(51) International Patent Classification ^{6} : C07C 17/38, 41/34, C07D 301/32, C07C 21/18, 19/08, 43/17, C07D 303/08, B01D 53/22	A1	(11) International Publication Number: WO 98/50331 (43) International Publication Date: 12 November 1998 (12.11.98)

(54) Title: CO$_2$ REMOVAL FROM FLUOROCARBONS BY SEMIPERMEABLE MEMBRANE

(57) Abstract

A process for removing carbon dioxide from a fluorocarbon carbon dioxide mixture in which the fluorocarbon carbon dioxide mixture is contacted with a semipermeable polyimide membrane to form at least one exit stream having an increased concentration of carbon dioxide and at least on exit stream having a reduced concentration of carbon dioxide.

TITLE
CO$_2$ Removal from Fluorocarbons by Semipermeable Membrane

Field of the Invention

5   This invention relates to a process for removing quantities of
carbon dioxide from fluorocarbons.

Background of the Invention

Conventional methods of manufacturing and purifying non-
10   chlorine-containing fluorocarbons typically result in a product containing at
least a small amount of undesired impurities. These fluorocarbons are
useful as refrigerants, blowing agents, cleaning agents and many other
applications. When any of these compounds are used as an etchant in
electronics applications, purity requirements are unusually high. Even trace
15   impurities can markedly affect the reject rate for miniaturized electronic
circuits or optical disks, in some cases affecting the reject rate a thousand-
fold. As a result, highly purified fluorocarbons used for such applications
typically require unusually stringent purification procedures and command a
premium market position and price. Two of the compounds so used are
20   trifluoromethane (HFC-23) and hexafluoroethane (FC-116).

It is known that HFC-23 can be made in a mixture with
chlorofluoromethanes by intensive fluorination of chloromethane
compounds under special conditions, or by disproportionation of
chlorodifluoromethane (HCFC-22). These reactions are costly to carry out
25   on a small scale because of the small volume of HFC-23 required, and the
reaction products require extensive purification to obtain a product of
sufficient purity for the etchant market.

It is also known that commercial processes to make the
important refrigerant chlorodifluoromethane (HCFC-22) on a large scale by
30   catalytic reaction of chloroform with HF typically also produce several
percent of HFC-23 as a byproduct. Depending on the size and design of the
plant, this HFC-23 can be vented to the atmosphere or recovered. The
environmentally desirable recovery of HFC-23 for sale to the etchant
market is costly because of the small percentage produced and the number
35   of impurities which must be removed.

It is also known that FC-116 can be made by similar catalytic
processes involving the reaction of HF or fluorine with perchloroethylene or

other two-carbon halocarbons. Again, these processes yield a product that
requires extensive purification for the etchant market.

Other fluorocarbons such as perfluoroepoxides are useful in
preparation of various fluoropolymers. One of the most important

5   perfluoroepoxides is hexafluoropropylene oxide, or HFPO, which is used to
make a variety of specialty fluorochemical polymers with complex
structures. The presence of small amounts of impurities interferes with
many of the subsequent processing steps, particularly in polymerization,
where low levels of impurities can have a serious limiting effect on

10   achieving the desired molecular weight polymer. Hexafluoropropylene
oxide (HFPO) is typically manufactured by oxidation of
hexafluoropropylene (HFP) using oxidizing agents such as hydrogen
peroxide, sodium hypochlorite, oxygen or ozone.

Most of the bulk impurities from the above reactions to make

15   HFC-23, FC-116 or HFPO can be readily removed from the desired
fluorocarbon by careful fractional distillation and/or scrubbing to remove
acids, followed by drying by passing through a silica gel bed. When HFPO
is manufactured by oxidation of HFP, HFP can be present in the stream to
be purified but would usually not be considered to be an impurity.

20   However, even after careful purification, these compounds typically contain
small amounts of carbon dioxide (CO_2). This may result from the presence
of CO_2 in the water used for scrubbing acidic impurities, as a byproduct of
the reaction, or from other sources. For generally non-reactive
fluorocarbons such as HFC-23 and FC-116, the amount of CO_2 can be

25   reduced by scrubbing the fluorocarbon with an excess of caustic solution
(relative to the CO_2), or by passing it through a fixed bed of soda-lime
pellets, also present in excess relative to the amount of CO_2. The reactions
involved are shown below:

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

30   $$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
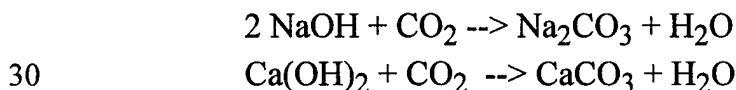
However it is difficult to achieve reliably low levels of CO_2
with either of these approaches because the needed excess of alkali results
in an alkali-alkali carbonate mixture, the composition of which must be
carefully and continually monitored for maximum effective removal of the

35   CO_2. That is, if the proportion of alkali carbonate in the resulting alkali-
alkali carbonate mixture becomes too high, the mixture becomes less
effective in removing CO_2, and the product no longer meets specifications
[a current goal is 50 parts per million (ppm) of CO_2 on a molecular or

volume basis, with a future goal of 10 ppm]. If the alkali-alkali carbonate mixture is replaced with fresh alkali while the proportion of alkali carbonate is too low, the cost of the operation becomes excessive. In addition, either -approach creates an alkali-alkali carbonate mixture which must be disposed

5   of. Furthermore, either of these steps introduces some water (from the scrubbing solution and/or as neutralization byproduct) into the dry fluorocarbon which must then be removed in an additional step.

For more reactive fluorocarbons such as HFPO, scrubbing with an alkali may give rise to unwanted side reactions and yield losses.

10   Processes have been proposed for removing trace quantities of impurities from etchant gases by contacting them at high temperatures with special Zr-V-Fe alloys as disclosed in EP 501 933 A2, or by contacting with hydrogenated Ni-NiO catalysts as disclosed in JP 06116180 A2, in order to react with and remove the impurities. These methods of treatment are

15   costly.

It is also known to carry out polymerizations of fluorinated monomers in media comprising CO_2. See, for example, U.S. Patent 5,674,957. Unreacted monomers from such processes are desirably recovered from mixtures with CO_2 for recycle to the polymerization

20   reaction.

There is a need for a process to remove low or trace quantities of CO_2 from fluorocarbons such as HFC-23, FC-116 or HFPO in a reliable manner without contacting them with other chemicals which can introduce water or other impurities and create waste disposal problems or problems in

25   polymerization for polymerizable monomers, or require costly alloy or catalyst reaction treatments.

Description of the Related Art

The use of semipermeable membranes to separate gases other than CO_2 and fluorocarbons is well known. Many of the separations

30   disclosed in the literature are based on polyimide membranes. For example, Kim et al., "Relationship between Gas Separation Properties and Chemical Structure in a Series of Aromatic Polyimides", Journal of Membrane Science, 37 (1988), 45-62, discloses various polyimide structures tested for a number of gas separations.

35   Many other such references describe polyimide structures for gas permeation. U.S. Patent 5,015,270 discloses a process for separation of gases using a polyimide membrane having phenylindane residues incorporated in the polyimide backbone chain. A preferred polyimide is

"MATRIMID" 5218 polyimide resin, made by Ciba-Geigy and based on
5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane. Examples to
demonstrate selectivity were made with common atmospheric gases (O_2,
N_2, CO_2, He).

5   U.S. Patent 5,085,676 discloses a process for preparing a
multicomponent membrane comprising a porous polymeric substrate and a
separating layer of various polyimide or other structures. Example 40
utilizes "MATRIMID" 5218 as the separating layer and "ULTEM" 1000, a
polyetherimide made by GE as substrate. Its selectivity was measured with
10   O_2/N_2 mixtures.

        U.S. Patent 5,042,992 discloses a novel class of polyimides
based on a partially fluorinated polyimide. It is said to be useful for making
semipermeable membranes which have a high permeability and acceptable
selectivity for CO_2 from mixtures of CO_2 and methane. The examples used
15   to determine selectivity were either made using pure CO_2 and methane, a
mixture of 30% CO_2 and 70% methane, or of 10% CO_2 and 90% methane.

        U.S. Patent 5,120,329 discloses a method for providing a
controlled atmosphere in a food storage facility using a semipermeable
membrane which has a higher permeability to CO_2 than to nitrogen. Typical
20   CO_2 levels are given as about 0 to 20%, with 2% CO_2 used as the dividing
line between low and high concentrations for various applications.
Polyimide membranes are cited as examples of suitable membranes for this
application.

        In an article by Schell et al, "Membranes can Efficiently
25   Separate CO_2 from Mixtures", Oil & Gas Journal, August 15, 1983, page
83, an example is given of removing low concentrations of CO_2 from a
refinery off-gas containing hydrogen by using a commercially available but
unspecified membrane that allows CO_2 to permeate more rapidly than
hydrogen. A two-stage membrane system was required to reduce the CO_2
30   concentration from 6% to 0.2% (60,000 ppm to 2000 ppm), with 50% of the
hydrogen still retained in the non-permeate stream.

        The problems inherent in removing low concentrations of
impurities by gas permeation techniques are discussed in some detail in the
Membrane Handbook, written by W. S. Winston Ho and K. K. Sirkar,
35   published by Van Nostrand Reinhold, 1992. On pages 22 and 23 of this
reference, it is noted that an externally applied field such as an electrical or
magnetic field may be used to provide an additional driving force across the
membrane for such cases, and states: "This makes it feasible to separate

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electrochemically gases that have a low feed concentration. Carbon dioxide, oxygen, and sulfur oxides have been separated in the laboratory by this technique." This laboratory method of removing low concentrations of CO_2 has the disadvantage of requiring special equipment which would be

5   expensive and not easily available on a commercial scale.

Summary of the Invention

In accordance with the invention, a process is provided for removing carbon dioxide from a fluorocarbon carbon dioxide mixture in which the fluorocarbon carbon dioxide mixture is contacted with a

10   semipermeable membrane to form at least one exit stream having an increased concentration of carbon dioxide and at least one exit stream having a reduced concentration of carbon dioxide.

In a preferred form of the invention, the fluorocarbon in the fluorocarbon carbon dioxide mixture consists essentially of non-chlorine

15   containing fluorocarbons. It is also preferred for the fluorocarbon to have at most one hydrogen atom. More preferably, the fluorocarbon carbon dioxide mixture contains a fluorocarbon selected from the group consisting of trifluoromethane (HFC-23), hexafluoroethane (FC-116), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), perfluoro(alkyl vinyl ethers) (PAVE)

20   wherein the alkyl group contains 1-3 carbon atoms, and hexafluoropropylene oxide (HFPO). A particularly preferred fluorocarbon is tetrafluoroethylene.

In a preferred form of the invention, the semipermeable membrane is a polyimide membrane having phenylindane residues

25   incorporated in the polyimide backbone chain. In another preferred mode, the semipermeable membrane is a polyaramid membrane.

The invention is advantageously used to remove low quantities of CO_2, i.e., less than 3 weight % carbon dioxide being present in the fluorocarbon carbon dioxide mixture. The invention is also advantageously

30   used to remove trace quantities of CO_2, i.e., less than 0.1 weight % carbon dioxide being present in the fluorocarbon carbon dioxide mixture.

In a preferred form of the invention, the exit stream with increased concentration of carbon dioxide contains less than about 10% by weight of the fluorocarbon present in the original fluorocarbon carbon

35   dioxide mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatical view of laboratory scale apparatus illustrating an embodiment of the present invention.

Figure 2 is a diagrammatical view of alternate laboratory scale apparatus illustrating an embodiment of the present invention.

DETAILED DESCRIPTION

In the context of the present invention, "fluorocarbon" means an
5   organic compound containing carbon and fluorine. Fluorocarbons in the
fluorocarbon carbon dioxide mixture for the practice of the present
invention may also contain hydrogen, oxygen and/or other halogens.
Preferably, the fluorocarbon consists essentially of non-chlorine containing
fluorocarbons. "Consisting essentially of non-chlorine containing
10   fluorocarbons" means that the chlorine content from chlorinated impurities
of the starting fluorocarbon carbon dioxide mixture is less than about
0.1 weight %. Preferably, in addition, the fluorocarbon contains at most one
hydrogen atom per molecule. More preferably, the fluorocarbon is selected
from the group consisting of trifluoromethane (HFC-23), hexafluoroethane
15   (FC-116), tetrafluoroethylene (TFE), hexafluoropropylene (HFP),
perfluoro(alkyl vinyl ethers) (PAVE) wherein the alkyl group contains 1-3
carbon atoms, and hexafluoropropylene oxide (HFPO). A particularly
preferred fluorocarbon is tetrafluoroethylene.

The fluorocarbon component of the fluorocarbon carbon dioxide
20   mixture from which CO_2 is removed by the process of the present invention
is comprised of at least one fluorocarbon compound. Thus, the
fluorocarbon component of the fluorocarbon carbon dioxide mixture can be
a mixture of fluorocarbon compounds. Such mixtures include, for example,
HFP/HFPO, TFE/HFP, TFE/PAVE, and TFE/HFP/PAVE. In the foregoing
25   mixtures, PAVE can be a single compound or a PAVE mixture, e.g., a
mixture of perfluoro(methyl vinyl ether) and perfluoro(propyl vinyl ether),
or, e.g., a mixture of perfluoro(ethyl vinyl ether) and perfluoro(propyl vinyl
ether). One skilled in the art will recognize that compounds other than
those defined above (chlorine-free, at most one hydrogen) can be present in
30   the mixture. Such other compounds can contain fluorine or can be fluorine-
free, and may or may not be separated from CO_2 by the process of the
present invention.

The invention is advantageously applied to process streams
which contain low quantities of CO_2. By "low quantities of CO_2" is meant
35   quantities below about 3 weight %. The invention is also advantageously
applied to process streams which contain trace quantities of CO_2. By "trace
quantities of CO_2" is meant quantities less than about 0.1 weight %, i.e.,
less than about 1000 parts per million (ppm) on a weight basis.

In the present process, the fluorocarbon gas containing CO_2 is contacted with a selected semipermeable membrane to form two exit streams, one of which is fluorocarbon depleted in CO_2 and the other is fluorocarbon enriched in CO_2. Usually, the reduced CO_2 stream is the

5   "non-permeate" stream, often called the "reject" stream, and does not pass through the membranes whereas the "permeate" stream passes through the membrane and has increased CO_2 content. Typically, the stream with reduced CO_2 content is recovered, i.e., shipped or sold in the form recovered, processed by contact with other semipermeable membranes, or

10   further processed by conventional means to achieve additional separation or recovery/removal of a desired component. The fluorocarbon enriched in CO_2 can be recycled to earlier stages in the purification process, subjected to further purification before recycling, blended with fluorocarbon used for less demanding markets, or disposed of by incineration or other means as

15   permitted by environmental regulations. The process of the invention can also be used to obtain purified fluorinated compounds from mixtures with CO_2 such as the TFE/CO_2 shipping mixture disclosed in U.S. Patent 5,345,013. Other components, organic or inorganic, may be present during the contacting step of the instant invention.

20   The membrane separation device useful in the present invention can be any such device as known in the art and may be in any shape which has a feed side and a permeate side. Included in this description are membranes which can be formed into films (with or without support), tubular devices, spiral wound devices, hollow fibers and the like.

25   The semipermeable membrane useful in the instant invention preferably is polyimide membrane or polyaramid membrane. Such membrane may be made of any polyimide or polyaramid material capable of preferentially passing the CO_2 relative to the fluorocarbon. That is, the ratio of permeation rates of the CO_2 to that of the fluorocarbon should be

30   greater than 1. Obviously, the higher the ratio, the more efficient will be the separation process.

                Polyimide membranes typically used in commercial use for conventional gas separations may be used. Preferably, the polyimide has phenylindane residues incorporated in the polyimide backbone chain. One

35   membrane of this type is "MATRIMID" 5218 polyimide resin, manufactured by Ciba-Geigy and based on 5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane. The membrane may be a composite of a porous substrate and the polyimide resin. For example, hollow fibers of "Ultem"

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1000, a polyetherimide made by General Electric, are a particularly suitable
support for "Matrimid" 5218. Such membranes and their manufacture are
described in U.S. Patent 5,085,676. Polyaramid membranes that can be
used include those of the types disclosed in U.S. Patent 5,085,774.

5   As in known permeation separation process, parameters which
are usually considered as variables to enhance the separation process are the
temperature, the pressure differential and pressure ratio between the feed
side of the membrane and the permeate side of the membrane, and the
residence time of the feed stream on the feed side of the membrane and the

10   residence time of the permeate on the permeate side of the membrane. In
the instant invention, these parameters may be varied to enhance the
separation so long as the values selected are not are not damaging to the
membrane material. Temperature can be any convenient temperature,
usually from about -50 to 150°C. The primary temperature limitations are

15   that the temperature should be below any temperature at which the
membrane is affected adversely and above the dew point of the
fluorocarbon. Preferably, the temperature range will be from about 0 to
about 75°C.

The pressure differential between the feed side of the membrane

20   and the permeate side is preferably at least about 0.1 atmosphere (10 kPa).
The process may be operated at a lesser pressure differential but the
separation process will be slower. The pressure differential can be the
result of higher pressure on the feed side of the semipermeable membrane
or the result of reduced pressure on the permeate side of the membrane or a

25   combination of both. Useful feed pressures can vary substantially with the
mode in which the membrane device is employed and with the materials
being separated. For hollow fiber membranes, for example, feed pressure
might be as high as 1000 psig (7 MPa) for feed to the outside of the fibers
(shell-side feed) but might be limited to 200-250 psig (1.5-1.8 MPa) for

30   bore-side feed. Additionally, choice of pressure should be consistent with
safe handling of the various streams.

The present process can be carried out as a batch process or as a
continuous process. Since this permeation separation process is a
differential process producing a substantial reduction in CO_2, multiple pass

35   or multiple stage processes may be the most efficient system to achieve very
high purity fluorocarbons. In such multiple stage arrangements, an output
stream from one stage can be fed to another stage either as the primary feed
to that other stage or as a recycle stream. The term "stage" as used in the

present application is intended to encompass a stage in which gases are fed
to a separate membrane separation devices or a pass in which gases are
returned to the same device. When low or trace levels of CO_2 are present,
removal to a few ppm can be achieved in a one or two stage process.

5   Preferably, at least about 50%, more preferably at least about 75%, by
weight of the CO_2 present is removed in each stage. The present invention
provides separation without the purchase and addition of extraneous
materials and without creating additional waste disposal problems.

Preferred processes in accordance with the invention can provide

10   low "losses" of the fluorocarbon. "Loss" is determined from the weight of
the fluorocarbon in the stream with increased carbon dioxide concentration
(usually the permeate stream) in relation to the weight of the fluorocarbon
present in the original fluorocarbon carbon dioxide mixture. Preferably, the
exit stream with increased concentration of carbon dioxide contains less

15   than about 10% by weight, more preferably less than about 5 percent, and
most preferably less than about 2%, of the fluorocarbon present in the
original fluorocarbon carbon dioxide mixture. The aforesaid low losses can
be achieved in multiple stage processes, but preferably are achieved in a
single stage.

20   The following examples are presented for illustrative purposes
only and in no way are intended to limit the present inventive process.

Example 1

This example illustrates the invention for removal CO_2 from a

25   mixture of HFC-23 and CO_2.

With reference to Figure 1 illustrating laboratory scale
apparatus 10 for carrying out the present invention, a 1 kg mixture of HFC-
23 containing 1.11 weight % CO_2 is placed in a pressure cylinder 12 at
25°C and about 200 psig (1400 kPa) . The pressure cylinder 12 is

30   connected to a flow meter 14 and then to a hot water heated coil 16 to adjust
the temperature of the HFC-23 mixture. After leaving the coil 16, the gases
enter the inlet side of a permeation separator 18 with a commercial
polyimide membrane in the form of 360 hollow fibers 73 cm long having
outside diameter of 160 μm and bore diameter of 90 μm. The membrane

35   used is Ciba Geigy's "MATRIMID" 5218 polyimide skin covering a bulk
porous fiber wall made of General Electric's "ULTEM" 1000. The
permeate gas is fed via line 20 to a flowmeter 22 and vacuum pump 24 to
collection cylinder 26. The non-permeate gas or product is fed via line 28

to a flowmeter 30 and to a vacuum pump 32 for recycling back to the line from feed cylinder 12. Thus, the feed concentration changes from the original value of 1.11 weight % CO_2 to very low values during the course of the test, permitting us to evaluate the separation system under a variety of

5   inlet feed concentrations. Under conditions of the test, the feed pressure into the permeator is initially about 120 psig (930 kPa) and the pressure at the non-permeate discharge is about 110 psig (860 kPa). While these pressures drop slightly during the course of the test, the pressure differential of 10 psig (170 kPa) is maintained throughout the test. The permeate

10   pressure at the vacuum pump is maintained at about 0.5 psia (3 kPa) during the test. However, when drawing off permeate samples, the vacuum pump is turned off for a few minutes, allowing pressure to build up to about 5 psia (35 kPa) to permit a sample to be taken, after which the test is resumed under the original 0.5 psia (3 kPa) pressure.

15   Permeate sample analyses are checked against the calculated values obtained by mass balance calculations from flow measurements and the analyses of feed and non-permeate analyses as shown in Figure 2, and found to be in reasonably good agreement. The permeate concentrations found by analysis are all slightly lower than the mass balance values,

20   perhaps because of the momentarily higher permeate pressures during sampling. Samples are analyzed by gas chromatograph using a POREPAK-T column. Flowrates are measured with a Hastings transducer, with results corrected to standard temperature and pressure (STP) for the specific gases uses.

25   In Table 1 below, flowrates are given in liters/minute at STP, and concentrations of CO_2 in HFC-23 given in parts per million (ppm) by volume. The CO_2 concentrations given for the permeate gas are those calculated from the mass balance data, since permeate samples are not taken every time period.

30

TABLE 1

Time Hrs.	Flowrates (Liter/min.)			Feed Pressure kPa	CO₂ Concentr. (ppm by vol.)		
	Feed	Perm.	Non-Perm.		Feed	Permeate	Product
0.50	1.066	0.292	0.763	930	17,517	63,941	16.4
1.50	1.066	0.268	0.736	930	16,338	64,964	21.3
2.25	1.244	0.259	0.899	930	14,249	68,265	59.2
3.25	1.244	0.246	0.954	930	11,431	57,524	79.6
5.75	1.096	0.208	0.872	930	7,000	36,749	35.0
7.00	0.859	0.213	0.681	930	4,322	17,378	16.4
10.25	1.155	0.155	0.954	840	2,218	16,351	30.6
11.50	1.096	0.143	0.899	805	1,530	11,521	33.5
12.25	0.770	0.130	0.627	710	1,049	6,171	9.1
14.25	0.710	0.115	0.627	680	714	4,401	2.3
14.75	0.710	0.111	0.627	620	589	3,681	16.2
17.50	0.651	0.091	0.627	600	483	3,388	10.3
18.25	0.651	0.081	0.627	565	261	2,082	2.3
19.00	0.533	0.080	0.517	570	126	830	1.4
21.00	0.533	0.068	0.517	495	105	816	1.0

Although there is some variation in results for individual time
periods, the general results may be divided into clear groups, as shown by
5   the horizontal lines in the table above. When the initial concentration of
CO_2 in the HFC-23 range from about 11,400 to 17,500 ppm by volume
(7,200 to 11,100 ppm by weight), the purified product (the non-permeate)
has a CO_2 content ranging from only 16 to 80 ppm by volume (10 to 50
ppm by weight). With a feed concentration of 1,100 to 7,000 ppm CO_2 by
10   volume in HFC-23 (600 to 4,400 ppm by weight), the purified product has a
CO_2 content ranging from 9 to 35 ppm by volume (6 to 22 ppm by weight).
With a feed concentration of 110 to 710 ppm CO_2 by volume in HFC-23
(70 to 400 ppm by weight), the purified product has a CO_2 content ranging
from 1 to 16 ppm by volume (0.6 to 10 ppm by weight).
15   The above results show that HFC-23 with a CO_2 content of up to
about 1.2 weight % can be reduced in CO_2 content to a few ppm by one or
two passes through a polyimide membrane separator, depending in part on
the size/residence time of the separators, the exact process conditions, the
desired recovery rate for HFC-23, and the future treatment of the permeate
20   gas (HFC-23 with a high percent of CO_2).

Example 2

This example illustrates removing CO_2 from a mixture of HFPO and CO_2.

5   As illustrated in Figure 2, apparatus 10a is the apparatus of Example 1 but modified by adding separate feed cylinders 12a and 12b and feed lines controlled by flowmeters 14a and 14b for each of the two components, CO_2 and HFPO respectively. A packed cylinder 15 is also added for thorough mixing. After calibration, the mass flow units are set to

10   give an combined composition of 1.2 weight % of CO_2 in a mixture with HFPO. As in Example 1, the mixture of gases is connected to the inlet side of the same permeation separator 18. The permeate CO_2 gas is captured by direct reaction with NH_3 in cylinder 26. The non-permeate HFPO product is captured by dry ice condensation in cylinder 34 which is added in place

15   of the recycle of the apparatus of Figure 1. The test is conducted for 3.5 hours. For the first 10 minutes, a feed pressure of 100 psig (700 kPa) is used, but some signs of HFPO condensation and erratic flow are noted. This is eliminated by dropping the feed pressure to 90 psig (620 kPa) and adding supplemental HFPO heating.

20   Weight changes on the feed tanks, corrected for the amount of material required to fill the system, showed a total feed of 298.0 g of HFPO and 5.0 gm of CO_2, for an average feed composition of 1.6 weight % CO_2. The permeate captured is 2.6 g, and the non-permeate captured is 290.0 g, for an overall mass balance (feed vs recovery) of 96.6%. Colorimetric tests

25   are carried out on the products, based on the observation that the CO_2/NH_3 reaction product stays water clear with time, while the HFPO/NH_3 reaction product darkens in minutes to faint yellow, and then to dark yellow, red/orange and eventually black over a 24 hour period. These tests indicate that the permeate is essentially all CO_2, with less than 1% HFPO, and that

30   the non-permeate is HFPO with about 0.8 weight % CO_2, about a 50% reduction. Direct infra-red measurements indicate that the CO_2 content of the non-permeate is below 0.1 weight %, an even greater reduction in CO_2 content.

35   **Example 3**

This example illustrates removing CO_2 from a mixture of HFPO and CO_2 using collection of the permeate by liquid nitrogen condensation.

The apparatus used in Example 2 is modified to collect the permeate in cylinder 26 by liquid nitrogen condensation, enabling the permeate side of the membrane to operate under vacuum. Improved results are noted compared to Example 2, presumably due to operation under

5   reduced pressure. The CO_2 in the feed is estimated to be about 3.0 weight %. The CO_2 in the permeate is again estimated at above 99 weight %. By colorimetric analysis, the CO_2 in the non-permeate product is estimated at about 0.6 weight %, for an approximate 80% reduction in CO_2 content with negligible HFPO loss. Direct infra-red measurements indicates that the

10   CO_2 content of the non-permeate is below 0.1 weight %, an even greater reduction in CO_2 content.

Example 4

A permeator similar to that of Example 1 except that fiber length

15   is 41 cm is used to separate a mixture of 48 wt% TFE and 52 wt% CO_2 at $23°±2°C$. The experimental arrangement differs from that shown in Figure 1. With reference to Figure 1, the TFE/CO_2 source 12 is a cylinder initially charged with 3800 g of the gas mixture at 420 psig (3.0 MPa) and recharged only as necessary. The cylinder is equipped with a pressure

20   regulator set to deliver the feed gas at 60 psig (0.52 MPa). A GC sample is taken between the mass flow meter 14 and the permeator 18. The heated coil 16 is not used. On the reject (i.e., non-permeate) side, the exit pressure is controlled by a throttle valve to create a range of feed-side pressure differences, Δp. The reject stream passes through volumetric flow meter 30

25   to atmospheric pressure. Vacuum pump 32 and the recycle line to the feed cylinder 12 are not used. On the permeate side, the permeate passes through volumetric flow meter 22 to atmospheric pressure. Vacuum pump 24 collection cylinder 26 are not used. GC samples are taken in both the permeate and reject streams upstream from the flow meters. The combined

30   flow and GC measurements lead to a good mass balance, enhancing confidence in the flow and GC data. Flow rate and compositional data summarized in Table 2 show that a TFE/CO_2 stream rich in CO_2 can be separated effectively with a polyimide membrane. "Loss" is the fraction (%) of total TFE flow that is in the permeate stream. There is no evidence

35   of reaction between the membrane and the highly reactive TFE. I.e., there is no evidence of attack of the membrane by the TFE, and no evidence of TFE polymerization which is known in CO_2 media (no initiation by the membrane).

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Table 2. Separation of TFE and CO_2 with Polyimide Membrane

Δp		TFE in Reject Stream		TFE in Permeate Stream	
(psi)	(kPa)	Rate (g/min)	Purity (wt%)	Rate (g/min)	Loss (%)
59.0	407	8.604	60.0	0.0520	0.60
25.0	172	5.233	71.4	0.0786	1.48
12.8	88	3.912	82.7	0.0967	2.41
5.6	39	1.977	91.2	0.1046	5.02
2.7	19	0.960	95.8	0.1225	11.3
1.1	8	0.334	98.5	0.1204	26.5

5 **Example 5**

The procedure of Example 4 is essentially repeated, except that a permeator made with polyaramid hollow fibers is used and feed pressure values of 100 and 145 psig (0.79 and 1.10 MPa) are tested in addition to 60 psig. The fiber membranes are made generally according to

10 Examples 9-12 of U.S. Patent 5,085,774 and the permeator incorporates 200 such fibers 73 cm long having outside diameter of 200 μm and bore diameter of 80 μm. Flow rate and compositional data summarized in Tables 3-5 show that a TFE/CO_2 stream rich in CO_2 can be separated effectively with a polyaramid membrane. Note, in comparison with

15 Example 4, that polyaramid provides less "loss" at a given purity but has lower productivity despite higher membrane area. However, productivity can be enhanced by increased feed pressure without significant impact on loss. There is no evidence of reaction between the membrane and the highly reactive TFE. I.e., there is no evidence of attack of the membrane by

20 the TFE, and no evidence of TFE polymerization which is known in CO_2 media (no initiation by the membrane).

Table 3. TFE/CO$_2$ Separation at 60 psig with Polyaramid Membrane

Δp		TFE in Reject Stream		TFE in Permeate Stream	
(psi)	(kPa)	Rate (g/min)	Purity (wt%)	Rate (g/min)	Loss (%)
4.8	33	0.3409	56.0	0.00068	0.20
2.8	19	0.2140	60.7	0.00071	0.33
1.8	12	0.1440	66.0	0.00069	0.48
1.0	7	0.0937	78.9	0.00079	0.83
0.5	3	0.0559	85.5	0.00073	1.29

5   ### Table 4. TFE/CO$_2$ Separation at 100 psig with Polyaramid Membrane

Δp		TFE in Reject Stream		TFE in Permeate Stream	
(psi)	(kPa)	Rate (g/min)	Purity (wt%)	Rate (g/min)	Loss (%)
4.9	34	0.5435	58.1	0.00110	0.20
3.7	23	0.4318	60.5	0.00112	0.26
2.7	19	0.3358	63.6	0.00120	0.36
1.8	12	0.2532	69.7	0.00123	0.48
0.8	6	0.1398	82.1	0.00137	0.97
0.5	3	0.0972	90.2	0.00149	1.51

Table 5. TFE/CO$_2$ Separation at 145 psig with Polyaramid Membrane

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Δp		TFE in Reject Stream		TFE in Permeate Stream	
(psi)	(kPa)	Rate (g/min)	Purity (wt%)	Rate (g/min)	Loss (%)
5.1	35	0.8438	59.9	0.00192	0.23
4.2	29	0.7101	62.2	0.00196	0.27
3.2	22	0.5777	65.7	0.00196	0.34
2.0	14	0.4086	72.9	0.00210	0.51
1.0	7	0.2393	84.0	0.00233	0.96
0.5	3	0.1509	89.8	0.00227	1.49

Example 6

This example illustrates separation of TFE and CO$_2$ using a two-
15   stage permeator setup. Two permeators similar to that described in

Example 4 are arranged in series, with the reject stream from the first permeator being the feed stream to the second permeator. Feed pressures p_1 to stage 1 of 60, 100 and 140 psig (0.52, 0.79, and 1.07 MPa) are tested at various total Δp with Δp regulated so that $\Delta p_1 = 2\Delta p_2$, wherein the

5   subscripts identify the stage. Tables 6 and 7 show data for total Δp of 6 and 12 psi (41 and 83 kPa). Note that total "loss" can be limited to first-stage "loss" by recycling second-stage permeate with appropriate pressure increase to the first-stage feed, which is especially convenient when the second-stage permeate composition is close to that of the first-stage feed.

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Table 6. Data for Stage 1 of Example 6

p_1 (MPa)	Δp_1 (kPa)	TFE in Reject Stream Rate (g/min)	Purity (wt%)	TFE in Permeate Stream Rate (g/min)	Loss (%)
0.52	27.6	1.078	87.2	0.0333	2.99
0.52	55.2	2.073	75.1	0.0350	1.66
0.79	27.6	2.121	88.9	0.0678	3.10
0.79	55.2	3.563	78.0	0.0544	1.50
1.07	27.6	2.082	94.7	0.1256	5.69
1.07	55.2	4.778	82.4	0.1043	2.14

15   ## Table 7. Data for Stage 2 of Example 6

p_2 (MPa)	Δp_2 (kPa)	Stream TFE Purity (wt%) Reject	Permeate	TFE in Permeate Stream Rate (g/min)	Loss (%)
0.49	13.8	89.3	22.5	0.0072	0.67
0.46	27.6	81.4	4.2	0.0063	0.30
0.77	13.8	92.6	18.0	0.0152	0.71
0.74	27.6	85.3	3.7	0.0127	0.36
1.04	13.8	95.9	45.2	0.0248	1.19
1.01	27.6	90.1	5.7	0.0248	0.53

Example 7

The experimental arrangement of Example 6 is used to generate

20   a feed stream to the second-stage permeator that is low in CO_2. This is done by feeding a TFE/CO_2 mixture containing 50.3 wt% of CO_2 to the first stage at 180 psig (1.34 MPa), using low Δp_1 of 1.0 and 0.8 psi (6.9 and 5.5 kPa),

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and using reduced pressure (partial vacuum) on the permeate side of the first stage permeator. The resulting streams containing 2.96 and 1.14 wt% of CO_2, respectively, are processed through the second-stage permeator at Δp_2 of 0.5 psi (3.4 kPa). Data in Table 8 show that the process of this

5   invention can be used effectively to separate TFE and CO_2 even when the CO_2 concentration is low to obtain TFE of even higher purity.

Table 8. Polyimide Membrane at Low CO_2 Concentration (Example 7)

CO_2 Conc. (wt%)		TFE Rate (g/min)		CO_2 Rate (g/min)		Removed
Feed	Reject	Feed	Reject	Feed	Reject	CO_2 (%)
2.96	1.03	1.589	1.582	0.0485	0.0165	66.0
1.14	0.58	1.172	1.148	0.0135	0.0067	50.4

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Claims

1. A process for removing carbon dioxide from a fluorocarbon carbon dioxide mixture comprising contacting said fluorocarbon carbon dioxide mixture with a semipermeable polyimide membrane to form at least

5   one exit stream having an increased concentration of carbon dioxide and at least one exit stream having a reduced concentration of carbon dioxide.

2. The process of claim 1 wherein said fluorocarbon of said fluorocarbon carbon dioxide mixture consists essentially of non-chlorine containing fluorocarbons.

10   3. The process of claim 1 wherein said fluorocarbon has at most one carbon atom.

4. The process of Claim 1 wherein said fluorocarbon carbon dioxide mixture comprises a fluorocarbon selected from the group consisting of trifluoromethane (HFC-23), hexafluoroethane (FC-116),

15   tetrafluoroethylene, hexafluoropropylene, perfluoro(alkyl vinyl ethers) wherein the alkyl group contains 1-3 carbon atoms, and hexafluoropropylene oxide (HFPO).

5. The process of claim 1 wherein said fluorocarbon is tetrafluoroethylene.

20   6. The process of claim 1 wherein said semipermeable membrane is a membrane selected from the group consisting of polyimide membranes and polyaramid membranes.

7. The process of Claim 1 in which the semipermeable membrane is a polyimide membrane having phenylindane residues

25   incorporated in the polyimide backbone chain.

8. The process of claim 1 wherein less than 3 weight % carbon dioxide is present in said fluorocarbon carbon dioxide mixture.

9. The process of claim 1 wherein less than 0.1 weight % carbon dioxide is present in said fluorocarbon carbon dioxide mixture.

30   10. The process of claim 1 wherein said process is performed in one or more stages and at least 50% of said CO_2 present is removed in a stage.

11. The process of claim 1 wherein said exit stream with increased concentration of carbon dioxide contain less than about 10% by

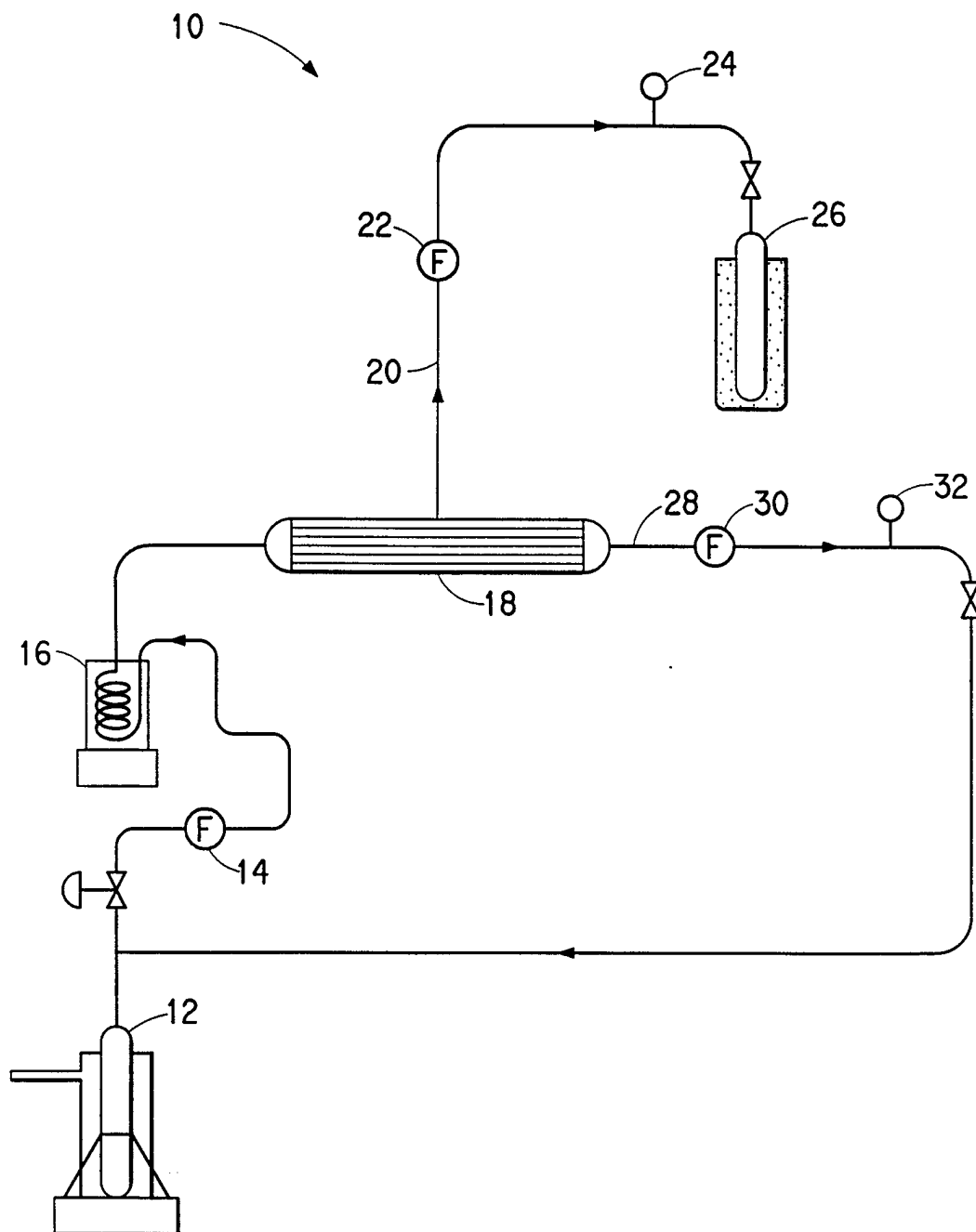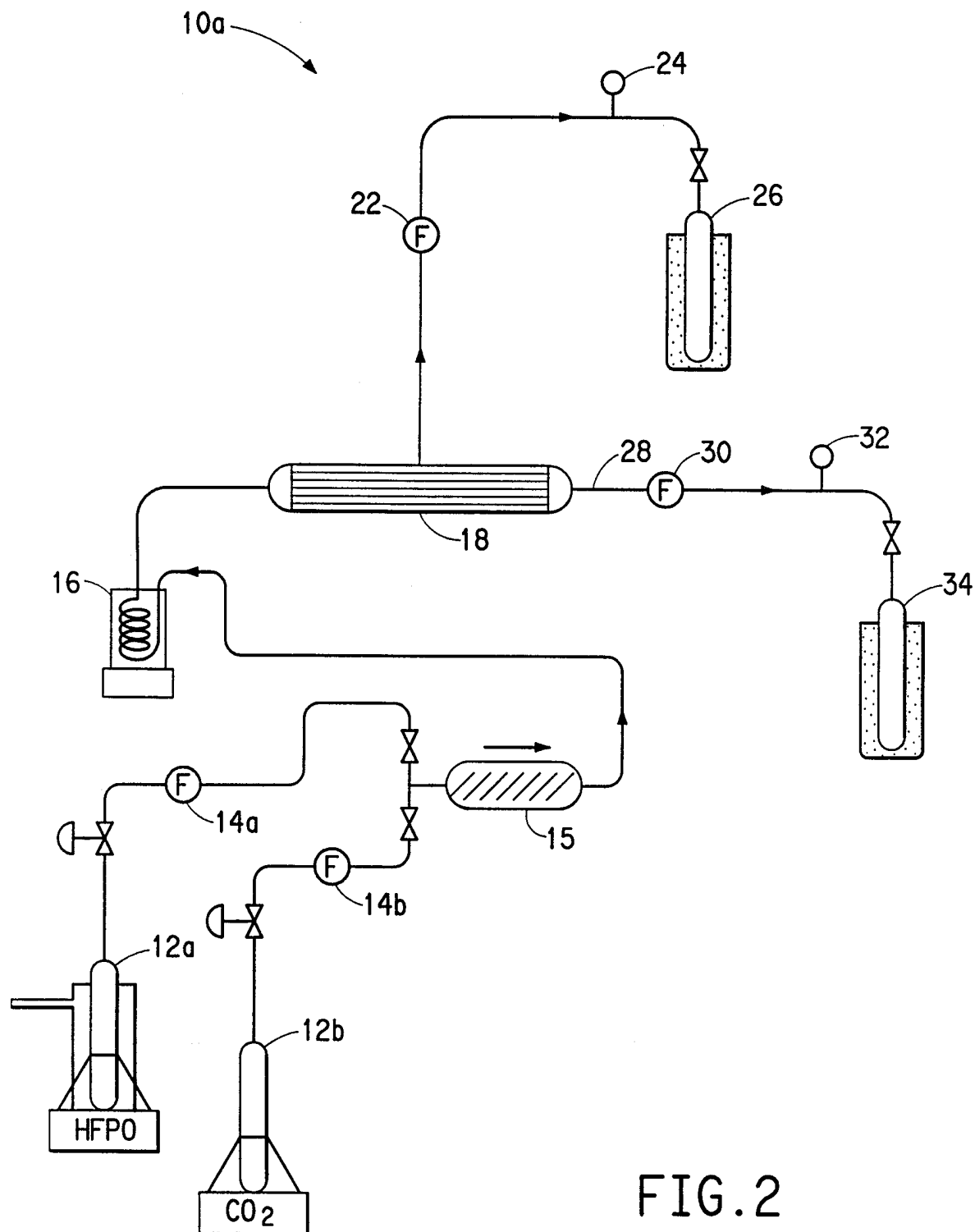35   weight of the fluorocarbon present in said original fluorocarbon carbon dioxide mixture.

12. The process of claim 1 wherein said exit stream with increased concentration of carbon dioxide contain less than about 5% by

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weight of the fluorocarbon present in said original fluorocarbon carbon dioxide mixture.

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FIG.1

FIG.2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C17/38   C07C41/34   C07D301/32   C07C21/18   C07C19/08
         C07C43/17   C07D303/08   B01D53/22

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 6   C07C   C07D   B01D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 373 683 A (SHELL INT RESEARCH) 20 June 1990 -----	1-12

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

Date of the actual completion of the international search	Date of mailing of the international search report
20 July 1998	29/07/1998

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