

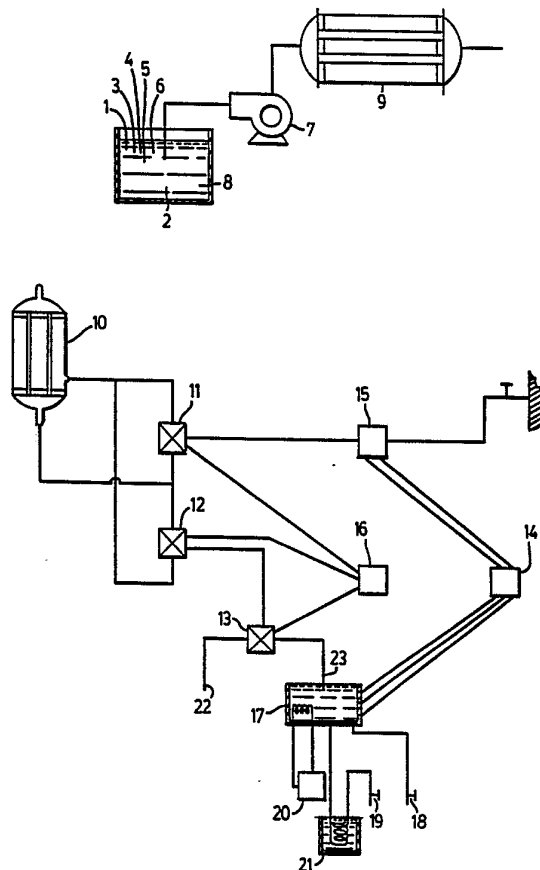


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/CA90/00090 (22) International Filing Date: 16 March 1990 (16.03.90) (30) Priority data: 89101659.7 18 March 1989 (18.03.89) EP <i>(34) Countries for which the regional or international application was filed:</i> CH et al. (71) Applicant (for all designated States except US): INTERNATIONAL APPLIED SCIENCES, INC. [US/US]; 44 East Cheryl Road, Pinebrook, NJ 07058 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : WANG, Ying [CN/CA]; YANG, Qilian [CN/CA]; Unit 2, 4150 Midland Avenue, Scarborough, Ontario M1V 4S6 (CA).		(74) Agent: ROGERS, BERESKIN & PARR; 40 King Street West, 40th Floor, Toronto, Ontario M5H 3Y2 (CA). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), + CH, CH (European patent), CM (OAPI patent), DE, + DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i>

(54) Title: ULTRAFILTRATION MEMBRANE**(57) Abstract**

An ultrafiltration membrane is formed on an extrafiltrator for use in a water purification system. The ultrafiltration membrane has a membrane material which may be furan, furfural, furfona, furfonal and furfuryl alcohol. The membrane has a thickness of from 50 microns to 40,000 microns and contains pores having a diameter of from 50 Å to 100 Å. A method for forming such a membrane dynamically within the pores of an extrafiltrator is also provided. The method includes the preparation of a membrane forming solution containing a membrane forming material, a solvent, a diluent, a plasticizer, a curing agent and a pore forming agent and passing the membrane forming solution through the extrafiltrator to cause a membrane to deposit within the pores of the extrafiltrator, to crosslink and fixate in the pores. A method for filtering water using such an ultrafiltration membrane is provided. The method includes the steps of passing water through an extrafiltrator having such an ultrafiltration membrane deposited thereon and periodically stopping the flow of water into the extrafiltrator to allow unfiltered water to drain from the extrafiltrator.



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Title: Ultrafiltration Membrane

FIELD OF THE INVENTION

This invention relates to the field of
5 filtration membranes for use in purification of water.

BACKGROUND OF THE INVENTION

Commercial drinking water systems, such as those
used in offices, generally consist of a water purifier and
either a cooler or heater. There are two common types of
10 purifier for use in such systems. One such purifier is a
fibre filter. Another such purifier is more comprehensive
and includes an activated charcoal filter, a germicidal
system which may use ultraviolet light and a hollow fibre
extrafiltrator. Either of these purification systems are
15 connected to a building's water system and the purified
water is typically consumed after it has either been
heated or cooled.

The benefits of the previous systems include the
removal of pigment, suspended matter and free chlorine.
20 These systems however have some shortcomings. Firstly,
eventually the ability of the activated charcoal to adsorb
the organic substances will be diminished, necessitating
replacement of the activated charcoal filter after
adsorption saturation. Prior to replacement, however,
25 harmful nitrous salts and more bacteria may be formed by
long-term interaction between the activated charcoal in
the filter and bacteria in contact therewith.

Another disadvantage with these prior systems is
that the hollow fibre extrafiltrators presently
30 commercially available are not able to remove the low
molecular weight organic substances in the tap water
completely. These may include potentially carcinogenic
substances such as trichloromethane, tetrochloromethane
and non polar organic materials.

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SUMMARY OF THE INVENTION

The present invention provides an ultrafiltration membrane formed on an extrafiltrator for use in a water purification system, said ultrafiltration
5 membrane comprising:

a membrane material selected from the group of resins consisting of furan, furfural, furfurone, furfural and furfuryl alcohol;

said membrane having a thickness of from 50
10 microns to 40,000 microns;

said membrane having pores with a diameter of from 50Å to 100Å; and,

said membrane having been formed dynamically within the pores of said extrafiltrator.

15 A method is also provided for forming an ultrafiltration membrane on an extrafiltrator, said method comprising the steps of:

preparing a membrane forming solution by dissolving a membrane forming material in a solvent and
20 adding to the solution so obtained, a diluent, a plasticizer, a curing agent and a pore forming agent; and,

passing said membrane forming solution through said extrafiltrator to cause a membrane to deposit within the pores of said extrafiltrator, and permitting the
25 membrane so deposited to crosslink and fixate in said pores.

A method is provided for filtering water using an ultrafiltration membrane deposited on an extrafiltrator, said method including the steps of:

30 passing water through an extrafiltrator having an ultrafiltration membrane deposited thereon; and

periodically stopping the flow of water into said extrafiltrator and allowing unfiltered water to drain from said extrafiltrator.

35 BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described below with

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reference to the appended drawings which form a part of the specification and in which:

Fig. 1 is a schematic diagram showing a process for membrane formation according to the present invention;
5 and,

Fig. 2 is a schematic diagram showing a water purification system using a membrane filter according to the present invention.

BRIEF DESCRIPTION OF PREFERRED EMBODIMENTS

10 According to the present invention, a polymer material is used to form a membrane layer within the pores of the extrafiltrator of commercially available drinking water purification systems. The extrafiltrators may be any of the types comprising hollow fibres, spirally wound
15 modules, or flat filters made from polypropylene, nylon, cellulose or aromatic amides having a pore diameter of from 0.02Å to 1.0Å and being of a thickness from about 8 to 200 microns. The ultrafiltration membrane is an extra thick film which is able not only to remove low molecular
20 weight organic substances that cannot be removed by the commercial extrafiltrator, but also the nitrous salts, metal salts, radioactive substances and suspended bacteria. Due to the thickness of the film, water can pass through with relatively small resistance thereby giving a
25 relative high productivity per unit.

Referring to Figure 1, the process of dynamic membrane formation is illustrated. A membrane forming material 1 is dissolved in a solvent 2, and a diluent 3, plasticizer 4, curing agent 5 and pore forming agent 6 are
30 added to the solution 8.

Generally, a commercial extrafiltrator 9 is connected by a pump 7 to the solution 8. When the pump is activated, the solution 8 is passed through the pores of the extrafiltrator and causes deposition of membrane
35 forming material in the pores of the extrafiltrator. The membrane forming material condenses in the pores and is

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cross linked and fixated therein. This results in an ultrafiltration membrane having a pore size significantly less than the original pore size of the extrafiltrator.

The amount of polymerization of the pore forming agent and, accordingly, the size of the pore forming agent, is controlled by controlling the pH of the membrane forming solution. Sodium hydroxide may be added at the outset to increase the pH of the solution which tends to suppress the molecular weight of the pore forming material. As the solution is passed through the extrafiltrator, the pH of the solution is gradually reduced by the addition of sulphuric acid. This causes an increase in the amount of polymerization and, accordingly, an increase in the molecular weight of the pore forming material. Eventually, the pore forming material will have the optimum molecular weight to deposit in the pores of the extrafiltrator to give a membrane of the desired separation qualities.

In order to monitor the separation ability of the membrane, an indicator such as phenolphthalein or xylenobluue may be added to the solution. The indicator concentration in the solution passing through the membrane may then be monitored, for example, using photometric means. Once the indicator concentration shows that the membrane has achieved the desired amount of separability, the passing of solution through the extrafiltrator is stopped.

After membrane formation has been completed, the membranes may be stored in a disinfectant and preservative solution. A suitable solution contains 1% ethyl alcohol, 5% glycerol and 1% formalin in water.

Ultrafiltration membranes may be produced as described above using an extrafiltrator having the following properties as a substrate:

35	thickness of substrate	8 - 200 microns;
	pore diameter of substrate	0.02-1 microns;

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	material of substrate	polypropylene, nylon, cellulose, aromatic amide; and
5	shape of substrate	hollow fibre, spiral- wound module and flat.

Such membranes typically have a thickness of from 50 microns to 40,000 microns and a pore size of from 50Å to 100Å. Suitable membrane forming materials include
10 furan resins such as furfural resin, furfuran resin, furfural resin, and furfuryl alcohol resin in concentrations of from 1 to 200 mg/l.

Suitable diluents include lower alcohols and ketones such as C1 to C5 alcohols, in an amount of from 1
15 to 99% per volume of the membrane forming liquid.

A suitable plasticizer is phthalic phosphoric ester in a concentration of from 0.5-500 mg/l.

Suitable curing agents include benzene sulfonylchloride, ethyl sulfate and sulphuric acid in a
20 concentration of from 0.9-5% by volume of the membrane forming solution.

Water is typically used as the solvent and forms from 1 to 99% by volume of the membrane forming solution.

The pore forming agent may be a neutral soluble
25 inorganic salt in a concentration of from 20-1500 mg/l and a surfactant in a concentration of from 20-1500 mg/l. Suitable surfactants include alkyl sodium sulphate, quaternary ammonium salts and polyoxyethylene.

A water purification system incorporating an
30 ultrafiltration membrane as described above is illustrated in Figure 2. The system consists of a dynamically formed membrane module 10, three three-way electromagnetic valves 11, 12 and 13, a two-way electromagnetic valve 15 controlled by relay 14 for controlling water level, a
35 relay or micro-computer 16 for controlling time, a water tank 17 and hot and cold water valves 18 and 19 respectively.

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In use, when the tank 17 is empty, relay 14 opens the two way electromagnetic valve 15 to permit tap water to pass therethrough. The tap water flows through the three-way electromagnetic valve 11 and into the membrane module 10. Purified water passing from the membrane module 10 flows into the two three-way electromagnetic valves 12 and 13. Valve 13 is controlled by either a time relay or micro-computer indicated by reference 16. For the first two to five minutes, the valve 13 is positioned so as to discharge water through a waste outlet 22 in order to flush the system. Once the system flushing time has expired, valve 13 is positioned so as to stop discharge through the waste outlet 22 and to cause purified water to drain into the tank 17 from the clean water outlet 23.

Cool water is provided at outlet 18 through the use of water cooler 20.

Hot water is provided at outlet 19 by means of water heater 21.

When the water tank 17 is filled with purified water, the relay 14 for controlling water level will close the two-way electromagnetic valve 15 thereby shutting off water entry into the system from the water source.

The three-way electromagnetic valves 11, 12 and 13 may periodically be activated so as to cause waste water from the membrane module 10 to be drained through the waste water outlet 22. Such periodic draining of the membrane module removes a portion of the contaminants from the non-filtered side of the module thereby reducing blockage and deposition of waste substances in the membrane module, increasing the life span of the module and optimizing both the flow rate through the module and the purified water quality.

The present invention may be further illustrated by reference to the following examples:

Example 1

An extrafiltrator made of the cellulose hollow

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fibres manufactured in U.S.A. by Microgon and having a thickness of 50 microns and a pore size of .02 microns was used.

To make the membrane forming solution, 50 ppm
5 furfurol alcohol was added to water. To this solution was
added 1% ethyl alcohol, 0.1% polyoxyethylene. Sodium
hydroxide was then added to this solution to adjust the pH
to 8 and xylenobblue was added as an indicator. The pump
was activated and operated at a pressure of 3 kg/cm². After
10 approximately 2-3 minutes, small amounts of sulphuric acid
were added to lower the pH and the indicator concentration
was measured with a photometer. After approximately 30
minutes, the solution had a pH of approximately 3 and the
concentration of indicator in the permeate water as
15 compared with the concentration of indicator remaining in
the feedwater was approximately 95%.

At this point, the pump was stopped and a
solution of 1% ethyl alcohol, 5% glycerol and 1% formalin
was introduced into the membrane.

20 Example 2

The extrafiltrator in this example contained a
polypropylene hollow fibre module having a membrane
thickness of 50 microns and a pore size of .6 microns.

The membrane solution contained 50 ppm furool,
25 .7% dibutic phthalate, water, acetone, ethyl sulphate,
sodium dodecyl sulfonate and phenolphthalein. The solution
was made by dissolving furool in acetone, dibutic phthalate
and ethyl sulphate to form a first solution. This first
solution was poured into water to achieve the above
30 concentration and sodium dodecyl sulfonate was dissolved
in the solution while adding phenolphthalein. The pump was
turned on and operated at a pressure of approximately 3
kg/cm². The pump was operated for approximately 60 minutes
and the concentration of indicator measured using a
35 photometer. After approximately 60 minutes the indicator
concentration in the permeate was approximately 95% of
that in the feedwater. The pump was stopped and the

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membrane was treated with a preserving solution containing 1% ethyl alcohol, 5% glycerol and 1% formalin in water.

It is to be understood that variations to the embodiment described above may be apparent to persons
5 skilled in the relevant arts without departing from the spirit and scope of the invention as set out in the appended claims. It is to be understood that such variations or modifications are intended to be covered by this specification.

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We CLAIM:

1. An ultrafiltration membrane formed on an extrafiltrator for use in a water purification system, said ultrafiltration membrane comprising:
 - 5 a membrane material selected from the group of resins consisting of furan, furfural, furfurone, furfural and furfuryl alcohol;
said membrane having a thickness of from 50 microns to 40,000 microns;
 - 10 said membrane having pores with a diameter of from 50Å to 100Å; and,
said membrane having been formed dynamically within the pores of said extrafiltrator.
2. An ultrafiltration filter as claimed in claim 1,
 - 15 wherein said membrane formation is achieved by passing a solution containing a membrane forming material, a solvent, a diluent, a plasticizer, a curing agent and a pore forming agent through said extrafiltrator;
said extrafiltrator is made from a material
 - 20 selected from the group consisting of polypropylene, nylon, cellulose and aromatic amides;
said extrafiltrator has a thickness of from 8 to 200 microns and a pore size of from .02 to 1 microns.
3. An ultrafiltration filter as claimed in claim 1 or 2, wherein said dynamically formed membrane material is a resin selected from the group consisting of furan resin, furfural resin, furfurone resin, furfural resin and furfuryl alcohol resin in a concentration of from 1 to 200 mg/l;
 - 25
 - 30 said diluent is selected from the group consisting of lower alcohols and ketones in an amount of from 1 to 99% by volume of the membrane forming liquid;
said plasticizer is phthalic phosphoric ester in a concentration of from 0.5 to 500 mg/l;

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said curing agent is selected from the group comprising benzene sulfonyl chloride, ethyl sulfate, sulphuric acid in an amount from 0.9 to 5% by volume of the membrane forming solution;

5 said solvent is water in an amount of from 1 to 99% of said membrane forming solution; and,

 said pore forming agent is a neutral soluble inorganic salt in a concentration of from 20 to 1500 mg/l and a surfactant in a concentration of from 20 to 1500
10 mg/l.

4. A method for forming an ultrafiltration membrane on an extrafiltrator, said method comprising the steps of:
 preparing a membrane forming solution by combining a membrane forming material, a solvent, a
15 diluent, a plasticizer, a curing agent and a pore forming agent; and,

 passing said membrane forming solution through said extrafiltrator to cause a membrane to deposit within the pores of said extrafiltrator, to crosslink and to
20 fixate in said pores.

5. A method according to claim 4 wherein:

 said membrane material is a resin selected from the group consisting of furan resin, furfural resin, furfurone resin, furfural resin and furfuryl alcohol
25 resin in an amount of from 1 to 200 mg/l;

 said diluent is selected from the group consisting of lower alcohols and ketones in an amount of from 1 to 99% by volume of said membrane forming solution;

 said plasticizer is phthalic phosphoric ester in
30 an amount of from 0.5 to 500 mg/l.

 said curing agent is selected from the group consisting of benzene sulfonyl chloride, ethyl sulfate and sulphuric acid in an amount of from 0.9 to 5% by volume of said membrane forming solution;

35 said solvent is water in an amount of from 1 to

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99% by volume of said membrane forming solution; and
said pore forming agent is a neutral soluble
inorganic salt in an amount of from 20 to 1500 mg/l and a
surfactant in an amount of from 20 to 1500 mg/l.

5 6. A method according to claim 5 wherein:
said surfactant is selected from the group
consisting of alkylsodium sulfate, quaternary ammonium
salt and polyoxyethylene; and
the pH of the membrane forming solution is
10 adjusted during membrane deposition to gradually increase
the amount of polymerization of the membrane forming
material.

7. A method according to claim 6 wherein an
indicator is further added to the membrane forming
15 solution and the indicator concentration in the membrane
forming solution permeating through the extrafiltrator is
monitored to determine the completeness of membrane
deposition.

8. A method according to claim 7 wherein:
20 said extrafiltrator is a cellulose hollow fiber
module having a thickness of about 50 microns and a pore
size of about 0.02 microns;

said surfactant is polyoxyethylene in an amount
of about 1% by weight of the membrane forming solution;

25 sodium hydroxide is added to the membrane
forming solution to give an initial pH of approximately 8;
and,

during membrane deposition the pH of the
membrane forming solution is decreased to approximately 3
30 by the addition of sulphuric acid.

9. A method for forming an ultrafiltration membrane
on an extrafiltrator which is a polypropylene hollow fibre
module having a thickness of about 50 microns and a pore

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size of about 6 microns, said method comprising the steps of:

5 diluting furol with acetone, dibutic phthalate and ethyl sulfate to form a first solution which is subsequently combined with water to give a concentration of 50 ppm furol, .7% dibutic phthalate; 2% acetone and 1.5% ethyl sulfate;

10 dissolving 1000 ppm sodium dodecyl sulfonate in said first solution and adding phenolphthalein to give a second solution;

passing said second solution through said extrafiltrator at a pressure of about 3 kg/cm²;

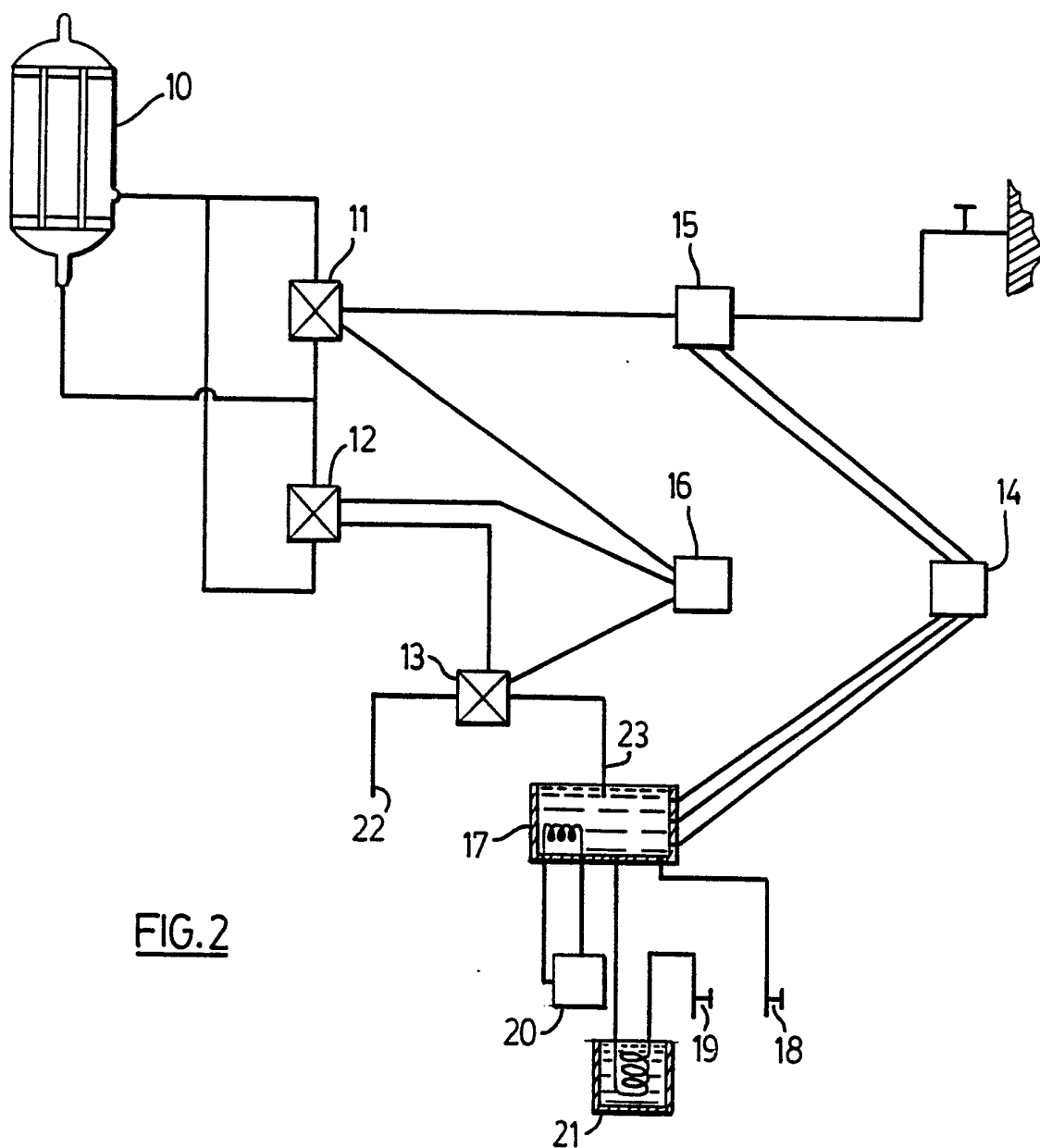
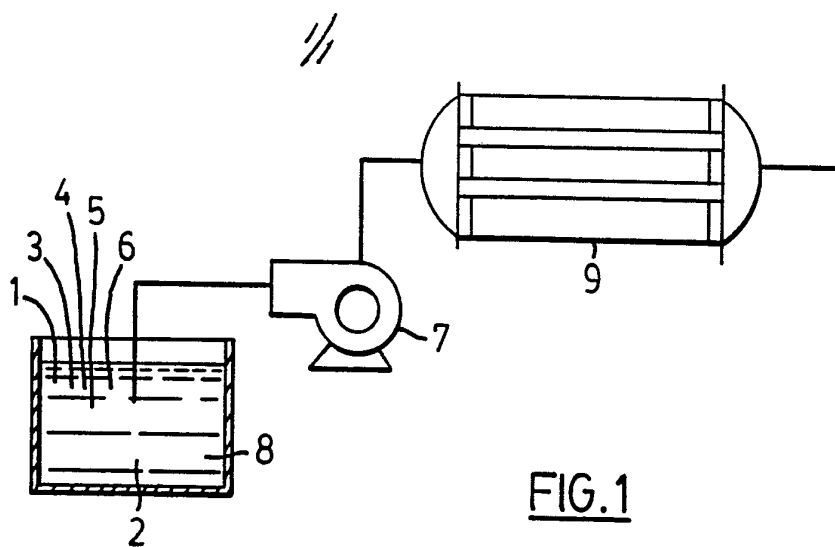
photometrically measuring the concentration of said indicator permeating through said extrafiltrator;

15 ceasing passing of said second solution through said extrafiltrator when the concentration of indicator in said permeate reaches a desired value.

10. A method for purifying water using an ultrafiltration membrane deposited on an extrafiltrator, said method including the steps of:

20 passing water through an extrafiltrator having an ultrafiltration membrane deposited thereon; and

periodically stopping the flow of water into said extrafiltrator and allowing unfiltered water to drain from ultrafiltration membrane deposited on said extrafiltrator.



INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 90/00090

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : B 01 D 69/14, 67/00, 71/52, C 02 F 1/44		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	B 01 D, C 02 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3926798 (J.E. CADOTTE) 16 December 1975 see the whole document --	1
A	US, A, 2593540 (R.T.K. CORNWELL) 22 April 1952 see column 1, lines 1-5, 45-53; column 5, line 75 - column 6, line 4; column 6, line 60 - column 7, line 5; column 4, line 61 - column 5, line 16 --	1
A	US, A, 4214020 (R.R. WARD) 22 July 1980 see abstract; column 4, lines 39-66; column 7, lines 24-26; column 12, lines 22-29 --	1
A	US, A, 4187333 (A. REMBAUM) ./.	1, 4
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
25th June 1990		18. 07. 90
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		<div style="display: flex; align-items: center;"> <div style="margin-right: 20px;">M. Peis</div> <div style="border: 1px solid black; padding: 2px 5px;">M. PEIS</div> </div>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	<p>5 February 1980 see abstract; figures 1,2; column 3, lines 3-10; column 4, lines 25-33; column 6, line 67 - column 7, line 17; column 9, lines 27-36; claim 1</p> <p>--</p>	
A	<p>Patent Abstracts of Japan, volume 6, no. 158 (C-120)(1036, 19 August 1982, & JP, A, 5778908 (KURARAY K.K.) 17 May 1982 see the abstract</p> <p>--</p>	1
A	<p>WO, A, 85/01222 (MEMTEC LTD) 28 March 1985 see abstract; page 5, lines 21-25; page 7, line 25 - page 10, line 5</p> <p>--</p>	1,4
A	<p>US, A, 3849305 (S. MANJIKIAN) 19 November 1974 see abstract; figures; column 2, line 58 - column 3, line 7; column 3, lines 50-54</p> <p>--</p>	10
A	<p>Patent Abstracts of Japan, volume 4, no. 38 (C-4)(520), 27 March 1980, & JP, A, 5511014 (HITACHI SEISAKUSHO K.K.) 25 January 1980 see the abstract</p> <p>-----</p>	10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

CA 9000090

SA 35586

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/07/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3926798	16-12-75	None	
US-A- 2593540		DE-C- 852838 GB-A- 655663	
US-A- 4214020	22-07-80	None	
US-A- 4187333	05-02-80	US-A- 3944485 US-A- 4045352	16-03-76 30-08-77
WO-A- 8501222	28-03-85	AU-B- 570508 AU-A- 3398184 EP-A- 0156840 JP-T- 60502145	17-03-88 11-04-85 09-10-85 12-12-85
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