

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



11 Publication number: **0 515 936 A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: **92108302.8**

51 Int. Cl.<sup>5</sup>: **B01D 71/02**, B01D 71/04,  
//B01D69/02

22 Date of filing: **16.05.92**

30 Priority: **27.05.91 DE 4117284**

71 Applicant: **Studiengesellschaft Kohle mbH**  
**Kaiser-Wilhelm-Platz 1**  
**W-4330 Mülheim/Ruhr(DE)**

43 Date of publication of application:  
**02.12.92 Bulletin 92/49**

72 Inventor: **Maier, Wilhelm F.**  
**Steingatt 20**  
**W-4300 Essen 17(DE)**

84 Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI LU NL SE**

74 Representative: **von Kreisler, Alek,**  
**Dipl.-Chem. et al**  
**Patentanwälte Von Kreisler-Selting-Werner,**  
**Deichmannhaus am Hauptbahnhof**  
**W-5000 Köln 1(DE)**

54 **Procedure for the preparation of microporous ceramic membranes for the separation of gas and liquid mixtures.**

57 Gas and liquid separation with membranes has either been achieved by organic polymer membranes, which are limited by low temperature stability and a separation mechanism through adsorption or solubility in the membrane matrix, or by inorganic membranes, whose gas and liquid separation efficiency is limited by Knudsen diffusion. The membranes of this invention show a temperature stability up to 500 °C and a gas separation with separation factors better than the Knudsen limit.

Continuous microporous inorganic membranes of any desirable thickness can be prepared by e-beam evaporation of metal oxides on a support membrane, which has substantially larger pores than the metal oxide membrane. It is advantageous when the support membrane consists of the same material as the microporous membrane. The membranes are of porous structure with a narrow pore size distribution of pores, where the majority of the pores have diameters smaller than 1 nm.

The membranes can be used in all areas of gas and liquid separation, where the selective separation of smaller molecules from mixtures is desired (f.e. gas concentration by removal of water from natural gas, hydrogen from synthesis gas). The membranes can also be used for the concentration of aqueous solutions (fruit juices with retention of aroma compounds, vitamins and other compounds important for the flavor and nutritional value of the juice; biological liquids like lymph, blood, or others with retention of valuable compounds including small peptides, hormones, antibiotics and others) and for the concentration of organic solutions with retention of molecules larger than the solvent including oligomers and polymers. The membranes can also be used for the concentration of waste water with retention of organic contaminants like phenol resins and coal oil at coking plants. If the membranes have been made catalytically active, the membranes can also be used for the selective and poison resistant conduction of heterogeneously catalyzed three phase reactions by having the reaction gas diffusing through the catalytically active membrane to react at the other side of the membrane with the liquid, consisting of molecules too large to penetrate the pores.

EP 0 515 936 A1

This invention is concerned with the preparation and the use of continuous microporous inorganic membranes of controlled pore size by electron beam evaporation. Such membranes are of great practical interest for the transport of gas and water because of the potential application to many separation problems in the liquid and the gas phase, where separation by molecular size differences is desirable or required.

5 In numerous processes individual gases have to be separated from mixtures like water in natural gas, hydrogen from carbon monoxide, hydrogen from methane or oxygen from nitrogen. This is usually achieved by distillation or by cryogenic procedures, both of which require a lot of energy. Concentration of solutions through the removal of small molecules like water from fruit juice or from biological fluids like milk or blood with retention of larger molecules like oligo- and polysaccharides, proteins, aroma compounds, vitamins  
10 and others are as much of general importance as are the removal of solvent from process solutions or the preparation of ultrapure water by pervaporation through inorganic membranes (Suzumura, Yanaka, JP 63134093 A 2, June 1988).

The membranes used for gas separation are commonly polymer membranes, which do not separate by pore size but by the different solubility of the gases in the polymer matrix. So is the separation of nitrogen  
15 from natural gas improved upon by the use of polymer membranes (M.S.A. Baksh, A. Kapoor, R.T. Yang, Sep. Sci. Technol. 25 (1990) 845). A problem of polymer membranes is their inselectivity for the separation of in-polar small gases like hydrogen from argon or methane from other hydrocarbons. Another disadvantage of polymer membranes is their low thermal resistance, which usually forbids the separation at temperatures above 150 °C. Alternative membranes are being prepared by SOL-GEL procedures, but the separation  
20 factors are commonly below the Knudsen limit (square root of the molar weight ratio of the gases (Klein, Gizpec Ceram. Bull. 69 (1990) 1821; Suzuki, Ononato, Kurokawa, J. Noncryst. Solids 94 (1987), 160). This indicates that the pores are still too large (>1nm) to observe a sieving effect. Smaller pores are approached by the preparation of zeolite membranes (Bein, Brown, Enzel, Brinker, Mter. Res. Soc. Symp. Proc 121 (1988), 761; Oayama, Masatsugu, JP 63291809-A 2, 1988); technical application of zeolite membranes is  
25 obstructed by the apparently unavoidable formation of pin-holes. Another method for the preparation of ceramic membranes is CVD (chemical vapor deposition) (Mori, Fujita, JP 61238303 A 2, Oct. 86; Lin, Fransen, DeVries, Burggraf, Proc. Electrochem. Soc. 90-12 (1990) 539), which produces pore size distributions of 1 - 50 nm, but due to the high production costs and low separation effectivity CVD is not competitive to other methods. Sintered ceramic membranes made of a wide range of metal oxides (U.S.  
30 4,946,592) provide rather large pores (20 - 20,000 nm). In another procedure for the preparation of inorganic membranes with the aid of polymers, that are burned off after preparation (U.S. 4,980,062) give membranes with pore diameters of 100 to 500 nm, incorrectly claimed as microporous.  $\alpha$ -alumina ceramic membranes with effective pore sizes of about 50 nm can be made from boehmite sols seeded with varying  $\alpha$ -alumina particles (U.S. 4,968,426). Multilayered ceramic films with pore sizes in the upper mesopore range (10 - 20  
35 nm) have been prepared from metal oxide particles (EP 0 426 546 A 2) without giving examples of separations. A SOL-GEL procedure for the preparation of metal oxide ceramics (EP 0 425 252 A 1) gives membranes with mean pore diameters, not exceeding 4 nm. Hydrogen selective inorganic membranes of unknown separation mechanism have been prepared by closing the pores of the support membrane by CVD (Tsapatsis, Kim, Nam, Gavalas, Ind. Eng. Chem. Res. 30 (1991), 2151).

40 Membranes composed of a separation membrane on a support membrane are reported in EP 0 195 549 B 1. Herein the preparation of separation membranes of a thickness of 1 nm to 100  $\mu$ m and uniform pore sizes of 5 nm and larger are described. The average pore size is claimed to be 0.5 to 20 nm, however, there is no upper pore size limit. The separation factors achieved with these membranes do not reach the Knudsen limit, which means that the medium free path length of the molecules is still smaller than the  
45 larger pores in the membranes prepared. The flow of permeate through a membrane is dominated by the largest pores. The separation efficiency of a membrane is therefore not dependent on the smallest, but on the largest pores available. To utilize a potential molecular sieving effect and/or surface diffusion for separation and membrane catalysis, it is crucial to limit the upper pore size of the material. We have found that pores larger than 1.2 nm cannot be tolerated. There are many artificial and synthetic materials with micropores (pores smaller 1 nm), which can essentially not be used, because a major portion of their pore  
50 volume is due to pores larger than 1.2 nm (mesopores). The only well-known materials without mesopores are the crystalline zeolites. The preparation of non-crystalline materials with very small pore sizes is described in U.S. 5,006,248. However, although the lower pore size is described as 0.5 nm, the upper limit of 4 nm make these materials essentially mesoporous. In the membranes according to the instant invention,  
55 however, more than 90 % of all pores have an effective pore diameter of less than 1.2 nm and a separation factor as good or better than the Knudsen limit supporting our claims.

Materials and membranes with micropores of pore diameters between 0.3 and 1 nm have been known for a long time. Most clays and many ceramic materials prepared by the SOL-GEL-method have such

pores. However, the porosity of such materials has always been dominated by the larger mesopores, which are responsible for their separation characteristics. Good separation properties depend on the larger pore size limits.

No methods have been known to produce continuous inorganic membranes with confirmed pore diameters of less than 1.2 nm. We have found, however, that continuous inorganic membranes with pore diameters below 1 nm can be prepared by e-beam evaporation of inorganic oxides. (With continuous we mean a homogeneous uniform material even at the nm-scale.) According to this invention continuous microporous materials can be prepared by e-beam evaporation in a vacuum chamber by heating the starting material with an e-beam of at least 2 kW until it evaporates and condenses on a suitable support material. In this procedure the porosity of the material produced is not sensitive to the method of evaporation. Thin continuous films of any thickness with a better than nm precision can be prepared by this condensation method. Layer thickness can be controlled by a film thickness monitor. The pore size distribution of the membrane is determined by the nitrogen adsorption isotherm with many data points in the pressure range below 10 torr. The data treatment can be done with the t-plot method or by the method of Horvath and Kawazoe. Figure 1 shows the size distribution of such a membrane determined by the nitrogen adsorption isotherm in an equipment with high sensitivity in the pressure range below 10 torr. The data were treated by the method of Dubinin (Dubinin Co. Interface Sci. 23 (1967) 478) and the t-plot-method (Mikhail, Brunauer, Bodor J. Coll. Int. Sci. 26 (1968) 45). Aerosil 200 was used as an unporous reference material.

Membranes suitable for gas separation can be prepared by condensation of the membrane on a mesoporous support membrane with symmetrical or asymmetrical pores of pore diameters larger than 5 nm, but smaller than 2  $\mu$ m. Such support membranes, made of alumina or silica, are available commercially. Only flat membranes or capillary membranes qualify. The microporous membrane for the separation has to be deposited on the outside of the capillary and on the side of the bottle neck pores on asymmetrical flat membranes. Mesoporous capillary membranes have to be rotated stepwise or continuously during the condensation to achieve a homogeneous layer formation on the outer surface.

Such membranes can be used in commercial filtration units or capillary reactors for liquid or gas separation at temperatures up to 500 °C. The separation efficiency increases with increasing pressure difference between permeate and feed. Best separation results are achieved by excess pressure on the feed and reduced pressure on the permeate side.

Suitable materials for the membranes are metal oxides of high thermal and chemical resistance like silica, alumina, titania, zirconia and cer oxide.

The membranes can principally be used for the following applications:

Separation of ethane/ethene, propane/propene, methane/nitrogen, methane/water, oil/asphalt, ammonia/hydrogen/nitrogen, hydrogen/carbon monoxide. The membranes can be used to separate the water from fruit juices without loss of larger molecules like aroma compounds, fruit acids, vitamins and other important juice components. Similarly biological fluids can be concentrated by the removal of water while biologically important compounds like small peptides, hormones and others will be retained. The membranes can also be used for the preparation of ultrapure water. The removal of water from waste water, like the retention of the coal oil from the waste water from a coking plant should be possible with such a membrane. The membranes can also be used for the separation of solvents with retention of dissolved compounds like oligomers, polymers, unknown hazardous compounds or side products. If the membranes contain catalytically active centers like catalytically active metals, the membranes can be used for three phase reactions, where the reactant gas (hydrogen, oxygen, carbon monoxide or halogen) pass the membrane and react with the reactant liquid on the other side of the membrane.

#### EXAMPLE 1:

A mesoporous BIORAN-glass capillary from the SCHOTT company (pore diameter 10 nm) was coated with silica at  $10^{-5}$  to  $10^{-4}$  torr e-beam evaporation of quartz in an evaporation chamber. The capillary was turned continuously 40 times/min during the deposition to assure a uniform deposition of the silica on the outer side of the capillary. The deposition at a rate of about 10 nm/min was controlled by a film thickness monitor and terminated at a layer thickness of 500 nm, which corresponds to a layer thickness of 160 nm on the capillary. The capillary was mounted in the apparatus shown in Figure 2 and sealed by a silicon polymer. The gas permeation of several gases was determined at various pressures. The results, shown in the following table, demonstrate that at these conditions only the gas isobutane is strongly hindered in its diffusion, while all other gases can be characterized by Knudsen diffusion. This indicates a molecular sieving diameters of the size of molecules.

Table: Separation factors relative to hydrogen determined by gas separation through a glass capillary covered by a microporous silica membrane at various pressures. The permeation factors are given as the ratio of the space velocities  $V_{H_2}/V_{gas}$ .

Gas	0.5 bar	1 bar	2 bar	theor. Value*
CO	3.2	3.3	3.6	3.7
N <sub>2</sub>	3.0	3.1	3.3	3.7
i-butane	10.7	178.0	339.0	5.4
Ar	3.6	3.8	4.4	4.4
CH <sub>4</sub>	2.2	2.3	2.5	2.8
He	1.8	1.6	1.6	1.4

\* $(M_1/M_2)^{0.5}$

#### EXAMPLE 2:

A mesoporous BIORAN-glass capillary (pore diameter 10 nm) was coated with a silica membrane as in Example 1. The capillary was mounted in an apparatus shown in Figure 3, sealed by silicon. The separation of the membrane with several gas mixtures was determined at various pressure gradients with an on-line quadrupole. The composition was obtained through the calibrated ion pressure. All mixtures show separation factors better than Knudsen supporting the high separation efficiency of the small pores of these membranes (see Table).

P 2(Torr)	dp(Torr)	H <sub>2</sub> /Ar	H <sub>2</sub> /CO	H <sub>2</sub> /i-Bu	H <sub>2</sub> /N <sub>2</sub>
760	310	2.8	3.9	1.1	3.5
50	930	6.4	15.3	1.3	3
10	980	10.9	-	7.1	7
1	1010	28.2	29.6	8.5	-

#### EXAMPLE 3:

A flat alumina membrane (diameter 48 mm, pore size 20 nm) from the company ANOTEC was coated with a silica membrane through e-beam evaporation of quartz in an evaporation chamber as described in Example 1. The evaporation at a rate of 15 nm/min was terminated at a layer thickness of 520 nm. The membrane on the alumina support was mounted in an apparatus as shown in Figure 4. The gas permeation of helium and of hydrogen showed a separation factor of 1.7 - 1.9 at 0.2 bar excess pressure and 1.6 - 1.7 at 0.5 bar excess pressure, which is significantly better than the Knudsen limit of 1.4.

#### EXAMPLE 4:

A Vycor glass membrane from Corning (diameter 47 mm, thickness 2 mm) was coated with a silica membrane, thickness 1000 nm, by e-beam evaporation of quartz as described in Example 1. This membrane was mounted in a stainless steel filtration unit (Sartorius) and apple juice with pH of 5.4 was filtered through this membrane at a hydrostatic pressure of 1 m. The permeate was clear colorless water of neutral pH and taste.

#### Claims

## EP 0 515 936 A1

1. A supported continuous inorganic membrane, where at least 90% of the pores have an effective pore diameter of 1.2 nm or less, consisting of metal oxides, metal carbides or metal nitrides of high thermal stability and chemical resistance or mixtures thereof.
- 5 2. The membrane of claim 1 with a pore diameter between 0.3 and 0.8 nm.
3. The membrane of claims 1 and 2 with a porosity between 5 and 70 %.
- 10 4. The membrane of claims 1 - 3, where the support consists of porous glass, glass ceramic, silica or alumina with pore diameters larger than 3 nm and smaller than 3000 nm.
5. The membrane of claims 1 to 4, consisting of more than 70%, preferably at least 80 % of silicon oxide (silica), titanium oxide (titania), aluminium oxide (alumina), zirconium oxide (zirconia), ceric oxide, spinel, mullite, silicon carbide, silicon nitride, titanium carbide, titanium nitride, zirconium carbide, zirconium nitride, boron carbide, boron nitride or mixtures thereof.
- 15 6. The membrane of claims 1 - 5 with a membrane thickness of 10 - 10,000 nm.
- 20 7. The membrane of claims 1 - 5 with a membrane thickness of 50 - 200 nm.
8. Process for the preparation of the membrane of claims 1 - 7, where the membrane is prepared by simultaneous evaporation of the membrane materials by an e-beam in a vacuum (pressure smaller 10 torr) or by thermal evaporation onto the porous support material, which has a temperature of at least -20 °C and not more than 400 °C.
- 25 9. Process of claim 8 producing a Sol-Gel, the membrane material after calcination is free of mesopores (pores larger than 1.2 nm).
- 30 10. Process of claim 8, whereby the temperature for the use of the membrane of claims 1 - 7 does not exceed 500 °C.
11. The use of the membrane of claims 1 - 7 for gas separation with separation factors, that are larger than the Knudsen limit  $(M_1/M_2)^{-2}$ .
- 35 12. The use of the membrane of claims 1 - 7 for the concentration of solutions.
13. The use of the membrane of claims 1 - 7 for the selective separation of solvents and water from solutions of organic compounds and polymers, biological materials and inorganic compounds with molecular diameters smaller or equal the pore diameter of the membrane.
- 40 14. The use of the membranes of claims 1 - 7 for the concentration of fruit juices.
15. The use of the membranes of claims 1 - 7 for the purification of water by selectively separating water from contaminants.
- 45

50

55

Figure 1

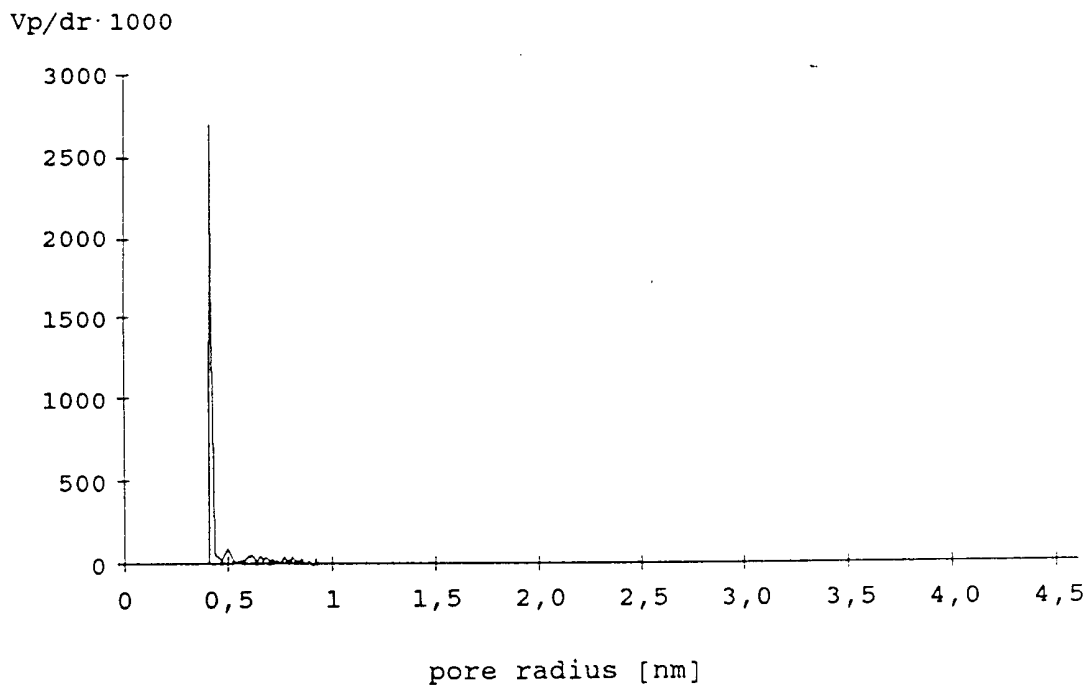


Figure 2: Reactor for gas permeation through microporous capillaries

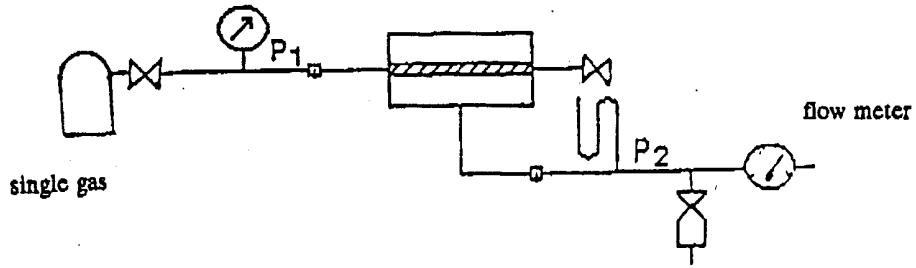


Figure 3: Reactor for gas separation of gas mixtures on microporous capillaries

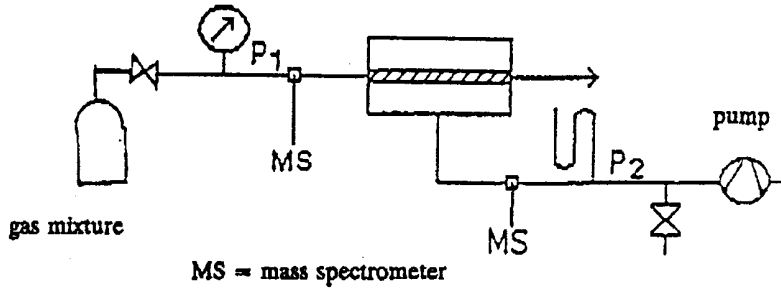
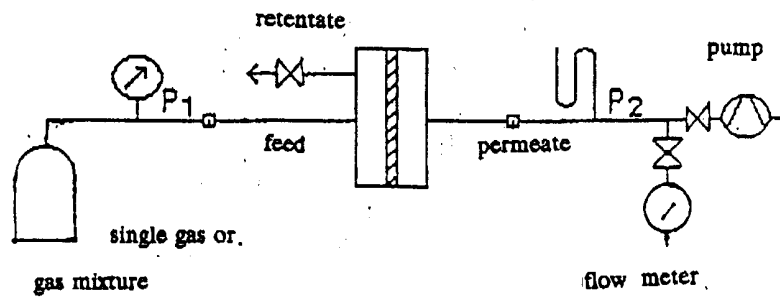


Figure 4: Reactor for gas permeation on microporous membranes





European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 8302

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A, D	EP-A-0 195 549 (NGK INSULATORS, LTD.) ---		B01D71/02
A	EP-A-0 428 052 (AIR PRODUCTS AND CHEMICALS, INC.) )		B01D71/04 //B01D69/02
A	EP-A-0 397 216 (ALCAN INTERNATIONAL LTD.) ---		
A	EP-A-0 097 770 (KABUSHIKI KAISHA TOSHIBA) ---		
A	US-A-3 692 087 (R. E. EBERTS) -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01D
Place of search	Date of completion of the search	Examiner	
THE HAGUE	06 AUGUST 1992	DEVISME F. R.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03.82 (P0401)