

deasphalted oils require the use of dilution dewaxing solvents to facilitate handling reduced temperature conditions. When a dewaxing solvent is employed any of the well
25 suitable. For example, there may be used at least one member selected from alkane hydrocarbons having 2 to 10 carbon atoms in the molecule, such as ethane, propane, hexane and octane or mixtures thereof. Some of these hydrocarbons can also be refrigerative solvents e.g., propane and propylene. Ketones containing from 3 to 8 acetone, dimethyl ketone, methyl ethyl ketone, methyl propyl ketone and methyl is
30 mixtures thereof may also be used. Mixtures of the ketones with at least one member aromatic hydrocarbons such as benzene and toluene, e.g. methyl ethyl ketone/toluene ketone/toluene are also suitable. Halogenated hydrocarbons such as methyl chloride, and ethylene dichloride can also be used. Further, N-methylpyrrolidone and N-ethylp used as dewaxing solvents. Useful solvent combinations include mixtures of autorefrig
35 solvents, such as mixtures of acetone and propylene.

Any waxy hydrocarbon oil stock, petroleum oil stock or distillate fraction thereof employing dewaxing aids. Illustrative but nonlimiting examples of such stocks are (a) distillates have a boiling range within the broad range of from about 500 to 1300 °F (260 to 700 °C) stocks or deasphalted oils having an initial boiling point above about 800 °F (426.7 °C).
40 are the lubricating oil fraction or transformer oil fraction. Additionally, any of these hydrocracked prior to distilling, or deasphalting. These may come from any source of crudes obtained from Aramco, Kuwait, Panhandle, North Louisiana, etc., naphthenic crudes from Juana, Coastal crudes, etc., as well as the relatively heavy feedstocks such as bright stock having a range of 1050 + °F (565.6 + °C) and synthetic feedstocks derived from Athabasca tar sands
45 etc.

Well-known dewaxing aids are condensation polymers of chlorinated paraffins, polyalkylacrylates, polyalkylmethacrylates, alphaolefin copolymers, ethylene-vinyl acetate, fumarate-vinyl acetate copolymers, polyethylene-oxides, polyvinyl-pyrrolidones, polyisobutadienes, polystyrene-butadiene copolymers, alkali metal stearates, polyalkylene glycol
50 glycerides, etc. These dewaxing aids may be used either alone or in mixtures of two or more aids, typical examples of such mixtures being polyalkylmethacrylates and chlorinated paraffins condensation polymers; or polyalkylmethacrylates and ethylene-vinylacetate copolymers in various proportions. In order for these dewaxing aids to be efficient in that their use reduces fine particles produced and, thereby, the wax separation (filtration) rate is increased, the aids should have relatively high molecular weight and possess a broad distribution of molecular weight. De
55 molecular weights from 1,000 to approaching or exceeding 5,000,000, preferably 2,000 to 10,000, more preferably about 10,000 to 500,000, have been successfully employed. These aids are typically employed in an amount of active ingredient ranging from about 500 to 50,000 ppm

without dewaxing aid mixed therein, is introduced into the top of an elongated, stage
25 plurability of stages therein while maintaining a high degree of agitation in said stages to
achieve substantially instantaneous mixing of the solvent and wax/oil mixture as they pass
zone. The chilling rate in the mixing zone takes place at an average of about 2° F (1.1° C)
slurry comprising solid particles of wax and a dewaxed oil solution. The slurry exits at
some elevated temperature and is then passed optionally through a scraped surface heat exchanger
30 3,775,288) wherein it is further cooled down to the desired temperature for wax filtration. The
slurry is passed to a rotary drum wax filter to separate the solid particles of wax from the
solution. The use of dewaxing aids in such a system is contemplated.

In typical solvent dewaxing processes (including both autorefrigerative solvent systems and
liquid solvent systems) the dewaxing aid employed is left in the wax and is not recovered.
35 is so because the standard recovery techniques, e.g., distillation, are either uneconomical or
to the components employed. High temperatures degrade the dewaxing aid rendering it unusable for
recycle and re-use.

Failure to recover and recycle dewaxing aid, beyond involving the loss of such aid, the
expense of the continual addition of new aid, alters the nature and purity of the wax product
40 present in the wax and can impart color or other objectionable character to the wax product.

Any dewaxing process employing dewaxing aids may be improved by utilization of a
(preferably polysulfone membrane) separation process of the present invention. Dewaxing processes
commonly practiced are those utilizing dewaxing solvents.

45 Description of The Figures

Figure I presents the effect of polymer glass transition temperature on flux decline.

Figure II presents the effect of pressure on flux.

Figure III presents the effect of pressure on membrane compaction and accompanying

50 Figure IV presents the effect on the relation between pressure and flow exerted by the
substitutes.

Figure V presents the effect on the relation between pressure and flow exerted by the
element feed and permeate flows.

Figure VI presents a preferred embodiment of the present process.

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The Present Invention

By the practice of the instant invention, the dewaxing aid, rather than being discarded,

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55 50 45 40 35 Table I 28

MEMBRANE SELECTION

This Table shows that within a range of membrane materials, a choice of membrane can be attained and that proper choice of membrane operability of the process.

Feed: 600N + 5 wt% dewaxing aid (a 50/50 mixture of 1/1 DWA used on 34% active ingredient basis)

Membrane	Pore size μm	Flux (l) 1/m ² . d	% A. Permeate
Regenerated Cellulose	0.01 μm	30	<
Polycarbonate	0.2	125	<
Cellulose Acetate	0.1	280	<
Nylon	0.1	220	<
Polysulfone	0.1	300	<
Tranne ME	0.45	230	2

	Polysulfone	190	1.9 x 10
25	Polyethersulfone	>190 (220*)	0.4 x 10

30 *Chemical Engineering Science, Vol. 38, No. 1,
Table III lists the characteristics of a few
waxes.

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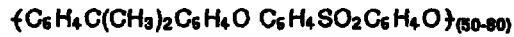
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(1) B.S. Bright Stock (2500N)

25 DWA = 1:1 Paraflo 149/Acryloid 150 (used on
received basis which contains about 35-40%
active ingredient).

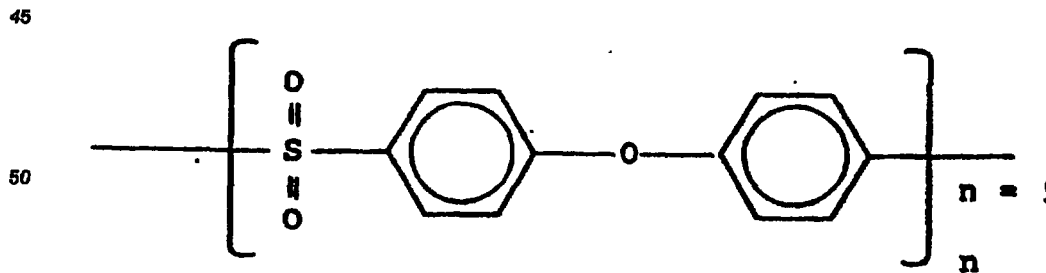
30 The membranes which have proven useful in the process of the present invention are available from commercial sources. Polysulfone and polyethersulfone membranes were secured from DuPont Chemicals Inc. The Nylon membranes from Pall Canada, Ltd. (the Ultipore series) and the acetate membranes from Schleicher and Schuell.

35 The polysulfone membranes of choice are prepared from polysulfone polymers made of the repeating unit:



40 and is special in that the phenylene units are linked by three different chemical groups: ether, sulfone, and sulfone.

The polyether sulfone polymer used to produce the polyethersulfone membrane (having a glass transition temperature above 190°C) is made of the repeating unit:



55 Elevated temperatures are needed to melt the wax into the liquid form, but too high a temperature should be avoided to insure that the membrane does not experience polymer creep which would reduce the flux.

Process operating (gauge) pressure is about 50 psig (344.8 kPa). Although low pressure is preferred.

As the velocity of the feed across the membrane surface increases, the flux is increased. However, there is a decrease in gel thickness on the membrane surface. Values above 4 GPM (15.14 liter/minute) result in very high pressure drops and destruction of the membrane/element package.

TABLE IV

EFFECT OF FEED FLOW RATE ON FLUX

	<u>Flow Rate,</u> <u>(GPM) liter/minute</u>	<u>Flux,</u> <u>($l/m^2 \cdot d$)</u>	<u>Waxing aid in Permeate</u>
	(0) 0	20	-
	(0.5) 1.89	163	<0.02
	(1.0) 3.79	235	<0.02
	(2.0) 7.57	302	<0.02
	(4.0) 15.14	235	<0.02

The above table is for Polysulfone membrane at 100° C and 50 psig (344.8 kPa gauge) pressure, 26" (66.04 cm) long element package, using 800N slack wax feed (see Table III).

As previously stated it is preferred to use the polysulfone membrane in the form of a spiral wound element. Spiral wound elements are described in US-A-3,417,870, US-A-3,173,876, US-A-3,386,583 and US-A-3,397,780 to name just a few. Spiral wound elements for use in a wax recovery process are fabricated from materials which are resistant to elevated temperatures, to the action of the wax and dewaxing aid, plus any dewaxing solvent and dewaxed oil which may be present. A spiral wound element therefore employs a central mandril-permeate tube made of metal or resistant plastic such as polycarbonate or nylon and an anti-telescoping device also of metal or resistant plastic such as nylon or polycarbonate. The fabrication of spiral wound elements employs various adhesives as to seal different membrane edges thereby defining permeate channels and feed-retentate channels. The adhesives used in fabricating the element are high temperature epoxies such as Fuller F-100. A feed channel is defined by a layer of permeate spacer material typically Simplex, (Dacron).

aid system) channel heights of up to 0.125 inch (3.175 mm) may be employed in pressure drop. In preparing spiral wound elements, permeate cloths, e.g., tricot
25 traditionally been used in water systems which have viscosities 1 cst at 25° C. Hot wax ranging between about 7.5-18 cS (7.5×10^{-6} to 18×10^{-6}) at the permeating temperature, preferably about 70-100° C. Thus, one would expect to see several times the resistance of a cloth.

Figure V shows that there is not much difference between a standard tricot (213) and a
30 thickness at typical flux levels (for hot wax) of 300 l/m².d. However, at higher flow rates, the resistance becomes larger. Therefore, in order to compensate for higher viscosities of waxy streams, a spiral wound element was shortened from about 40 inches (101.6 cm) to 20 inches (50.8 cm). The permeate cloth thickness doubled. Of course, by shortening the leaf length the number of elements increased from 4 to between 5 and 8.

35 Further, it has been discovered that in fabricating spiral wound elements the feed spacer does not extend the entire length of the feed/retentate channel in the elements. Elements with open feed channels have been found to exhibit superior flux to those elements wherein the feed spacer extends the entire length of the element. These open feed channels, however, do require a feed spacer material positioned at the forward edge of the membrane so as to define the
40 feed channel, when the membrane permeate spacer and feed spacer layers, described above, are wound into an element. The feed spacer material need be only wide enough to resist movement along the element length down the feed channel under the pressures and flow velocity of the feed in the element. This material can be held in place either by the friction created when the element is wound or by the use of an adhesive. The spacer material (as recited above) is thick enough to define
45 membrane layers and define feed channels.

For example, in a 26 inch (66.04 cm) long element, spacer material only 2 inches (5.08 cm) wide, positioned at the leading edge of the feed channel when the element was wound, was found to be sufficient to keep the membrane layers separated and define feed channels. Feed spacer material of a width between about 2-10%, preferably about 5-8%, of the overall element length, defined by the
50 and positioned at the feed inlet end of the elements are sufficient to produce elements with open feed channels. Feed spacer materials can be the PE-25 or other spacer materials previously described. Feed spacer materials at the leading edge of the feed channels, as well as materials such as small diameter inert rods positioned in the feed channels parallel to the direction of feed flow.

In an experiment Bright Stock Slack wax was combined with 0.3 wt.% dewaxing agent and
55 comprising a 1:1 mix of Parafflow 149/Acryloid 144 and used as a test feed. Three different element configurations employing polysulfone membrane were evaluated. The test runs were conducted at a temperature of 70° C. at a flow rate of 2 GPM (7.57 liter/minute) in a 4 inch (10.2 cm) diameter, 26 inch (66 cm) long element. The tests evaluated elements wherein the feed spacer material extended along the entire length of the element.

Figure VI is a schematic of an embodiment for the practice of dewaxing aid recovery. The various pumps and valves which would typically be employed in a process scheme to maintain adequate pressure as well as any insulation and heat sources to keep the wax in liquid form have been omitted from the figure since their placement and operation are within the capacity of those skilled in the art. Heated slack wax stream from the dewaxing operation via line 1 to a bank of polysulfone spiral wound elements (2A-2D) the number of such banks based on the total volume of slack wax to be ultrafiltered. In this description 4 elements are arbitrarily selected as exemplative. The first bank separates a major portion of the wax, the slack wax/dewaxing aid stream with the wax permeate being collected via line 3 and the filter aid retentate being sent for further processing via line 4. This residual retentate goes to a second bank of polysulfone spiral wound elements (5A-5C) wherein additional wax is separated as permeate (line 6) while retentate containing dewaxing aid and a much reduced level of wax goes for recycle to the dewaxing operation. Optionally a portion of this retentate stream can be sent to a third bank of elements for removal of additional wax. The number of banks of elements and the recycle is left to the discretion and judgment of the practitioner. The purified wax is collected via line 5 and 6 and combined and sent via line 9 to storage or further processing.

A typical concentration of aid in the slack wax stream is 0.3% which when processed by a membrane unit produces a wax stream being 95% of the original feed stream volume and an aid stream (of about 10% aid in wax) which is about 5% of the original feed stream volume.

Dewaxing aid was concentrated from a slack wax feed in the laboratory and in a plant. The results are shown in Table VI.

The laboratory results using a 600N slack wax feed containing aid (Parafflow/Acrylowax) at an equivalent feed filter rate, to the same system using fresh aid at essentially the same feed rate versus 21.2 m³/m²*d. This shows that there is essentially no difference between the two feed filter rate values the more potent the aid.

The plant results were obtained using 500 gallons (1892.7 liter) of membrane recovery at a concentration of 6.5% aid. This was tested both in the laboratory and in the plant. The process showed any change in potency. This was confirmed both using a testing apparatus (at the laboratory).

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Table VI
POTENCY OF RECOVERED AID

Test System	Lab	Lab
Feed to Membrane (1) Unit	None (STD)	600N + 0.3% Aid
Concentration of Aid, %	2.5 (fresh)	2.5 (recovered)
Feed Filter Rate m3/m2.d	21.2	22.9
Relative Feed Filter Rate	1.0	1.08
Potency, Remarks	Equal to Fresh Aid	Equal or Better Than Fresh

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Claims

- 30 1. A method for separating dewaxing aid from wax comprising contacting a selective membrane in spiral wound element form with a hot mixture of wax and dewaxing aid of between about 70 to 150° C and at a feed flow velocity through the element of about 0.1 to 1.0 ft/min and thereby selectively permeating said wax through the spiral wound membrane to produce a permeate rich in wax and a retentate rich in dewaxing aid, the membrane being made of polysulfone, nylon and cellulose acetate and spiral wound membrane element construction feed and retentate spacers made of polyester, nylon or inert material in the form of small diameter rods.
- 40 2. The method according to claim 1 wherein the feed- and retentate-spacer material is PE-25 and PE-15 which are polyester monofilament weaves of 25 and 15 strands per inch or Nylon 20 which is a nylon (polyamide) monofilament weave of 20 strands per inch.
- 45 3. The method according to claim 2 wherein the polyester feed-spacer material and the retentate-spacer material are each PE-25 having 23.9 strands per inch (9.4094 strands/cm) in its weave and each strand has a diameter of 350 μm (350 x 10⁻⁴cm), and wherein the material has a thickness of 780 μm (780 x 10⁻⁴cm) with 44.75% open area.
- 50 4. The method of any one of claims 1 to 3 wherein the polysulfone polymer making up the membrane has a glass transition temperature of about 140° C and higher.
- 55 5. The method of claims 4 wherein the polysulfone polymer making up the membrane has a glass transition temperature of about 190° C and higher.
6. The method of any one of claims 1 to 5 wherein the polysulfone membrane is about 0.001 to 0.01 inch thick and has an average pore diameter of about 500 to 2,000 Å (500 x 10⁻¹⁰m).
7. The method of any one of claims 1 to 6 wherein the hot dewaxing aid and wax mixture is contacted with the membrane in the spiral wound membrane element at a temperature of about 70 to 150° C.

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Claims

1. A method for separating dewaxing aid from wax comprising contacting a select
30 membrane in spiral wound element form with a hot mixture of wax and dewaxing aid
of between about 70 to 150 °C and at a feed flow velocity through the element of about
and thereby selectively permeating said wax through the spiral wound membrane el
permeate rich in wax and a retentate rich in dewaxing aid, the membrane being
polysulfone, nylon and cellulose acetate and spiral wound membrane element
35 construction feed and retentate spacers made of polyester, nylon or inert material in
or small diameter rods.
2. The method according to claim 1 wherein the feed- and retentate-spacer material is s
25 and PE-15 which are polyester monofilament weaves of 25 and 15 strands per 2.54
40 or Nylon 20 which is a nylon (polyamide) monofilament weave of 20 strands per 2.54 c
3. The method according to claim 2 wherein the polyester feed-spacer material and the
material are each PE-25 having 23.9 strands per inch (9.4094 strands/cm) in its wea
strand has a diameter of 350 μm ($350 \times 10^{-4}\text{cm}$), and wherein the material has a fr
45 780 μm ($780 \times 10^{-4}\text{cm}$) with 44.75% open area.
4. The method of any one of claims 1 to 3 wherein the polysulfone polymer making up th
a glass transition temperature of about 140 °C and higher.
- 50 5. The method of claims 4 wherein the polysulfone polymer making up the membr
transition temperature of about 190 °C and higher.
6. The method of any one of claims 1 to 5 wherein the polysulfone membrane is about
to 381 μm thick and has an average pore diameter of about 500 to 2,000 Å ($500 \times 10^{-10}\text{m}$).
55 10⁻¹⁰m).
7. The method of any one of claims 1 to 6 wherein the hot dewaxing aid and wax mix
with the membrane in the spiral wound membrane element at a temperature of about 7

1. Procédé de séparation d'adjuvant de déparaffinage d'avec de la cire, comprenant
 25 d'une membrane sélectivement perméable sous forme d'élément enroulé en spirale
 chaud de cire et d'adjuvant de déparaffinage, à une température comprise entre 70° C
 et à une vitesse d'écoulement de charge à travers l'élément d'environ 1 à 100 ml/min
 perméation sélective de ladite cire à travers l'élément de membrane enroulé en spirale
 perméat riche en cire et un rétentat riche en adjuvant de déparaffinage, la membrane
 30 parmi la polysulfone, le Nylon et l'acétate de cellulose, et l'élément de membrane enroulé
 utilisant dans sa construction des espaceurs de charge et de rétentat constitués de
 ou d'un matériau inerte sous la forme de bandes ou de tiges de faible diamètre.
2. Procédé selon la revendication 1, dans lequel le matériau espaceur de charge est
 35 parmi PE-25 et PE-15 qui sont des tissages monofilaments de polyester de 25 et 15
 mils, par 2,54 cm, ou le Nylon 20, qui est un tissage monofilament de Nylon (polyamide)
 par 2,54 cm.
3. Procédé selon la revendication 2, dans lequel le matériau espaceur de charge et le
 40 matériau espaceur de rétentat en polyester sont chacun un PE-25 comportant 25 brins
 (9,4094 brins/cm) dans son tissage, chaque brin ayant un diamètre de 350 μ m (35
 mils) et le matériau ayant une épaisseur de tissu de 780 μ m (780×10^{-4} cm) avec 44,75 % de
 rétentat.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le polymère
 45 constituant la membrane a une température de transition vitreuse d'environ 140° C et plus.
5. Procédé selon la revendication 4, dans lequel le polymère polysulfone constituant la
 membrane a une température de transition vitreuse d'environ 190° C et plus.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la membrane
 50 a une épaisseur d'environ 3 à 15 mils (76,2 à 381 μ m) et a un diamètre de pore moyen de
 2 000 Å (500×10^{-10} m à $2\,000 \times 10^{-10}$ m).
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'adjuvant
 55 chaud et le mélange à base de cire sont mis en contact avec la membrane enroulée en
 spirale, à une température d'environ 70 à 100° C.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'adjuvant

Ansprüche

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1. Verfahren zum Trennen von Entparaffinierungshilfsmittel von Paraffin, bei dem eine Membran in Form eines spiralartig gewundenen Elements mit einer heißen Mischung Entparaffinierungshilfsmittel bei einer Temperatur zwischen etwa 70 und 150 °C und einer Strömungsgeschwindigkeit durch das Element von etwa 1 bis 4 cm/s kontaktiert, das Paraffin selektiv durch das spiralartig gewundene Membranelement dringt, was einen Permeat und einem Entparaffinierungshilfsmittel reichen Retentat führt, wobei die Membran ausgewählt ist aus Polysulfon, Nylon und Cellulose-acetat und die Konstruktion des Membranelements Zufluß- und Retentatabstandhalter aus Polyester, Nylon oder in Form von Streifen oder Stäben mit kleinem Durchmesser aufweist.
2. Verfahren nach Anspruch 1, bei dem das Zufluß- und Retentat-Abstandhaltermaterial PE-25 und PE-15, die Polyester-Einzelfaser-Gewebe mit 25 bzw. 15 Strängen pro cm sind, Nylon 20, das ein Nylon (Polyamid)-Einzelfasergewebe mit 20 Strängen pro 2,54 cm ist.
3. Verfahren nach Anspruch 2, bei dem das Polyester-Zufluß-Abstandhaltermaterial PE-25 mit 9,4094 Strängen/cm (23,9 Stränge pro inch) ist, wobei jeder Strang einen Durchmesser von 350 µm (350×10^{-4} cm) hat, und eine Gewebedicke von 780 µm (780×10^{-4} cm) mit 44,75 % offener Fläche hat.
4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem das die Membran bildende Material eine Glasübergangstemperatur höher hat.
5. Verfahren nach Anspruch 4, bei dem das die Membran bildende Polysulfonpolymer eine Glasübergangstemperatur von etwa 190 °C und höher hat.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem die Polysulfonmembran etwa 0,001 bis 0,0038 cm (15 mils) dick ist und einen durchschnittlichen Porendurchmesser von etwa 500×10^{-10} m (500 bis 2000 Å) hat.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem die heiße Entparaffinierungsmischung mit der Membran in dem spiralartig gewundenen Membranelement bei einer Temperatur von 70 bis 100 °C kontaktiert wird.

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