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(54) **Title:** MEMBRANE POLYMER COMPOSITIONS

(57) **Abstract:** The invention relates to a terpolymer of tetrafluoroethylene (TFE) monomer, polyvinylidene fluoride (PVDF) monomer and hexafluoropropylene (HFP) monomer for forming an ultrafiltration or microfiltration membrane, method of forming said membranes, and to the ultrafiltration or microfiltration membranes themselves. The invention also relates to a method of forming a polymeric ultrafiltration or microfiltration membrane including preparing a leachant resistant membrane dope which incorporates a leachable pore forming agent, casting a membrane from the dope and leaching the pore forming agent from the membrane. The invention also relates to a method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure including the step of adding a nucleating agent to the membrane dope before casting.

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10   TITLE: MEMBRANE POLYMER COMPOSITIONS

TECHNICAL FIELD

The invention relates to compositions suitable for use in forming membranes, in

particular for forming hollow fibre membranes for use in microfiltration. The invention

15   also relates to membranes prepared from such compositions, and to methods of their

preparation.

BACKGROUND ART

The following discussion is not to be construed as an admission with regard to

the common general knowledge in Australia.

20   Synthetic membranes are used for a variety of applications including

desalination, gas separation, filtration and dialysis. The properties of the membranes

vary depending on the morphology of the membrane i.e. properties such as symmetry,

pore shape and pore size and the polymeric material used to form the membrane.

Different membranes can be used for specific separation processes, including

microfiltration, ultrafiltration and reverse osmosis. Microfiltration and ultrafiltration are

pressure driven processes and are distinguished by the size of the particle or molecule

that the membrane is capable of retaining or passing. Microfiltration can remove very

5   fine colloidal particles in the micrometer and submicrometer range. As a general rule,

microfiltration can filter particles down to 0.1μm, whereas ultrafiltration can retain

particles as small as 0.01μm and smaller. Reverse Osmosis operates on an even smaller

scale.

As the size of the particles to be separated decreases, the pore size of the

10   membrane decreases and the pressure required to carry out the separation increases.

A large surface area is needed when a large filtrate flow is required. One known

technique to make filtration apparatus more compact is to form a membrane in the shape

of a hollow porous fibre. Modules of such fibres can be made with an extremely large

surface area per unit volume.

15   Microporous synthetic membranes are particularly suitable for use in hollow

fibres and are produced by phase inversion. In this process, at least one polymer is

dissolved in an appropriate solvent and a suitable viscosity of the solution is achieved.

The polymer solution can be cast as a film or hollow fibre, and then immersed in

precipitation bath such as water. This causes separation of the homogeneous polymer

20   solution into a solid polymer and liquid solvent phase. The precipitated polymer forms a

porous structure containing a network of uniform pores. Production parameters that

affect the membrane structure and properties include the polymer concentration, the

precipitation media and temperature and the amount of solvent and non-solvent in the

polymer solution. These factors can be varied to produce microporous membranes with

a large range of pore sizes (from less than 0.1 to 20μm), and altering chemical, thermal and mechanical properties.

Microporous phase inversion membranes are particularly well suited to the application of removal of viruses and bacteria. Of all types of membranes, the hollow

5   fibre contains the largest membrane area per unit volume.

Flat sheet membranes are prepared by bringing a polymer solution consisting of at least one polymer and solvent into contact with a coagulation bath. The solvent diffuses outwards into the coagulation bath and the precipitating solution will diffuse into the cast film. After a given period of time, the exchange of the non-solvent and

10   solvent has proceeded such that the solution becomes thermodynamically unstable and demixing occurs. Finally, a flat sheet is obtained with an asymmetric or symmetric structure.

Hydrophobic surfaces are defined as "water hating" and hydrophilic surfaces as "water loving". Many of the polymers that porous membranes are made of are

15   hydrophobic polymers. Water can be forced through a hydrophobic membrane by use of sufficient pressure, but the pressure needed is very high (150-300 psi), and a membrane may be damaged at such pressures and generally does not become wetted evenly.

Hydrophobic microporous membranes are characterised by their excellent chemical resistance, biocompatibility, low swelling and good separation performance.

20   Thus, when used in water filtration applications, hydrophobic membranes need to be hydrophilised or "wet out" to allow water permeation. Some hydrophilic materials are not suitable for microfiltration and ultrafiltration membranes that require mechanical strength and thermal stability since water molecules can play the role of plasticizers.

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Currently, poly(tetrafluoroethylene) (PTFE), Polyethylene (PE), Polypropylene
(PP) and poly(vinylidene fluoride) (PVDF) are the most popular and available
hydrophobic membrane materials.   Poly(vinylidene fluoride) (PVDF) is a semi-
crystalline polymer containing a crystalline phase and an amorphous phase. The

5   crystalline phase provides good thermal stability whilst the amorphous phase adds some
flexibility to the membrane. PVDF exhibits a number of desirable characteristics for
membrane applications, including thermal resistance, reasonable chemical resistance (to
a range of corrosive chemicals, including sodium hypochlorite), and weather (UV)
resistance.

10   While PVDF has to date proven to be the most desirable material from a range of
materials suitable for microporous membranes, the search continues for membrane
materials which will provide better chemical stability and performance while retaining
the desired physical properties required to allow the membranes to be formed and
worked in an appropriate manner.

15   In particular, a membrane is required which has a superior resistance (compared to
PVDF) to more aggressive chemical species, in particular, oxidising agents such as
sodium hypochlorite and to conditions of high pH i.e. resistance to caustic solutions.

DESCRIPTION OF THE INVENTION

According to a first aspect the invention provides the use of polymer suitable for

20   forming into an ultrafiltration or microfiltration membrane, said polymer being a
terpolymer of tetrafluoroethylene (TFE), PVDF and hexafluoropropylene monomers.

Preferably, the polymer includes from 20-65% PVDF monomer, from 10-20%
hexafluoropropylene monomer and 30-70 % TFE.

More preferably, the polymer includes from 30-50% PVDF monomer, from 15-20% hexafluoropropylene, and from 30-55% TFE. Even more preferably, the polymer includes from 35-40% PVDF and 17-20% HFP and 40-48% TFE.

Most preferably, the polymer is a terpolymer of 44.6% tetrafluoroethylene (TFE) monomers, 36.5% PVDF monomers, and 18.9% hexafluoropropylene monomers.

Unless otherwise indicated, all percentages are expressed as weight percentages.

According to a second aspect the invention provides an ultrafiltration and/or microfiltration membrane formed from a terpolymer including TFE monomers, PVDF monomer and hexafluoropropylene monomer. Preferably the monomer composition is approximately 44.6% tetrafluoroethylene (TFE) monomer, 36.5% PVDF monomer and 18.9% hexafluoropropylene monomer.

The membranes of the second aspect have an improved chemical stability to oxidising agents and caustic soda relative to a membrane formed from PVDF alone.

According to a third aspect the invention provides a method of manufacturing a microfiltration or ultrafiltration membrane including the step of casting a membrane from a composition including a terpolymer of 44.6% tetrafluoroethylene (TFE) monomer, 36.5% PVDF monomer and 18.9% hexafluoropropylene monomer.

Preferably, the membrane is in the form of a hollow fibre, cast by the TIPS procedure, or more preferably by the DIPS procedure.

Most preferably, the polymer used is THV 220G, obtained from Dyneon® (3M) as a solvent soluble fluoropolymer. The polymer is a combination of approximately 44.6% tetrafluoroethylene (TFE) monomer, 36.5% PVDF monomer, and 18.9% hexafluoropropylene monomer.

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According to a fourth aspect, the invention provides a method of forming a

polymeric ultrafiltration or microfiltration membrane including the steps of:

preparing a leachant resistant membrane dope;

incorporating a leachable pore forming agent into the dope;

5   casting a membrane; and

leaching said leachable pore forming agent from said membrane with said

leachant.

Preferably, the leachant resistant membrane polymer includes a terpolymer of

TFE, PVDF and hexafluoropropylene. More preferably, the polymer includes 44.6%

10   tetrafluoroethylene (TFE) monomers, 36.5% PVDF monomers, and 18.9%

hexafluoropropylene monomers.

Preferably, the leachable pore forming agent is silica, and the leachant is a caustic

solution, but the pore forming agent may for preference be any inorganic solid with an

average particle size less than 1 micron while the leachant may be any material/solution

15   that leaches the said pore forming agent from the membrane.

According to fifth aspect, the invention provides a method of improving the

structure of a polymeric ultrafiltration or microfiltration membrane by the addition of a

nucleating agent to a membrane dope. Preferably the nucleating agent is added in

catalytic amounts and most preferably it is TiO_2, however, any insoluble/inert

20   (unleachable) inorganic solid with an average particle size less than 1micron may be

used.

According to a sixth aspect, the invention provides an elastic polymeric

ultrafiltration or microfiltration membrane having an asymmetric cross section defining a

large-pore face and a small-pore face; said membrane having a higher flux at a given

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pressure from said large-pore face to said small-pore face than from said small-pore face

to said large-pore face.

Preferably the elastic membrane is formed from the preferred membrane forming

mixtures of the preceding aspects, and may also be formed using the addition of

5   leachable pore forming agents and/or nucleating agents.

The invention will now be described with particular reference to specific examples.

It will be appreciated, however, that the inventive concept disclosed therein is not limited

to these specific examples

BEST MODE FOR CARRYING OUT THE INVENTION

10   MEMBRANE FORMATION

DIPS PROCEDURE

THV 220G, obtained from Dyneon® Corp (3M) was dissolved in N-

methylpyrrolidone (NMP) at approximately 20 wt%. A flat sheet membrane was cast

from this solution and precipitated in water at 60°C before being examined using

15   scanning electron microscopy (SEM).

A standard DIPS process was employed as follows: Polymer solutions were mixed

and heated to around 50°C and pumped (spun) through a die into a 5 metre water-filled

quench (or solidification) bath at 65°C. Non-solvent (lumen) consisting of 20% NMP,

10% water and 70% polyethylene glycol (PEG200) was fed through the inside of the die

20   to form the lumen. The hollow fibre was then spun into the quench bath and solidified,

before being run out of the bath over driven rollers onto a winder situated in a secondary

water bath at room temperature to complete the quench and washing of the fibre.

The membrane structure was reasonable although a skin was found on the surface

of the membrane that prevented exposure of surface pores.

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The caustic resistance of the membrane was tested by placing a sample of the flat

sheet into 5 wt% caustic solution and comparing the appearance with a control of PVDF

membrane cast by the TIPS process.

Both samples were thoroughly wet out with alcohol prior to immersion in the

5   caustic solution. The THV samples become transparent upon complete wetting. The

results of the caustic immersion test are shown in table 1.

Table 1 shows the results of the caustic resistance tests. The results indicate that

while the membranes are not impervious to caustic, as would be the case for a material

like Teflon, they show extremely limited degradation for an extended period of time in a

10   comparatively strong caustic solution. All subsequent exposures to 5% solutions have

shown the same result, that a slight yellowing occurs upon immediate contact with the

solution but no further degradation (either visually or affecting the membrane properties)

occurs.

In addition to colour changes, the stiffness of both the PVDF and the THV samples

15   were examined. The PVDF membrane had lost a marked amount of flexibility and was

quite brittle, while by contrast, the THV sample appeared to be relatively unaffected.

The results strongly suggest that no detrimental modification of the polymer

membranes takes place as a result of such caustic immersion.

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TABLE 1

Date/Time elapsed	THV 200 Sheet	PVDF Fibre (TIPS)
5 mins	Colourless	Light brown
10 mins	Colourless	Light brown
1 hr	Colourless	Darker brown
2 days 19 hrs	Colourless	Dark brown/reddish
3 days	Very slight yellowing	Very dark brown
3 days 18 hrs	Very slight yellowing	Very dark brown
4 days	Very slight yellowing	Very dark brown
5 days	Very slight yellowing	Slightly darker/coppery
6 days	Very slight yellowing	Slightly darker/coppery
7 days	Very slight yellowing	Very dark turning black
10 days	Very slight yellowing	Very dark turning black
11 days	Very slight yellowing	Very dark turning black

MODIFICATION OF MEMBRANE HYDROPHOBICITY/HYDROPHILICITY

Those skilled in the art will appreciate the desirability of preparing membranes that

are hydrophilic in character. For instance, as described earlier hydrophilic membranes

are simpler to operate than hydrophobic membranes as they do not require an additional

wetting step.

It was established in the present case that THV 220G is compatible with Lutonal

A25 (Polyvinylethylether) at concentrations of around 2%. Lutonal A25 makes the DIPS

membranes of the present application less hydrophobic.

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Other than modifying hydrophobicity, the addition of Lutonal A25 appeared to make little difference in the physical structure of the membrane, apart from opening the membrane structure slightly. However membranes prepared with or without Lutonal are still acceptable in terms of their structure.

The addition of Lutonal A25 reduced the mixing time of the dopes quite dramatically.

Other elements of the DIPS process have also been investigated in conjunction with the use of THV 220G as a membrane polymer. It was found that non solvents can be used in a dope mix such as the addition of 5% glycerine triacetate (GTA) into the mixture without undue detrimental effects.

LEACHABLE DOPANTS

In order to produce membranes without a dense surface skin and having a more hydrophilic nature, silica was added to the dope with the intention of leaching the silica out of the matrix by the use of a caustic solution.

A hydrophilic silica Aerosil 200 and a hydrophobic silica Aerosil R972 were tested separately as additives to the THV 220G membrane mixture. The dopes were cast into flat sheet membranes, and were quenched in hot water at 60°C as described previously. Once the membranes had been cast, a portion thereof was leached in a 5% aqueous caustic solution at room temperature for 14 hours. Without wishing to be bound by theory, it is believed that the silica reacts with caustic to make the membrane hydrophilic as discussed below. Also, the leaching using caustic soda provides a membrane of good open structure. A number of membranes containing silica were cast. The results are shown in Table 2.

TABLE 2

Dope	Hydrophilicity	Dope Viscosity
18% THV, 8% Aerosil R972, 2% Lutonal A25, 72% NMP	Extremely hydrophilic	Very high viscosity
21% THV, 5% Aerosil 200, 2% Lutonal A25, 72% NMP	Hydrophilic	Moderate (honey-like) viscosity
20% THV, 10% R972, 2% Lutonal A25, 68% NMP	Extremely hydrophilic	Extremely viscous (paste-like)
20% THV, 5% R972, 75% NMP	Extremely hydrophilic	Moderate (honey-like) viscosity
20% THV, 0.5% R972, 2% Lutonal A25, 77.5% NMP	Hydrophobic	Low viscosity
20% THV, 80% NMP	Extremely Hydrophobic	Low viscosity
18% THV, 5% R972, 2% Lutonal A25, 75% NMP		Moderate (honey-like) viscosity
20% THV, 5% R972, 5% Mg(OH)$_2$, 2% Lutonal A25, 68% NMP	—	Extreme viscosity — Far too high to cast

Table 2 demonstrates that the silica is required in reasonably high concentrations to make the membranes hydrophilic. It also shows the trend of increasing viscosity with

5   increasing silica content.

After the membranes were cast, and prior to leaching, the membranes were examined using scanning electron microscopy. The structures were generally extremely promising with the surface of the sheets completely open and totally free of any skin. The cross-sectional appearance was more like a conglomerate of precipitated particles, rather than a true honeycomb like structure.

The best form of the silica appeared to be the hydrophobic Aerosil R972, although both forms of silica produced a hydrophilic membrane with a highly porous structure.

Subsequently placing the sample in caustic soda to leach the silica provided a dramatic opening up in the membrane structure even further. The result of the leaching was a change in the cross-section from the abovementioned conglomerate-like structure to the more traditional lace or sponge-like formation.

The optimal dope for forming a DIPS polymer appears to be from a mixture of 72% NMP, 20% THV, 6% silica and 2% Lutonal. This provides a hydrophilic membrane from a dope possessing a viscosity in the range that can be easily pumped.

A number of hollow fibre membranes were prepared from the above dope. The wetting characteristics were as desired and the membrane structure showed an extremely open surface. While 6% silica was used in the present invention, it will be appreciated that the quantity can vary significantly without departing from the present inventive concept.

Fibres incorporating silica with thicker walls were prepared and the current properties of the fibre membranes were examined. The fibre was then subject to leaching with a 5% caustic solution at room temperature for 18 hours.

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It can be seen that leaching the membrane changes the permeability and bubble points significantly without altering the desirable physical properties of the membrane. The leaching of the silica from the membranes has a positive effect upon permeability.

Thus, before leaching, the membrane had very few pores and extremely low flows. After leaching, however, the situation is reversed and there are a multitude of pores and a high flux.

A long leaching time is not necessarily required and can be incorporated in the production process as a post-treatment of the final modular product. The leaching process can be carried out at any time, however there is an advantage to postponing the leaching process as long as possible, since any damage to the surface of the fibres during handling can be overcome by leaching which physically increases the porosity of the membrane. Existing PVDF membrane surfaces can be damaged irreconcilably during production, resulting in a decrease in permeability and flux of the fibres.

SEM analysis of the membranes showed a high degree of asymmetry. Asymmetry is defined as a gradual increase in pore size throughout the membrane cross-section, such that the pores at one surface of the hollow fibre are larger than the other. In this case, the pore size increase was seen from the outer surface where the pores were smallest (and a quite dense surface layer was present) to the inner surface where the pores were significantly larger than those on the outer surface.

Preparation of the fibres was run at 65°C rather than 50°C as in a typical DIPS process. Increasing the quench bath temperature by 10-15°C dramatically affects the surface structure. The higher temperature gives a much more open surface. The use of the higher temperatures therefore accordingly means it is feasible to increase the polymer

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concentrations and possibly the silica concentration if it is desired to bolster the existing

membrane and increase the mechanical strength.

Further it has been found that a more particular mixing procedure contributes to

the success of forming a membrane of high permeability. Mixing constituents together

5   in a random manner does not produce such a good result as following a more stringent

procedure whereby the Aerosil R972 is dissolved in the total quantity of NMP and this

solution is allowed to degas. The polymer pellets are mixed with the liquid Lutonal A25

to coat the pellets. When these two procedures are complete, the two mixtures are

combined. The advantage of this appears to be that the silica is dispersed effectively and

10   does not clump (which can lead to macrovoids) and also, the pellets do not clump (which

has the effect of increasing mixing time and consistency of the dope) since they are

coated with a sufficient quantity of Lutonal A25 for a sufficient time to allow them to

dissolve individually.

As well as silica, the leaching process allows for the introduction of other

15   functionalities into the membrane, such as introducing hydrolysable esters to produce

groups for anchoring functional species to membranes.

Surprisingly, it has also been found that the membrane remains hydrophilic after

leaching. Again, without wishing to be bound by theory, the silica particles have a size

in the order of nanometres so consequently the silica disperses homogeneously

20   throughout the polymer solution. When the polymer is precipitated in the spinning

process, there is a degree of encapsulation of the SiO_2 particles within the polymer

matrix. Some of the particles (or the conglomerates formed by several silica particles)

are wholly encapsulated by the precipitating polymer, some are completely free of any

adhesion to the polymer (i.e. they lie in the pores of the polymer matrix) and some of the

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particles are partially encapsulated by the polymer so that a proportion of the particle is
exposed to the 'pore' or to fluid transfer.

When contacted with caustic, it is believed that these particles will be destroyed
from the accessible side, leaving that part of the particle in touch with the polymer

5   matrix remaining. The remainder of the silica particle adheres to the polymer matrix by
hydrophobic interaction and/or mechanical anchoring. The inside of the particle wall is
hydrophilic because it consists of OH groups attached to silica. Because the silica is
connected to hydrophobic groups on the other side, it cannot be further dissolved.

Thus, when the membranes are treated with caustic solution, the free

10   unencapsulated SiO_2 reacts to form soluble sodium silicates, while the semi-exposed
particles undergo a partial reaction to form a water-loving surface (bearing in mind that
given the opportunity, such particles would have dissolved fully). It is believed that the
pores in the polymer matrix formed during the phase inversion stage yet filled with SiO_2
particles are cleaned out during leaching, giving a very open, hydrophilic membrane.

15   NUCLEATING AGENTS

TiO_2 (titania) was also added to the membrane at a variety of concentrations.
TiO_2 has been added to membrane forming mixtures previously as a filler to provide
abrasion resistance or to act as a nucleating agent, to increase the rate of fibre
solidification.

20   However, surprisingly in the present case, it was found that the addition of TiO_2 in
concentrations below that used for reinforcement of membranes, a high degree of
asymmetry was introduced into the membranes. In particular, this was as a result of the
formation of a dense outer layer. Without wishing to be bound by theory, the applicant
believes that the TiO_2 particles provide a site for phase inversion or precipitation to

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begin. In hollow fibre membranes prepared by the DIPS process, the high number of fast

solidification sites at which precipitation occurs means that the pores formed near the

membrane surface are smaller, fewer and further between.

The use of too much titania can cause a dense outer layer on the membrane to

5   restrict permeability. Further, as the titania disperses very well throughout the dope, only

of the order of a catalytic amount is required. For example, only about 0.1-0.2 wt%

titania need be incorporated into the membrane, although as much as 3% can be used

depending on the desired effect.

A dope formulation giving good results is 20 wt% THV 220G, 6 wt% Aerosil

10   R972, 2 wt% Lutonal A25, 0.2% TiO_2 and 71.8% N-methylpyrrolidone.

A dope having the above formulation was mixed and cast according to the DIPS

method. They were then leached in 5% caustic soda solution for approximately 24 hours

and then soaked in glycerol. Soaking fibres in glycerol or the like is a highly desirable

step, since the material is relatively flexible and will allow pores to collapse. The results

15   for the TiO_2 trial fibres are given as Table 3.

TABLE 3

Property	Results for THV 200
Permeability (LMH)	3771
Bubble Point (kPa)	150
Burst Point (kPa)	150-160
Break Extension (%)	245
Break Force(N)	0.72
Fibre Dimensions (μM)	1080 OD, 535 ID

Break Force per unit area (N/cm^2)	105

Table 3 lists the properties of the membranes made which incorporate a small proportion of TiO$_2$. The most apparent property to note is the high permeability of the membrane.

5   HIGH POLYMER CONCENTRATIONS

Attempts at making polymer concentrations above 20 wt% were attempted. Doing so however caused alternative problems mainly based around a dramatic increase in viscosity. Once the polymer portion rises to above 25 wt%, viscosity becomes too high to pump in conventional pumps. However, high polymer concentrations were seen to

10   correlate with an increase in the mechanical strength of the membrane. Optimal results of workability and strength were achieved with the hollow fibre having a polymer concentration of 22%. The best was seen to be 22 wt% THV 220G, 6 wt% Aerosil R972, 2% Lutonal A25 and 70% N-methylpyrrolidone. Concentrations as high as 30 wt% polymer did produce a feasible membrane. The high polymer concentration

15   membranes were leached in a 5% caustic solution for 24 hours and then soaked in glycerol. The results are shown in Table 4. A point of note is that the increase in polymer concentration or the addition of TiO$_2$ does not appear to improve the bubble point or burst pressure of the fibres in any way. The mechanical strength of the fibre appears to be mainly a function of wall thickness and lumen diameter.

20   TABLE 4

Property	Results for THV 200
Permeability (LMH)	2821
Bubble Point (kPa)	150

Burst Point (kPa)	150-160
Break Extension (%)	240
Break Force (N)	0.64
Fibre Dimensions (μM)	930 OD, 542 ID
Break Force per unit area (N/cm^2)	145

Table 4 lists the properties of the membrane made using 22% polymer (without

TiO$_2$). Comparing the results to Table 3, the membrane exhibit very similar

characteristics with the exception that Table 3 indicates possibly a higher

5   permeability/flux for titania containing membranes.

PHYSICAL PROPERTIES OF MEMBRANES

The bubble point measurements in Tables 3 and 4 do not give an entirely accurate

determination of the bubble point, the pore size or molecular weight cut off of the

membrane because the membranes are somewhat rubbery and flexible so that under

10   pressure the membrane expands and hence the pores stretch like a rubber band. It has

been observed that the fibres increase in size slightly under a backwash pressure of as

low as 100 Kilopascals.

This behaviour is apparently due to the high elastic nature of the polymer which

also gives extremely high break tension described in Table 4. This elastic behaviour

15   would adequately describe the apparently low bubble point recorded for the membrane,

since as the membrane is stretched by the pressure applied, the pores would be stretching

proportional to the overall size increase of the fibre. This property is extremely valuable

for cleaning a membrane, since the pores may be opened up by the application of a liquid

backwash and any material fouling the pores may be easily dislodged and flushed away.

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The elastic behaviour also indicates that the membrane (and hence the pores) may

recover up to 100% of such a deformation, thus the pores would return to their original

size.

To demonstrate this characteristic behaviour, the permeability and fluxes of the

5   fibres were measured. Permeability and flux are typically measured with a filtration

direction (direction of the filtrate flow relative to the membrane surfaces) outside-in with

the filtrate collected from the inside of the hollow fibre. To prove that the pore structure

is increasing in size, the flow was reversed so that the filtration direction was inside-out,

with filtrate emerging on the outer side of the fibre.

10   Table 5 shows the results of these "outside-in" and "inside-out" tests

TABLE 5

Pressure (kPa)	Flux Outside-In (L/m^2.hr)	Flux Inside-Out (L/m^2.hr)
22	919	1134
48	1550	2695
58	1374	3575
67	1327	4734
73	1353	5308
98	1322	7616
124	1283	11301

Table 5 and Figure 1 show that the flux for inside-out flow increases as the

pressure increases, while the outside-in flow remains almost completely constant. This

15   indicates that the pressure applied from the inside is expanding the pores to allow far

- 20 -

higher flows. This elasticity described is one of the most desirable properties of the membranes discussed.

POTTING

As a result of this one of the desirable features of the membranes according to the present invention is their ability to be potted directly into epoxy. PVDF membranes require a more flexible potting material such as polyurethane to prevent damage to the fibres. PVDF fibres can break with relative ease if the fibers are potted in a potting material which lacks any flexibility. If there is no flexibility in the potting material there can be breakage of the fiber at the point where the fiber enters the pot. By contrast, the membranes of the invention can be potted into epoxy potting material and the fibers will not be significantly damaged during use. In fact, the membranes of the present invention can be stretched to the normal break extension of the fibre when pulled parallel to the pot surface i.e. 90° to the potted direction.

The comparison of the properties of the THV membranes of the present application and PVDF prepared with the DIPS process are shown in Table 6.

TABLE 6

Property	THV 200 (after leaching)	DIPS PVDF
Hydrophilicity	Spontaneous Wetting	Satisfactory
Chlorine Resistance	Highly Resistant	Resistant
Caustic Resistance	Highly resistant	No resistance
Break Extension (%)	245	<145
Break Force (N)	0.73	<1.0
Permeability (LMH @	3000-4000	ca. 300

100kPa)		
Bubble Point (kPa)	ca. 150	ca. 350-400
Surface structure	Extremely open	Good
Asymmetry	Excellent	Excellent

Table 6 gives a comparison between THV membranes manufactured using the DIPS process and the best (to date) PVDF membranes manufactured using the DIPS process. The main differences are the spontaneous wetting of the THV membrane and also the high clean water permeability, both of which are lacking in current PVDF membranes. The other difference lies in comparing the stiffness of the membranes, which is directly attributable to the polymers used to produce the membrane.

It would be appreciated by those skilled in the art that while the invention has been described with particular reference to one embodiment, many variations are possible without deviating from the inventive concept disclosed herein.

THE CLAIMS OF THE INVENTION ARE AS FOLLOWS

1.   The use of a polymer for forming an ultrafiltration or microfiltration membrane, said polymer being a terpolymer of tetrafluoroethylene (TFE) monomer, polyvinylidene fluoride (PVDF) monomer and hexafluoropropylene (HFP) monomer.

2.   The use of claim 1 wherein the polymer includes, by weight, from 20-65% PVDF monomer, from 10-20% HFP monomer and from 30-70 % TFE monomer.

3.   The use according to claim 1 or claim 2 wherein the polymer includes, by weight, from 30-50% PVDF monomer, from 15-20% HFP monomer and from 30-55% TFE monomer.

4.   The use according to any one of the preceding claims wherein the polymer includes, by weight, from 35-40% PVDF monomer, from 17-20% HFP monomer and from 40-48% TFE monomer.

5.   The use of a polymer for forming into an ultrafiltration or microfiltration membrane, said polymer being a terpolymer of 44.6% tetrafluoroethylene (TFE) monomers, 36.5% polyvinylidene fluoride (PVDF) monomers, and 18.9% hexafluoropropylene (HFE) monomers by weight.

6.   An ultrafiltration and/or microfiltration membrane formed from a terpolymer including tetrafluoroethylene (TFE) monomer, polyvinylidene fluoride (PVDF) monomer and hexafluoropropylene (HFE) monomer.

7.   An ultrafiltration and/or microfiltration membrane according to claim 6 wherein the polymer includes, by weight, from 20-65% PVDF monomer, from 10-20% HFP monomer and 30-70 % TFE monomer.

8.   An ultrafiltration and/or microfiltration membrane according to claim 6 or 7 wherein the polymer includes, by weight, from 30-50% PVDF monomer, from 15-20% HFP monomer and from 30-55% TFE monomer.

9. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 8 wherein the polymer includes, by weight, from 35-40% PVDF monomer, from 17-20% HFP monomer and from 40-48% TFE monomer.

10. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 9 wherein the polymer is a terpolymer of 44.6% tetrafluoroethylene (TFE) monomers, 36.5% PVDF monomers, and 18.9% hexafluoropropylene monomers.

11. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 10 having an asymmetric cross section defining a large-pore face and a small-pore face; said membrane having a higher flux at a given pressure from said large-pore face to said small-pore face than from said small-pore face to said large-pore face.

12. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 11 wherein the membrane is in the form of a hollow fibre.

13. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 12 cast by a thermally induced phase separation procedure.

14. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 13 or cast by a diffusion induced phase separation procedure.

15. An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 14 further including a hydrophobicity modifying agent.

16. An ultrafiltration and/or microfiltration membrane according to claim 15 wherein the hydrophobicity modifying agent is polyvinylethylether.

17. An ultrafiltration and/or microfiltration membrane according to claim 15 or 16 wherein the hydrophobicity modifying agent is present in an amount of 2%.

18.   An ultrafiltration and/or microfiltration membrane according to any one of claims 6 to 17 having an improved chemical stability to oxidising agents and caustic soda relative to a membrane formed from PVDF alone.

19.   A method of manufacturing a microfiltration or ultrafiltration membrane including the step of casting a membrane from a polymer composition including tetrafluoroethylene (TFE) monomer, polyvinylidenefluoride (PVDF) monomer and hexafluoropropylene (HFP) monomer.

20.   A method of manufacturing a microfiltration or ultrafiltration membrane according to claim 19 wherein the polymer includes from 20-65% PVDF monomer, from 10-20% HFP monomer and 30-70 % TFE monomer.

21.   A method of manufacturing a microfiltration or ultrafiltration membrane according to claim 19 or 20 wherein the polymer includes from 30-50% PVDF monomer, from 15-20% HFP monomer and from 30-55% TFE monomer.

22.   A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 21 wherein the polymer includes from 35-40% PVDF monomer, from 17-20% HFP monomer and from 40-48% TFE monomer.

23.   A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 22 wherein the polymer is a terpolymer of 44.6% TFE monomers, 36.5% PVDF monomers, and 18.9% HFP monomers.

24.   A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 23 wherein the polymer is in the form of a membrane dope and further includes as a solvent N-methylpyrrolidone.

25.   A method of manufacturing a microfiltration or ultrafiltration membrane according to claim 24 wherein N-methylpyrrolidone is present in an amount of 70-80% by weight of the dope.

26. A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 25 further including the step of adding a hydrophobicity modifying agent.

27. A method of manufacturing a microfiltration or ultrafiltration membrane according to claim 26 wherein the hydrophobicity modifying agent is polyvinylethylether.

28. A method of manufacturing a microfiltration or ultrafiltration membrane according to claim 26 or 27 wherein the hydrophobicity modifying agent is present in an amount of 2%.

29. A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 28 including the step of using as a non-solvent a mixture of 20% N-methylpyrrolidone, 10% water and 70% polyethylene glycol.

30. A method of manufacturing a microfiltration or ultrafiltration membrane according to any one of claims 19 to 29 including the step of using water as a quench fluid.

32. A microfiltration or ultrafiltration membrane when formed by a method according to any one of claims 19 to 30.

32. A method of forming a polymeric ultrafiltration or microfiltration membrane including the steps of:

　　preparing a leachant resistant membrane dope;

　　incorporating a leachable pore forming agent into the dope;

　　casting a membrane; and

　　leaching said leachable pore forming agent from said membrane with said leachant.
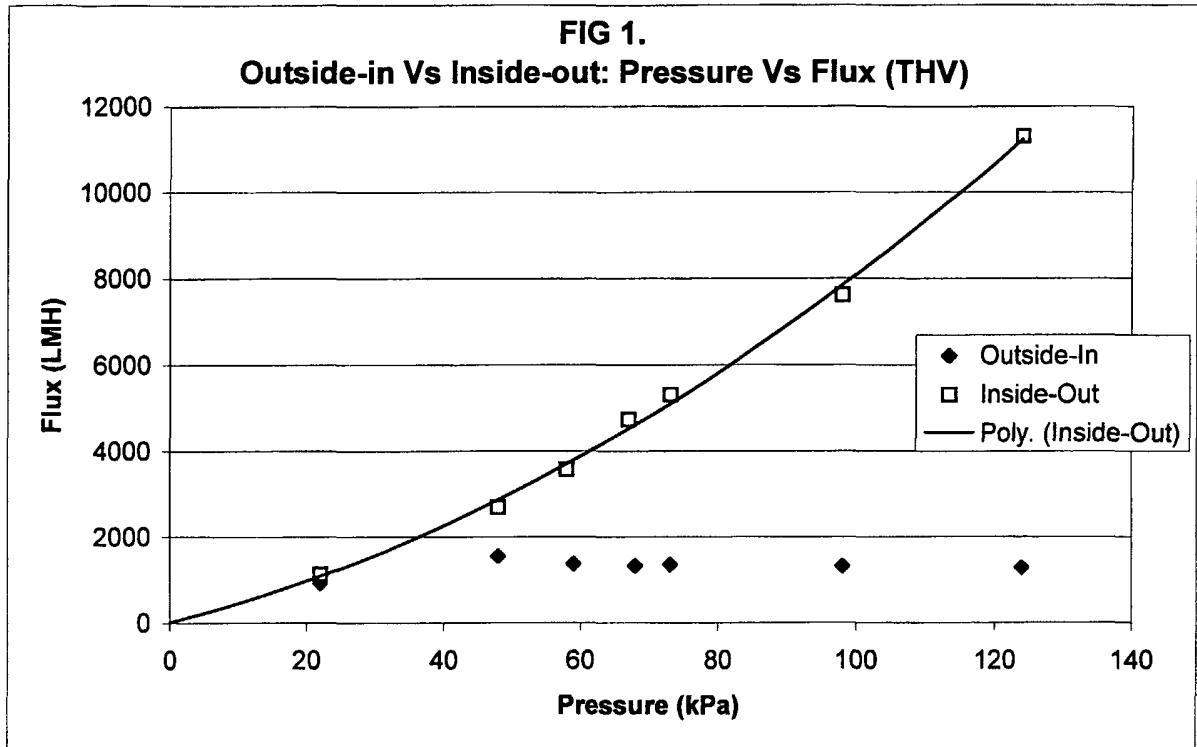
33.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 32 wherein the leachant resistant membrane dope includes a

polymer composition including tetrafluoroethylene (TFE) monomer,

polyvinylidenefluoride (PVDF) monomer and hexafluoropropylene (HFP) monomer.

34.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 33 wherein the polymer includes from 20-65% PVDF monomer,

from 10-20% HFP monomer and 30-70 % TFE monomer.

35.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 33 or 34 wherein the polymer includes from 30-50% PVDF

monomer, from 15-20% HFP monomer and from 30-55% TFE monomer.

36.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 33 to 35 wherein the polymer includes from 35-40%

PVDF monomer, from 17-20% HFP monomer and from 40-48% TFE monomer.

37.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 33 to 36 wherein the polymer is a terpolymer of 44.6%

TFE monomers, 36.5% PVDF monomers, and 18.9% HFP monomers.

38.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 33 to 37 wherein the polymer is in the form of a

membrane dope and further includes as a solvent N-methylpyrrolidone.

39.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 38 wherein N-methylpyrrolidone is present in an amount of 70-

80% by weight of the dope.

40.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 39 further including the step of adding a

hydrophobicity modifying agent.

41.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 40 wherein the hydrophobicity modifying agent is

polyvinylethylether.

42.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to claim 40 or 41 wherein the hydrophobicity modifying agent is present in

an amount of 2%.

43.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 42 including the step of using as a non-solvent a

mixture of 20% N-methylpyrrolidone, 10% water and 70% polyethylene glycol.

44.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 43 including the step of using water as a quench

fluid.

45.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 44 wherein the leachable pore forming agent is

an inorganic solid with an average particle size less than 1 micron.

46.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 45 wherein the leachable pore forming agent is

leachable silica.

47.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 46 wherein the leachable pore forming agent is

present in an amount of 8%

48.   A method of manufacturing a microfiltration or ultrafiltration membrane

according to any one of claims 32 to 47 wherein the leachant is a caustic solution.

49.   A microfiltration or ultrafiltration membrane when prepared by a method of any

one of claims 32 to 48.

50.   An elastic polymeric ultrafiltration or microfiltration membrane having an asymmetric cross section defining a large-pore face and a small-pore face; said membrane having a higher flux at a given pressure from said large-pore face to said small-pore face than from said small-pore face to said large-pore face when prepared by a method of any one of claims 32 to 48.

51.   A method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure including the step of adding a nucleating agent to a membrane dope prior to casting said membrane.

52.   A method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure according to claim 51 wherein the nucleating agent is added in catalytic amounts.

53.   A method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure according to claim 51 or 52 wherein the nucleating agent is an insoluble and or inert inorganic solid.

54.   A method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure according to any one of claims 51 to 53 wherein the nucleating agent is an insoluble and or inert inorganic solid with an average particle size less than 1micron.

55.   A method of preparing a polymeric ultrafiltration or microfiltration membrane of improved structure according to any one of claims 51 to 54 wherein the nucleating agent is TiO_2.

56.   An elastic polymeric ultrafiltration or microfiltration membrane having an asymmetric cross section defining a large-pore face and a small-pore face; said membrane having a higher flux at a given pressure from said large-pore face to said

small-pore face than from said small-pore face to said large-pore face when prepared

by the method of any one of claims 51 to 55.

57.   An elastic polymeric ultrafiltration or microfiltration membrane having an

asymmetric cross section defining a large-pore face and a small-pore face; said

membrane having a higher flux at a given pressure from said large-pore face to said

small-pore face than from said small-pore face to said large-pore face.

FIG 1.
Outside-in Vs Inside-out: Pressure Vs Flux (THV)

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   B01D 71/76, 67/00, 69/00

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC B01D 67/00, 69/00, 71/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent WPAT: IPC OR MEMBRANE + ULTRAFILT, MICROFILT, LEACH, NUCLEAT, TI02, ASYMMETR

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 98-095747/09, JP 09324067 (SHINETSU POLYMER KK) 16 December 1997	1, 6, 18, 19, 32a
X	Derwent Abstract Accession No. 1999-262453, RD 420013 (ANONYMOUS) 10 April 1999	1, 6, 18, 32a
A	WO 88/06200 (WHITFORD PLASTICS LIMITED) 25 August 1988 See whole document	

X	Further documents are listed in the continuation of Box C	X	See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
8 August 2002	1 4 AUG 2002

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	**MATTHEW FRANCIS** Telephone No : (02) 6283 2424

Form PCT/ISA/210 (second sheet) (July 1998)

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 1999-359314/31, DE 29906389 U (CRAMER WEBEREI HEEK NIENBORG GMBH & CO C) 17 June 1999	
X	US 5275766 A (GADKAREE et al) 4 January 1994 Abstract, claims	32b, 45, 49
X	EP 12557 B1 (ABCOR, INC.) 16 February 1983 Claim 6	32b, 40, 49
X	EP 395133 B1 (X-FLOW B.V.) 1 February 1995 Column 2, lines 20-32	32b, 40, 49
X	EP 492446 B1 (THE DOW CHEMICAL COMPANY) 29 November 1995 Page 1, lines 40-57, page 8, lines 37-46	32b, 40, 44, 49
X	US 5015275 A (BECK et al) 14 May 1991 Column 1, line 60-column 2, line 32	32b, 44, 49
X	US 4963304 A (IM et al) 16 October 1990 Column 2, lines 7-48	32b, 49
X	US 4904426 A (LUNDGARD et al) 27 February 1990 Column 1, line 61-column 2, line 26, column 8, line 25	32b, 44, 49
X	EP 492942 B1 (AMOCO CORPORATION) 16 February 2000 Page 3, lines 44-55	51, 52
X	US 4702840 A (DEGEN et al) 27 October 1987 Column 2, lines 54-61	51
X	US 4431545 A (PALL et al) 14 February 1984 Column 5, lines 34-36	51
X	Derwent Abstract Accession No. 92-366945/45, DE 4113420 A, Class A14 F01 J01 (BAYER AG)	57

C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4629563 A (WRASIDLO) 16 December 1986 Whole document	57

Box I	**Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos :

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos :

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II	**Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

   See separate sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☒ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)) (July 1998)

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

The application is considered to claim 4 separate inventions:

1)   Claims 1-32 and 33-39 relate to membranes produced from a terpolymer of tetrafluoroethylene monomer, polyvinylidene fluoride monomer and hexafluoropropylene monomer.

2)   Claim 32 (second instance as there are two such claims) and dependant claims 40-50 relate to a method of forming a membrane characterised by the steps of preparing a leachant resistant membrane dope, incorporating a leachable pore forming agent, casting the membrane and leaching out the pore forming agent. These claims are in no way limited to the terpolymer of claim 1.

3)   Claims 51-56 relate to the addition of a nucleating agent to a casting dope, which is also not limited to the terpolymer of claim 1.

4) Claim 57 relates to an asymmetric membrane characterised by physical properties and is no way restricted by its dope composition.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian 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			Patent Family Member				
JP	9324067	NONE					
WO	8806200	AU	14201/88	DK	5894/88	EP	348425
		ES	2006088	NO	884679	US	5171611
DE	29906389	NONE					
US	5275766	EP	595201				
EP	12557	CA	1132312	JP	55102635	US	4248913
		US	4302334				
EP	395133	CA	2015413	HK	1007697	JP	2302449
		NL	8901090	US	5076925		
EP	492446	US	5227101	CA	2058182	JP	4293533
		US	4904426	US	5064580	US	5200078
		US	5205968	AU	51628/90	CA	2009836
		EP	407684	NO	920164	WO	9101339
		ZA	9001039				
US	5015275	AU	58999/90	BR	9003375	CA	2021165
		EP	408046	JP	3068432	US	4980101
US	4963304	NONE					
US	4904426	US	5064580	US	5200078	US	5205968
		US	5227101	AU	51628/90	CA	2009836
		EP	407684	NO	920164	WO	9101339
		ZA	9001039				
EP	492942	AU	88386/91	CA	2056875	CN	1064491
		JP	4309546	NZ	241070	US	5176953
		US	5317035	US	5594070	US	5236963
		US	5272744	JP	5055120		
US	4702840	AU	10973/83	CA	1200158	CH	656887
		EP	90483	ES	519537	ES	8403326
		FR	2521028	GB	2116107	JP	58145740
		PT	76200	ZA	8300775		
US	4431545	CA	1209057	CH	654758	EP	94226
		ES	522148	ES	8406891	FR	2526327
		GB	2120116	JP	59026116	PT	76616

INTERNATIONAL SEARCH REPORT

Information on patent family members

DE	4113420	NONE					
US	4629563	BR	8101508	CA	1202837	EP	36315
		EP	144493	JP	56154051	JP	2002844
		US	4900443	US	4774039		

END OF ANNEX