

DescriptionDescription of the Invention

Hydrocarbon solvents used for dewaxing and/or deasphalting oils can be recovered by the selective permeation of the solvent through an interfacially polymerized membrane under reverse osmosis conditions.

The hydrocarbon solvents which can be recovered are the C_3 to C_6 aliphatic alkanes and alkenes, i.e., propane, propylene, butane, butene, hexane, hexene, heptane, heptene and mixtures thereof, preferably the C_3 - C_4 alkanes and alkenes and mixtures thereof, most preferably propane, butane and mixtures thereof.

These solvents are employed for the dewaxing and/or deasphalting of hydrocarbon oils, e.g., lubes and specialty oils, transformer oils, refrigerator oils, turbine oils, as well as the dewaxing of fuels fraction such as diesel, and jet. The hydrocarbon oils can come from any natural or synthetic source. Mineral oil distillates or hydrocracked oils ranging from light fuels fractions to Bright Stocks are dewaxed and/or deasphalted by the techniques known in the art. Similarly oils obtained by the isomerization of natural slack waxes or Fischer-Tropsch waxes as well as oils obtained from tar sands, coal liquification, and shale can be subjected to treatment as needed.

The C_3 to C_6 hydrocarbon solvents are recovered for use by the selective permeation of the solvent through an interfacially polymerized membrane.

The membranes are prepared by depositing an aqueous (or conversely non-aqueous) solution of a first reactant component on the microporous backing support layer, draining off the excess quantity of this first solution and then applying a second reactant component in the form of a non-aqueous (or conversely aqueous) solution. The two components interact and polymerize at the interface between the aqueous phase and the non-aqueous phase to produce a highly crosslinked thin polymer layer on the microporous ultrafiltration support backing layer.

In this invention the membranes are generally prepared by reacting multi-functional amino compounds dissolved in water with a second polyfunctional agent dissolved in organic solvents. The amino compounds can be aliphatic, alicyclic or aromatic. The polyfunctional agents with which the amines are reacted can include di- and tri- acid halides, acid anhydrides, aliphatic and aromatic diisocyanates, thioisocyanates, haloformates and sulfonyl halides. Backings which can be used include nylon (e.g., nylon 66), cellulose, polyester, teflon, polypropylene and other insoluble polymers.

Background of the Invention

The separation and recovery of C_3 - C_6 hydrocarbon dewaxing and/or deasphalting solvents from dewaxed and/or deasphalted oils is an important process consideration. It is uneconomical to simply discard the solvents after one use and similarly, in most applications their continued presence in the product oil can give rise to product quality concerns.

Such solvents have been recovered by simple distillation as well as by the simple expedient of permitting the normally gaseous solvents such as propane and butane merely vaporize. Such processes are not efficient requiring the expenditure of considerable energy to affect the distillates and, in the case of propane and butane, the recompression of the solvents before reuse is possible.

The recovery of such solvents by more energy efficient means has been explored. The use of membranes to effect the separation has generated much interest. See U.S. Patent 4,595,507 and U.S. Patent 4,617,126.

Interfacially polymerized membranes were initially discovered in the 1970's for use in water desalination (see "In situ-formed Condensation Polymers for Reverse Osmosis Membranes: Second Phase", North Star Research Institute, prepared for Department of the Interior, July 1974, available from NTIS, report #PB-234 198; "Continued Evaluation of In Situ-formed Condensation Polymers for Reverse Osmosis Membranes", Midwest Research Institute, prepared for Office of Water Research and Technology, April 1976, available from NTIS, report #PB-253 193; "Interfacially Synthesized Reverse Osmosis Membrane", U.S. Patent 4,277,344, July 7, 1981, assn. to Film Tec Corporation). Prior art only describes the use of these membranes for the separation of aqueous solutions by reverse osmosis.

Interfacially polymerized membranes are composed of a highly crosslinked and generally insoluble condensation polymer which is formed in situ on a micro-porous film. Most of these membranes are formed with di- or polyamines which are reacted with multi-functional iso-cyanates or acid chlorides. Amines react very readily with both of these reactants. Several of these membranes have been commercialized for water desalination purposes by companies such as UOP, Film Tec and Desalination Systems Inc. All of the commercial membranes use a polysulfone ultrafiltration membrane (0.02 to 0.1 micron pore size) for the

microporous support film. Prior art does describe the use of some other microporous support films such as polyvinylchloride ultrafiltration membranes.

These membranes are formed by using the following procedures. A thin layer of a dilute solution of one component, usually an aqueous solution of the amine, is put on one side of the microporous support film. A thin layer of a dilute solution of the second component, usually in a water immiscible solvent, is then put on top of the water solution layer. The order of applying the solutions can be reversed. The two components react at the water/solvent interface forming a thin (less than 1 micron thick) highly crosslinked polymer layer. This polymer layer is the active layer of the membrane at which separation occurs. Some examples of formulations mentioned in the prior art are reacting polyethylenimine with toluene diisocyanate, reacting polyethylenimine with isophthaloyl dichloride and reacting m-phenylene diamine with trimesoyl chloride.

These membranes exhibit high salt rejections from water (>95%).

EP-A-0 013 834 describes the sequential permeation under different pressures of a hydrophilic, water-containing regenerated cellulose membrane with solvents of decreasing polarity. A typical preconditioning sequence is:

water-methanol-MEK-pentane-propane. The said membrane is selectively permeable to a dewaxing solvent of a mixture comprising dewaxed oil and dewaxing solvent.

EP-A-0 427 452 of earlier priority date (cited under Article 54(3)EPC) describes a process for separating ketonic and aromatic dewaxing solvents from dewaxed oil using a membrane including a polyimine layer which has been cross-linked on a porous support layer with a cross-linking agent, e.g. polyisocyanate.

EP-A-0 421 676 of earlier priority date (cited under Article 54(3)EPC) similarly describes a process for separating ketonic and aromatic dewaxing solvents from dewaxed oil using an interfacially polymerised membrane e.g. of polyimine prepared on a support layer from a multifunctional amino reactant and a polyfunctional agent reactant, e.g. a diisocyanate.

The present invention provides a method for separating hydrocarbon solvents selected from C_3 to C_6 aliphatic alkanes and alkenes and mixtures thereof used for dewaxing and/or deasphalting oils from said dewaxed and/or deasphalted oil by contacting the dewaxed and/or deasphalted oil containing said hydrocarbon solvent with a membrane under reverse-osmosis conditions, whereby said solvent is selectively permeated through the membrane, characterised in that the said membrane is an interfacially-polymerized cross-linked membrane on a microporous ultrafiltration support backing, said interfacially-polymerized membrane comprising the reaction product of a multi-functional amino compound dissolved in water with a polyfunctional amine-reactive agent dissolved in an organic solvent.

In the method of the invention, the interfacially polymerized membranes are prepared by reacting multifunctional amino reactants dissolved in water with polyfunctional amine-reactive agent reactants dissolved in organic solvents. The interfacially polymerized membrane is produced on a non-selective, microporous ultrafiltration support layer which is inert in the organic media to which it will be exposed. This support layer is selected from nylon, cellulose, polyester, teflon (polytetrafluoroethylene), polypropylene, polyethylene terephthalate, ultrafiltration membranes having pores in the range 0.02 to 0.1 microns.

A few examples of multi-functional amino group reactants include polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, amine modified polyepihalohydrins, and other amine containing polymers, m-phenylene diamine, p-phenylene diamine, triaminobenzene, piperazine, piperidine, 2,4-bis (p-aminobenzyl) aniline, cyclohexane diamine, cycloheptane diamine, and mixtures thereof.

The polyfunctional agents that the amines are reacted with can include di- and tri- acid halides, (e.g., chlorides), polyfunctional acid anhydrides, aliphatic and aromatic diisocyanates, polyfunctional thioisocyanates, haloformates (e.g., chloroformates) and sulfonyl halides (e.g., sulfonyl chlorides), and mixtures thereof. A few examples of these agents are trimesoyl chloride, cyclohexane-1,3,5 tricarboxyl chloride, isophthaloyl chloride, terephthaloyl chloride, diisocyanatohexane, cyanuric chloride, diphenylether disulfonyl chloride, oxalyl chloride, malonyl chloride, succinyl chloride, glutaryl chloride, fumaryl chloride, glutaconyl chloride, phthalic anhydride, ethylene diisocyanate, propylene diisocyanate, benzene diisocyanate, toluene diisocyanate, naphthalene diisocyanate, methylene bis (4-phenylisocyanate), ethylene thioisocyanate, toluene thioisocyanate, naphthalene thioisocyanate, ethylene bischloroformate, propylene bischloroformate, butylene bischloroformate, 1,3-benzenedisulfonyl chloride, 1,4 benzene disulfonyl chloride, 1,3-naphthalene disulfonyl chloride and 1,4-naphthalenedisulfonyl chloride, and mixtures thereof.

A crosslinked membrane is used in the present invention to ensure stability. A crosslinked polymeric film is formed if these membranes are prepared with one of the reactants being at least trifunctional. The degree of crosslinking is primarily controlled by the concentration of the reactant solution with higher concentrations leading to higher degrees of cross-linking.

In general the interfacially polymerized membranes are produced using 0.1 to 10 wt% aqueous solutions of the amines, preferably 0.25 to 5 wt% aqueous solutions of the amines; and 0.1 to 5 wt% non-aqueous solutions of the poly-functional agents, preferably 0.15 to 0.5 wt% non-aqueous solution of the poly-functional agent.

Following the sequential deposition of the two solutions, the resulting film can be heated to promote crosslinking of any unreacted amine. This post heating step can be at a temperature of about 60 to 150 °C, preferably 80 to 120 °C for from 1 to 20 minutes. The concentrations of components used and drying/cross-linking times and temperatures will be selected from the above ranges by the practitioner in response to the membrane casting procedures actually employed and the casting machines or other mechanisms or equipment used.

The C₃-C₆ and mixtures thereof hydrocarbon dewaxing and/or deasphalting solvents are selectively permeated through the interfacially polymerized membranes under reverse osmosis conditions.

Reverse osmosis conditions include contacting the then, interfacially polymerized crosslinked face of the membrane with the raffinate phase, extract phase, or both, preferably extract phase at a temperature between about -24 to 200 °C, preferably 40 to 150 °C and under an applied pressure sufficient to overcome the osmotic pressure. Pressures on the order of 0 to 6.90 MPa (0 to 1000 psig) can be used, preferably about 2.76 to 4.14 MPa (400 to 600 psig).

The separation process could employ the interfacially polymerized membrane in the form of a spiral wound element. Fabrication of a spiral wound element would employ adhesives as disclosed in U.S. Patents 4,464,494 and 4,582,726.

Examples

Two interfacially polymerized membranes were prepared designated Membrane A and Membrane B. The membranes were prepared as follows:

Membrane A:

- Dissolve 4.00 grams of phenylene diamine (PDA) from Aldrich in 100 grams of deionized water.
- Dissolve 0.15 grams of trimesoyl chloride (TMC) from Aldrich in 100 grams of hexane.
- Install a disc of the 0.04 µm Ultipor nylon 66 membrane in a wash coat cell, leave one side of the membrane exposed.
- Pour the PDA solution over the exposed side of the membrane.
- Drain off excess solution for one minute.
- Pour the TMC solution over the exposed side.
- Drain off the excess solution for one minute.
- Bake the nylon membrane in an oven at 110 °C for 10 minutes.

Membrane B

- Dissolve 0.50 grams of PEI in 100 grams of deionized water.
 - Dissolve 0.50 grams of TDI in 100 grams of toluene.
 - Install a disc of the 0.04 µm Ultipor nylon 66 membrane in a wash coat cell, leave one side of the membrane exposed.
 - Pour the PEI solution over the exposed side of the membrane.
 - Drain off excess solution for one minute.
 - Pour the TDI solution over the exposed side.
 - Drain off the excess solution for one minute.
 - Bake the nylon membrane in an oven at 110 °C for 10 minutes.
- PEI = polyethylenimine (Aldrich #18, 197-8th)
TDI = toluene diisocyanate (BASF)

These membranes were evaluated for the separation of propane from a deasphalted oil. The oil was a Singapore 2500 Neutral deasphalted oil. The feeds used to evaluate Membrane A and B ranged from 8-19.6 wt% oil.

The results are presented below.

Membrane	A	B	B
Temperature °C:	60	60	60
Feed Pressure, psi (MPa)	950 (6.55)	450 (3.10)	600 (4.14)
Permeate Pressure, psi (MPa)	350 (2.41)	350 (2.41)	350 (2.41)
Feed Oil Concentration, wt%	8	13	19.6
Performance			
Flux, L/M ² -Day	510,000	20,950	130,500
Oil Rejection, %	29	73	65

Claims

1. A method for separating hydrocarbon solvents selected from C₃ to C₆ aliphatic alkanes and alkenes and mixtures thereof used for dewaxing and/or deasphalting oils from said dewaxed and/or deasphalted oil by contacting the dewaxed and/or deasphalted oil containing said hydrocarbon solvent with a membrane under reverse-osmosis conditions, whereby said solvent is selectively permeated through the membrane, characterised in that the said membrane is an interfacially-polymerized cross-linked membrane on a microporous ultrafiltration support backing, said interfacially-polymerized membrane comprising the reaction product of a multi-functional amino compound dissolved in water with a polyfunctional amine-reactive agent dissolved in an organic solvent.
2. The method of claim 1 wherein the multifunctional amino group reactant is selected from polyethylenimine, polyvinylamine, polyvinylaniline, polybenzylamine, polyvinylimidazolines, amine modified polyepihalohydrines, m-phenylenediamine, p-phenylenediamine, triaminobenzene, piperazine, piperidine, 2,4-bis-(p-aminobenzyl) aniline, cyclohexane diamine, cycloheptane diamine and mixtures thereof.
3. The method of claim 1 or claim 2 wherein the polyfunctional amine-reactive agent is selected from di- and tri- acid halides, polyfunctional acid anhydrides, aliphatic diisocyanates, aromatic diisocyanates, polyfunctional thioisocyanates, haloformates, and sulfonylhalides and mixtures thereof.
4. The method of any one of claims 1 to 3 wherein the multifunctional amine compound in water is at a concentration of 0.1 to 10 wt.%.
5. The method of any one of claims 1 to 4 wherein the polyfunctional agent reactant in organic solvent is at a concentration of 0.1 to 5 wt.%.
6. The method of any one of claims 1 to 5 wherein the backing is selected from nylon, cellulose, polyester, polytetrafluoroethylene, polypropylene, polyethylene, polyethylene terephthalate ultrafiltration membranes.
7. The method of claim 6 wherein the ultrafiltration membrane support layer has pores in the range 0.02 to 0.1 microns (0.02 to 0.1 µm).
8. The method of any preceding claim wherein the hydrocarbon dewaxing and/or deasphalting solvent is selected from propane, propylene, butane, butene, hexane, hexene and mixtures thereof.

Patentansprüche

1. Verfahren zum Abtrennen von Kohlenwasserstofflösungsmitteln ausgewählt aus aliphatischen C₃- bis C₆-Alkanen und -Alkenen und Mischungen derselben, die zum Entparaffinieren und/oder Entasphaltieren von Ölen verwendet werden, von dem entparaffinierten und/oder entasphaltierten Öl, indem das entparaffinierte und/oder entasphaltierte Öl, das das Kohlenwasserstofflösungsmittel enthält, unter Umkehrosmosebedingungen mit einer Membran kontaktiert wird, wobei das Lösungsmittel selektiv durch die Membran permeiert wird, dadurch gekennzeichnet, daß die Membran eine an der Grenzfläche polymerisierte vernetzte Membran auf einer mikroporösen Ultrafiltrationsträgerunterlage ist, wobei



Membrane	A	B	B
Temperature °C:	60	60	60
Feed Pressure, psi (MPa)	950 (6.55)	450 (3.10)	600 (4.14)
Permeate Pressure, psi (MPa)	350 (2.41)	350 (2.41)	350 (2.41)
Feed Oil Concentration, wt%	8	13	19.6
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1. A method for separating hydrocarbon solvents selected from C₃ to C₆ aliphatic alkanes and alkenes and mixtures thereof used for dewaxing and/or deasphalting oils from said dewaxed and/or deasphalted oil by contacting the dewaxed and/or deasphalted oil containing said hydrocarbon solvent with a membrane under reverse-osmosis conditions, whereby said solvent is selectively permeated through the membrane, characterised in that the said membrane is an interfacially-polymerized cross-linked membrane on a microporous ultrafiltration support backing, said interfacially-polymerized membrane comprising the reaction product of a multi-functional amino compound dissolved in water with a polyfunctional amine-reactive agent dissolved in an organic solvent.
2. The method of claim 1 wherein the multifunctional amino group reactant is selected from polyethylenimine, polyvinylamine, polyvinylaniline, polybenzylamine, polyvinylimidazolines, amine modified polyepihalohydrines, m-phenylenediamine, p-phenylenediamine, triaminobenzene, piperazine, piperidine, 2,4-bis-(p-aminobenzyl) aniline, cyclohexane diamine, cycloheptane diamine and mixtures thereof.
3. The method of claim 1 or claim 2 wherein the polyfunctional amine-reactive agent is selected from di- and tri- acid halides, polyfunctional acid anhydrides, aliphatic diisocyanates, aromatic diisocyanates, polyfunctional thioisocyanates, haloformates, and sulfonylhalides and mixtures thereof.
4. The method of any one of claims 1 to 3 wherein the multifunctional amine compound in water is at a concentration of 0.1 to 10 wt.%.
5. The method of any one of claims 1 to 4 wherein the polyfunctional agent reactant in organic solvent is at a concentration of 0.1 to 5 wt.%.
6. The method of any one of claims 1 to 5 wherein the backing is selected from nylon, cellulose, polyester, polytetrafluoroethylene, polypropylene, polyethylene, polyethylene terephthalate ultrafiltration membranes.
7. The method of claim 6 wherein the ultrafiltration membrane support layer has pores in the range 0.02 to 0.1 microns (0.02 to 0.1 µm).
8. The method of any preceding claim wherein the hydrocarbon dewaxing and/or deasphalting solvent is selected from propane, propylene, butane, butene, hexane, hexene and mixtures thereof.

Patentansprüche

1. Verfahren zum Abtrennen von Kohlenwasserstofflösungsmitteln ausgewählt aus aliphatischen C₃- bis C₆-Alkanen und -Alkenen und Mischungen derselben, die zum Entparaffinieren und/oder Entasphaltieren von Ölen verwendet werden, von dem entparaffinierten und/oder entasphaltierten Öl, indem das entparaffinierte und/oder entasphaltierte Öl, das das Kohlenwasserstofflösungsmittel enthält, unter Umkehrosmosebedingungen mit einer Membran kontaktiert wird, wobei das Lösungsmittel selektiv durch die Membran permeiert wird, dadurch gekennzeichnet, daß die Membran eine an der Grenzfläche polymerisierte vernetzte Membran auf einer mikroporösen Ultrafiltrationsträgerunterlage ist, wobei



die an der Grenzfläche polymerisierte Membran das Reaktionsprodukt einer in Wasser gelösten multifunktionalen Aminoverbindung mit einem in einem organischen Lösungsmittel gelösten polyfunktionalen, mit Amin reaktiven Mittel umfaßt.

2. Verfahren nach Anspruch 1, bei dem der multifunktionale Amingruppenreaktant ausgewählt ist aus Polyethylenimin, Polyvinylamin, Polyvinylanilin, Polybenzylamin, Polyvinylimidazolin, mit Amin modifizierten Polyepihalogenhydrinen, m-Phenylendiamin, p-Phenylendiamin, Triaminobenzol, Piperazin, Piperidin, 2,4-Bis(p-aminobenzyl)anilin, Cyclohexandiamin, Cycloheptandiamin und Mischungen derselben.
3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem das polyfunktionale, mit Amin reaktive Mittel ausgewählt ist aus Di- und Trisäurehalogeniden, polyfunktionalen Säureanhydriden, aliphatischen Diisocyanaten, aromatischen Diisocyanaten, polyfunktionalen Thioisocyanaten, Halogenformiaten und Sulfonylhalogeniden und Mischungen derselben.
4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die multifunktionale Aminverbindung in Wasser in einer Konzentration von 0,1 bis 10 Gew.% vorliegt.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das polyfunktionale Mittel als Reaktant in organischem Lösungsmittel in einer Konzentration von 0,1 bis 5 Gew.% vorliegt.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem die Unterlage ausgewählt ist aus Nylon-, Cellulose-, Polyester-, Polytetrafluorethylen-, Polypropylen-, Polyethylen- und Polyethylenterephthalat-Ultrafiltrationsmembranen.
7. Verfahren nach Anspruch 6, bei dem die Ultrafiltrationsmembranträgerschicht Poren im Bereich von 0,02 bis 0,1 μm aufweist.
8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Kohlenwasserstoffentparaffinierungs- und/oder -entasphaltierungslösungsmittel ausgewählt ist aus Propan, Propylen, Butan, Buten, Hexan, Hexen und Mischungen derselben.

Revendications

1. Procédé destiné à séparer des solvants hydrocarbonés, sélectionnés à partir d'alcane et d'alcènes aliphatiques en $\text{C}_3\text{-C}_6$ et des mélanges de ceux-ci utilisés pour le déparaffinage et/ou le désasphaltage des huiles, de l'huile déparaffinée et/ou désasphaltée en mettant en contact l'huile déparaffinée et/ou désasphaltée contenant ledit solvant hydrocarboné avec une membrane dans des conditions d'osmose inverse, le solvant traversant ainsi de manière sélective la membrane par perméation, caractérisé en ce que ladite membrane est une membrane réticulée fabriquée par polymérisation interfaciale sur un support d'ultrafiltration microporeux, ladite membrane fabriquée par polymérisation interfaciale comprenant le produit de réaction d'un composé d'amine multifonctionnel dissous dans de l'eau avec un agent amino-réactif polyfonctionnel dissous dans un solvant organique.
2. Procédé selon la revendication 1, dans lequel le réactif à groupe d'amine multifonctionnel est sélectionné à partir de la polyéthylèneimine, de la polyvinylamine, de la polyvinylaniline, de la polybenzylamine, des polyvinylimidazolines, des polyépihalogénohydrines amino-modifiées, de la m-phénylènediamine, de la p-phénylènediamine, du triaminobenzène, de la pipérazine, de la pipéridine, de la 2,4-bis-(p-aminobenzyl)aniline, de la cyclohexanediamine, de la cycloheptanediamine et des mélanges de ceux-ci.
3. Procédé selon la revendication 1 ou la revendication 2 dans lequel l'agent amino-réactif polyfonctionnel est sélectionné parmi des di- ou trihalogénures d'acides, des anhydrides d'acide polyfonctionnels, des diisocyanates aliphatiques, des diisocyanates aromatiques, des thioisocyanates polyfonctionnels, des formiates halogénés, et des sulfonylhalogénures et des mélanges de ceux-ci.
4. Procédé selon l'une quelconque des revendications 1 à 3 dans lequel le composé amine multifonctionnel dans l'eau est à une concentration de 0,1 à 10 % en poids.



5. Procédé selon l'une quelconque des revendications 1 à 4 dans lequel le réactif polyfonctionnel dans le solvant organique est à une concentration de 0,1 à 5 % en poids.
6. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel le support est sélectionné parmi les membranes d'ultrafiltration en nylon, cellulose, polyester, polytétrafluoréthylène, polypropylène, polyéthylène, et polyéthylène téréphtalate.
7. Procédé selon la revendication 6 dans lequel la couche support de membrane d'ultrafiltration a des pores compris entre 0,02 et 0,1 micron (0,02 à 0,1 μm).
8. Procédé selon l'une quelconque des revendications précédentes dans lequel le solvant hydrocarboné de déparaffinage et/ou de désasphaltage est sélectionné parmi le propane, le propylène, le butane, le butène, l'hexane, l'hexène et des mélanges de ceux-ci.