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(54) **Title:** THIN FILM COMPOSITE MEMBRANES FOR SEPARATION OF ALKENES FROM ALKANES

(57) **Abstract:** Composite membranes comprised of at least two layers, one of the layers being a silver ionomer and a second layer which is a fluorinated polymer with certain permeability properties, are especially useful for the separation of alkanes from alkenes, Particularly useful is a three-layer composite membrane in which a porous layer is laminated to the second layer.

THIN FILM COMPOSITE MEMBRANES FOR SEPARATION OF ALKANES AND
ALKENES

Field of the Invention

Thin film composite membranes which have one or more layers of a certain type

5   of silver ionomer, and which can separate alkanes from alkenes, are described.

Government Rights

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Technical Background

10   Membranes containing layers of silver ionomers of certain sulfonic acid
containing polymers, especially fluorinated polymers, have been used to separate
alkanes from alkenes. The separation of these types of compounds, especially those
having the same number of carbon atoms, such as ethylene from ethane, propylene
from propane, and pentene from pentane are often difficult by other methods, because

15   for instance the boiling points of the alkane and alkene are similar, resulting in high
energy requirements. This is especially true for lower boiling materials containing 2 to
four carbon atoms, which would require cryogenic distillation, usually very energy
intensive.

In membrane separation processes, thin film composite membranes are often

20   used. Thin-film composite membranes (TFCs) usually consist of layers of dissimilar
materials joined together to form a single membrane. This layered construction permits
use of material combinations that optimize the performance and durability of the
membrane. The same is true of alkane-alkene separation processes using silver
ionomers, described herein are new TFCs for such separations.

25   As a minimum requirement one might believe that a membrane having a single
layer, a "separation layer" (SL), of silver ionomer would be useful. However, such a type
of membrane has two important drawbacks, the silver ionomer is expensive, and in
thicker membranes which are required for the membrane to have sufficient strength, the
permeance to the alkene, the amount of alkene which can pass through the membrane

30   per unit time is relatively low. Therefore one (or more) thin separation layers are
required for practical membranes. A composite membrane with another layer of material
which physically supports the entire TFC, and which is laminarly contacting the
separation layer can be added. This other layer is nonporous and the material passing

through the TFC (in this case one or more alkenes), should also preferably diffuse through this other layer rapidly. Herein this other layer is called the high diffusion rate layer (HDR).

The use of various composite membranes with silver ionomer separation layers for the separation of alkanes from alkenes is known, see for instance A. van Zyl, *et al.*, *Journal of Membrane Science*, 133, (1997), pp. 15-26, O.I. Eriksen, *et al.*, *Journal of Membrane Science*, 85 (1993), pp. 89-97, and A.J. van Zyl, *Journal of Membrane Science*, 137 (1997), pp. 175-185, and U.S. Patent 5,191,151. However none of these references describe a TFC in which a separation layer of a silver ionomer is used in combination an HDR layer described herein.

Certain layers in TFCs, layers, sometimes termed "gutter layers" are used, and are generally described in M. Kattula, *et al.*, *Designing ultrathin film composite membranes: the impact of a gutter layer, Scientific Reports*, 5, Article Number 15016 (2015). There is no specific information concerning alkane-alkene separations using silver ionomers.

Summary of the Invention

This invention concerns, a thin film composite membrane for the separation of alkanes from alkenes, comprising:

(a) a separation layer comprising a silver ionomer of a polymeric sulfonic acid; and

(b) a high diffusion rate layer of a fluorinated polymer having a permeance to nitrogen of at least about 250 GPU wherein said separation layer and said high diffusion rate layer are laminated to each other.

Details of the Invention

Herein certain terms are used and some of them are defined below.

What is meant by a fluorinated polymer or ionomer is of the total of the carbon-hydrogen groups and the carbon fluorine groups in the ionomer, about 20% or more are carbon-fluorine groups, preferably about 50% or more, very preferably about 70% or more, especially preferably about 90% or more, and very especially preferably about 95% or more are carbon fluorine groups, or most preferably are perfluoropolymers. By a carbon-hydrogen group is meant a hydrogen atom bound directly to a carbon atom, while a carbon-fluorine group is a fluorine atom bound directly to a carbon atom. Thus -CF_2- groups contains 2 carbon fluorine groups, while a -CH_3 group contains 3

carbon-hydrogen groups. Thus in a homopolymer of vinylidene fluoride, in which the repeat groups are $-CH_2CF_2-$the carbon-hydrogen groups and the carbon fluorine groups are each 50% of the total of carbon-hydrogen plus carbon-fluorine groups present. In a copolymer of 50 mole percent perfluoro(2,2-dimethyl-1,3-dioxole) and 50 mole percent

5   ethylene the carbon-hydrogen groups are 33.3% of the total of the carbon-fluorine plus carbon hydrogen groups present, and the carbon-fluorine groups are 66.7% of the carbon-fluorine and carbon-hydrogen groups present. The relative amount of carbon-fluorine and carbon hydrogen groups present can be determined by elemental analysis, NMR spectroscopy, for instance using ^{14}C NMR, or a combination of any of these.

10   By a "driving force" in the separation of the alkene and alkane in the gaseous state is generally meant that the partial pressure of alkene on the first ("feed") side of the membrane is higher than the partial pressure of alkene on the second ("product") side of the membrane. For instance this may be accomplished by several methods or a combination thereof. One is pressurizing first side to increase the partial pressure of

15   alkene on the first side, second is sweeping the second side by inert gas such as nitrogen to lower the partial pressure of the alkene on the second side, and third is reducing pressure of second side by vacuum pump to lower the partial pressure of the alkene on the second side. These and other known methods in the art of applying a driving force may be used.

20   This may be quantified for a separation of gases to some extent by a mathematical relationship:

$$Q_a \propto F_a(P1_a - P2_a)$$

wherein Q_a is the flow rate of component "a" through the membrane, F_a is the permeance of component a through the membrane, $P1_a$ is the partial pressure on the

25   first (feed) side, and $P2_a$ is the partial pressure on the second (product) side.

By "laminated" is meant the two layers concerned are in intimate contact with each other. This is often referred to as "bonded together" although usually no separate adhesive is employed.

Preferably the SL is about 0.1 μm to about 1.0 μm thick, more preferably about

30   0.2 μm to about 0.5 μm thick. As mentioned above the relative thinness of this layer help to improve the productivity of the overall separation process per unit area of membrane.

Polymers useful for the SL are silver ionomers of sulfonic acid containing polymers. Such ionomers are well known in the art, and in some instances known to

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separate alkanes from alkenes, see for instance US Patent Application 14/334,605, US

Provisional Applications 62/159,646, 62/159,668, and 62/262,169 (now PCT applications

_____, respectively), A. van Zyl, *et al.*, *Journal of Membrane*

Science, **133**, (1997), pp. 15-26, O.I. Eriksen, *et al.*, *Journal of Membrane Science*, **85**

(1993), pp. 89-97, and A>J. van Zyl, *Journal of Membrane Science*, **137** (1997), pp. 175-

185, and U.S. Patent 5,191,151, all of which are hereby included by reference. A

preferred grade of Teflon® AF is AF 2400, which is reported to contain 83 mole percent

PDD, and 17 mole percent tetrafluoroethylene. Polymers of PDD with other

comonomers, such as perfluoro(propylvinyl ether) and

$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, may also be employed. In copolymers of PDD

with these alternative monomers, it is preferred that the PDD content be at least 90 mole

percent.

The sulfonic acid containing polymers that form the silver ionomers in the SL,

and of course the ionomers themselves, are preferably fluorinated polymers, and more

preferably 50% or more, very preferably 70% or more, and truly preferably 90% or more

are carbon fluorine groups. Especially preferably this polymer is a perfluoropolymer, that

is all the monomer being polymerized to repeat unit contain no hydrogen. Such

perfluoropolymers may have very small amounts of "adventitious" carbon hydrogen

groups from impure monomers, or groups such as initiator fragments bonded to chains.

In the fluorinated polymers in the HDL, and preferably 50% or more, more

preferably 70% or more, and very preferably 90% or more are carbon fluorine groups.

Especially preferably this polymer is a perfluorinated polymer, that is all the monomer

being polymerized to repeat unit contain no hydrogen. Such perfluoropolymers may

have very small amounts of "adventitious" carbon hydrogen groups from impure

monomers, or groups such as initiator fragments bonded to chains.

Preferably the HDL layer is about 0.05 μm to about 0.5 μm thick, more preferably

about 0.05 μm to about 0.2 μm thick.

Particularly preferred polymers for the HDL are copolymers of

perfluoro(2,2-methyl-1,3-dioxoole), (PDD) particularly if included in a perfluoropolymer.

In any copolymer of the PDD it is preferred that at least about 50 mole percent of the

total repeat units are derived from PDD, more preferably at least 80 mole percent.

Generally speaking higher molar percentages of PDD are desired in all PDD

copolymers, consistent with being able to process the polymers into a layer in the

membrane.   A preferred copolymer is that of PDD with tetrafluoroethylene, available as

Teflon® AF (The Chemours Co., Wilmington, DE 19899, USA) and for further information about Teflon® AF, see P.R. Resnick, et al., *Teflon AF Amorphous Fluoropolymers*, J. Schiers, Ed., *Modern Fluoropolymers*, John Wiley & Sons, New York, 1997, p. 397-420, which is hereby included by reference. A preferred grade of Teflon®
5   AF is AF 2400, which is reported to contain 83 mole percent PDD, and 17 mole percent tetrafluoroethylene.

Other potentially useful polymer in the HDL include Cytop® fluoropolymer resin (reportedly a homopolymer f 1,1,2,4,4,5,5,6,7,7-decafluoro-3-oxa-1-,6-heptadiene) available from Asahi Glass, 1-5-1, Marunouchi, Chiyoda-ku, Tokyo 100-8405, Japan,
10   and Hyflon® DA-type fluoropolymer resin, (reportedly a copolymer of tetrafluoroethylene and perfluoro(3-methoxy-1,3-dioxole) available from Solvay, SA, RUE DE RANSBEEK , 310, 1120 Bruxelles, Belgium.

Preferably the polymer(s) in of the HDL are so-called "glassy" polymers. By that is meant the polymer has no melting point above about 30°C with a heat of fusion of 3
15   J/g or more when measured by Differential Scanning calorimetry using ASTM Test D3418-12e1 using a heating and cooling rate of 10°C/min, and measured on the second heat.. Also a glassy polymer has a Glass Transition Temperature (Tg) above about 40°C,more preferably about 40°C. The Tg is measured according to ASTM Test D3418-12e1 at a heating and cooling rate of 10°C/min, and the Tg is taken as the midpoint
20   (inflection point) of the transition on the second heat. Preferably the Tg is less than about 220°C, because for instance if the Tg is too high it may be difficult to dissolve the polymer to form a coating or layer.

The polymers for the HDL may contain functional groups but preferably these functional groups are relatively difficult to oxidize and will not complex or react with the
25   silver ion in the SL. Useful groups include perfluoroether and choro (particularly when present as chlorotrifluoroethylene). Groups which preferably are not present are primary and secondary alcohol. Iodo, bromo, and aldehyde..

The HDL has a permanence to nitrogen of at least 250 GPU at about 25°C Preferably this permanence should be at least about 500 GPU and more preferably at
30   least about 1000 GPU, especially preferably about 1500 GPU, and very preferably at least about 2500 GPU, and most preferably at least about 5000 GPU. If the permanence to alkenes is high enough a relatively thick layer of the HDL material may be used, and this would support a membrane having only two layers, the HDL and SL.

However such nonporous very highly permeable materials are difficult to find and so in many instances a third layer is added a (micro)porous layer, a layer containing many small pores through which the desired may flow relatively unobstructed, while the HDL is very thin so that the productivity of the TFC is high per unit area. This porous

5   layer (PL) may be made thick enough to physically support the entire three (or more) layer TLC without sacrificing much productivity.

When these three types of layers, the SL, HDL and PL are combined into a single TLC, the structure of the TLC, in order of layers, is typically SL/HDL/PL (the slashes indicating where layer surfaces are laminated together)L, with the SL being

10   exposed to the mixture from which one or more components is to be separated, and the separated product passing through the HDL and emerging from the "free surface" of the PL or vice versa In this type of configuration, the HDL is often termed the "gutter layer". It is known that this gutter layer often improves the throughput of the TLC per unit area of TLC, see M. Kattula, *et al.*, *Designing ultrathin film composite membranes: the impact*

15   *of a gutter layer*, *Scientific Reports*, 5, Article Number 15016 (2015), which is hereby included by reference.

In the present invention however the gutter layer has another unexpected effect, improving the separation of the TLC as a whole. Not wishing to be bound by theory, generally speaking materials (usually polymers) chosen for the various layers of a TLC

20   are chosen partially because under the conditions the TLC will be used they are chemically and physically stable. Unfortunately the silver ionomers of the SL layer are not very chemically stable, especially in the presence of organic compounds which can be relatively readily oxidized. Most materials for the PLs, organic polymers which often contain small amounts of adventitious chemical materials or oxidizable groups in the

25   polymers themselves, which are oxidized by Ag^+, the silver often being reduced the metal, and thereby becoming ineffective in separate ng alkanes from alkenes.

This is why it is believed that the fluoropolymers, especially perfluoropolymers, described herein for the HDL are effective in not only perhaps improving productivity of the membrane, but in the proper configuration help protect the integrity of the SL,

30   improving its "separation properties" initially and over a longer period of time, see for instance Table 1 below.

Other layers and layer configurations may be present in the HDL. For instance an additional HDL layer may be present, preferably in the HDL/SL/HDL/PL configuration wherein the additional HDL layer protects the "exposed" surface of the three layer HDL

with a SL/HDL/PL from contamination and perhaps degradation from materials in the mixture which is to be (partially) separated. Other useful layers and configurations will be apparent to those skilled in the art.

The use of these types of membranes which have one or more dense silver
5   ionomer layers to separate alkanes from alkenes is well known in the art. On side of the membrane is exposed to a gaseous or liquid mixture of one or more alkanes and one or more olefins and a driving force is provided. An eluate stream comes out of the other side of the membrane which is enriched on alkene(s), that is the concentration of the alkane(s) in the alkene(s) is reduced. It is preferred if the mixture of alkane(s) and
10 alkene(s) is gaseous. Such separation process are described in US Patent Application 14/334,605, US Provisional Applications 62/159,646, 62/159,668, and 62/262,169 (now PCT applications _____, respectively), A. van Zyl, *et al.,* *Journal of Membrane Science,* *133,* (1997), pp. 15-26, O.I. Eriksen, *et al., Journal of Membrane Science,* *85* (1993), pp. 89-97, and A.J. van Zyl, *Journal of Membrane*
15 *Science,* *137* (1997), pp. 175-185, and U.S. Patent 5,191,151, all of which are hereby included by reference.

The HDL must have a minimum permeance to nitrogen at about 25°C of at least about 500 GPU, preferably at least about 1000 GPU, more preferably at least about 1500 GPU and very preferably at least about 2000. To obtain high permeances for such
20 layers these layer are typically made out of polymers which have a high permeability to the gas being tested, in this instance nitrogen, and are generally quite thin, because the higher the thickness the lower the permeance. Thus these SLs can be about 0.1 to about 1.0 μm thick, preferably about 0.2 to about 0.5 μm thick. It may be difficult to measure permeances on layer by themselves that are so thein because of damage from
25 forming and handling such thin layers. Thus the measurement of the permeance of the HDL can be measured with the HDL supported by a porous layer, the porous layer having a much higher "permeance" to the gas being tested than the HDL itself. If possible a membrane having HDL layer, and for instance the porous layer, are both made by the same process used to make the actual membrane which is to be used to
30 the olefin/alkane separation, see for instance the preparation of the as "Teflon AF/PAN" substrate in Example 3 below.

One can search for potential polymers useful in SDLs by finding the permeabilities to nitrogen of various otherwise suitable polymers. GPU units herein have the units of (1×10^{-6}) sec/cm$^2 \cdot$ s $\cdot$ cm Hg, while permeability units are often in Barrer,

which are (1×10^{-10}) sec·cm/cm²·s·cm H<u>Method of Measuring Nitrogen Permeance of the HDL</u>

A 47 mm flat disc membrane containing only gutter layer material as a membrane on a porous support is punched from a larger 3 inch flat sheet membrane.

5   The 47 mm disc is then placed in a stainless steel cross flow testing cell comprised of a feed port, retentate port, a sweep inlet port, and a permeate port. Four hex bolts are used to tightly secure the membrane in the testing cell with a total active area of 13.85 cm².

The feed port of the cell is connected to a gas manifold consisting of 4 gases:

10   nitrogen, oxygen, helium, and carbon dioxide. The retentate port is connected to a ball valve to dead end the gas flow as well as the purge the gas. One of the two permeate ports is shut and the other is connected to a flow meter.

Nitrogen is brought up to pressure by a gas regulator and allowed to purge slowly for 1 minute. The retentate port is closed and a flow measurement can be taken from the

15   permeate which is at atmospheric pressure. This process is repeated for three different feed pressures between 5 to 10 psig so that an average permeance can be calculated. The feed pressure, permeate flowrate, and temperature are recorded for the calculation. The permeance can be calculated by the equation:

$$Q = F/(A \cdot \Delta p)$$

20   where, Q = gas permeance, F = permeate flow rate, ΔP = transmembrane pressure difference, and A is the effective area of the membrane, in this instance 13.85 cm².

<u>Determination of Permeance and Selectivity for Olefin/Alkane Separations</u>

For determinations of permeance (GPU, reported in units of sec/cm²·s·cm Hg) and selectivity the following procedure was used. A 47 mm flat disc membrane was punched

25   from a larger flat sheet 3 inch composite membrane. The 47 mm disc is then placed in a stainless steel cross flow testing cell comprised of a feed port, retentate port, a sweep inlet port, and a permeate port. Four hex bolts were used to tightly secure the membrane in the testing cell with a total active area of 13.85 cm².

The cell was placed in a testing apparatus comprising of a feed line, a retentate

30   line, a sweep line, and a permeate line. The feed consisted of a mixture of an olefin (propylene) gas and a paraffin (propane) gas. Each gas was supplied from a separate cylinder. For olefin, polymer grade propylene (99.5 vol% purity) was used and for paraffin, 99.9 vol% purity propane was used. The two gases were then fed to their respective mass flow controllers where a mixture of any composition can be made. The

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standard mixing composition was 20 vol% olefin and 80 mol% paraffin at a total gas flow

rate of 200 mL/min. The mixed gas was fed through a water bubbler to humidify the gas

mixture bringing the relative humidity to greater than 90%. A back pressure regulator is

used in the retentate line to control the feed pressure to the membrane. The feed

5   pressure was normally kept at 60 psig (0.41 MPa) after the back pressure regulator the

gas is vented.

The sweep line consisted of a pure humidified nitrogen stream. Nitrogen from a

cylinder was connected to a mass flow controller. The mass flow controller was set to a

flow of 300 mL/min. The nitrogen was fed to a water bubbler to bring the relative

10   humidity to greater than 90%. After the bubbler the nitrogen was fed to the sweep port of

the membrane to carry any permeating gas through to the permeate port.

The permeate line consisted of the permeated gas through the membrane and

the sweep gas as well as water vapor. The permeate was connected to a three way

valve so flow measurements could be taken. A Varian® 450 GC gas chromatograph

15   (GC) with a GS-GasPro capillary column (0.32mm, 30m) was used to analyze the ratio

of the olefin and paraffin in the permeate stream. The pressure in the permeate side was

typically between 1.20 and 1.70 psig (8.3 to 11.7 kPa), but for Examples herein was 0.0

to 0.3 psig ("0" to 2.1 kPa). Experiments were carried out at room temperature.

During experiment the following were recorded: feed pressure, permeate

20   pressure, temperature, sweep-in flow rate (nitrogen + water vapor) and total permeate

flow rate (permeate + nitrogen + water vapor).

From the results recorded the following were determined: all individual feed

partial pressures based on feed flows and feed pressure; all individual permeate flows

based on measured permeate flow, sweep flows, and composition from the GC; all

25   individual permeate partial pressures based on permeate flows and permeate pressures.

From these the transmembrane partial pressure difference of individual component

were calculated. From the equation for permeance

$$Q_i = F_i / (A.\Delta p_i)$$

wherein, Q_i = permeance of species 'i', F_i = Permeate flow rate of species 'i' Δp_i =

30   transmembrane partial pressure difference of species 'i', and A is the area of the

membrane (13.85 cm^2), the permeance(Q_i) was calculated.

In the Examples, the following abbreviations are used:

HFPO – hexafluoropropylene oxide (For preparation of HFPO dimer peroxide see US Patent 7,112,314, which is hereby included by reference. HFPO dimer [2062-98-8] is available from Synquest Laboratories, Alachua, Fl., USA)

PDD – perfluoro(2,2-dimethyl-1,3-dioxole) or

SEFVE - $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$

PPSF- $CF_2=CFOCF_2CF_2SO_2F$

VF2 – vinylidene fluoride ($H_2C=CF_2$)

VF- vinyl fluoride ($H_2C=CHF$)

PPVE – perfluoro(propylvinyl ether)

Example 1

Synthesis of PDD/VF/SEFVE (feed ratio 100:100:150) copolymer and hydrolysis

Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66g PDD, 10.04 g SEFVE, 12 mL of Vertrel ®XF, (reportedly 1,1,1,2,2,3,4,5,5,5-deafluoropentane and available from The Chemours Co., Wilmington, DE 19899, USA) 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.69 g of vinyl fluoride gas at 0 °C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After 3 hours of reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100 °C overnight to yield 5.5 g PDD/VF/SEFVE terpolymer as a colorless solid (Tg 37 °C).

Into a 250 mL round bottom flask, were added 3.75 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.85 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60 °C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60 °C for 3 hours. A brownish solid (2.7 g) containing free sulfonic acid groups was obtained.

Example 2

Synthesis of PDD/VF/PPSF (feed ratio 100:100:150) copolymer and hydrolysis

Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66g PDD, 6.3 g PPSF, 12 mL of Vertrel ®XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.96 g of vinylidene fluoride gas at 0 °C. The reaction mixture was sealed in the pressure vessel and stirred

5   at room temperature in a water bath. After overnight reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100 °C overnight to yield 6.0 g PDD/VF/PPSF terpolymer as a colorless solid (Tg 58 °C).

10   Into a 250 mL round bottom flask, were added 4.0 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.5 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60 °C. . After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was

15   evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60 °C for 3 hours. A slight brownish solid (3.0 g)

20   containing free sulfonic acid groups was obtained.

<u>Example 3</u>
Membrane Formation and Testing
Into a glass bottle, were added 0.1g of the polymer from example 1, 20mg of silver nitrate, 3.5g of isopropyl alcohol and 1.5g of Novec®7300 (reportedly

25   1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluromethylpentane and available from 3M Corp., Electronic Markets Materials Div., St. Paul, MN, 55144, USA). The resulting solution was stirred for 1-2 hours, and then filtered through a glass fiber filter having a pore size of 1.2 μm. This solution is denoted as "Solution 1".

Into a glass bottle, were added 0.1g of the polymer from example 2, 20mg of

30   silver nitrate, 3.5g of isopropyl alcohol and 1.5g of Novec®7300. The resulting solution was stirred for 1-2 hours, and then filtered through a glass fiber filter having a pore size of 1.2 μm. This solution is denoted as "Solution 2".

Into a glass bottle, were added 0.4g of Aquivion®D79-25BS (obtained from
Sigma-Aldrich, USA, and reportedly containing 25 weight percent polymer in water, 1.23-
1.30 meq/ g of acid capacity on a polymer basis), 20mg of silver nitrate, 4.6g of isopropyl
alcohol. The resulting solution was stirred for 1-2 hours, and then filtered through a
5   glass fiber filter having a pore size of 1.2 μm. This solution is denoted as "Solution 3".

Into a glass bottle, were added 0.5g of Nafion®D2020 (obtained from DuPont
Fuel Cells, P.O. Box 80701, Wilmington, DE, 19880-0701, USA, and reportedly
containing 20 weight percent polymer, about 34wt% of water, and about 46 wt. % of 1-
propanol, 1.03-1.12 meq/ g of acid capacity on a polymer basis), 20mg of silver nitrate,
10   4.5g of isopropyl alcohol. The resulting solution was stirred for 1-2 hours, and then
filtered through a glass fiber filter having a pore size of 1.2 μm. This solution is denoted
as "Solution 4".

A substrate was prepared by coating a 0.2 weight % solution of Teflon® AF2400
(available from the DuPont Co, Wilmington, DE 19898, USA) (for further information
15   about Teflon® AF, see P.R. Resnick, et al., *Teflon AF Amorphous Fluoropolymers*, J.
Schiers, Ed., *Modern Fluoropolymers*, John Wiley & Sons, New York, 1997, p. 397-420,
which is hereby included by reference) in Fluorinert® 770 (available from 3M Corp., 3M
Center, Sty. Paul, MN, USA) on a PAN350 membrane made by Nanostone Water,
10250 Valley View Rd., Eden Prairie, MN 53344, USA) (The PAN350 membrane is
20   ultrafilter made from polyacrylonitrile). This substrate is denoted as "Teflon AF/PAN".

Another substrate was prepared by coating 10% Sylgard®184 in n-hexane on
PAN350 membrane made. This substrate is denoted as PDMS/PAN.

The Solution 1 was coated on directly PAN350 membrane and coated on Teflon
AF/PAN respectively at < 30% relative humidity.
25   The Solution 2 was coated on PAN350 membrane, coated on Teflon AF/PAN
and coated on PDMS/PAN respectively at < 30% relative humidity.

The Solution 3 was coated on PAN350 membrane, coated on Teflon AF/PAN
and coated on PDMS/PAN respectively at < 30% relative humidity.

The Solution 4 was coated on PAN350 membrane and coated on Teflon AF/PAN
30   respectively at < 30% relative humidity.

Obtained composite membranes are measured the propane and propylene
permeances as following method.

The permeance measurement membrane was a 47mm diameter, a flat sheet.
The feed gas composition, 20 mole % propylene (polymer synthesis grade), and 80%

propane was humidified by passing it through a water bubbler. The total flow rate of both gases was 200 mL/min. The feed gas (mixture of propylene and propane) was 60 psig, and the sweep gas on the second side of the membrane was humidified nitrogen at a pressure of 0.0 to 0.3 psig. The permeate from the second side of the membrane was

5   analyzed by GC to determine the molar ratio of propane and propylene. Permeances (GPU) are given in $cm^3/cm^2/sec/cm$ Hg x 10^6.

Table-1 shows the permeance measurements result

Table 1

Membrane Material	Permeance (GPU)		Selectivity
	C_3H_8	C_3H_6	C_3H_6/C_3H_8
Solution 1 on PAN	2.71	78.9	29.1
Solution 1 on Teflon AF/PAN	5.29	247.6	46.8
Solution 2 on PAN	2.9	79.3	27.4
Solution 2 on Teflon®AF/PAN	2.9	276	95.7
Solution 2 on PDMS /PAN	4.5	120.1	26.7
Solution 3 on Teflon®AF/PAN	5.97	311.4	52.1
Solution 3 on PAN	4.45	143.7	32.3
Solution 3 on PDMS /PAN	11.1	219.7	29.2
Solution 4 on PAN	7.3	58.2	8.0
Solution 4 on Teflon®AF/PAN	5.69	212.3	37.3

10   It is clear from Table 1 that incorporation of the fluoropolymer HDL in the composite membrane results in a consistent increase in both the propylene permeance and the propylene/propane selectivity.

Example 4

Synthesis of a PDD/PPVE High Diffusion Rate polymer

15   A glass pressure tube was charged 8.0 g PDD, 872 mg PPVE, 0.8 mL HFPO dimer peroxide solution (0.12 M) in Vertrel XF and 15 mL Vertrel XF. After degassing the mixture for 5 minutes with argon at 0 °C, the glass tube was sealed, allowed to warm to room temperature in a water bath and the reaction mixture was stirred overnight. The tube was opened to air and 30 mL acetone is added into the mixture. After stirring for 5

20   minutes, the mixture was filtered and 30 mL fresh acetone was added to rinse everything

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out of the vessel. The solid on the filter paper was transferred to a watch glass. After drying in oven at 100 °C overnight, 7.4 g of white solid was collected as the PDD/PPVE polymer.

<div align="center">Example 5</div>
<div align="center">Synthesis of a PDD/SEFVE High Diffusion Rate Polymer</div>

A glass pressure tube was charged with 4.88 g PDD, 892 mg SEFVE, 0.4 mL HFPO dimer peroxide solution (0.12 M) in Vertrel XF and 15 mL Vertrel XF. After degassing the mixture for 5 minutes with argon at 0 °C, the glass tube was sealed, allowed to warm to room temperature in a water bath and the reaction mixture is stirred overnight. The tube was opened to air and 30 mL acetone was added into the mixture. After stirring for 5 minutes, the mixture was filtered and 30 mL fresh acetone was added to rinse everything out of the vessel. The solid on the filter paper was transferred to a watch glass. After drying in oven at 100 °C overnight, 4.1 g of white solid was collected as the PDD/SEFVE polymer.

<div align="center">Example 6</div>

<div align="center">High Diffusion Rate Layer Permeability Measurements</div>

Solutions were prepared from Teflon® AF 2400 in Fluorinert®770 at various concentrations (Table 2) and coated on a PAN350 membrane as described in example 3. It is believed lower polymer concentration results in formation of thinner membranes. These supported membranes were tested for nitrogen permeance at feed pressures of 10, 20 and 30 psig (68.9, 137.8 and 207.7 kPa) and at ambient (atmospheric) pressure on the product side. The results shown in Table 2 for each solution are averages of the three feed pressures.

<div align="center">Table 2</div>

Teflon® AF 2400 concentration in Fluorinert®770 (wt %)	Nitrogen Permeance (GPU)
0.3	2578
0.1	6184
0.05	12445

Claims

1. , A thin film composite membrane for the separation of alkanes from alkenes, comprising:

(a) a separation layer comprising a silver ionomer of a polymeric sulfonic acid;

5   and

(b) a high diffusion rate layer of one or more fluorinated polymers having a permeance to propylene of at least about 250 GPU, and

wherein said separation layer and said high diffusion rate layer are laminated to each other.

10   2. The thin film composite membrane of claim 1 wherein said silver ionomer is a fluorinated polymer.

3. The thin film composite membrane of claim 1 wherein said silver ionomer is a perfluoropolymer.

4. The thin film composite membrane of any one of claims 1 to 3 wherein said

15   high diffusion rate layer is a fluorinated polymer wherein about 50% or more of the total of the carbon fluorine groups and carbon-hydrogen groups are carbon fluorine groups.

5. The thin film composite membrane any one of claim 1 to 3 wherein said high diffusion rate layer fluorinated polymer is a perfluoropolymer.

6. The thin film composite membrane any one of claims 1 to 3 wherein said high

20   diffusion rate layer fluorinated polymer is a perfluorocopolymer of perfluoro(2,2-trifluoromethyl-1,3-dioxole).

7. The thin film composite membrane any one of claims 1 to 3 wherein said high diffusion rate layer fluorinated polymer is a copolymer of perfluoro(2,2-trifluoromethyl-1,3-dioxole). and tetrafluoroethylene.

25   8. The thin film composite membrane of any one of claims 1 to 3 wherein said high diffusion rate layer is about 0.1 to about 1.0 μm thick.

9. The thin film composite membrane of any one of claims 1 to 3 additionally comprising a porous layer which is laminated to said high diffusion rate layer.

10. The thin film composite membrane of claim 4 additionally comprising a

30   porous layer which is laminated to said high diffusion rate layer.

11. The thin film composite membrane of claim 5 additionally comprising a porous layer which is laminated to said high diffusion rate layer.

12. The thin film composite membrane of claim 6 additionally comprising a porous layer which is laminated to said high diffusion rate layer.

13. The thin film composite membrane of claim 7 additionally comprising a porous layer which is laminated to said high diffusion rate layer.

14. The thin film composite membrane of claim 13 wherein said high diffusion rate layer is about 0.1 to about 1.0 μm thick.

15. A membrane process for the separation of alkanes from alkenes, wherein the improvement comprises, using the membrane of any one of claims 1 to 14.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/31135

Box No. II   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.: 15
       because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III   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:

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 additional fees, this Authority did not invite payment of additional fees.

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 and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/31135

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 7/144; B01D 69/12; B01D 69/10; B01J 47/12; B01D 71/06; B01D 53/22 (2016.01)
CPC - C07C 7/144; B01D 53/228; B01D 71/76; B01D 71/82; B01D 71/32; B01J 47/12; B01D 69/12
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(8) - C07C 7/144; B01D 69/12; B01D 69/10; B01J 47/12; B01D 71/06; B01D 53/22 (2016.01)   CPC - C07C 7/144; B01D 53/228; B01D 71/76; B01D 71/82; B01D 71/32; B01J 47/12; B01D 69/12
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   Patents and non-patent literature (classification, keyword; search terms below)
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)   PatBase, Google Scholar (NPL), Google Patents; search terms: thin film, composite membrane, separating alkenes, olefins, alkanes, paraffins, silver, Ag, ionomer, sulfonic, high diffusion, fluorinated polymer, perfluoropolymer, permeance, propylene, GPU, laminate, perfluoro(2,2-trifluoromethyl-1,3-dioxole), tetrafluoroethylene, porous layer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/0025293 A1 (FEIRING et al.) 22 Jan 2015 (22.01.2015) para [0001], [0014], [0017]-[0022], [0025]-[0027], [0037]-[0038], [0040]-[0042], [0047], [0050]-[0052], [0055], [0060]-[0065]	1-14
Y	US 2003/0033929 A1 (PINNAU et al.) 20 February 2003 (20.02.2003) para [0002], [0004], [0052], [0064]-[0065], [0195], [0197]-[0201], [0244]-[0245]	1-14
A	US 5,670,051 A (PINNAU et al.) 23 September 1997 (23.09.1997) entire document, especially col 1, ln 12-15; col 3, ln 35-45, 59-65; col 4, ln 15-18, 22-33; col 8, ln 48-52; col 9, ln 52-66; col 10, ln 15-20, 57-60	1-14
A	US 5,914,154 A (NEMSER) 22 June 1999 (22.06.1999) entire document, especially col 4, ln 30-31, 37 38, 41, 47-55, 57-59; col 5, ln 34-40, 43-51; col 6, ln 62-63; col 9, ln 35-38	1-14

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	
"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	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 July 2016 (07.07.2016)	**05 AUG 2016**

Name and mailing address of the ISA/US	Authorized officer:
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