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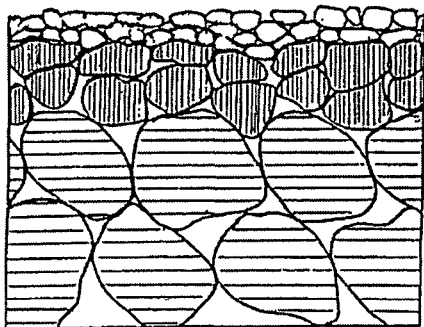
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(54) **Title:** CERAMIC MEMBRANE, ITS PREPARATION AND USE



(57) **Abstract:** The invention relates to a method for preparing a ceramic microporous membrane made of ZrO_2 and/or TiO_2 on a support membrane, comprising the steps of: i) forming a polymeric solution comprising polymeric ZrO_2 particles, TiO_2 particles and mixtures thereof, an alcohol amine and a solvent; ii) applying the polymeric solution on the support membrane; and iii) drying and firing the support membrane applied with the polymeric solution, thereby forming the microporous membrane on the support membrane, to the obtainable ceramic membrane and to its use.

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CERAMIC MEMBRANE, ITS PREPARATION AND USE

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The present invention relates to novel thermally and chemically stable ceramic microporous membranes, to a method for preparing these membranes and to the use of these membranes in liquid separation processes.

10 Liquid separation processes are widely practiced in a number of technological fields. Frequently, the separation of a mixture of liquids is achieved by distillation, but especially at lower concentrations of the minor compound, this is a relatively expensive technique.

15 When the liquid mixture has a relative volatility of 1 and forms an azeotropic mixture or also in the case when it has close-boiling components, efficient separation is also not possible by conventional distillation and a third compound, an entrainer, has to be added. A drawback of using this type of distillation processes is that additional separation steps are required to recover the entrainer and that a great deal of energy is consumed.

20 Moreover, in many cases, there is no suitable entrainer available and other separation techniques must be used like, for example, adsorption or extraction. A drawback of such techniques is the fact that they frequently require also a great deal of energy and significant investment and maintain cost. From an energy, environmental and cost point of view, the replacement
25 of a traditional liquid separation unit by a membrane, more specifically a pervaporation membrane, is proven to be very beneficial.

Frequently, the membrane employed in a pervaporation device consists of a polymeric material having the significant disadvantages in that the thermal and chemical stability of the material is restricted. As an alternative for the
30 polymeric membranes, microporous ceramic membranes have been developed, but problems with too strong acid or alkaline liquids are encountered in such membranes. It is the object of the present invention to

provide a thermally stable microporous ceramic membrane suitable for separating liquid mixtures. This membrane shows a high chemical stability with respect to all types of organic liquids and to acid and alkaline liquids.

A substantial amount of work has already been done in the field of the development of membranes which can be applied for pervaporation. These
5 membranes are generally classified into organic polymeric membranes and inorganic ceramic membranes, among which polymeric membranes represent the main group in both the commercial industrial field and the academic field. A considerable number of studies has been published in the literature
10 reporting the preparation of polymeric membranes and describing their performance for a number of organic solvent/water and organic solvent/organic solvent separations. Initially, membrane materials prepared were simple hydrophilic or hydrophobic polymers such as, for example, polyvinyl alcohol or rubbery polymers. These membranes have found
15 application at an industrial scale in the dehydration of alcohols, containing a small amount of water, and in the separation of small amounts of organic compounds from water.

An important problem hindering the development of pervaporation processes as a viable alternative to distillation in a larger number of
20 applications was the lack of polymeric membranes able to withstand sustained exposure to aggressive organic liquids, especially at higher temperatures. Later, a lot of research has been done on the development of more advanced polymeric membranes with improved properties. Research has been focused, for example, on improving the flux and the selectivity, but also on the solvent
25 stability and the corrosion resistance of the membranes for certain applications.

A number of advanced membranes have been proposed with a potential for more advanced pervaporation applications, but also these membranes do not cover a wide range of solvents and/or acid and alkaline
30 liquids and there are still a number of restrictions to the feed mixtures that can be handled.

5 Microporous ceramic membranes made from zeolite or SiO_2 have been proposed as an alternative for polymeric pervaporation membranes, because they have some well-known advantages including a greater chemical and thermal stability and a significantly longer service-life. They can operate reliably in all types of organic solvents, due to the inorganic nature of the membrane material, and temperatures up to 250°C can be handled.

10 Reported is the performance of both academic-scale and commercially available zeolite membranes for pervaporation applications. Some of these membranes show an extremely narrow pore size distribution around 0.5 nm and can separate very effectively water from all types of organic solvents. Also mixtures of organic solvents, for example benzene/cyclohexane, have been successfully separated with zeolite membranes.

15 Microporous SiO_2 pervaporation membranes are similar to well-known SiO_2 gas separation membranes and have been introduced on the market a few years ago. The membranes comprise of a microporous SiO_2 membrane layer with a pore size of for instance 0.4 nm, which is applied on a mesoporous carrier made of $\gamma\text{-Al}_2\text{O}_3$ by a polymeric sol-gel procedure. Since they appeared, these membranes have found increasing attention, especially, because they offer a rather good separation factor in combination with a relatively high flux. The main drawback of commercially available zeolite and SiO_2 pervaporation membranes, which have been introduced as alternatives for polymeric membranes, is, however, their limited resistance to acid and alkaline liquids.

25 In order to improve this resistance, SiO_2 membranes with ZrO_2 or TiO_2 added as a second component have been proposed, but membranes with a demonstrable improved corrosion resistance and having a pore size suitable for use in pervaporation have not been described or obtained.

30 The present invention relates to novel microporous ceramic membrane layers, which can be applied for pervaporation, and to methods for their production. In particular, the invention provides microporous membrane layers made of ZrO_2 and/or TiO_2 , displaying a high thermal stability, a chemical stability in all types of organic solvents and in acid and alkaline liquids and a

good separation efficiency in pervaporation. The invention furthermore relates to a method for preparing such microporous membrane layers according to a polymeric sol-gel dip-coating method, in which an alcohol amine is applied as a modifier and as a coating and drying controlling additive preparing.

5 Accordingly, the invention provides a method for preparing a ceramic microporous membrane made of ZrO_2 and/or TiO_2 on a support membrane, comprising the steps of:

- 10 i) forming a polymeric solution comprising polymeric ZrO_2 particles, TiO_2 particles and mixtures thereof, an alcohol amine and a solvent;
- ii) applying the polymeric solution on the support membrane; and
- 15 iii) drying and firing the support membrane applied with the polymeric solution, thereby forming the microporous membrane on the support membrane.

The method of the invention is simple in procedure, in required chemicals, in application method (dip-coating) and in conventional utilities (drying and firing oven). The method is similar for using Zr-precursor, Ti-precursor or both.

20 Examples of suitable alcohol amines are mono-, di-, and/or trialcohol amine having a C_1 - C_5 alkyl chain, preferably a C_2 - C_3 alkyl chain.

Preferably, the alcohol amine is monoethanol amine, diethanol amine and/or triethanol amine, preferably diethanol amine.

25 Any suitable solvent may be used, such as alcohols, hydrocarbons (benzene and hexane), methyl ethyl keton and acetic acid.

The polymeric ZrO_2 particles, TiO_2 particles and mixtures thereof may be formed by polymeric sol preparation from a precursor solution. Such precursor solution comprises as a precursor a metal alkoxide of formula (1)



and/or alkylated metal alkoxide of formula (2)



wherein:

5 M= Zr and/or Ti

n= 1 to 5

R= d-Cs-alkyl

x= 1 or 2

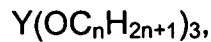
10 Preferably, the metal alkoxide may be ethoxide or butoxide. Alkoxides derived from ethanol, propanol and butanol may be used as well. The alkyl group may be straight or branched. When used as a mixture, the ratio between the Zr-alkoxide and Ti-alkoxide varies between 0.9 and 0.1, preferably the Zr-alkoxide is the predominant component and preferably present in a percentage varying from 60-99%, such as 70-95%.

15 In relation to the alkylated metal alkoxide it is preferred that one or two alkyl groups may be present with preferably a C₂ or C₃ alkyl group.

As a support for the microporous membrane, a mesoporous membrane made of $\gamma\text{-Al}_2\text{O}_3$, ZrO₂, TiO₂ or a combination of these materials can be used. In a preferred preparation method, diethanol amine is added to a solution of a zirconia and/or titania precursor, after which a sol containing nanometer-sized particles of these materials can be obtained. A stable microporous membrane layer comprising ZrO₂ and/or TiO₂ can be made by dip-coating these structures on the carrier, followed by a drying and firing process in air.

25 Preferably, such coatings are fired at a temperature of 400 °C or higher. The firing temperature normally ranges from 350-750 °C, preferably 400-600 °C. In order to avoid cracking or breakage of the microporous membrane it is preferred to add a pore growth restricting agent, such as an yttrium compound. Accordingly, it is preferred that the polymeric solution comprises an yttrium compound as a pore growth restricting agent. When the yttrium compound is added to the precursor solution then a preferred yttrium compound is yttrium alkoxide of formula (3)

30



wherein $n = 1$ to 8 , preferably $2-4$.

The polymeric solution then contains an yttrium compound as a dopant,
5 which restricts pore growth during firing at the desired temperatures. The
membrane layers prepared in this manner show a small pore size suitable for
pervaporation applications, a high thermal and a high chemical stability.

The polymeric solution may be applied by the known gel dip coating
method. Other methods for applying the polymeric solution may be used
10 provided that the intended thickness and/or amount of polymeric solution is
applied.

It is preferred that the ceramic microporous membrane is applied on a
support membrane which is a mesoporous membrane comprising $\gamma\text{-Al}_2\text{O}_3$,
 TiO_2 and/or ZrO_2 .

15 Another aspect of the present invention relates to ceramic microporous
membranes obtainable by the method according to the invention. Similarly,
the present invention relates to ceramic membranes comprising a
microporous membrane applied on a support membrane.

Finally, another aspect of the invention is the use of such ceramic
20 microporous membranes and ceramic membranes according to the invention,
particular in the liquid separation processes.

Mentioned and other features of the present invention will be further
discussed in detail with reference to the annexed drawing and the following
examples. However, it will be understood that the drawing and the examples
25 are given for illustration purposes and are not intended to restrict the present
invention to any extent.

In the drawing, figure 1 is a schematic cross-sectional view of a
ceramic membrane according to the invention comprising a ceramic
microporous membrane (layer 1) applied on the support membrane.

30 Referring to the figure 1, layer 1 is a microporous membrane layer,
having a pore size smaller than 1 nm and a thickness in the range $30 - 200$
 nm . Layer 2 is a mesoporous carrier, preferably having a pore size in the

range 2 to 10 nm and a thickness less than 10 μm . This layer is present on the surface of a porous support material 3, generally having a thickness of a few millimeters. The support material 3 may be present in all common configurations such as a flat, a tubular or a multichannel monolithic configuration and in the case of a tubular configuration, layer 2 can be present at the inside or outside surface.

Methods for preparing the support material 3 and layer 2 have been developed by various manufacturers and are well-known. The support material 3 is generally made of $\gamma\text{-Al}_2\text{O}_3$, by means of a conventional ceramic powder technique. Also other common support materials, such as TiO_2 , ZrO_2 , SiO_2 or a metal compound, can be used rather than $\gamma\text{-Al}_2\text{O}_3$. Layer 2 is generally made of $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , ZrO_2 or a combination of these materials, by means of a colloidal sol-gel dip-coating procedure.

Layer 1 is the active pervaporation layer of the membrane. Most preferably, layer 1 is made of ZrO_2 or TiO_2 or a combination of these materials. The especially preferred preparation method a polymeric sol-gel dip-coating method followed by a thermal treatment at a temperature of 400°C or higher, starting from a zirconium or titanium sol-gel precursor, which is modified by chelation with a slowly hydrolyzing ligand.

In order to obtain a microporous material with a pore size smaller than 1 nm, a sol comprising of nanometer-sized particles is required. Generally, precursor modifying ligands that find use in sol-gel processing, such as acetylacetone, carboxylic acids, alcohol amines, and the like, can be used to provide such as a sol. In the present invention, a polymeric sol-gel dip-coating procedure with an alcohol amine as precursor modifier is proposed as a suitable preparation route for a pervaporation membrane layer.

It has been found that the preparation of ZrO_2 and TiO_2 membranes for pervaporation or gas separation, starting from precursor modified polymeric sols, fails, not because these sols do not contain the required nanometer-sized particles, but rather due to the poor quality of the coated membrane layer. This failure may be due to the unfavorable layer formation and the strong tendency for cracking in the sol-gel dip-coating procedure. Binders or

other large molecular weight organic additives can not be added, because these compounds create too large voids in the coated layer after the firing process. The novel membrane of the invention can be made, because of an improvement in the coating, drying and firing processes is obtained by
5 incorporating an alcohol amine in the sol. Clearly, the precursor modifying additive can also impart the ideal coating properties to the sol and prevent the formation of cracks during the critical drying process.

A suitable polymeric sol preparation route for the membrane of the invention is as follows. A polymeric sol containing nanometer-sized zirconia,
10 titania or mixed zirconia-titania polymeric structures is prepared starting from a Zr and/or Ti metal-organic precursor. The precursor is a metal-alkoxide, $M(\text{OC}_n\text{H}_{2n+1})_4$, or an alkylated metal-alkoxide, $\text{MR}_x(\text{OC}_n\text{H}_{2n+1})_{4-x}$, wherein $M = \text{Zr}$ or Ti , R is an organic ligand, $n = 1$ to 8 and $x = 1$ to 2 . The most preferred are commercially available simple metal-alkoxides with $n = 2$ to 4 . The metal-
15 organic precursor can be dissolved in any suitable organic solvent, including aliphatic and aromatic hydrocarbons, alcohols, organic acids, ketones and in mixtures of such solvents. Preferably, the solvent is a lower alcohol, $\text{C}_n\text{H}_n\text{W}\text{iOH}$, with $n = 1$ to 8 and the most preferred are those with $n = 2$ to 4 .

The alcohol amine is added to the precursor solution, prior to the
20 hydrolysis reaction, with the molar ratio of alcohol amine to precursor in the range 0.2 to 3.0 . The most appropriate sols for dip-coating are obtained by reacting the precursor with 1 to 15 moles of H_2O in the presence of diethanol amine as a modifier and with or without the presence of a mineral acid, such as HNO_3 . Alternatively, also other alcohol amines, such as monoethanol
25 amine and triethanol amine can be used. It would also be possible to use mono-, di- and tri-alcohol amines comprising a longer alkyl chain.

The size of the polymeric structures consisting of zirconia and/or titania in the sols, prepared in this manner, is in the range 3 to 15 nm and will usually not exceed 10 nm.

30 An especially preferred preparation method, which provides reproducible formation of smooth and crack-free membrane layers, involves first preparing a sol from a Zr- and/or Ti-alkoxide precursor, alcohol as a

solvent, diethanol amine and 5 - 10 mole of H_2O . The water may be acidified or not acidified at all. The sol is then coated on the surface of a mesoporous carrier. The layer can be dried in ambient air and converted into a stable microporous membrane layer consisting of ZrO_2 and/or TiO_2 by a conventional firing treatment. A firing temperature of $400^{\circ}C$ or higher is preferred, to give a toplayer with a sufficient thermal stability. It has also become apparent that such a firing treatment provides a chemically stable microporous layer, which can be properly used in a pH range from 1 to 13. Alternatively, the coated layer may also be dried at higher temperatures and/or with forced air circulation over the surface.

In an alternative membrane preparation procedure, which is even more preferred, a doping material is incorporated in the coated layer to retard grain growth during firing at the desired temperatures. A similar polymeric sol-gel dip-coating method can be used to prepare such a coating. In this method as a doping material an yttrium compound, is introduced into the sol. A preferred procedure involves the preparation of a doped polymeric sol starting from a mixture of a Zr- and/or Ti-alkoxide and an Y-alkoxide, $Y(OC_nH_{2n+1})_3$, dissolved in a lower alcohol. Alternatively, it would also be possible to add the Y-alkoxide as a doping material to the above described polymeric sol prior to the dip-coating procedure. It is also possible to add an yttrium salt as a doping material.

Examples

Example 1

Separation of isopropanol and water with an Y-doped ZrO_2 membrane

A polymeric ZrO_2 sol was prepared in a glove box with He-atmosphere starting from $Zr(OC_3H_7)_4$, $Y(OC_3H_7)_3$ and diethanol amine (DEA), with the yttrium compound as the dopant and DEA as the precursor modifier. The modified precursor was hydrolysed by adding 7.14 mole of H_2O at ambient

temperature. The H₂O was acidified by adding HNO₃ until a 1 M HNO₃ solution was obtained, prior to the hydrolysis reaction. In the sol preparation, the molar ratio of the components Zr(OC₃H₇)₄, Y(OC₃H₇)₃, DEA, H₂O and n-C₃H₇OH was 1.00:0.058:1.78:7.14:0.09, respectively. The particle size of the resultant sol measured ca. 5 nm in dynamic laser beam scattering, with a very narrow size distribution, and the sol was found to be stable for several months. The dip-coating procedure was carried out in a class 100 clean-room under a constantly flowing air-stream.

First, the sol was diluted by adding a volume of n-C₃H₇OH, equal to half the volume of the sol. Then, the diluted sol was contacted with a mesoporous Y-Al₂O₃ membrane with an average pore size in the range 3 - 5 nm during 15 s. State of the art mesoporous membranes, prepared by colloidal sol-gel dip-coating procedures on porous γ -Al₂O₃ support disks with a diameter of 39 mm and a thickness of 2 mm, were used as used as a carrier for the coating. The coating was allowed to dry for a few minutes and the coated carrier was subsequently placed in an oven and fired at 500°C in air for 2 hours. The temperature was increased by 0.5°C/min to 500°C and decreased by 0.5°C/min to room temperature. If necessary, the quality of the resultant ZrO₂ membrane layer was improved by repeating the sol-gel dip-coating and firing procedure.

The prepared membranes were tested for their quality in a pervaporation test with a water/isopropanol mixture. In a representative test, a feed stream containing 95 % of isopropanol and 5% of water could be converted into a permeate stream containing 5 % of isopropanol and 95 % of water by using the prepared membranes at an operation temperature of 70°C.

Example 2

Separation of isopropanol and water with an Y-doped TiO₂ membrane

30

A polymeric TiO₂ sol was prepared in a similar manner as described in Example 1 starting from Ti(OC₃H₇)₄, Y(OC₃H₇)₃, diethanol amine (DEA) and 1

M HNO₃, with the yttrium compound as the dopant and DEA as the precursor modifier. In the sol preparation, the molar ratio of the components Ti(OCaHy)₄, Y(OC₃H₇)₃, DEA, H₂O and n-C₃H₇OH was 1:0.04:1.4:5:85, respectively. The properties of the resultant TiO₂ sol were similar to those described for the ZrO₂ sol in Example 1. Then, a similar dip-coating procedure could be used, with a mesoporous γ-Al₂O₃ membrane with an average pore size in the range 3 - 5 nm as a carrier, followed by a similar drying and firing procedure. In a representative test, the properties of this type of membrane were also found similar to the properties of the ZrO₂ membrane: a feed stream containing 95 % of isopropanol and 5% of water could be converted into a permeate stream containing 5 % of isopropanol and 95 % of water by using the prepared membranes at an operation temperature of 70⁰C.

15 Example 3

Preparation of Y-doped membranes with an yttrium salt

Another possible preparation method of the Y-doped membranes consisting of ZrO₂ or TiO₂ starts with the synthesis of a polymeric zirconia or titania sol in its undoped form. In the sol preparation, Y(NO₃)₃.6H₂O was added to the resultant polymeric sol as the yttrium compound and the molar ratio of Y(NO₃)₃.6H₂O and precursor was the same as for Y(OC₃H₇)₃ and precursor. A similar membrane as described in Example 1 and 2 was obtained according to the same dip-coating, drying and firing procedure, with a mesoporous γ-Al₂O₃ membrane with an average pore size in the range 3 - 5 nm as a carrier.

30 Example 4

Preparation of membranes without doping material.

Polymeric sols were prepared in their undoped form starting from $Zr(OC_3H_7)_4$, $Ti(OC_3H_7)_4$ and a mixture of $Zr(OC_3H_7)_4$ and $Ti(OC_3H_7)_4$ in a similar way as described in Examples 1 and 2. An undoped form of the
5 membrane containing ZrO_2 , TiO_2 or a mixture of these compounds could be obtained according to the same dip-coating, drying and firing procedure, by using one of the resultant sols and a mesoporous $\gamma-Al_2O_3$ membrane with an average pore size in the range 3 - 5 nm as a carrier.

10

Example 5

Preparation of a membrane for application in strong acid and alkaline feed mixtures

15

A second type of membrane configuration that is more preferred for application in a mixture comprising an aggressive aqueous component is achievable by depositing the membranes described in Example 1 - 4 on a ZrO_2 or TiO_2 membrane as a carrier. Membranes having a microporous ZrO_2
20 and TiO_2 toplayer, deposited on mesoporous ZrO_2 and TiO_2 membranes with an average pore size of 3 - 4 nm, respectively, were successfully tested in long-term nanofiltration tests with corrosive aqueous HNO_3 and $NaOH$ feed solutions having a pH in the range 1 - 13. In these tests the corrosive feed solutions were permeated under a pressure of 5 - 7 bar through the
25 membranes. Starting from a ZrO_2 or TiO_2 membrane as a carrier, a similar dip-coating, drying and firing procedure could be used as described in the previous Examples, resulting in a membrane with a potential for application in acid and alkaline feed mixtures.

30

CLAIMS

5

1. Method for preparing a ceramic microporous membrane made of ZrO_2 and/or TiO_2 on a support membrane, comprising the steps of:

- iv) forming a polymeric solution comprising polymeric ZrO_2 particles, TiO_2 particles and mixtures thereof, an alcohol amine and a solvent;
- 10 v) applying the polymeric solution on the support membrane; and
- vi) drying and firing the support membrane applied with the polymeric solution, thereby forming the microporous
- 15 membrane on the support membrane.

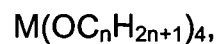
2. Method as claimed in claim 1, wherein the alcohol amine is a mono-, di-, and/or trialcoholamine having a C_1 - C_5 alkyl chain, preferably a C_2 - C_3 alkyl chain.

3. Method as claimed in claim 2, wherein the alcohol amine is

20 monoethanol amine, diethanol amine and/or triethanol amine, preferably diethanol amine.

4. Method as claimed in claim 1-3, wherein the polymeric ZrO_2 particles and/or TiO_2 particles are formed by polymeric sol preparation from a precursor solution comprising as a precursor a metal alkoxide of formula (1)

25



and/or alkylated metal alkoxide of formula (2)



wherein:

M= Zr and/or Ti

n= 1 to 5

R= d-C β -alkyl

x= 1 or 2

5 5. Method as claimed in claim 4, wherein

n = 2-4

6. Method as claimed in claim 4 or 5 wherein

n = 2 or 4

R = C₂ or C₃

10 x= 1

7. Method as claimed in claim 4-6, wherein the precursor solution is subjected to a hydrolysis reaction, preferably an acidic hydrolysis reaction.

8. Method as claimed in claim 7, wherein the molar ratio of metal alkoxide of formula (1) and/or alkylated metal alkoxide of formula (2) to water
15 is 1 to 15, preferably 5 to 10.

9. Method as claimed in claim 1-8 comprising a precursor modifying ligand.

10. Method as claimed in claim 4-9, wherein the alcohol amine is added to the polymeric solution.

20 11. Method as claimed in claim 1-9, wherein the alcohol amine is added to the precursor solution.

12. Method as claimed in claim 1-11, wherein the molar ratio of the alcohol amine to the metal alkoxide of formula (1) and/or alkylated metal alkoxide of formula (2) is 0.2 to 3.0, preferably ...

25 13. Method as claimed in claim 1-12, wherein the polymeric solution comprises an Yttrium compound as a pore growth restricting agent.

14. Method as claimed in claim 13, wherein the Yttrium compound is added to the precursor solution as an Yttrium alkoxide of formula (3)

30 Y(OC_nH_{2n+1})₃,

wherein n = 1 to 8, preferably 2-4.

15. Method as claimed in claim 1-14, wherein the dried microporous membrane is fired at a temperature of 350 - 750 °C, preferably of 400 - 600°C.

16. Method as claimed in claim 1-15, wherein the polymeric solution is
5 applied by gel dip coating.

17. Method as claimed in claim 1-16, wherein the support membrane is a mesoporous membrane comprising γ -AL-2O₃, TiO₂ and/or ZrO₂.

18. Ceramic microporous membrane obtainable by the method of claim
1-17.

10 19. Ceramic membrane comprising a microporous membrane of claim 18 on a support membrane.

20. Use of a ceramic microporous membrane of claim 18 or a ceramic membrane of claim 19 in liquid separation processes.

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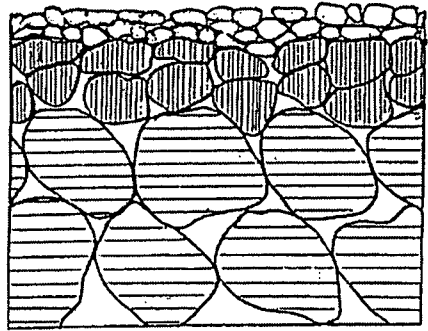


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/010594

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D71/02 B01D67/00

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)
BOID

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

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

EPO-Internal , WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	DE 102 08 276 A1 (CREAVIS GESELLSCHAFT FUER TECHNOLOGIE UND INNOVATION MBH) 4 September 2003 (2003-09-04) abstract example 2c	1-20
A	----- JIAGUO YU, XIUJIAN ZHAO, QINGNAN ZHAO, GAO WANG: "Preparation and characterization of super-hydrophilic porous TiO2 coating films" MATERIALS CHEMISTRY AND PHYSICS, vol. 68, 15 February 2001 (2001-02-15), pages 253-259, XP002380061 abstract page 253, column 2, line 16 - page 254, column 1, line 21 ----- -/-	1-12, 15-20

Further documents are listed in the continuation of Box C

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
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Date of the actual completion of the international search

6 February 2007

Date of mailing of the international search report

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Lançon, Eveline

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/010594

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHANGRONG X ET AL: "Sol-gel synthesis of yttria stabilized zirconia membranes through controlled hydrolysis of zirconium alkoxide"</p> <p>JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 162, no. 1-2, 1 September 1999 (1999-09-01), pages 181-188, XP004178895 ISSN: 0376-7388 the whole document</p> <p style="text-align: center;">-----</p>	1-20
A	<p>WO 97/10045 A (INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DL; CUPERUS, FOLKERT,) 20 March 1997 (1997-03-20) abstract page 3, line 3 page 4, lines 18,19 page 5, lines 30,31 page 6, line 5 - page 7, line 32</p> <p style="text-align: center;">-----</p>	1-20
A	<p>OKUBO T ET AL: "Crack-free porous YSZ membrane via controlled synthesis of zirconia sol"</p> <p>JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL. COMPANY. AMSTERDAM, NL, vol. 118, no. 2, 18 September 1996 (1996-09-18), pages 151-157, XP004041796 ISSN: 0376-7388 the whole document</p> <p style="text-align: center;">-----</p>	1-20
A	<p>KIM J ET AL: "Sol-gel synthesis and characterization of yttria stabilized zirconia membranes"</p> <p>JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL. COMPANY. AMSTERDAM, NL, vol. 139, no. 1, 4 February 1998 (1998-02-04), pages 75-83, XP004113691 ISSN: 0376-7388 the whole document</p> <p style="text-align: center;">-----</p>	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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