter determination.

FIG. 7 shows the preferred testing equipment 700 for determining the maximum pore sizes of porous membranes in accordance with this embodiment of the present invention. The porous membrane 701 is first impregnated with a liquid, mounted in a suitable holder 705 and placed into the cell 702. The cell 702 containing the porous membrane 701 is installed into a sealed vessel 703. The lower part of the cell 702 has holes hydraulically connecting the cavity under the porous membrane 701 with the vessel 703. The vessel 703 is filled with liquid up to the level fully covering cell 702. The liquid is then gradually pumped out of vessel 703 through an outlet 715. In so doing, the impregnated porous membrane 701 retains liquid at the expense of the action of the capillary forces. Consequently, a difference appears between the levels of liquid in the cell 702 and the vessel 703, which is recorded by a differential pressure transducer 704. The pumping of the liquid stops upon reaching the assigned pressure difference on porous membrane 701. Vapor of the same liquid is fed into the vessel 703 via an inlet 710 under the porous membrane 701 at some excess pressure. The vapor pressure that is increasing is continuously measured in the vessel 703 using a pressure gauge 720. A thin layer of liquid appears on the surface of the porous membrane 701. The temperature of this layer increases as the pressure in the vessel 703 increases. Since the convective heat transfer to the surface of the porous membrane 701 by condensation greatly exceeds the heat discharge from the porous membrane 701 to the liquid, the surface temperature of the porous membrane 701 assumes a value equal to the ambient vapor temperature and can be determined based on the pressure in the vessel 703 by the equation of the condition of saturated vapor. As the temperature of the porous membrane 701 increases, the surface tension of the impregnating liquid in the porous membrane 701 decreases. At some time, the pressure difference on porous membrane 701 exceeds the capillary holding capacity of the porous membrane 701. At this point, vapor breaks through the porous membrane 701 and the pressure difference on the porous membrane 701 disappears. The pressure in the vessel 703 at which the pressure on the porous membrane 701 disappears is recorded. On reaching that pressure, the value of the liquid surface tension coefficient is

determined based on the saturated vapor curve and the value of the maximum pore size is calculated using Laplace's formula.

The example below was carried out to demonstrate the foregoing testing method.

Example 5

The maximum pore size of a fluoropolymeric membrane 701 was measured using Freon 12 as working liquid (gaseous) medium. A pressure differential of 7.5 kPa was maintained on the porous membrane 701 at an initial pressure in the vessel 703 of 5.4 bar. The pressure difference disappeared at a Freon pressure increase to 7.52 bar in the vessel 703. The value of surface tension coefficient equaled $7.5 \cdot 10^{-3}$ N/m based on this pressure. The maximum pore diameter was calculated to be $d = 1.0 \mu\text{m}$ using Laplace's formula:

$$d = \frac{4\sigma}{P}$$

Where: d is the pore diameter, m;

σ is the surface tension force of the liquid, N/m;

P is the pressure, Pa

It is understood in this calculation that cosine of the contact angle on the membrane was equal to 1.