#### (19) World Intellectual Property Organization

International Bureau



## 

(43) International Publication Date 26 May 2005 (26.05.2005)

PCT

#### (10) International Publication Number WO 2005/046835 A1

B01D 19/00 (51) International Patent Classification<sup>7</sup>:

(21) International Application Number:

PCT/US2004/037306

(22) International Filing Date:

5 November 2004 (05.11.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10/702,013

5 November 2003 (05.11.2003)

(71) Applicant (for all designated States except US): SYSTEC, INC. [US/US]; 213 Old Highway 8, New Brighton, MN 55112 (US).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): GURNER, Yuri [US/US]; 2086 Timmy Street, Mendota Heights, MN 55120 (US). SIMS, Carl, W. [US/US]; 1136 Colette Place, St. Paul, MN 55116 (US). THIELEN, Thomas [US/US]; 12120- 53rd Avenue North, Plymouth, MN 55422 (US).
- (74) Agent: BURNS, Mark, J.; Haugen Law Firm PLLP, 121 South Eighth Street, Suite 1130, Minneapolis, MN 55402 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,

KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,

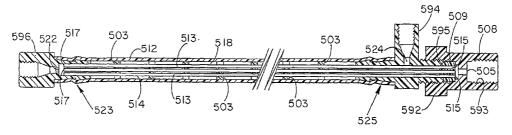
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### **Declarations under Rule 4.17:**

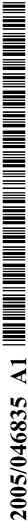
- as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GO, GW, ML, MR, NE, SN, TD, TG)
- as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE,

[Continued on next page]

(54) Title: AXIAL TRANSFER DEGASSING



(57) Abstract: An elongated flow-through degassing apparatus includes an elongated gas and liquid impermeable outer tube (512) and one or more gas-permeable, liquid-impermeable elongated inner tubes (514) extending within the outer tube (512) and at least partially through a chamber (518) defined within the outer tube (512). The apparatus also includes inlet (594) and outlet (596) connection structures operably coupled to respective portions of the outer tube (512) and the inner tubes (514) to further enable a sealed engagement between the outer tube (512) and the inner tubes (514), and to provide for connection devices to operably couple the degassing apparatus of the present invention to respective spaced apart components. The degassing apparatus is sufficiently flexible so as to be readily manipulatable into desired configurations.





#### WO 2005/046835 A1

DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,

LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

#### **Published:**

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/046835 PCT/US2004/037306

# AXIAL TRANSFER LINE DEGASSING Field of the Invention

The present invention relates generally to systems for degassing fluids utilized in a wide variety of applications, including the degassing of chromatographic fluids, inks, semiconductor processing fluids, beverages, and laboratory-grade fluids, and more particularly to a flow-through transfer line degassing apparatus wherein transfer lines extending between respective components in systems incorporating such an apparatus simultaneously act to operably degas fluids passing therethrough.

## Background of the Invention

15

20

25

30

There are many chemical applications, particularly analytical applications involving the use of liquid solvents, reactants or the like in which the presence of dissolved gases, and particularly air, is undesirable. prime example of such an application relates to the fluids utilized in liquid chromatography where the presence of even small amounts of dissolved gases interferes with the accuracy and sensitivity of the results obtained. example, air dissolved in the mobile phase can manifest itself in the form of bubbles which causes noise and drift as the mobile phase passes through the chromatographic In situations where the dissolved gases are detector. chemically active, unwanted modifications or deterioration in the chromatographic fluids can occur. Therefore, it is desirable to remove such species through a degassing process.

The degassing of liquid materials has been necessary to the success of many processes, and, consequently, various degassing methods have been employed for some time. Techniques have included heating or boiling the fluid to be degassed, exposing the material to a reduced pressure environment or vacuum, and using combination of heat and vacuum to reduce the amount of dissolved gases in the fluid. Ultrasonic energy has also been employed for such degassing purposes. As conventionally applied, however, these traditional techniques have generally fallen short of the desired degree of separation efficiency.

Vacuum degassing through a membrane apparatus has long been known, and generally utilizes a length of relatively small diameter, thin-walled, semi-permeable synthetic polymer resin material contained within an enclosed chamber held under a reduced pressure or vacuum in which the fluid to be degassed is caused to flow through the tube. One such apparatus is shown by Sims in U.S. Patent No. 5,340,384, assigned to the same Assignee as in the present invention. Other such devices are shown in U.S. Patent Nos. 5,183,486; 4,430,098; and 3,668,837.

10

15

20

25

30

While each of these devices employ a vacuum degassing approach, there remains a need, particularly with devices associated with liquid chromatography instruments, provide a fluid degassing capability in fluid transfer lines respective components of such operably coupling chromatographic instruments. In conventional degassing systems, chromatographic fluids are routed into a distinct vacuum chamber for performing the degassing function In such a manner, a separate and distinct thereat. component must be incorporated into the chromatographic instrument assembly. Moreover, fluid transfer lines must be routed from respective fluid reservoirs to a distinct vacuum chamber prior to such fluid flow through the chromatographic instruments.

WO 2005/046835 PCT/US2004/037306

It is therefore a principle object of the present invention to provide fluid transfer lines as axially-disposed individual degassing chambers.

It is another object of the present invention to provide chromatographic fluid transfer lines which are operably coupled to vacuum sources so as to enable vacuum-type degassing upon the fluids passing therethrough.

It is a yet further object of the present invention to provide an elongated flow-through vacuum degassing apparatus having an outer impermeable tube and one or more semi-permeable inner tubes disposed therewithin, with fluids passing either through or around the inner semi-permeable tubes in a relatively low-pressure environment between the outer tube and the inner tubes so as to effect a vacuum degassing characteristic upon the semi-permeable inner tubes.

10

15

20

25

30

It is a still further object of the present invention to provide an elongated flow-through transfer line vacuum degassing apparatus having an outer tube and one or more inner tubes disposed therewithin, and wherein the inner tubes are formed solely from an amorphous perfluorinated copolymer material.

It is another object of the present invention to provide an elongated transfer line vacuum degassing apparatus that is sufficiently flexible so as to be readily manipulatable into desired configurations.

It is a further object of the present invention to provide a transfer line fluid degassing apparatus having an outer impermeable tube and one or more semi-permeable inner tubes disposed therewithin, and wherein the one or more inner tubes are formed solely from amorphous perfluorinated copolymers.

It is another object of the present invention to provide a transfer line apparatus having an outer impermeable tube and one or more semi-permeable inner tubes disposed therewithin, with the transfer line apparatus preventing regassing of fluids passing therethrough.

## Summary of the Invention

By means of the present invention, fluids may be operably degassed in distinct transfer lines extending between respective components in an associated fluid flow system. The transfer lines of the present invention are preferably configured as axially-disposed individual degassing units having an elongated outer tube fabricated from liquid and gas impermeable material, and one or more semi-permeable inner tubes disposed therewithin. The outer and inner tubes, in combination, are preferably sufficiently flexible so as to be readily manipulatable into desired configurations.

10

15

20

25

30

In a particular embodiment of the present invention, the elongated flow-through fluid treatment apparatus includes an elongated outer tube that is gas and liquid impermeable, and has an inlet end, an outlet end, and a vacuum source coupling aperture formed in a side wall thereof. The degassing apparatus further includes an elongated inner tube extending within the outer tube, with the inner tube being formed of a gas-permeable, liquid-impermeable polymeric material, and which has an inlet portion and an outlet portion corresponding to the inlet and outlet ends of the outer tube. In addition, a vacuum source adaptor extends from the side wall of the outer tube and coextensively with the vacuum source coupling aperture such that a hollow channel extending through the vacuum source

adaptor provides for fluid connection from a space defined between the outer tube and the inner tube to locations external to the vacuum source adaptor. The apparatus of the present invention further includes an inlet connection apparatus operably coupled to the inlet end of the outer tube and the inlet portion of the inner tube, and an outlet connection apparatus operably coupled to the outlet end of the outer tube and the outlet portion of the inner tube. The apparatus is preferably sufficiently flexible so as to be readily manipulatable into desired configurations. The inner tube is preferably fabricated from an amorphous perfluorinated copolymer material, while the outer tube is selected from the group consisting of Tefzel®, FEP, PEEK and the like.

10

15

20

25

30

Another embodiment of the invention provides for a method for treating a fluid involving a transfer line apparatus having an outer tube defining a first chamber that includes a length, an inlet, and an outlet, with the outer tube being substantially gas and liquid impermeable. apparatus further includes one or more inner tubes extending within the outer tube and at least partially through the first chamber, with the one or more inner tubes each being formed solely of a gas-permeable, liquid-impermeable material. Each of the one or more inner tubes have an open end and a substantially opposed closed end. The method further provides for operably coupling the open end of each of the one or more inner tubes into communication with a vacuum source so as to substantially evacuate respective second chambers that are defined within the one or more inner tubes. The fluid is transported through the first chamber from the inlet through the outlet so as to effect a 15

25

30

vacuum degassing or regassing prevention operation on the fluid.

In a still further aspect of the present invention, a method of treating a fluid includes providing a transfer line apparatus having an outer tube defining a first chamber which has a length, an inlet, and an outlet, with the outer tube being substantially gas and liquid impermeable. apparatus further includes one or more inner tubes extending within the outer tube and at least partially through the 10 first chamber, with the one or more inner tubes each being formed solely of a gas-permeable, liquid-impermeable material. Each of the one or more inner tubes have first and second substantially opposed open ends. The method further includes operably coupling respective first open ends of the one or more inner tubes to a first fluid source such that the first fluid is transported through respective chambers that are defined within the one or more inner tubes. Additionally, a second fluid is operably transported through the first chamber from the inlet through the outlet. Where the second fluid has a lower target gas concentration then the first fluid, the target gas is accordingly caused to operably pass through respective walls of the one or more inner tubes from the first fluid to the second fluid. contrast, where the second fluid has a higher target gas concentration than the first fluid, the target gas is correspondingly caused to operably pass through respective walls of the one or more inner tubes from the second fluid to the first fluid.

#### Brief Description of the Drawings

Figure 1 is a cross-sectional view of a transfer line degassing apparatus of the present invention;

Figure 2 is a partial cut-away view of a degassing apparatus of the present invention incorporating a particular configuration for the inlet and outlet connection means;

Figure 3 is a partial cut-away view of a degassing apparatus of the present invention incorporating a particular configuration for the inlet and outlet connection means;

Figure 4 is a partial cut-away view of a degassing apparatus of the present invention incorporating a particular configuration for the inlet and outlet connection means;

Figure 5 is a cross-sectional view of a transfer line degassing apparatus of the present invention;

Figure 6 is an enlarged view of a portion of the degassing apparatus illustrated in Figure 5;

Figure 7 is a cross-sectional view of a sealing mechanism of the present invention;

Figure 8 is a cross-sectional view of a sealing 20 mechanism of the present invention;

Figure 9 is a cross-sectional view of a transfer line degassing apparatus of the present invention; and

Figure 10 is a cross-sectional view of a transfer line degassing apparatus of the present invention.

25

10

## Detailed Description of the Preferred Embodiments

The objects and advantages enumerated above together with other objects, features, and advances represented by the present invention will now be presented in terms of detailed embodiments described with reference to the attached drawing figures which are intended to be

representative of various possible configurations of the invention. Other embodiments and aspects of the invention are recognized as being within the grasp of those having ordinary skill in the art.

With reference now to the drawings, and first to Figure 1, a transfer line degassing apparatus 10 of the present invention includes an outer tube 12 and an inner tube 14 disposed within outer tube 12. Outer tube 12 preferably forms an elongated sealed chamber through which inner tube 14 extends. 10

5

15

20

25

As illustrated in Figure 1, outer tube 12 includes an inlet end 22 and an outlet end 24, with inner tube 14 having a corresponding inlet portion 32 and outlet portion 34. Inlet and outlet connection devices 41, 43 are preferably operably coupled to respective inlet and outlet ends 22, 24 of outer tube 12, and to inlet portions 32, 34 of inner tube Inlet and outlet connection devices 41, 43 are preferably configured so as to operably provide a gas-tight coupling at respective inlet and outlet ends 22, 24 of outer tube 12, as between outer tube 12, respective connection devices 41, 43 and inner tube 14 thereat. As such, the portion of outer tube 12 between inlet end 22 and outlet end 24 forms a sealed chamber 18 through which inner tube 14 passes.

A vacuum source coupling aperture 48 is preferably formed in the sidewall of outer tube 12 and extends therethrough, such that the space between outer tube 12 and inner tube 14 is fluidly connected to an environment external to apparatus 10 via aperture 48. In preferred embodiments of the present invention, a vacuum source 30 adapter 52 extends from the sidewall 13 of outer tube 12 and coextensively with aperture 48. Vacuum source adaptor 52 is

preferably configured so as to be operably coupled to a vacuum source, whereby open space with chamber 18 may be substantially evacuated during use. In such a manner, fluids flowing through inner tube 14 at locations within the chamber 18 are caused to be degassed, as governed by Henry's Law of partial pressure. As such, gas entrained within fluids passing through inner tube 14 will have the tendency to be drawn through the gas-permeable, liquid-impermeable material forming inner tube 14, and into the relatively low pressure environment within chamber 18. Gas that is so drawn from the fluid within inner tube 14 is consequently removed from chamber 18 via aperture 48, which is operably coupled to a vacuum source.

10

15

20

25

30

It is also contemplated by the present invention that the apparatus described herein for degassing one or more fluids may also be utilized in preventing the regassing of such fluids. For example, a fluid that has previously been substantially degassed may be directed through apparatus 10 such that, for the length of apparatus 10, the fluid passing therethrough does not absorb gaseous components. is important where pre-degassed fluids must be transferred from a source to a destination without absorbing gaseous components therein. The apparatus of the present invention, therefore, enables such transportation of predegassed fluids without risk of regassing due to the fact that the vacuum prevents gaseous components from entering into the fluid stream. In such a manner, the apparatus of the present invention may be termed a fluid treatment apparatus which may be utilized to degas fluids and/or prevent the regassing of such fluids in a transfer line device.

In another embodiment of the present invention, and as illustrated in Figure 9, the fluids to be degassed may instead be directed through chamber 518, as defined between inner tubes 514 and outer tube 512, while a low pressure 5 environment is obtained within inner tubes 514. In such a manner, the degassing function operates in the reverse direction, with target gas entrained within the fluid being drawn by partial pressure through inner tubes 514, and into the relatively low pressure environment within the respective chambers defined by inner tubes 514.

10

15

20

30

As shown in Figure 9, outer tube 512 preferably has an inlet end 523 a substantially opposed outlet and 525. Similarly to apparatus 10 described with reference to Figure 1, outer tube 512 is preferably substantially gas and liquid impermeable, and most preferably is less permeable than the combined permeability's of inner tubes 514. materials useful in outer tube 512 include Tefzel®, PEEK, FEP, PFE, Tygon®, and the like. In addition to having a relatively low permeability characteristic, outer tube 512, as well as all other outer tubes described in this application, preferably exhibit inertness and physical flexibility, such that the transfer line apparatus of the present invention is relatively flexible so as to allow ready manipulation of the transfer line apparatus with relatively little effort. As such, the transfer line 25 apparatus of the invention may be manipulated by the user into a wide variety of configurations to best conform to the desired application.

Inner tupes 514 of transfer line apparatus 510 extend within outer tube 512 and at least partially through chamber 518. In the embodiment illustrated in Figure 9, inner tubes 514 each have an open end 515 and a substantially opposed closed end 517. Vacuum line coupler 592 is preferably engaged with fluid inlet coupler 594, which itself is engaged with outer tube 512. Vacuum coupler 592 forms a gas-tight plenum 508 adjacent to respective open ends 515 of inner tubes 514. Such a plenum 508 is gas-tight only with respect to chamber 518, in that ferrule 509 sealingly engages with second end 595 of fluid inlet coupler 594 when vacuum coupler 592 is firmly seated upon fluid inlet coupler 594. Vacuum coupler 592 is preferably operably coupled to a vacuum source (not shown) at first end 593, which is in fluid connection with plenum 508 via passage 505 in vacuum coupler 592. Through such an arrangement, plenum 508 is operably coupled into communication with the vacuum source so as to substantially evacuate respective chambers 513 defined within inner tubes 514.

10

15

20

25

The fluid to be degassed is preferably directed into chamber 518 via inlet coupler 594, which is sealingly engaged with outer tube 512. Fluid entering chamber 518 at inlet 524 through fluid inlet coupler 594 is directed by fluid pressure about inner tubes 514, and eventually out from chamber 518 at outlet 522 through fluid outlet coupler 596. By passing fluid around the semi-impermeable inner tubes 514, which are substantially evacuated as described above, entrained gas within the fluid is drawn by Henry's Law of partial pressure through respective inner tubing walls and into the respective chambers 513 defined by inner tubes 514. The vacuum source acts to remove gas from within chambers 513 that permeate through the sidewalls of inner tubes 514.

30 As further illustrated in apparatus 510, baffles 503 may be disposed in chamber 518 to direct and/or redirect fluid flow through chamber 518 from inlet 524 to outlet 522.

Applicants have determined that by placing structure such as baffles 503 in the fluid path through chamber 518, laminar flow of the fluid through chamber 518 may be disrupted. Such a laminar flow disruption assists in mixing entrained gas throughout the fluid flow volume, thereby enhancing the degassing efficiency of apparatus 510.

Certain advantages are incorporated into the degassing system when the fluid to be degassed is directed through chamber 518 between outer tube 512 and inner tubes 514. For instance, the fluid to be degassed is exposed to a relatively larger gas-permeable separation media surface area, in that the outer diameter of inner tubes 514 is greater than the inner diameter thereof. By directing the fluid about the outer surfaces of the inner tubes 514, therefore, a relatively higher degassing efficiency for a particular system is achieved. In addition, the degassing toward the inner tubes 514 may be used to counteract influx of gases through outer tube 512, where outer tube 512 is not completely gas-impermeable.

10

15

20

25

30

In other embodiments of the present invention, fluids may be degassed by interaction with a sweep fluid. Such a sweep fluid may be in a gaseous or liquidous form, and preferably flows adjacent to the fluid to be degassed but separated by the gas permeable, liquid impermeable walls of the inner tubes of the present invention. In some embodiments, such sweep fluid flows counter to the flow direction of the liquid being degassed, such that the efficiency of liquid degassing is enhanced. To effectively degas the liquid, the sweep fluid preferably has a relatively low partial pressure (gas) or concentration (liquid) with respect to the target gaseous species being operably removed from the liquid.

A particular example of an apparatus arranged to degas a fluid through the use of a sweep fluid is illustrated in Figure 10. As shown therein, apparatus 610 includes an outer substantially impermeable tube 612 and a gaspermeable, liquid-impermeable tube 614 extending therewithin and at least partially through chamber 618 defined within outer tube 612. First and second end portions 623, 625 of outer tube 612 are each preferably sealingly engaged with respective inlet and outlet couplers 694, 696, which each include an open channel 688, 689 axially formed therethrough. As such, chamber 618 is open through inlet and outlet couplers 694, 696.

10

15

20

Inlet and outlet couplers 694, 696 are each engaged with inlet and outlet manifolds 672, 674, respectively. In the embodiment illustrated in Figure 10, inlet manifold 672 includes a first fluid inlet bore 673 and a second fluid inlet bore 675. Inner tube 614 preferably sealingly engages within fluid inlet adapter 652, such that the first fluid entering fluid inlet adapter 652 is transported without leakage into open end 617 of chamber 613 defined within inner tube 614. Fluid pressure within chamber 613 operably directs the first fluid through inner tube 614 through first fluid outlet bore 681 in outlet manifold 674.

A second fluid is brought into apparatus 610 via second fluid inlet bore 675, which enables fluid connection with chamber 618 within outer tube 612. An open plenum 677 within inlet manifold 672 operably directs the second fluid into open channel 688 in inlet adapter 652, which leads to chamber 618. Fluid pressure in plenum 677 directs the second fluid through chamber 618, and ultimately through second fluid outlet bore 679 in outlet manifold 674.

The target gas concentration that is to be operably decreased in a designated one of the first and second fluids should be higher in the designated removal fluid than in the receiving fluid in order for transfer of the target gas 5 through the one or more semi-permeable tubes to efficiently take place. For example, where target gas is to be removed from the first fluid passing through inner tube 614, the second fluid passing about inner tube 614 in chamber 618 should have a target gas concentration lower than that of the first fluid. When such conditions are present, the second fluid acts as a sweep fluid removing at least a portion of the gas entrained within the first fluid.

10

15

20

The gas transfer between the two fluids can, of course, be opposite of that described above, wherein the first fluid has a target gas concentration less than that of the second In this case, the target gas will be caused to transfer through respective walls of inner tube 614 from the second fluid passing about inner tube 614 to the first fluid passing through chamber 613 within inner tube 614.

The present invention further contemplates that the flow directions of the first and second fluids can be opposite with respect to one another. In fact, such an arrangement is preferred, wherein the first or second fluid enters apparatus 610 through outlet manifold 674, and the other of the first or second fluid enters apparatus 610 "counterflow" through inlet manifold 672. a Such arrangement has been found to increase the rate of gas transfer between the first and second fluids across the walls of inner tube 614.

In a particularly preferred mode of the invention, one 30 of the first and second fluids is a liquid to be degassed, with the other of the first and second fluids being a gas or liquid having a target gas partial pressure or concentration substantially less than the target gas concentration in the liquid to be degassed. Since gases typically have a higher capacity to receive gaseous materials, a particular embodiment of the invention incorporates a liquid to be degassed with a sweep gas flowing counter to the flow direction of the liquid.

10

15

20

25

30

An important aspect of the present invention, such as is shown in Fig. 1, is in providing the transfer line degassing apparatus of the present invention with a flexibility characteristic that is sufficient so as to be readily manipulatable into desired configurations. transfer line for operably effectively used as a transporting, i.e., chromatographic fluids from one point to another within a respective chromatographic system, the apparatus is preferably flexible and conformable, whereby inlet connection device 41 may be operably coupled to an upstream component such as a fluid reservoir, and the outlet connection device 43 operably coupled to a downstream as a blending valve apparatus component, such Since connections between such chromatographic column. by manufacturer as well by components vary chromatographic system type, the apparatus of the invention preferably conform to a user's particular configurational needs. Accordingly, for example, outer tube 12 may be fabricated from a variety of materials, so long as the material exhibits a substantial flexibility, relatively low gas and liquid impermeability, and is formed in a to obtain the above-stated caliber thickness so as characteristics. Outer tube 12 may therefore be fabricated from, for example, Tefzel®, FEP, PEEK, PFE, Tygon®, and the like.

In preferred embodiments of the present invention, the one or more inner tubes are fabricated from a gas-permeable, liquid-impermeable material that is relatively inert and is relatively flexible. A particularly preferred material for inner tubes is an amorphous in fabricating the perfluorinated copolymer, such as that marketed by DuPont under the trade name Teflon® AF. Such materials have gas permeabilities of up to about 2 or 3 orders of magnitude higher than conventionally-utilized PTFE. Due to the relatively higher gas-permeabilities of the Teflon® AF material, greater gas mass transfer rates may be achieved with tubes of Teflon® AF having increased wall thicknesses, thereby permitting the undertaking of applications requiring relatively high pressure differentials. Advantageously, tubes of smaller internal diameter and shorter length offer reduced internal volumes, which thereby assist in reducing such amorphous Moreover, startup times. perfluorinated copolymers are sufficiently flexible so as to abide by the flexibility characteristics desired in the present invention.

10

15

20

25

30

A further important aspect of the inner tubes of the present invention is in the fact that such tubes are preferably solely fabricated from one or more gas-permeable, liquid impermeable materials, such as the amorphous perfluorinated copolymers described above. Due to the permeability and strength characteristics of the Teflon AF® material, the inner tubes may be extruded or otherwise formed as monolithic, free-standing elements that do not require support structures along their length to remain viable in a wide range of operating conditions, including those involved in vacuum degassing. In preferred embodiments of the present invention, each of the inner

tubes of the present invention have a wall thickness of between about 0.003 and about 0.015 inches, with smaller or larger tubing calipers being envisioned by the Applicants as useful in certain applications. Additionally, the inside diameter of such inner tubes is preferably between about 0.01 and about 0.5 inches in dimension. Applicants, however, contemplate the use of smaller or larger inside diameter tubing, as required.

A variety of configurations for inlet and outlet connection devices 41, 43 are contemplated by the present 10 invention. In the embodiment illustrated in Figure 1, inlet and outlet connection devices 41, 43 include dual-shrink tubing 71, 73 disposed in surrounding relationship to respective inlet and outlet portions 32, 34 of inner tube 14. Such tubing sections 71, 73 are preferably heat shrunk about respective portions of inner tube 14, while inlet and outlet ends 22, 24 of outer tube 12 are preferably sealingly engaged with an outer surface of respective tubing sections 71, 73 so as to obtain a sealed engagement between outer tube 12, respective tubing sections 71, 73, and inner tube Inlet and outlet connection devices 41, 43 further include nuts 45, 47 in conjunction with a pair of ferrules 49, 50 and which, in combination, are formed in surrounding relationship to tubing sections 71, 73 for connecting apparatus 10 between respective chromatographic system 25 components.

15

20

30

Figures 2-4 illustrate alternative configurations for the inlet and outlet connection means of the present Specifically, apparatus 110 in Figure 2 invention. illustrates a female-type fitting comprising inlet and outlet connection means 141, 143. As shown in the enlarged view of outlet connection means 143 in figure 2, nut 147 operably engages a seat 150, which seat 150 acts as an intermediary object to transmit force against double sided ferrule 152. Progressive threaded engagement of nut 147 within receptacle 154 results in compressive contact between nut 147 and seat 150, which, in turn, results in compressive contact between seat 150 and first end 158 of double ended ferrule 152. Such compressive contact forces ferrule 152 against a tapered base of receptacle 154, so as to form a liquid and a gas-tight seal surrounding inner tube 114 at both sides of double ended ferrule 152. Receptacle 154 further includes a threaded opening 156 that is specifically configured for threadably receiving a fluid transfer line connector component (not shown) therein.

10

25

30

Apparatus 210 and apparatus 310 illustrated in Figures 3 and 4 depict male fittings of various configurations for respective inlet and outlet connection means 241, 243 and 341, 343. Such configurations illustrated in Figures 2-4 are exemplary only, and do not in any way restrict the scope of the present invention in its utilization of connection 20 means having various known configurations. Preferably, however, the respective connection means utilized in a particular degassing apparatus of the present invention operably correspond and engage with respective components of an associated chromatographic system.

Another embodiment of the present invention is illustrated in figures 5-6, wherein an apparatus 410 incorporates a plurality of semi-permeable inner tubes 414 extending through outer tube 412. In such a manner, a relatively higher surface area of semi-permeable tubing is exposed to the low pressure environment within the interior space defined by outer tube 412. As may be seen more clearly in figure 6, connection means 443 incorporates first

nut 447 having a first barbed end 449 and a second threaded end 451 extending divergently with respect to first end 449. First nut 447 includes a central bore 453 through which semi-permeable tubes 414 extend.

5

10

15

20

25

30

In preferred embodiments, outlet end 424 of outer tube 412 is preferably operably press fit about first barbed end 447 so as to obtain a gas-tight seal 449 of nut Barbed end 449 of nut 447 assists therebetween. retaining outer tube 412 in a fixed engagement therewith, in that annular barb 450 inhibits movement of outer tube 412 with respect thereto. Second threaded end 451 of first nut 447 is preferably threadably engageable with second nut 463. In particular, threaded end 451 of nut 447 is threadably engageable with threaded opening 465 of second nut 463. shown in figure 6, threaded engagement of first nut 447 into nut 463 results in compressive contact between end 452 of nut 447 and ferrule 470. Such compressive contact operably forces ferrule 470 against first inner boss 482 of second nut 463 so as to obtain a fluid-tight seal therebetween. As such, fluid exiting respective inner tubes 414 flows through second open end 485 of second nut 463, and does not leak into and out from threaded opening 465 thereof. Preferably, a fluid transfer line connector (not shown) may be operably coupled to second open end 485 of second nut 463 so as to maintain fluid containment throughout the associated chromatographic system. Preferably, first and second nuts 447, 463 and ferrule 470 are fabricated from relatively durable and inert materials such as stainless steel and the like. Ferrule 470 is also preferably fabricated so as to moderately deform under contact pressure generated through the progressive threaded engagement of nut 447 into nut 463.

Such deformation of ferrule 470 accommodates the fluid-tight engagement to first bossed portion 482 of second nut 463.

aspect of the present invention further illustrated in Figures 7 and 8, wherein a sealing apparatus 710 may be utilized to operably crimp outer tube 712 against inner tube 714 so as to create a gas and/or liquid tight seal therebetween. Apparatus 710 preferably includes a ferrule 718 that may be operably installed about outer tube 712 by sliding ferrule 718 over the outer diameter of outer tube 712 to a desired sealing position. In the embodiment illustrated in Figure 7, first and second clamping rings 722, 724 are brought into engagement with respective first and second sides 719, 720 of ferrule 718. Since each of first and second clamping rings are tapered with a minimum inside diameter less than the outside diameter of first and second sides 719, 720 of ferrule 718, the operation of engaging first and second clamping rings 722, 724 onto ferrule 718 causes at least first and second sides 719, 720 of ferrule 718 to compress inwardly against outer tube 712. Such compression acts to displace a portion of outer tube 712 against inner tube 714, and with a force sufficient to create a gas and/or liquid tight seal therebetween.

10

15

20

30

To effectuate the displacement of ferrule 718, first and second clamping rings 722, 724 are preferably a 25 relatively strong and rigid material such as stainless steel.

Apparatus 810 illustrated in Figure 8 is similar to that described with reference to apparatus 710, except that ferrule 818 includes only a first side 819 such that only a first clamping ring 822 need be employed. Apparatus 810, therefore, obtains only a single sealing point between outer tube 812 and inner tube 814, while apparatus 710 operably

WO 2005/046835 PCT/US2004/037306

obtains two sealing points between outer tube 712 and inner tube 714. It is contemplated by the Applicants that apparatus 710 may preferably be employed in applications having a need for a relatively high level of assurance that sealing between outer tube 712 and inner tube 714 has been accomplished.

The invention has been described herein in considerable detail in order to comply with the patent statutes, and to provide those skilled in the art with the information needed to apply the novel principles and to construct and use embodiments of the invention as required. However, it is to be understood that the invention can be carried out by specifically different devices and that various modifications can be accomplished without departing from the scope of the invention itself.

#### Claims

What is claimed is:

- 1. An elongated flow-through fluid treatment apparatus for treating one or more fluids passing therethrough, said fluid treatment apparatus comprising:
- (a) an elongated outer tube defining a first chamber therewithin, and being relatively gas and liquid impermeable;
- (b) one or more elongated inner tubes extending within said outer tube and at least partially through said first chamber, said one or more inner tubes each being formed solely of one or more gas-permeable, liquid-impermeable materials, and having an inlet portion and an outlet portion;
- (c) one or more adapters extending from a side wall of said outer tube and coextensively with one or more apertures therein such that a hollow channel extending through said one or more adapters provides for fluid connection between said first chamber and locations external to said one or more adapters;
  - (d) sealing means for mechanically creating gastight junctions of said outer tube adjacent said inlet and outlet portions of said one or more inner tubes;
- (e) inlet connection means operably coupled to 25 said outer tube and said inlet portion of said one or more inner tubes; and
  - (f) outlet connection means operably coupled to said outer tube and said outlet portion of said one or more inner tubes,
- said fluid treatment apparatus being sufficiently flexible so as to be readily manipulatable into desired configurations.

20

- 2. A fluid treatment apparatus as in Claim 1 wherein said inner tubes are an amorphous perfluorinated copolymer material.
- 3. A fluid treatment apparatus as in Claim 1 wherein said outer tube is selected from the group consisting of Tefzel® stainless steel, FEP, and PEEK.
  - 4. A method for treating a fluid, comprising:
- (a) providing a transfer line apparatus having an outer tube defining a first chamber having a length, an inlet, and an outlet, said outer tube being substantially gas and liquid impermeable, and one or more inner tubes extending within said outer tube and at least partially through said first chamber, said one or more inner tubes each being formed solely of one or more gas-permeable, liquid-impermeable materials, each of said one or more inner
- liquid-impermeable materials, each of said one or more inner tubes having an open end and a substantially opposed closed end;
  - (b) operably coupling said open end of each of said one or more inner tubes into communication with a vacuum source so as to substantially evacuate respective second chambers defined within said one or more inner tubes; and
  - (c) transporting said fluid through said first chamber from said inlet through said outlet.
- 5. A method as in Claim 4 wherein said inlet is disposed at a first end of said outer tube, and said outlet is disposed at a second substantially opposed end of said second outer tube.
- 6. A method as in Claim 4 wherein said one or more inner tubes extend along said length of said chamber.
  - 7. A method as in Claim 4 wherein said one or more inner tubes are amorphous perfluorinated copolymers.

10

15

20

25

30

- 8. A method of treating a fluid, comprising:
- (a) providing a transfer line apparatus having an outer tube defining a first chamber having a length, an inlet, and an outlet, said outer tube being substantially gas and liquid impermeable, and one or more inner tubes extending within said outer tube and at least partially through said first chamber, said one or more inner tubes each being formed solely of one or more gas-permeable, liquid-imperable materials, said one or more inner tubes each having first and second substantially opposed open ends;
- (b) operably coupling respective first open ends of said one or more inner tubes to a first fluid source, such that said first fluid is transported through respective second chambers defined within said one or more inner tubes; and
- (c) transporting a second fluid through said first chamber from said inlet through said outlet, said second fluid having a lower target gas concentration than said first fluid, such that target gas is caused to operably pass through respective walls of said one or more inner tubes from said first fluid to said second fluid.
- 9. A method as in Claim 8 wherein said one or more inner tubes are amorphous perfluorinated copolymers.
  - 10. A method for treating a fluid, comprising:
- (a) providing a transfer line apparatus having an outer tube defining a first chamber having a length, an inlet, and an outlet, said outer tube being substantially gas and liquid impermeable, and one or more inner tubes extending within said outer tube and at least partially through said first chamber, said one or more inner tubes each being formed solely of one or more gas-permeable,

liquid-impermeable materials, said one or more inner tubes each having first and second substantially opposed open ends;

- (b) operably coupling respective first open ends of said one or more inner tubes to a first fluid source, such that said first fluid is transported through respective second chambers defined within said one or more inner tubes; and
- (c) transporting a second fluid through said

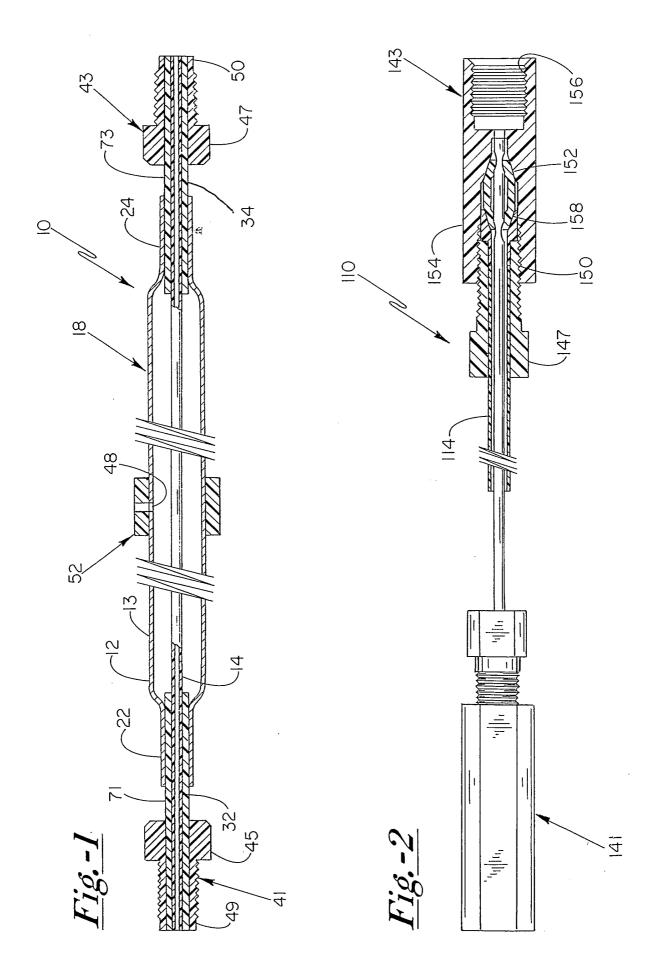
  first chamber from said inlet through said outlet, said

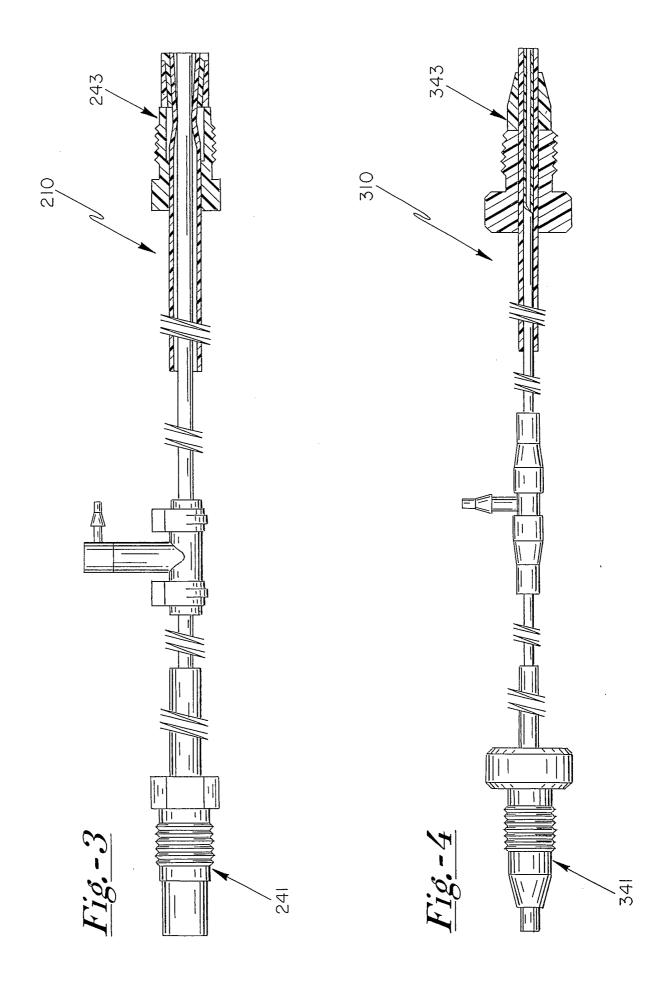
  second fluid having a higher target gas concentration than

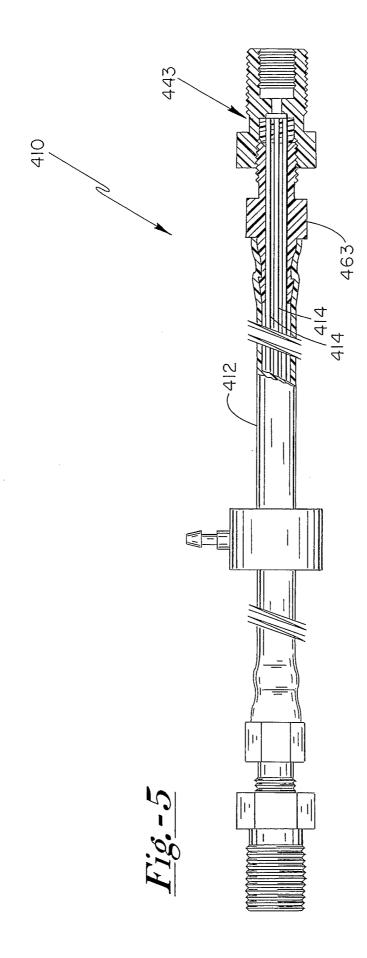
  said first fluid, such that target gas is caused to operably

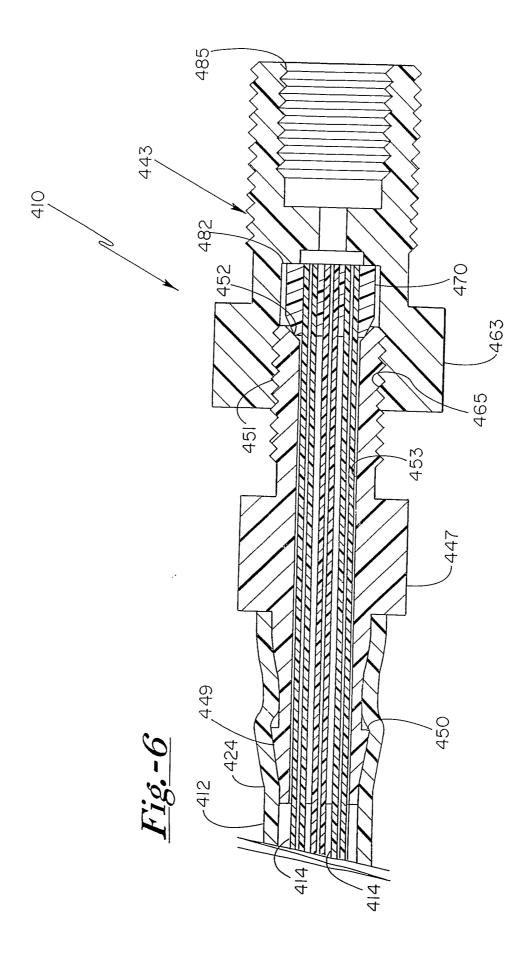
  pass through respective walls of said one or more inner

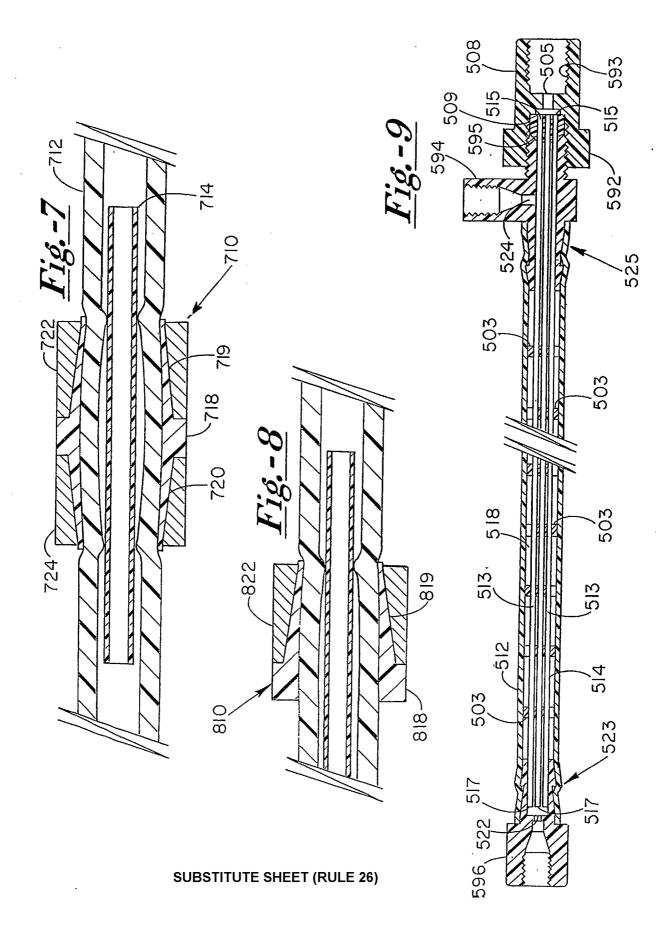
  tubes from said second fluid to said first fluid.
- 15 11. A method as in Claim 10 wherein said one ore more inner tubes are amorphous perfluorinated copolymers.

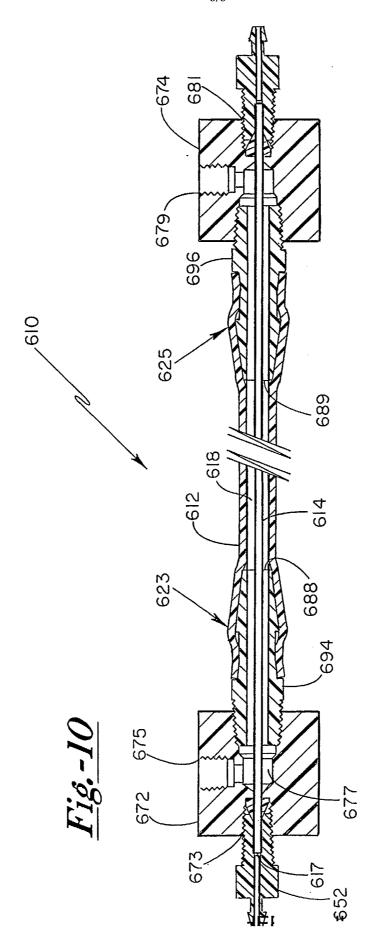












SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/37306

A. CLASSIFICATION OF SUBJECT MATTER			
IPC(7) : B01D 19/00			
US CL : 95/46; 96/6; 73/61.55			
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) U.S.: 95/46, 241; 96/6, 8, 10, 155; 73/61.55			
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 practicable, search terms used)			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category *	Citation of document, with indication, where a	ppropriate, of the relevant passages	Relevant to claim No.
Α	US 6,494,938 B2 (Sims et al.) 17 December 2002 (1 25	7.12.2002), Fig. 6 and col. 6, lines 5-	1, 2
Α	US 6,675,835 B2 (Gerner et al.) 13 January 2004 (13.1.2004)		1, 2
Α	US 6,248,157 B1 (Sims et al.) 19 June 2001 (19.6.2001)		1, 2
Α	US 6,837,992 B2 (Gerner et al.) 4 January 2005 (4.1.2005)		1, 2
A	US 6,309,444 B1 (Sims et al.) 30 October 2001 (30.10.2001)		1, 2
x	US 5,989,318 (Schroll) 23 November 1999 (23.11.1999), Fig. 1 and col. 2, line 3 to col. 4, line 15		4, 5, 6
X	US 5,788,742 (Sugimoto et al.) 4 August 1998 (4.8.1998), Fig. 1 and col. 2, line 53 to col.		8
3, line 65 X US 4,923, 679 (Fukasawa et al.) 8 May 1990 (8.5.19 6, line 29		990), Fig. 1 and col. 5, line 26 to col.	10
	0, the 29		
!			
Further	documents are listed in the continuation of Box C.	See patent family annex.	
* 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	
"A" document defining the general state of the art which is not considered to be of particular relevance		principle or theory underlying the inver	ntion
"E" earlier application or patent 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	
O" document referring to an oral disclosure, use, exhibition or other means		being obvious to a person skilled in the	
"P" document published prior to the international filing date but later than the priority date claimed		"&" document member of the same patent for	amily
Date of the actual completion of the international search		Date of mailing of the international search report	
16 February 2005 (16.02.2005)		11 MAR 2005	
Name and mailing address of the ISA/US		Authorized officer	
Mail Stop PCT, Attn: ISA/US Commissioner for Patents		Duane Smith	
P.O. Box 1450 Alexandria, Virginia 22313-1450		Telephone No. 571-272-0987	Jan
Facsimile No. (703) 305-3230			