

WO 2016/065132 A1



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, **Published:**
GW, KM, ML, MR, NE, SN, TD, TG).

— *with international search report (Art. 21(3))*

METHOD, SYSTEM, AND DEVICE FOR DELIVERY OF PROCESS GAS**TECHNICAL FIELD**

[1] Methods, systems, and devices for the vapor phase delivery of high purity process gases in micro-electronics and other critical process applications.

BACKGROUND

[2] Various process gases may be used in the manufacturing and processing of micro-electronics. In addition, a variety of chemicals may be used in other environments demanding high purity gases, e.g., critical processes, including without limitation microelectronics applications, wafer cleaning, wafer bonding, photolithography mask cleaning, atomic layer deposition, chemical vapor deposition, flat panel displays, disinfection of surfaces contaminated with bacteria, viruses and other biological agents, industrial parts cleaning, pharmaceutical manufacturing, production of nano-materials, power generation and control devices, fuel cells, power transmission devices, and other applications in which process control and purity are critical considerations. In those processes, it is necessary to deliver specific amounts of certain process gases under controlled operating conditions, e.g., temperature, pressure, and flow rate.

[3] For a variety of reasons, gas phase delivery of process chemicals is preferred to liquid phase delivery. For applications requiring low mass flow for process chemicals, liquid delivery of process chemicals is not accurate or clean enough. Gaseous delivery would be desired from a standpoint of ease of delivery, accuracy and purity. One approach is to vaporize the process chemical component directly at or near

the point of use. Vaporizing liquids provides a process that leaves heavy contaminants behind, thus purifying the process chemical. Gas flow devices are better attuned to precise control than liquid delivery devices. Additionally, micro-electronics applications and other critical processes typically have extensive gas handling systems that make gaseous delivery considerably easier than liquid delivery. However, for safety, handling, stability, and/or purity reasons, many process gases are not amenable to direct vaporization.

[4] There are numerous process gases used in micro-electronics applications and other critical processes. Ozone is a gas that is typically used to clean the surface of semiconductors (e.g., photoresist stripping) and as an oxidizing agent (e.g., forming oxide or hydroxide layers). One advantage of using ozone gas in micro-electronics applications and other critical processes, as opposed to prior liquid-based approaches, is that gases are able to access high aspect ratio features on a surface. For example, according to the International Technology Roadmap for Semiconductors (ITRS), current semiconductor processes should be compatible with a half-pitch as small as 20-22 nm. The next technology node for semiconductors is expected to have a half-pitch of 10 nm, and the ITRS calls for <7 nm half-pitch in the near future. At these dimensions, liquid-based chemical processing is not feasible, because the surface tension of the process liquid prevents it from accessing the bottom of deep holes or channels and the corners of high aspect ratio features. Therefore, ozone gas has been used in some instances to overcome certain limitations of liquid-based processes, because gases do not suffer from the same surface tension limitations. Plasma-based processes have also been employed to overcome certain limitations of liquid-based processes. However, ozone-

and plasma-based processes present their own set of limitations, including, inter alia, cost of operation, insufficient process controls, undesired side reactions, and inefficient cleaning.

[5] Other problems relate to the temperature necessary for successful deposition. With respect to silicon nitride (SiN) for example, ammonia (NH₃) is currently often used at temperatures in excess of 500 °C or even 600 °C. It is expensive to maintain such high temperatures for deposition and it would be preferable to deposit at lower temperatures. In addition, new semiconductor device technologies have stringent thermal budgets, which inhibit the use of elevated temperatures over 400 °C. Hydrazine (N₂H₄) presents an opportunity to explore lower temperatures in part because of the favorable thermodynamics of hydrazine resulting in lower deposition temperatures and a spontaneous reaction to form nitrides. Although reported in the literature (Burton et al. *J. Electrochem. Soc.*, 155(7) D508-D516 (2008)), hydrazine usage has not been adopted commercially due to the serious safety concerns with using hydrazine. Substituted hydrazines suffer from the drawback of leading to unwanted carbon contamination. Thus, there is a need to develop a safer method for using hydrazine for either deposition processes or for delivery to other critical process applications.

[6] The gas phase use of hydrazine has been limited by safety, handling, and purity concerns. Hydrazine has been used for rocket fuel and can be very explosive. Semiconductor industry protocol for safe handling of this material is very limited. Therefore, a technique is needed to overcome these limitations and, specifically, to provide substantially water-free gaseous hydrazine suitable for use in micro-electronics and other critical process applications.

[7] Similarly, as explained in PCT Publication No. 2014014511 by Rasirc, Inc., which is hereby incorporated by reference herein, the gas phase use of hydrogen peroxide in critical process applications has been of limited utility, because highly concentrated hydrogen peroxide solutions present serious safety and handling concerns and obtaining high concentrations of hydrogen peroxide in the gas phase has not been possible using existing technology.

SUMMARY OF CERTAIN EMBODIMENTS

[8] Methods, systems, and devices for delivering a substantially water-free process gas stream, particularly a hydrazine-containing gas stream, are provided. The methods, systems, and devices are particularly useful in micro-electronics applications and other critical processes. Generally, the methods comprise (a) providing a non-aqueous hydrazine solution having a vapor phase comprising an amount of hydrazine vapor; (b) contacting a carrier gas or vacuum with the vapor phase; and (c) delivering a gas stream comprising substantially water-free hydrazine to a critical process or application. In many embodiments, the amount of hydrazine in the vapor phase is sufficient to provide hydrazine directly to a critical process or application without further concentrating or processing the hydrazine-containing gas stream. In many embodiments, the non-aqueous hydrazine solution includes a stabilizer. In certain embodiments, the methods further include removing one or more stabilizers from the gas stream. By adjusting the operating conditions of the methods, e.g., the temperature and pressure of the carrier gas or vacuum, the concentration of the hydrazine solution, and the temperature and pressure of the hydrazine solution, hydrazine can be precisely

and safely delivered as a process gas. In certain embodiments, the amount of hydrazine in the vapor phase and delivered to the critical process or application can be controlled by adding energy to the hydrazine solution, e.g., thermal energy, rotational energy, or ultrasonic energy. In many embodiments of the invention, the non-aqueous hydrazine is neat hydrazine or hydrazine that is substantially free of water.

[9] Systems and devices for delivering hydrazine using the methods described herein are also provided. Generally, the systems and devices comprise (a) a non-aqueous hydrazine solution having a vapor phase comprising an amount of hydrazine vapor; (b) a carrier gas or vacuum in fluid contact with the vapor phase; and (c) an apparatus for delivering a gas stream comprising hydrazine to a critical process or application. In many embodiments, the non-aqueous hydrazine solution includes one or more stabilizers. In certain embodiments, the systems and devices further include an apparatus for removing one or more stabilizers from the gas stream. In many embodiments, the amount of hydrazine in the vapor phase is sufficient to provide hydrazine directly to a critical process or application without further concentrating or processing the hydrazine-containing gas stream. In certain embodiments, the apparatus for delivering a gas stream comprising hydrazine is an outlet of a head space, containing the vapor phase, that is connected directly or indirectly to a micro-electronics application or other critical process system, allowing the hydrazine containing gas stream to flow from the head space to the application or process in which it will be used. The hydrazine delivery assembly (HDA) described herein is one such device. By adjusting the operating conditions of the systems and devices, e.g., the temperature and pressure of the carrier gas or vacuum, the concentration of the

hydrazine solution, and the temperature and pressure of the hydrazine solution, hydrazine can be precisely and safely delivered as a process gas. In certain embodiments, the amount of hydrazine in the vapor phase and delivered to the critical process or application can be controlled by adding energy to the hydrazine solution, e.g., thermal energy, rotational energy, or ultrasonic energy.

[10] Many of the embodiments of the methods, systems, and devices disclosed herein utilize a membrane in contact with the hydrazine-containing solution. The use of the membrane has safety advantages. In certain embodiments, the membrane wholly or partially separates the hydrazine-containing solution from the hydrazine-containing vapor phase. By eliminating access between the vapor phase and the liquid phase, a sudden decomposition in the vapor phase of the hydrazine would be limited and not cause a corresponding decomposition in the liquid phase due to the presence of the membrane.

[11] Also disclosed herein are devices for containing a liquid comprising a volatile chemical or chemical composition (e.g., hydrazine, hydrogen peroxide, water, alcohols, amines, or ammonium hydroxide), wherein the device comprises a head space where vapor comprising the chemical or composition is accessible as a process gas to be incorporated into a process gas stream. The process gas stream comprising the chemical or composition is typically delivered to a critical process application. In certain embodiments, the device comprises (a) a chamber containing a liquid comprising a volatile chemical or chemical composition, (b) a head space comprising a vapor phase that includes the volatile chemical or chemical composition in the gas phase, (c) an inlet port through which a carrier gas stream can enter the chamber, and

(d) a protected outlet port through which a process gas stream comprising carrier gas and the volatile chemical or chemical composition can exit the head space. In certain embodiments, the head space is a portion of the chamber. In certain alternative embodiments, the head space is distinct from the chamber and in fluid communication with the chamber to allow the volatile chemical or chemical composition in the gas phase to move from the chamber into head space. In many embodiments, a membrane facilitates the transfer of the volatile chemical or chemical composition from the liquid into the gas phase. The configuration of the membrane may vary according to the particular application and process design. In some embodiments, the membrane wholly or partially separates the liquid from the head space. In certain embodiments, the membrane comprises a tube connected to the inlet port such that all or a portion of the carrier gas travels through the membrane. In such embodiments, the membrane tube may also travel through a portion of the liquid in the chamber and terminate in the head space. The protected outlet port comprises an apparatus to ensure that the volatile chemical or chemical composition entering the exit port is substantially in the gas phase, i.e., substantially free of liquid phase material, such as droplets, mists, or fogs.

[12] The methods, systems, and devices described herein are generally applicable to a wide variety of process gas streams, particularly non-aqueous hydrazine solutions wherein the hydrazine solutions contain non-aqueous components.

[13] In certain embodiments, the solution comprises substantially pure hydrazine, meaning hydrazine in which no other chemicals are deliberately included but allowing for incidental amounts of impurities. In certain embodiments, the solution comprises from about 5% to about 99% by weight of hydrazine, or from about 90% to

about 99%, from about 95% to about 99%, from about 96% to about 99%, from about 97% to about 99%, from about 98% to about 99%, or from about 99% to about 100% by weight of hydrazine, with the remaining components comprising solvents and/or stabilizers. In some embodiments, the solution comprises hydrazine at concentrations greater than 99.9% purity and, in some embodiments, the solution comprises hydrazine at concentrations of greater than 99.99%. Selection of an appropriate non-aqueous hydrazine solution will be determined by the requirements of a particular application or process.

[14] In certain embodiments, the non-aqueous hydrazine solution comprises, in addition to hydrazine, one or more suitable solvents. For example, the non-aqueous hydrazine solution may comprise a PEGylated solvent, wherein the PEGylated solvent is a liquid when at a temperature of about 25 °C. The term "PEGylated solvent" refers to a solvent containing a covalently attached poly(ethylene glycol) moiety. One exemplary PEGylated solvent is poly(ethylene glycol) dimethyl ether. In some embodiments, the suitable solvent is selected from low molecular weight polymers or oligomers of polyaniline, polypyrrole, polypyridine or polyvinylalcohol. A low molecular weight polymer is one such that when combined with hydrazine, the combined solution has a viscosity of about 35 centipoises (cp) or less. Other examples of solvents include glymes such as monoglyme, diglyme, triglyme, higlyme, and tetraglyme. Further examples include a range of PEGylated dimethyl ethers such as Polyglycol DME 200, Polyglycol DME 250, Polyglycol DME 500, Polyglycol DME 1000, or Polyglycol DME 2000. Still other solvents include hexamethylphosphoramide and hexamethylenetetramine. In some embodiments, the non-aqueous hydrazine solution

comprises from about 30% to about 69% by weight and ranges in between including between about 65% to about 69% by weight of hydrazine. The remainder of the solution may comprise, for example, one or more PEGylated solvents such as poly(ethylene glycol) dimethyl ether. For instance, the hydrazine solution may comprise from about 32% to 35% by weight of PEGylated solvent such as poly(ethylene glycol) dimethyl ether or other suitable solvents. In other embodiments, less than about 65% hydrazine is used and more than about 35% of a PEGylated solvent such as poly(ethylene glycol) dimethyl ether is used such as Polyglycol DME 250.

[15] The methods, systems, and devices provided herein can employ a variety of membranes. The membrane is typically a selectively permeable membrane, particularly a substantially gas-impermeable membrane, e.g., a perfluorinated ion exchange membrane, such as a NAFION® membrane. In certain embodiments, the NAFION® membrane may be chemically treated e.g., with an acid, base, or salt to modify its reactivity. For example, in certain embodiments, the NAFION® membrane may be treated in a way to form the ammonium species. By using certain selectively permeable membranes, which typically are substantially gas-impermeable membranes and specifically NAFION® membranes and its derivatives, the concentration of the hydrazine gas in the resultant gas stream may be altered relative to the hydrazine concentration that would be obtained directly from the vapor of the hydrazine solution in the absence of a membrane. In certain embodiments, the hydrazine gas concentration is amplified (i.e., higher than) the concentration that would be expected from the vapor of the hydrazine solution absent the membrane. Preferably, the concentration of hydrazine is amplified using the methods, systems, and devices disclosed herein.

[16] In another embodiment, the membrane is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether. One such example of such a membrane can be made from Aquivon® which is sourced from Solvay. A specific Aquivon® polymer is known as P98S and is provided as pellets.

[17] The methods, systems, and devices provided herein may further comprise removing one or more components from the hydrazine containing gas stream to produce a purified hydrazine containing gas stream, e.g., using a device that selectively or non-selectively removes components from the gas stream. Preferred devices would be devices that substantially remove a non-reactive process gas from the hydrazine containing gas stream, while the amount of hydrazine in the gas stream is relatively unaffected. For example, a device may remove any non-aqueous solvents or stabilizers from the gas stream, including without limitation any traces of water or non-aqueous solvents. For example, the devices may further comprise a purifier positioned downstream of the head space. Particularly preferred purifier devices are membrane contactors, molecular sieves, activated charcoal and other adsorbents, if they have the desired characteristics to meet the application or process requirements. A preferred characteristic of the gas removal device is the ability to remove certain component(s) in a relatively selective manner while allowing the remaining component(s) to remain in the hydrazine gas stream relatively unaffected.

[18] The systems and devices provided herein may further comprise various components for containing and controlling the flow of the gases and liquids used therein. For example, the systems and devices may further comprise mass flow controllers, valves, check valves, pressure gauges, regulators, rotameters, and pumps.

The systems and devices provided herein may further comprise various heaters, thermocouples, and temperature controllers to control the temperature of various components of the devices and steps of the methods.

[19] Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or maybe learned by practice of the invention. The objects and advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the embodiments and claims.

[20] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention.

[21] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several embodiments of the invention and, together with the description, serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[22] Figure 1A is a diagram illustrating a part of a membrane assembly useful in certain embodiments of the present invention.

[23] Figure 1B is a diagram illustrating an embodiment of a hydrazine delivery assembly (HDA) according to certain embodiments of the present invention.

[24] Figure 2A is a cross-sectional view of an embodiment of an HDA according to certain embodiments of the present invention.

[25] Figure 2B is a cross-sectional view of an embodiment of an HDA according to certain embodiments of the present invention.

[26] Figure 3 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

[27] Figure 4 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

[28] Figure 5 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

[29] Figure 6 is a diagram illustrating a membrane assembly and HDA according to certain embodiments of the present invention.

[30] Figure 7 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

[31] Figure 8 is a chart depicting hydrazine gas concentration and temperature over time according to an embodiment of the present invention, using substantially pure hydrazine as a liquid source.

[32] Figure 9 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

[33] Figure 10 is a chart depicting hydrazine gas concentration and temperature over time according to an embodiment of the present invention, using anhydrous 98% hydrazine as a liquid source.

[34] Figure 11 is a chart depicting hydrazine gas concentration and temperature over time according to an embodiment of the present invention, using 65% hydrazine in poly(ethylene glycol) dimethyl ether as a liquid source.

[35] Figure 12 is a diagram illustrating an HDA according to certain embodiments of the present invention.

[36] Figure 13 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

[37] The term “process gas” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to a gas that is used in an application or process, e.g., a step in the manufacturing or processing of micro-electronics and in other critical processes. Exemplary process gases are reducing agents, oxidizing agents, inorganic acids, organic acids, inorganic bases, organic bases, and inorganic and organic solvents. A preferred process gas is hydrazine.

[38] The term “reactive process gas” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and

is not to be limited to a special or customized meaning), and refers without limitation to a process gas that chemically reacts in the particular application or process in which the gas is employed, e.g., by reacting with a surface, a liquid process chemical, or another process gas.

[39] The term “non-reactive process gas” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to a process gas that does not chemically react in the particular application or process in which the gas is employed, but the properties of the “non-reactive process gas” provide it with utility in the particular application or process.

[40] The term “carrier gas” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to a gas that is used to carry another gas through a process train, which is typically a train of piping. Exemplary carrier gases are nitrogen, argon, hydrogen, oxygen, CO₂, clean dry air, helium, or other gases that are stable at room temperature and atmospheric pressure.

[41] The term “head space” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to a volume of gas in fluid contact with a hydrazine solution that provides at least a portion of the gas contained in the head space. There may be a permeable or selectively permeable barrier wholly or partially separating the head space that is optionally in direct contact

with the hydrazine solution. In those embodiments where the membrane is not in direct contact with the hydrazine solution, more than one head space may exist, i.e. a first head space directly above the solution that contains the vapor phase of the solution and a second head space separated from the first head space by a membrane that only contains the components of the first space that can permeate the membrane, e.g., hydrazine. In those embodiments with a hydrazine solution and a head space separated by a substantially gas-impermeable membrane, the head space may be located above, below, or on any side of the hydrazine solution, or the head space may surround or be surrounded by the hydrazine solution. For example, the head space may be the space inside a substantially gas-impermeable tube running through the hydrazine solution or the hydrazine solution may be located inside a substantially gas-impermeable tube with the head space surrounding the outside of the tube.

[42] The term “substantially gas-impermeable membrane” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to a membrane that is relatively permeable to other components that may be present in a gaseous or liquid phase, e.g., hydrazine, but relatively impermeable to other gases such as, but not limited to, hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulfide, hydrocarbons (e.g., ethylene), volatile acids and bases, refractory compounds, and volatile organic compounds.

[43] The term “ion exchange membrane” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without

limitation to a membrane comprising chemical groups capable of combining with ions or exchanging with ions between the membrane and an external substance. Such chemical groups include, but are not limited to, sulfonic acid, carboxylic acid, sulfonamide, sulfonyl imide, phosphoric acid, phosphinic acid, arsenic groups, selenic groups, phenol groups, and salts thereof.

[44] The term “permeation rate” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers without limitation to the rate at which a specific chemical, e.g., hydrazine, or a chemical composition a permeates a membrane. The permeation rate may be expressed as an amount of the chemical or composition of interest that permeates a particular surface area of membrane during a period of time, e.g., liters per minute per square inch (L/min/in²).

[45] The term “non-aqueous solution” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers to a solution comprising hydrazine and optionally other components and containing less than 10% by weight of water. Exemplary non-aqueous solutions include those containing less than 2%, 0.5%, 0.1%, 0.01%, 0.001% or less water.

[46] The term “stabilizer” as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a special or customized meaning), and refers to a chemical that prevents the decomposition or reaction of process chemical, such as hydrazine or hydrogen peroxide. In certain embodiments, the stabilizer is non-volatile and is not present in the

vapor phase in more than an insubstantial amount. In certain embodiments, the stabilizer can be removed from the process gas stream by exposing the process gas stream to an adsorbent or passing the process gas stream through a cold trap. In certain embodiments that include a membrane separating the non-aqueous hydrazine solution from the vapor phase, the stabilizer may not permeate the membrane.

[47] The methods, systems, and devices disclosed herein provide advantageous delivery of volatile process components to a critical process application. In many embodiments, the methods, systems, and devices disclosed herein are particularly applicable to hydrazine. Certain devices disclosed herein are also applicable to other volatile process components.

[48] In certain embodiments, the advantageous hydrazine delivery provided by the present invention, and specifically the methods, systems, and devices of certain embodiments described herein, may be obtained using a membrane contactor. In a preferred embodiment, a non-porous membrane is employed to provide a barrier between the hydrazine solution and the head space that is in fluid contact with a carrier gas or vacuum. Preferably, hydrazine rapidly permeates across the membrane, while gases are excluded from permeating across the membrane into the solution. In some embodiments the membrane may be chemically treated with an acid, base, or salt to modify the properties of the membrane.

[49] In certain embodiments, the hydrazine is introduced into a carrier gas or vacuum through a substantially gas-impermeable ionic exchange membrane. Gas impermeability can be determined by the "leak rate." The term "leak rate" as used herein is a broad term, and is to be given its ordinary and customary meaning to a

person of ordinary skill in the art (and is not to be limited to a specialized or customized meaning), and refers without limitation to the volume of a particular gas that penetrates the membrane surface area per unit of time. For example, a substantially gas-impermeable membrane could have a low leak rate of gases (e.g., a carrier gas) other than a process gas (e.g., hydrazine), such as a leak rate of less than about 0.001 cm³/cm²/s under standard atmospheric temperature and pressure. Alternatively, a substantially gas-impermeable membrane can be identified by a ratio of the permeability of a process gas vapor compared to the permeability of other gases. Preferably, the substantially gas-impermeable membrane is more permeable to such process gases than to other gases by a ratio of at least 10,000:1, such as a ratio of at least about 20,000:1, 30,000:1, 40,000:1, 50,000:1, 60,000:1, 70,000:1, 80,000:1, 90,000:1 or a ratio of at least 100,000:1, 200,000:1, 300,000:1, 400,000:1, 500,000:1, 600,000:1, 700,000:1, 800,000:1, 900,000:1 or even a ratio of at least about 1,000,000:1. However, in other embodiments, other ratios that are less than 10,000:1 can be acceptable, for example 1.5:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1; 50:1, 100:1, 500:1, 1,000:1, or 5,000:1 or more.

[50] In certain embodiments, the membrane is an ion exchange membrane, such as a polymer resin containing exchangeable ions. Preferably, the ion exchange membrane is a fluorine-containing polymer, e.g., polyvinylidene fluoride, polytetrafluoroethylene (PTFE), ethylene tetrafluoride-propylene hexafluoride copolymers (FEP), ethylene tetrafluoride-perfluoroalkoxyethylene copolymers (PFE), polychlorotrifluoroethylene (PCTFE), ethylene tetrafluorideethylene copolymers (ETFE), polyvinylidene fluoride, polyvinyl fluoride, vinylidene fluoride-trifluorinated ethylene

chloride copolymers, vinylidene fluoride-propylene hexafluoride copolymers, vinylidene fluoridepropylene hexafluoride-ethylene tetrafluoride terpolymers, ethylene tetrafluoridepropylene rubber, and fluorinated thermoplastic elastomers. Alternatively, the resin comprises a composite or a mixture of polymers, or a mixture of polymers and other components, to provide a contiguous membrane material. In certain embodiments, the membrane material can comprise two or more layers. The different layers can have the same or different properties, e.g., chemical composition, porosity, permeability, thickness, and the like. In certain embodiments, it can also be desirable to employ a layer (e.g., a membrane) that provides support to the filtration membrane, or possesses some other desirable property.

[51] The ion exchange membrane is preferably a perfluorinated ionomer comprising a copolymer of ethylene and a vinyl monomer containing an acid group or salts thereof. Exemplary perfluorinated ionomers include, but are not limited to, perfluorosulfonic acid/tetrafluoroethylene copolymers ("PFSA-TFE copolymer") and perfluorocarboxylic acid/tetrafluoroethylene copolymer ("PFCA-TFE copolymer"). These membranes are commercially available under the tradenames NAFION® (E.I. du Pont de Nemours & Company), 3M Ionomer (Minnesota Mining and Manufacturing Co.), FLEMION® (Asashi Glass Company, Ltd.), and ACIPLEX® (Asashi Chemical Industry Company), and Aquivon® (Solvay).

[52] In preparing a hydrazine containing gas stream, a hydrazine solution can be passed through the membrane. The term "passing a hydrazine solution through a membrane" as used herein is a broad term, and is to be given its ordinary and customary meaning to a person of ordinary skill in the art (and is not to be limited to a

special or customized meaning), and refers without limitation to contacting a first side of a membrane with the hydrazine solution, such that the hydrazine passes through the membrane, and obtaining a hydrazine containing gas stream on the opposite side of the membrane. The first and second sides can have the form of substantially flat, opposing planar areas, where the membrane is a sheet. Membranes can also be provided in tubular or cylindrical form where one surface forms the inner position of the tube and an opposing surface lies on the outer surface. The membrane can take any form, so long as the first surface and an opposing second surface sandwich a bulk of the membrane material. Depending on the processing conditions, nature of the hydrazine solution, volume of the hydrazine solution's vapor to be generated, and other factors, the properties of the membrane can be adjusted. Properties include, but are not limited to physical form (e.g., thickness, surface area, shape, length and width for sheet form, diameter if in fiber form), configuration (flat sheet(s), spiral or rolled sheet(s), folded or crimped sheet(s), fiber array(s)), fabrication method (e.g., extrusion, casting from solution), presence or absence of a support layer, presence or absence of an active layer (e.g., a porous prefilter to adsorb particles of a particular size, a reactive prefilter to remove impurities via chemical reaction or bonding), and the like. It is generally preferred that the membrane be from about 0.5 microns in thickness or less to 2000 microns in thickness or more, preferably from about 1, 5, 10, 25, 50, 100, 200, 300, 400, or 500 microns to about 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, or 1900 microns. When thinner membranes are employed, it can be desirable to provide mechanical support to the membrane (e.g., by employing a supporting membrane, a screen or mesh, or other supporting structure), whereas

thicker membranes may be suitable for use without a support. The surface area can be selected based on the mass of vapor to be produced.

[53] Certain embodiments of the methods, systems, and devices provided herein, in which a carrier gas or vacuum can be used to deliver substantially water-free hydrazine, are shown by reference to the Figures.

[54] According to certain embodiments of the present invention, a hydrazine delivery assembly (HDA) is provided. An HDA is a device for delivering hydrazine into a process gas stream, e.g., a carrier gas used in a critical process application, e.g., microelectronics manufacturing or other critical process applications. An HDA may also operate under vacuum conditions. An HDA may have a variety of different configurations comprising at least one membrane and at least one vessel containing a non-aqueous hydrazine solution and a head space separated from the solution by membrane.

[55] Figures **1A** and **1B** depict different views of one embodiment of an HDA **100** and a membrane assembly **110** that forms part of an HDA that can be used as provided herein. Figure **1A** shows membrane assembly **110** comprising a plurality of membranes **120**, for example, 5R NAFION® membrane, which can be configured as lumens. As depicted in Figure **1A**, membranes **120** configured into lumens are inserted into a collector plate **130** through a plurality of holes within collector plate **130**. Membrane assembly **110** also comprises a plurality of polytetrafluoroethylene (PTFE) rods **140** inserted into collector plate **130**. As shown in Figure **1B**, as part of HDA **100**, membrane assembly **110** comprises membrane lumens **120** spanning collector plates **130**. HDA **100** further comprises endcaps **150** at each end of membrane assembly **110**.

Endcaps **150** further include branches **160**, which can be fitted with tubing to provide access to the interior of HDA **100**, e.g., to fill, empty, clean, or refill the HDA.

[56] Figure **2A** and Figure **2B** show a cross-sectional view of two embodiments of HDAs according to certain embodiments of the present invention.

[57] HDA **200A**, as shown in Figure **2A**, comprises a membrane assembly **210A** within a shell housing **220A** and end caps **230A** configured to couple to shell housing **220A**. Membrane assembly **210A** comprises of a plurality of membranes **240A**, which can be configured as lumens. The number of lumens can vary depending on various factors, including the size of the lumens, the size of HDA **200A**, and the operating conditions of the HDA. In certain embodiments, an HDA may contain up to 1000 membrane lumens, up to 500 lumens, up to 200 lumens, up to 100 lumens, or up to 50 lumens. For example, HDA **200A** may have about 20-50 membrane lumens. The membrane lumens can be constructed from a perfluorinated sulfonic acid membrane, for example, 5R NAFION® membrane. The end caps **230A** and shell housing **220A** can be formed from a variety of materials, for example, PTFE, stainless steel (such as 316 stainless steel), or other suitable materials. Each end cap **230A** further comprises a gas connection **231A**. Gas connection **231A** can take the form of a variety of connection configurations and sizes, for example, 1/4" VCR, 1/4" NPT, or other suitable connectors.

[58] HDA **200B**, as shown in Figure **2B**, comprises a membrane assembly **210B** within a shell housing **220B** and end caps **230B** configured to couple to shell housing **220B**. Membrane assembly **210B** can be comprised of a plurality of membrane lumens (not shown). The number of lumens can vary depending on various factors,

including the size of the lumens, the size of HDA **200B**, and the operating conditions of the HDA. In certain embodiments, an HDA may contain up to 1000 membrane lumens, up to 500 lumens, up to 200 lumens, up to 100 lumens, or up to 50 lumens. For example, HDA **200B** may have about 20-50 membrane lumens. The membrane lumens can be constructed from a perfluorinated sulfonic acid membrane, for example, 5R NAFION® membrane. The end caps **230B** and shell housing **220B** can be formed from a variety of materials, for example, PTFE, stainless steel (such as 316 stainless steel), or other suitable materials. Each end cap **230B** can comprise a gas connection **231B**. Gas connection **231B** can take the form of a variety of connection configurations and sizes, for example, 1/4" VCR, 1/4" NPT, or other suitable connectors.

[59] According to the various embodiments, the HDA can be filled with a non-aqueous hydrazine containing solution, while maintaining a head separated from the hydrazine containing solution by a membrane. Because the membrane is permeable to hydrazine and substantially impermeable to the other components of the solution, the head space will contain substantially pure hydrazine vapor in a carrier gas or vacuum, depending upon the operating conditions of the process.

[60] According to various embodiments, an HDA can be constructed similarly to the devices described in commonly assigned U.S. Patent No. 7,618,027, which is herein incorporated by reference.

[61] According to certain embodiments, a device for containing liquid and a vapor phase comprising a volatile chemical or composition, which may be a non-aqueous hydrazine containing solution, is provided, wherein the membrane contacts the volatile chemical or composition on one side of the membrane and a carrier gas stream

on the other side of the membrane. Figure **12** depicts one example of such a device **1200**, comprising (a) a chamber containing a liquid comprising a volatile chemical or chemical composition, (b) a head space comprising a vapor phase that includes the volatile chemical or chemical composition in the gas phase, (c) a inlet port through which a carrier gas stream can enter the chamber, and (d) a protected outlet port through which a process gas stream comprising carrier gas and the volatile chemical or chemical composition can exit the head space.

[62] As shown in Figure **12**, carrier gas **1214** enters through the inlet port **1202**. Carrier gas **1214** then moves through the membrane **1208** which is attached to inlet port **1202** by seal **1216**. In certain embodiments, seal **1216** provides a leak tight connection between inlet port **1202** and **1208**. In certain embodiments, seal **1216** may not be leak tight or may be a partial seal to allow a portion of carrier gas **1214** to flow into head space **1210**. In certain embodiments, membrane **1208** is a tubular membrane, but the geometry of the may be adapted according to the requirements of the particular application or process in which the device is used. One side of membrane **1208** is configured to contact liquid **1212**, which comprises a volatile chemical or composition capable of diffusing across membrane **1208**. Carrier gas **1214** flows through membrane **1208** on a side opposite the side that is in contact with liquid **1212**. Process gas stream **1218**, comprising the volatile chemical or composition in the gas phase, is formed as the volatile chemical or composition diffuses across the membrane into the carrier gas stream. Membrane **1208** allows certain components of liquid **1212** to diffuse across the membrane into the carrier gas stream to provide a select process gas stream **1218**, while preventing other components of liquid **1212** from diffusing into the process gas

stream **1218** (e.g., water, metal ions, other ionic contaminants, and other contaminants). At the outlet **1222** of membrane **1208**, process gas stream **1218**, comprising carrier gas **1214** and a process chemical from liquid **1212**, enters headspace **1210**. Thus, the pressure inside of tubular membrane **1208** matches the pressure in head space **1210** and, thus, the vapor pressure of liquid **1212**, which prevents the collapse of the membrane when the outlet pressure is lower than the inlet pressure. Process gas **1220** contained in headspace **1210** exits the device through the splash guard **1206** and outlet port **1204** for delivery to a critical process **1224**. In this embodiment, splash guard **1206** retains the open end **1222** of the tubular membrane **1208** such that the process gas stream exiting passing through outlet port **1204** is substantially free of liquid contaminants, e.g., droplets, particles, mists, or fogs.

[63] In many embodiments, e.g., the embodiment shown in Figure **12**, the membrane is partially immersed in the liquid source. Submerging the membrane increases the mass transfer surface area and the residence time the carrier gas has to fully saturate with gas generated from the liquid source. The membrane may be long enough to reach the bottom of the canister and then back up to the surface above the liquid. The membrane can range from about 3.0 inches in length or less to about 72 inches in length or more, including lengths in between such as about 5, 10, 15, 20, 25, 30, or 35 inches to about 40, 45, 50, 55, 60, or 65 inches or more. The immersed part of the membrane can be coiled to increase liquid to membrane surface area. Multiple membranes can be used and run in parallel to further increase liquid to membrane surface area. The membrane may be about 0.002 inches thick or less to about 0.010 inches thick or more, including about 0.003, 0.004, or 0.005 inches thick to about 0.006,

0.007, 0.008, or 0.009 inches thick or more. The diameter of the membrane may be about 0.062 inches or less to about 0.250 inches or more, including 0.070, 0.080, 0.090, 0.100, 0.110, 0.120, 0.130, 0.140, or 0.150 inches to about 0.160, 0.170, 0.180, 0.190, 0.200, 0.210, 0.220, 0.230, or 0.240 inches or more.

[64] In many embodiments, e.g., the embodiment shown in Figure **12**, the device includes a splash guard. The splash guard limits the volume, velocity, or nature of the liquid exiting through the outlet of the device. The splash guard is capable of maintaining the outlet of the tubular membrane above the liquid. In several embodiments, the splash guard has a long narrow slit in the conductive path to the outlet barb which prevents droplets from entering the gas stream leaving the outlet port. The splash guard is made of a material compatible with the chemistries being used in the liquid source and carrier gas. For example, low-reactive materials such as, but not limited to, stainless steel, aluminum, or plastic may be used. The splash guard may be attached to the container by fitting onto the outlet barb. In some embodiments, the splash guard is about 1.50 inches in height, the slit is about 0.03 inches in width and about 1.25 inches in height, and the slit's length is the same as the diameter of the splash guard which is about 1.00 inch.

[65] Although a primary purpose of the present disclosure is gas phase delivery of non-aqueous hydrazine according the methods, systems, and devices provided herein, other process chemicals capable of diffusing across the membrane may be used in the liquid source and, therefore, may also be part of process gas stream **1218** exiting the outlet port, include hydrogen peroxide, water, alcohols (such as ethanol, methanol, ethylene glycol, pentanol, glycerol, xylitol, or isopropyl alcohol),

amines (such as hydrazine, methylamine, ethanolamine, dimethylamine, aniline, trimethylamine, triphenylamine, aziridine, or methylethanolamine), or ammonium hydroxide. These process chemicals, whether in the liquid source or in the process gas, may be used alone or in combination. In certain embodiments, the liquid source may include a polar solvent, whereas in certain other embodiments the liquid source may include a nonpolar solvent.

[66] The devices disclosed herein that are capable of containing a liquid source comprising at least one process chemical and delivering at least one process chemical in the gas phase to a critical process application, e.g., the device shown in Figure 12, may be used in conjunction with the methods, systems, and other devices of the present invention, or they may be used as standalone devices for delivering a process gas stream to a critical process application.

[67] An embodiment according to an aspect of the methods, systems, and devices provided herein is described below by reference to a manifold 300, as shown by reference to Figure 3. According to the embodiment shown by reference to Figure 3, a carrier gas 310 flows through the head space of HDA 320, which can be an HDA as described above. A mass flow controller (MFC) 330, for example, Unit UFC-1260A 1 slm, can be used to control the flow rate of carrier gas 310, which can be set to 1 slm, for example. Analysis of the amount of hydrazine in the gas stream may require dilution of the resultant gas stream, which can be accomplished with dilution gas 350. A mass flow controller (MFC) 340, for example, a Unit UFC-1260A 10 slm can be used to control the flow rate of dilution gas 350. Carrier gas 310 and dilution gas 350 can be supplied by a gas source 360, which can be typically nitrogen or other suitable carrier

gas. A valve **370** can be used to isolate the dilution line when it is not required. Check valves **371**, **372** can be placed downstream of both MFC **330** and MFC **340** to protect them from possible hydrazine exposure. A 60 psig pressure gauge **373** can be placed between MFC **330** and check valve **372** to insure that the manifold's pressure does not exceed the maximum pressure allowed by hydrazine analyzer **380**, e.g., 5 psig.

[68] The nitrogen pressure can be maintained with a forward pressure regulator **374**, typically set to 15 psig. A thermocouple **375** can measure the temperature of nitrogen carrier gas **310** before it enters HDA **320** for hydrazine addition. A thermocouple **376** can measure the temperature of the hydrazine solution in HDA **100**. A thermocouple **377** can measure the gas temperature before entering hydrazine analyzer **380**. Hydrazine analyzer **380** can pull in a sample of carrier gas **310** to measure the hydrazine concentration. Manifold **300** can further comprise a relative humidity/resistance temperature detector (RH/RTD) probe **378**. A heater tape **390** can be placed on certain sections as indicated in Figure 3. The manifold's temperature can be controlled in two separate zones, the membrane assemblies and the remaining tubing, with a Trilite Equipment & Technologies Controller and a Watlow 96 Controller, respectively. The entire manifold can be set up inside of a fume hood.

[69] The embodiment shown by reference to Figure 3 is set up as a test apparatus to measure the amount of hydrazine introduced into a carrier gas stream under various operating conditions of an HDA. It will be understood that a similar apparatus can be used to deliver hydrazine to a critical process application.

[70] Figure 4 is a P&ID of a test manifold **400**, according to another embodiment, used to demonstrate delivery of hydrazine under vacuum conditions,

according to the methods, systems, and devices provided herein. According to the embodiment shown by reference to Figure 4, a vacuum pump **410** removes gas from the hydrazine containing vapor side (i.e., head space) of HDA **420**, which can be an HDA as described above. For example, vacuum pump **410** can be maintained at about 24 mmHg using a valve **480** and a pressure gauge **430**. A gas source **440** can be maintained at a pressure of about 2 psig with a forward pressure regulator **450**. A valve **460** can be used as a flow restrictor. A thermocouple **470** can be placed inside the filling tube of a HDA **420** to measure the solution's temperature inside the shell of HDA **420**. The test involves contacting the vapor side, i.e., head space, of HDA **420** to a vacuum produced by vacuum pump **410** while holding HDA **420** at a constant temperature. A heat tape **490** can be placed around HDA **420** to allow for constant temperature control of the hydrazine containing solution within HDA **420**. This vacuum-based method, system, and device is particularly preferred in numerous micro-electronics and other critical process applications that are operated at relatively reduced pressures (i.e., under vacuum).

[71] The embodiment shown by reference to Figure **4** is set up as a test apparatus to measure the amount of hydrazine introduced into a carrier gas stream under various operating conditions of an HDA. It will be understood that a similar apparatus can be used to deliver hydrazine to a critical process application.

[72] Figure **5** is a P&ID of a test manifold **500**, according to another embodiment, used to demonstrate delivery of hydrazine, according to an aspect of the methods, systems, and devices provided herein. As shown in Figure **5**, a nitrogen carrier gas **510** can flow through the head space of HDA **520**, which can be an HDA as

described above. A mass flow controller (MFC) **530**, for example, a Brooks SLA5850S1EAB1B2A1 5 slm, can be used to control the flow rate of nitrogen carrier gas **510**, which can be set to 1 slm, for example. Analysis of the amount of hydrazine in the gas stream may require dilution of the resultant gas stream, which can be accomplished with dilution gas **550**. A mass flow controller (MFC) **540**, for example, a Brooks SLA5850S1EAB1B2A1 10 slm, can be used to control the flow rate of a nitrogen dilution gas **550**. Nitrogen carrier gas **510** and nitrogen dilution gas **550** can be supplied by a nitrogen gas source **560**. A valve **570** can be used to isolate the dilution line when desired. A pair of check valves **571**, **572** can be placed downstream of both MFC **530** and MFC **540** to protect them from possible hydrazine exposure. A pressure gauge **573**, for example, 100 psi gauge, can be placed between MFC **530** and HDA **520** to insure that the manifold's pressure does not exceed any maximum pressure allowed by an analyzer **580**.

[73] The nitrogen pressure can be maintained with a forward pressure regulator **574**, for example set to 25 psig. A thermocouple **575** can measure the temperature of nitrogen carrier gas **510** before it enters HDA **520** for hydrazine addition. Within HDA **520**, nitrogen carrier gas **510** can flow through the membrane tubes and hydrazine vapor can permeate through the membrane from the solution contained within the shell housing and combined with carrier gas **510**. A thermocouple **576** can measure the temperature of the hydrazine solution in HDA **520**. A thermocouple **577** can measure the gas temperature exiting HDA **520**. In this embodiment, an analyzer **580** can be used to measure the hydrazine concentration in the gas stream. Analyzer **580** can be, for example, a MiniRAE 3000, which has a photoionization detector with an

11.7eV gas discharge lamp. Analyzer **580** can, for example, pull a sample of the hydrazine containing gas stream to measure the hydrazine concentration. A thermocouple **578** can be used to measure the gas temperature before entering analyzer **580**. A thermocouple **581** can be used to measure the temperature of nitrogen dilution gas **550**.

[74] Manifold **500** can further comprise a catalytic converter **585** configured to remove the hydrazine by converting it into nitrogen and hydrogen. Downstream of catalytic converter **585** can be a probe **579**, for example, a E+E Elektronik EE371 humidity transmitter configured to measure the dew point (DP) and moisture concentration. Downstream of probe **579** can be a vent. A heater tape **590** can be placed on certain sections as indicated in Figure **5**. The manifold's temperature can be controlled in four separate zones, indicated by the dotted line boxes, with Watlow EZZone® 96 controllers, respectively. The entire manifold can be set up inside of a fume hood.

[75] The embodiment shown by reference to Figure **5** is set up as a test apparatus to measure the amount of hydrazine introduced into a carrier gas stream under various operating conditions of an HDA. It will be understood that a similar apparatus can be used to deliver hydrazine to a critical process application.

[76] Figure **6** is a diagram illustrating a cross-section of a membrane assembly useful in certain embodiments of the present invention when a single membrane is used. The membrane assembly may be incorporated into, for example, an HDA such as one shown in Figure **1B**. As shown in Figure **6**, in one embodiment of the invention, the membrane may be a single membrane lumen sleeved over a stainless steel tube

containing a calibrated number of holes to provide a specific membrane surface area available for permeation. The sleeved stainless steel tube is encased inside an outer tube to form the Hydrazine Delivery Assembly (HDA). Liquid hydrazine is filled inside the space between the inner and outer tubes. A carrier gas is directed to flow through the inner tube to carry hydrazine vapor which has permeated the membrane to the desired process.

[77] Figure 7 is a P&ID of a manifold that can be used to test methods, systems, and devices for hydrazine delivery according to certain embodiments of the present invention. According to this embodiment, a carrier gas (CG) flows through the head space of the HDA, labeled "Vaporizer," which can be an HDA as described above. A mass flow controller (MFC 1), for example, a 5 slm Brook's SLA5850S1EAB1B2A1 mass flow controller, can be used to control the flow rate of carrier gas into the HDA. Analysis of the amount of hydrazine in the gas stream exiting the vaporizer may involve first diluting the resultant gas stream, which can be accomplished with a dilution gas (DG-1). A mass flow controller (MFC 2), for example, a 10 slm Brook's SLA5850S1EAB1B2A1 mass flow controller, can be used to control the flow rate of dilution gas DG-1. A separate line of dilution gas DG-2 may be supplied to a portion of the manifold positioned within a Glove Bag.

[78] Carrier gas CG and dilution gases DG-1 and DG-2 can be supplied by a Gas Source, which can be typically nitrogen or other suitable carrier gas. In some embodiments such as the one shown in Figure 7, the carrier gas and dilution gases share the same gas source. In other embodiments, the carrier gas and dilution gases may have independent gas sources. Valves V-1 and V-2 can be used to control gas

flow into the HDA/DG-1 dilution line or into the DG-2 dilution line/Glove Bag, respectively. Check valves CV-1 and CV-2 can be placed downstream of MFC 2 and MFC 1, respectively, to protect them from possible hydrazine exposure. A pressure gauge PG-2 can be placed between CV-2 and the Vaporizer to measure pressure upstream of the Vaporizer.

[79] The carrier gas pressure can be maintained with a forward pressure regulator PR1 and measured with pressure gauge PG-1. A forward pressure regulator PR2 can be used to control the flow of dilution gas DG-2 through the Gas Bag. A thermocouple T-1 can measure the temperature of the hydrazine solution in the Vaporizer. A thermocouple T-2 can measure the gas temperature after a mixing loop and before entering a hydrazine analyzer. The MiniRAE 3000 is one example of a hydrazine analyzer. Heater tape HT can be placed on certain sections, such as on the Vaporizer, a portion of the dilution gas DG-1 line, and lines downstream of the Vaporizer as indicated in Figure 7. The manifold may also comprise catalytic converters downstream of the Vaporizer and Glove Bag to decompose hydrazine to nitrogen and hydrogen. The entire manifold can be set up inside of a fume hood.

[80] The embodiment shown by reference to Figure 7 is set up as a test apparatus to measure the amount of hydrazine introduced into a carrier gas stream under various operating conditions of an HDA. It will be understood that a similar apparatus can be used to deliver hydrazine to a critical process application.

EXAMPLE 1

Experimental

[81] In the examples of the disclosure, membranes were prepared by purchasing sulfonyl fluoride perfluorinated polymers, extruding them, and then hydrolyzing them by methods known in the art to form membranes. Such membranes are also referred to as NAFION® herein.

[82] The manifold illustrated in Figure 7 was utilized for a test procedure in this Example. The test procedure involved obtaining stable gas phase hydrazine readings utilizing a non-aqueous, substantially pure hydrazine solvent as a liquid source.

[83] A NAFION® vaporizer (P/N# 200801-01) was used for this experiment. This vaporizer included a single 5R NAFION® membrane sleeved over a 1/8" SS (stainless steel) tubing. The SS tubing had twenty 0.06" diameter holes, allowing for a total permeable area of 0.06 in². The tubing was enclosed by a 3/8" SS tubing with two 1/4" fill ports for the shell side. The volume of the shell side was approximately 8 ml.

[84] The manifold was setup in a fume hood. The nitrogen pressure was maintained at 25 psig with a forward pressure regulator (**PR-1**) and measured with a pressure gauge (**PG-1**). Two valves (**V-1** and **V-2**) were used to terminate gas flow through vaporizer and/or dilution line. A 5 slm Brook's SLA5850S1EAB1B2A1 Mass Flow Controller (MFC-1) was used to control the carrier gas flow rate. A 10 slm Brook's SLA5850S1EAB1B2A1 Mass Flow Controller (MFC-2) was used to control the dilution gas flow rate. Check valves (CV-1 and CV-2) were placed downstream of both MFCs to protect them from being exposed to hydrazine. A forward pressure regulator with gauge (PR-2) was used to control flow of nitrogen through gas bag. The pressure upstream of the vaporizer was measured with a pressure gauge (PG-2). A J-type thermocouple (TC-1) was attached to the vaporizer as a control point for the heater tape. The carrier

gas was mixed with the nitrogen from the dilution line downstream of the vaporizer. A J-type thermocouple (TC-2) was used to monitor gas temperature after mixing. A MiniRAE 3000, which has a photoionization detector (PID) with an 11.7eV gas discharge lamp, was used to measure the hydrazine concentration in the gas stream. The test manifold and glove bag vent lines had catalytic converters that decomposed the hydrazine to nitrogen and hydrogen. The vaporizer, a portion of the dilution line, and the test manifold downstream of the vaporizer was heat-traced with heater tape.

[85] For this experiment, the carrier gas flow was set to 1 slm. The dilution gas flow was initially set to 1 slm and would be increased if the concentration was above 2000 ppm (upper detection limit of the MiniRae 3000). The manifold was heated to keep the gas temperature at 30 °C at TC-2.

[86] Figure 8 represents the results from this experiment with the carrier gas flow and dilution gas flow at 1 slm. As shown, the hydrazine output was directly affected by the gas temperature once the system was stabilized. This effect was demonstrated when the temperature setpoint for this experiment was raised from 30 °C to 31 °C 78 minutes into the test. The average concentration of hydrazine was 2426 ppm for the last 26 minutes of the test. The result is a permeation rate of 0.04043 L/min/in² under these conditions.

EXAMPLE 2

[87] The manifold illustrated in Figure 9 was utilized for test procedures in this Example. The test procedures involved obtaining stable gas phase hydrazine readings using either an anhydrous 98% hydrazine solvent as a liquid source, or a solution of

65% hydrazine in poly(ethylene glycol) dimethyl ether solvent ($M_n=250$) as a liquid source.

[88] A NAFION® vaporizer (P/N# 200846-A) was used for these experiments. This vaporizer consisted of a single 5R NAFION® membrane sleeved over a 1/8" SS tubing. The SS tubing had ten 0.06" diameter holes, allowing for a total permeable area of 0.03 in². The tubing is enclosed by a 3/8" SS tubing with two 1/4" fill ports for the shell side. The volume of the shell side was approximately 8 ml.

[89] The manifold was setup in a fume hood. An Entegris 500KF Gatekeeper purifier was used to remove oxygen, water, and hydrocarbons from the gas stream. Two valves (V-1 and V-2) were used to terminate gas flow through glove box and the test manifold respectively. The nitrogen flow inside the glove box was maintained with a forward pressure regulator and the pressure measured with a pressure gauge (PG-1). A check valve (CV-1) was placed upstream of the glove box to prevent back streaming of the hydrazine. A forward pressure regulator with gauge was used to maintain a gas pressure of 25psig upstream of the MFCs. A 5 slm Brook's SLA5850S1EAB1B2A1 Mass Flow Controller (MFC-1) was used to control the carrier gas flow rate. A 10 slm Unit Mass Flow Controller (MFC-2) was use to control the dilution gas flow rate. Check valves (CV-2 and CV-3) were placed downstream of both MFCs to protect them from being exposed to hydrazine.

[90] A single-lumen vaporizer was used to add hydrazine vapor to the gas stream. The mixing loop was used to mix nitrogen from the dilution line and hydrazine vapor in the carrier gas downstream of the vaporizer. A J-type thermocouple (TC-1) was used to monitor gas temperature after mixing. A MiniRAE 3000, which has a

photoionization detector (PID) with an 11.7eV gas discharge lamp, was used to measure the hydrazine concentration in the gas stream. The test manifold and glove box vent lines had scrubbers that catalytically decompose the hydrazine to nitrogen and hydrogen. A valve (V-3) was used to create backpressure in the glove box and for isolation.

[91] For this Example, two solutions were tested at room temperature. One solution was anhydrous 98% hydrazine (Sigma Aldrich). The second solution was 65% w/w hydrazine ($\rho = 1.029 \text{ g/ml}$) in poly(ethylene glycol) dimethyl ether ($\rho = 1.03 \text{ g/ml}$). An 8ml solution was made with 5.2ml of anhydrous 98% hydrazine and 2.8ml of poly(ethylene glycol) dimethyl ether.

[92] Before each test run, the MiniRAE 3000 was calibrated with 100ppm isobutene gas standard. Once the analyzer was attached the test manifold, the solution was added to the vaporizer without gas flowing through the test manifold. Once filled, the carrier gas flow was set to 1slm and the dilution gas flow was to 1slm. The dilution gas flow would be increased if the concentration was above 2000ppm (upper detection limit of the MiniRAE 3000). Readings of the gas temperature and hydrazine concentration were recorded. Stabilization would be determined as when the vaporizer output change was less than 5ppm/min.

[93] Figure 10 represents the results from the anhydrous 98% hydrazine with the carrier gas flow and dilution gas flow at 1 slm for 330 minutes. After stabilization was reached in ten minutes, the average concentration was $1482.7 \text{ ppm} \pm 102.2 \text{ ppm}$ at an average temperature of $23.6 \text{ }^{\circ}\text{C} \pm 0.4 \text{ }^{\circ}\text{C}$. Thus, the concentration was stable to within less than 10% of the average concentration. The result is an average permeation

rate of 0.04942 L/min/in² under these conditions. This hydrazine permeation rate was close to the 0.04043 L/min/in² permeation rate measured during the previous test done in Example 1.

[94] Figure 11 represents the results from the 65% hydrazine in poly(ethylene glycol) dimethyl ether with the carrier gas flow and dilution gas flow at 1 slm for 320 minutes. After stabilization was reached in 30 minutes, the average concentration was 1190.6 ppm \pm 27.6 ppm with an average temperature of 24.5 °C \pm 0.3 °C. The result was an average permeation rate of 0.03969 L/min/in² under these conditions. Spikes in hydrazine concentration shown near time zero in Figures 10 and 11 reflect artifacts in the measuring instruments and are not deemed to be accurate or relevant.

[95] The permeation was 19.7% less with the 65% hydrazine/ poly(ethylene glycol) dimethyl ether solution in comparison to the 98% hydrazine solution. An encouraging attribute shown with the 65% hydrazine/solvent was that the output was more stable over time than the 98% hydrazine hydrate solution. In 290 minutes the 98% hydrazine solution concentration output decreased 263 ppm. However, the 65% hydrazine/ poly(ethylene glycol) dimethyl ether solution concentration output only decreased 23 ppm in 290 minutes. The overall result with the poly(ethylene glycol) dimethyl ether presents it as a viable solvent for safe hydrazine vapor delivery.

[96] By controlling the temperature of the hydrazine containing solution and, as applicable, the carrier gas or vacuum, particular hydrazine concentrations can be delivered. The stability of the hydrazine concentration in the process gas stream can be controlled to less than about 20%, e.g., less than about 18%, less than about 16%, less than about 14%, or less than about 12%, or less than about 10%. In a preferred

embodiment, the stability of the hydrazine concentration in the process gas stream can be controlled to less than about 10% of the average concentration within one standard deviation, e.g., less than about 9%, less than about 8%, less than about 7%, less than about 6%, less than about 5%, less than about 4%, less than about 3%, less than about 2%, or even less than about 1%. The average concentration does not include measurements by the instrument prior to achieving equilibrium. For example, the measurement in Figure 11 of hydrazine concentration includes what appears to be a spike of up to about 1900 ppm. This spike is an instrument factor and not an actual measurement as it takes on the order of about 10 minutes or more for the instrument to stabilize and all average concentration readings hereunder take such stabilization into account. The selection of a particular hydrazine concentration will depend on the requirements of the application or process in which the hydrazine containing process gas will be used. In certain embodiments, the hydrazine containing gas stream may be diluted by adding additional carrier gas. In certain embodiments, the hydrazine containing gas stream may be combined with other process gas streams prior to or at the time of delivering hydrazine to an application or process. Alternatively or additionally, any residual solvent or stabilizers, or contaminants present in the hydrazine containing process gas may be removed in a purification (e.g., dehumidification) step using a purifier apparatus.

EXAMPLE 3

[97] The manifold illustrated in Figure 13 was utilized for test procedures in this Example. The Brute™ vaporizer 1306 was assembled with a PTFE splash guard on the

outlet barb and a new lumen assembly. Brute™ vaporizer **1306** was filled with 200mL of a liquid source solution comprising hydrogen peroxide and the lid was assembled. The test system **1300** was assembled as shown in Figure **13**. Manometer **1310** was connected to the display readout. All valves **1302**, **1304**, **1308**, and **1312** were closed and vacuum pumps **1318**, **1320**, and **1322** were off. Cold trap bath **1316** was filled with liquid nitrogen. Outlet back pressure valve (BPV) **1304** was closed and valve **1312** was opened. Vacuum pumps **1318**, **1320**, and **1322** were turned on, the cold trap bath **1316** was opened, and the equilibrium pressure was recorded. Outlet BPV **1304** was quickly opened to shock vaporizer **1306** with low pressure. Observation perfluoroalkoxy (PFA) Tube **1324** was monitored for signs of droplets of the liquid source solution. Vaporizer **1306** was exposed to vacuum until the pressure was constant. Valve **1312** was turned off and the rate of rise was recorded in minute intervals. The test was repeated several times. The splash guard prevented liquid solution from entering the outlet of vaporizer **1306** at pressures below 1 torr.

[98] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A method comprising:

(a) providing a non-aqueous hydrazine solution having a vapor phase comprising an amount of hydrazine vapor;

(b) contacting a carrier gas or vacuum with the vapor phase; and

(c) delivering a gas stream comprising anhydrous hydrazine to a critical process or application.

2. The method of claim 1, further comprising changing the concentration of at least one component of the vapor phase by changing at least one of the following parameters: (a) the temperature of the hydrazine solution, (b) the pressure of the hydrazine solution, (c) the concentration of the hydrazine solution, (d) the temperature of the carrier gas, (e) the pressure of the carrier gas or vacuum, and (f) the flow rate of the carrier gas.

3. The method of any one of claims 1 or 2, wherein a membrane is in contact with the non-aqueous hydrazine solution.

4.. The method of any one of claims 1 to 3, wherein at least one membrane at least partially separates the vapor phase from the non-aqueous hydrazine solution.

5. The method of any one of claims 3 or 4, wherein hydrazine permeates the membrane at a faster rate than any other component of the non-aqueous hydrazine solution.
6. The method of any one of claims 3 to 5, wherein the membrane is a substantially gas-impermeable membrane.
7. The method of claim 6, wherein the substantially gas-impermeable membrane comprises an ion exchange membrane.
8. The method of any one of claims 3 to 7, further comprising changing the concentration of at least one component of the vapor phase by changing the surface area of the membrane,
9. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution further comprises a hydrazine stabilizer.
10. The method of claim 9, further comprising removing any residual stabilizer from the gas stream prior to the delivery to a critical process or application.
11. The method of any one of the preceding claims, further comprising removing contaminants from the gas stream.

12. The method of any one of the preceding claims, wherein the carrier gas comprises nitrogen, argon, hydrogen, clean dry air, helium, or other gases that are stable at room temperature and atmospheric pressure.
13. The method of any one of the preceding claims, further comprising changing the concentration of at least one component of the vapor phase by adding energy to the hydrazine solution.
14. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution further comprises a solvent selected from polymers or oligomers of polyaniline, polypyrrole, polypyridine or polyvinylalcohol wherein the viscosity of the solution is about 35 cp or less.
15. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution further comprises a solvent selected from monoglyme, diglyme, triglyme, higlyme, tetraglyme, Polyglycol DME 200, Polyglycol DME 250, Polyglycol DME 500, Polyglycol DME 1000, Polyglycol DME 2000, hexamethylphosphoramide or hexamethylenetetramine.
16. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution further comprises a PEGylated solvent, wherein the PEGylated solvent is a liquid when at a temperature of about 25 °C.

17. The method of claim 16, wherein the non-aqueous hydrazine solution comprises poly(ethylene glycol) dimethyl ether.
18. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution comprises from about 25% to about 69% by weight of hydrazine.
19. The method of any one of claims 1 to 18, wherein the non-aqueous hydrazine solution comprises from about 50% to about 69% by weight of hydrazine.
20. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution comprises from about 60% to about 69% by weight of hydrazine.
21. The method of any one of the preceding claims, wherein the non-aqueous hydrazine solution comprises from about 65% to about 69% by weight of hydrazine.
22. The method of any one of claims 1 to 12, wherein the non-aqueous hydrazine solution is substantially pure hydrazine.
23. The method of any one of the preceding claims, wherein the concentration of hydrazine delivered is stable to within about 20% of the average concentration delivered.

24. The method of any one of claims 1 to 22, wherein the concentration of hydrazine delivered is stable to within about 10% of the average concentration delivered.
25. The method of any one of claims 1 to 22, wherein the concentration of hydrazine delivered is stable to within about 5% of the average concentration delivered.
26. The method of any one of claims 1 to 22, wherein the concentration of hydrazine delivered is stable to within about 3% of the average concentration delivered.
27. A chemical delivery system comprising:
- (a) a non-aqueous hydrazine solution having a vapor phase comprising an amount hydrazine vapor;
 - (b) a carrier gas or vacuum in fluid contact with the vapor phase; and
 - (c) an apparatus for delivering a gas stream comprising at least one component of the hydrazine solution to a critical process or application.
28. The chemical delivery system of claim 27, configured to provide for changing the concentration of at least one component of the vapor phase by changing at least one of the following parameters: (a) the temperature of the hydrazine solution, (b) the pressure of the hydrazine solution, (c) the concentration of the hydrazine solution, (d) the temperature of the carrier gas, (e) the pressure of the carrier gas or vacuum, and (f) the flow rate of the carrier gas.

29. The chemical delivery system of any one of claims 27 or 28, wherein the non-aqueous hydrazine solution further comprises a hydrazine stabilizer.
30. The chemical delivery system of claim 29, further comprising an apparatus for removing the stabilizer from the gas stream prior to the delivery to a critical process or application.
31. The chemical delivery system of any one of claims 27 or 28, further comprising a membrane that is in contact with the non-aqueous hydrazine solution.
32. The chemical delivery system of any one of claims 27 or 28, wherein at least one membrane at least partially separates the vapor phase from the non-aqueous hydrazine solution.
33. The chemical delivery system of any one of claims 31 or 32, wherein hydrazine permeates the membrane at a faster rate than any other component of the non-aqueous hydrazine solution.
34. The chemical delivery system of any one of claims 31 to 33, wherein the membrane is a substantially gas-impermeable membrane.
35. The chemical delivery system of claim 34, wherein the substantially gas-impermeable membrane is an ion exchange membrane.

36. The chemical delivery system of any one of claims 31 to 35, further comprising a hydrazine stabilizer.
37. The chemical delivery system of claim 36, wherein the membrane is substantially impermeable to the stabilizer.
38. The chemical delivery system of any one of claims 36 or 37, further comprising an apparatus for removing the stabilizer from the gas stream prior to the delivery to a critical process or application.
39. The chemical delivery system of any one of claims 31 to 38, configured to provide for changing the concentration of at least one component of the vapor phase by changing the surface area of the membrane.
40. The chemical delivery system of any one of claims 27 to 39, wherein the carrier gas comprises nitrogen, argon, hydrogen, clean dry air, helium, or other gases that are stable at room temperature and atmospheric pressure.
41. The chemical delivery system of any one of claims 27 to 40, configured to provide for changing the concentration of at least one component of the vapor phase by adding energy to the hydrazine solution.

42. The chemical delivery system of any one of claims 27 to 41, wherein the apparatus for delivering a gas stream comprising at least one component of the hydrazine solution is an outlet of a head space, containing the vapor phase, that is connected directly or indirectly to a critical process or application.
43. The chemical delivery system of any one of claims 27 to 42, wherein the non-aqueous hydrazine solution further comprises a solvent selected from polymers or oligomers of polyaniline, polypyrrole, polypyridine or polyvinylalcohol wherein the viscosity of the solution is about 35 cp or less.
44. The chemical delivery system of any one of claims 27 to 43, wherein the non-aqueous hydrazine solution further comprises a solvent selected from monoglyme, diglyme, triglyme, higlyme, tetraglyme, Polyglycol DME 200, Polyglycol DME 250, Polyglycol DME 500, Polyglycol DME 1000, Polyglycol DME 2000, hexamethylphosphoramide or hexamethylenetetramine.
45. The chemical delivery system of any one of claims 27 to 44, wherein the non-aqueous hydrazine solution further comprises a PEGylated solvent, wherein the PEGylated solvent is a liquid when at a temperature of about 25 °C.
46. The chemical delivery system of claim 45, wherein the non-aqueous hydrazine solution comprises poly(ethylene glycol) dimethyl ether.

47. The chemical delivery system of any one of claims 27 to 46, wherein the non-aqueous hydrazine solution comprises from about 25% to about 69% by weight of hydrazine.

48. The chemical delivery system of any one of claims 27 to 46, wherein the non-aqueous hydrazine solution comprises from about 50% to about 69% by weight of hydrazine.

49. The chemical delivery system of any one of claims 27 to 46, wherein the non-aqueous hydrazine solution comprises from about 60% to about 69% by weight of hydrazine.

50. The chemical delivery system of any one of claims 27 to 46, wherein the non-aqueous hydrazine solution comprises from 65% to 69% by weight of hydrazine.

51. The chemical delivery system of any one of claims 27 to 42, wherein the non-aqueous hydrazine solution is substantially pure hydrazine.

52. A device comprising:

(a) a housing configured to contain a solution comprising a process chemical to be used in a critical process application;

(b) a solution comprising a process chemical to be used in a critical process application contained within the housing;

(c) a head space configured to contain vapor comprising the process chemical in the gas phase;

(d) an inlet port in fluid communication with the head space and configured to allow a carrier gas to flow into the device through at least one membrane connected to the inlet port, wherein at least a portion of the membrane contacts the solution; and

(e) an outlet port in fluid communication with the head space and configured to allow a process gas stream comprising the process chemical to flow out of the device.

53. The device of claim 52, further comprising a device for changing at least one of the following parameters: (a) the temperature of the solution, (b) the pressure of the solution, (c) the concentration of the solution, (d) the temperature of the carrier gas, (e) the pressure of the carrier gas, and (f) the flow rate of the carrier gas.

54. The device of any one of claims 52 or 53, wherein the process chemical is selected from the group consisting of hydrogen peroxide, alcohols, amines, and ammonium hydroxide.

55. The device of claim 54, wherein the process chemical is hydrogen peroxide.

56. The device of claim 55, wherein the solution is a non-aqueous hydrogen peroxide solution.

57. The device of any one of claims 55 or 56, wherein the solution further comprises a hydrogen peroxide stabilizer.
58. The device of claim 57, further comprising an apparatus for removing the stabilizer from the gas stream prior to the delivery to a critical process or application.
59. The device of any one of claims 52 to 53, wherein the process chemical is an alcohol selected from the group consisting of ethanol, methanol, ethylene glycol, pentanol, glycerol, xylitol, or isopropyl alcohol.
60. The device of claim 59, wherein the solution is non-aqueous.
61. The device of any one of claims 52 to 53, wherein the process chemical is an amine selected from the group consisting of hydrazine, methylamine, ethanolamine, dimethylamine, aniline, trimethylamine, triphenylamine, aziridine, or methylethanolamine.
62. The device of claim 61, wherein the solution is non-aqueous.
63. The device of claim 61, wherein the process chemical is hydrazine.
64. The device of claim 63, wherein the solution is a non-aqueous hydrazine solution.

65. The device of any one of claims 63 or 64, wherein the hydrazine solution further comprises a hydrazine stabilizer.
66. The device of claim 65, further comprising an apparatus for removing the stabilizer from the gas stream prior to the delivery to a critical process or application.
67. The device of any one of claims 57 or 66, wherein the at least one membrane is substantially impermeable to the stabilizer.
68. The device of any one of claims 52 to 66, wherein the at least one membrane at least partially separates the head space from the solution.
69. The device of any one of claims 52 to 68, wherein the process chemical permeates the membrane at a faster rate than any other component of the solution.
70. The device of any one of claims 52 to 69, wherein the at least one membrane is a substantially gas-impermeable membrane.
71. The device of claim 70, wherein the substantially gas-impermeable membrane is an ion exchange membrane.

72. The device of any one of claims 52 to 71, configured to provide for changing the concentration of at least one component of the vapor by changing the surface area of the membrane.
73. The device of any one of claims 52 to 72, wherein the one membrane comprises a plurality of membrane lumens.
74. The device of any one of claims 52 to 73, wherein the carrier gas comprises nitrogen, argon, hydrogen, clean dry air, helium, or other gases that are stable at room temperature and atmospheric pressure.
75. The device of any one of claims 52 to 74, configured to provide for changing the concentration of at least one component of the vapor phase by adding energy to the solution.
76. The device of any one of claims 52 to 75, wherein the head space is connected directly or indirectly to a critical process or application.
77. The device of any one of claims 52 to 76, wherein the solution is a non-aqueous solution that further comprises a solvent selected from polymers or oligomers of polyaniline, polypyrrole, polypyridine or polyvinylalcohol wherein the viscosity of the solution is about 35 cp or less.

78. The device of any one of claims 52 to 77, wherein the solution is a non-aqueous solution that further comprises a solvent selected from monoglyme, diglyme, triglyme, higlyme, tetraglyme, Polyglycol DME 200, Polyglycol DME 250, Polyglycol DME 500, Polyglycol DME 1000, Polyglycol DME 2000, hexamethylphosphoramide or hexamethylenetetramine.

79. The device of any one of claims 52 to 78, wherein the solution is a non-aqueous solution that further comprises a PEGylated solvent, wherein the PEGylated solvent is a liquid when at a temperature of 25 °C.

80. The device of claim 79, wherein the solution comprises poly(ethylene glycol) dimethyl ether.

81. The device of any one of claims 52 to 80, wherein the solution is a non-aqueous hydrazine solution that comprises from 25% to 69% by weight of hydrazine.

82. The device of any one of claims 52 to 80, wherein the solution is a non-aqueous hydrazine solution that comprises from about 50% to about 69% by weight of hydrazine.

83. The device of any one of claims 52 to 80, wherein the solution is a non-aqueous hydrazine solution that comprises from about 60% to about 69% by weight of hydrazine.

84. The device of any one of claims 52 to 80, wherein the solution is a non-aqueous hydrazine solution that comprises from about 65% to about 69% by weight of hydrazine.
85. The device of any one of claims 52 to 76, wherein the solution is a non-aqueous hydrazine solution that comprises substantially pure hydrazine.
86. The device of any one of claims 52 to 85, wherein the device further comprises a port for relieving pressure inside the container.
87. The device of claim 86, wherein the third port is attached to a pressure relief device.
88. The device of claim 87, wherein the third port contains a membrane barrier between the liquid in the container and the pressure relief device.
89. A method comprising using the device of any one of claims 52 to 88 to deliver a process chemical to a critical process application.
90. A method comprising:
- (a) providing a solution comprising a process chemical to be used in a critical process application;
 - (b) providing a head space in fluid communication with the solution to contain vapor comprising the process chemical in the gas phase, wherein the head space

contains at least a portion of at least one membrane that is at least partially in contact with the solution;

(c) contacting a carrier gas or vacuum with the vapor phase; and

(d) delivering a gas stream comprising the process chemical to a critical process or application.

91. The method of claim 90, further comprising changing the concentration of at least one component of the vapor phase by changing at least one of the following parameters: (a) the temperature of the solution, (b) the pressure of the solution, (c) the concentration of the solution, (d) the temperature of the carrier gas, (e) the pressure of the carrier gas, and (f) the flow rate of the carrier gas.

92. The method of any one of claims 90 or 91, wherein the process chemical is selected from the group consisting of hydrogen peroxide, alcohols, amines, and ammonium hydroxide.

93. The method of claim 92, wherein the process chemical is hydrogen peroxide.

94. The method of claim 93, wherein the solution is a non-aqueous hydrogen peroxide solution.

95. The method of any one of claims 93 or 94, wherein the solution further comprises a hydrogen peroxide stabilizer.

96. The method of claim 95, further comprising removing the stabilizer from the gas stream prior to the delivery to a critical process or application.
97. The method of any one of claims 90 or 91, wherein the process chemical is an alcohol selected from the group consisting of ethanol, methanol, ethylene glycol, pentanol, glycerol, xylitol, or isopropyl alcohol.
98. The method of claim 97, wherein the solution is non-aqueous.
99. The method of any one of claims 90 or 91, wherein the process chemical is an amine selected from the group consisting of hydrazine, methylamine, ethanolamine, dimethylamine, aniline, trimethylamine, triphenylamine, aziridine, or methylethanolamine.
100. The method of claim 99, wherein the solution is non-aqueous.
101. The method of claim 99, wherein the process chemical is hydrazine.
102. The method of claim 101, wherein the solution is a non-aqueous hydrazine solution.

103. The method of any one of claims 101 or 102, wherein the hydrazine solution further comprises a hydrazine stabilizer.

104. The method of claim 103, further removing the stabilizer from the gas stream prior to the delivery to a critical process or application.

105. The method of any one of claims 95 or 103, wherein the at least one membrane is substantially impermeable to the stabilizer.

106. The method of any one of claims 90 to 105, wherein the at least one membrane at least partially separates the head space from the solution.

107. The device of any one of claims 90 to 106, wherein the process chemical permeates the membrane at a faster rate than any other component of the solution.

108. The method of any one of claims 90 to 107, wherein the at least one membrane is a substantially gas-impermeable membrane.

109. The method of claim 108, wherein the substantially gas-impermeable membrane is an ion exchange membrane.

110. The method of any one of claims 90 to 109, further comprising changing the concentration of at least one component of the vapor phase by changing the surface area of the membrane.

111. The method of any one of claims 90 to 110, wherein the one membrane comprises a plurality of membrane lumens.

112. The method of any one of claims 90 to 111, wherein the carrier gas comprises nitrogen, argon, hydrogen, clean dry air, helium, or other gases that are stable at room temperature and atmospheric pressure.

113. The method of any one of claims 90 to 112, configured to provide for changing the concentration of at least one component of the vapor phase by adding energy to the solution.

114. The method of any one of claims 90 to 113, wherein the head space is connected directly or indirectly to a critical process or application.

115. The method of any one of claims 90 to 114, wherein the solution is a non-aqueous solution that further comprises a solvent selected from polymers or oligomers of polyaniline, polypyrrole, polypyridine or polyvinylalcohol wherein the viscosity of the solution is about 35 cp or less.

116. The method of any one of claims 90 to 115, wherein the solution is a non-aqueous solution that further comprises a solvent selected from monoglyme, diglyme, triglyme, higlyme, tetraglyme, Polyglycol DME 200, Polyglycol DME 250, Polyglycol DME 500, Polyglycol DME 1000, Polyglycol DME 2000, hexamethylphosphoramide or hexamethylenetetramine.

117. The method of any one of claims 90 to 116, wherein the solution is a non-aqueous solution that further comprises a PEGylated solvent, wherein the PEGylated solvent is a liquid when at a temperature of 25 °C.

118. The method of claim 117, wherein the solution comprises poly(ethylene glycol) dimethyl ether.

119. The method of any one of claims 90 to 118, wherein the solution is a non-aqueous hydrazine solution that comprises from 25% to 69% by weight of hydrazine.

120. The method of any one of claims 90 to 118, wherein the solution is a non-aqueous hydrazine solution that comprises from about 50% to about 69% by weight of hydrazine.

121. The method of any one of claims 90 to 118, wherein the solution is a non-aqueous hydrazine solution that comprises from about 60% to about 69% by weight of hydrazine.

122. The method of any one of claims 90 to 118, wherein the solution is a non-aqueous hydrazine solution that comprises from about 65% to about 69% by weight of hydrazine.
123. The method of any one of claims 90 to 114, wherein the solution is a non-aqueous hydrazine solution that comprises substantially pure hydrazine.
124. The method of any one of claims 90 to 114, further comprising relieving pressure inside the head space by exposing a port connected to the head space to a lower pressure environment.
125. The method of claim 124, wherein the port is attached to a pressure relief device.
126. The method of claim 125, wherein the port contains a membrane barrier between the liquid in the container and the pressure relief device.

FIGURE 1A

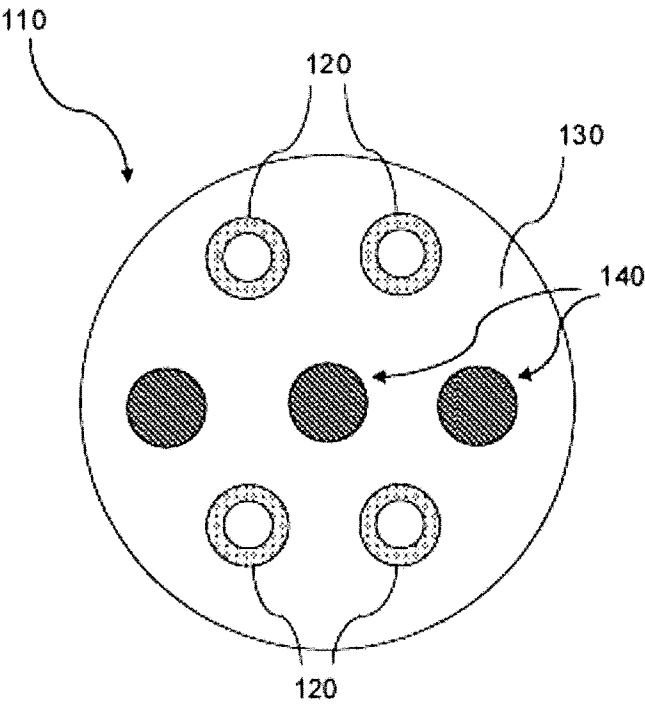


FIGURE 1B

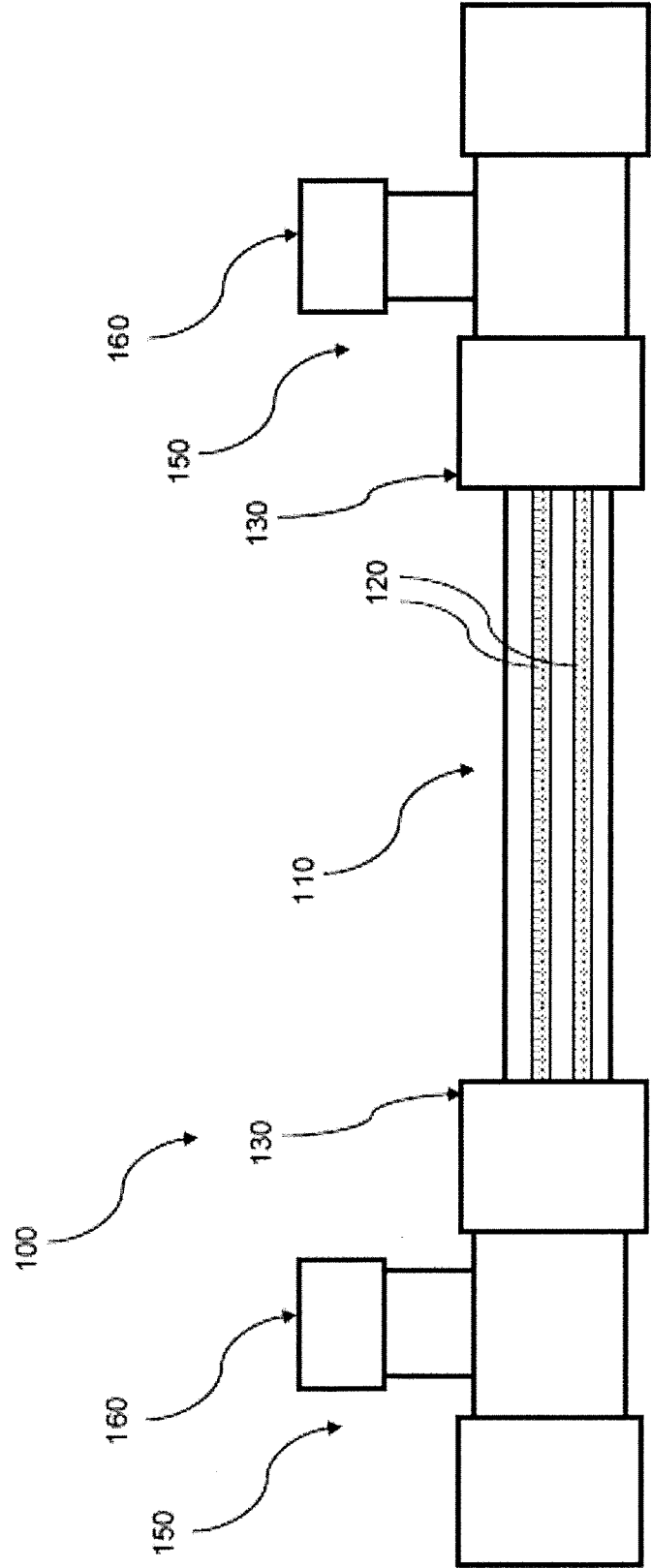


FIGURE 2A

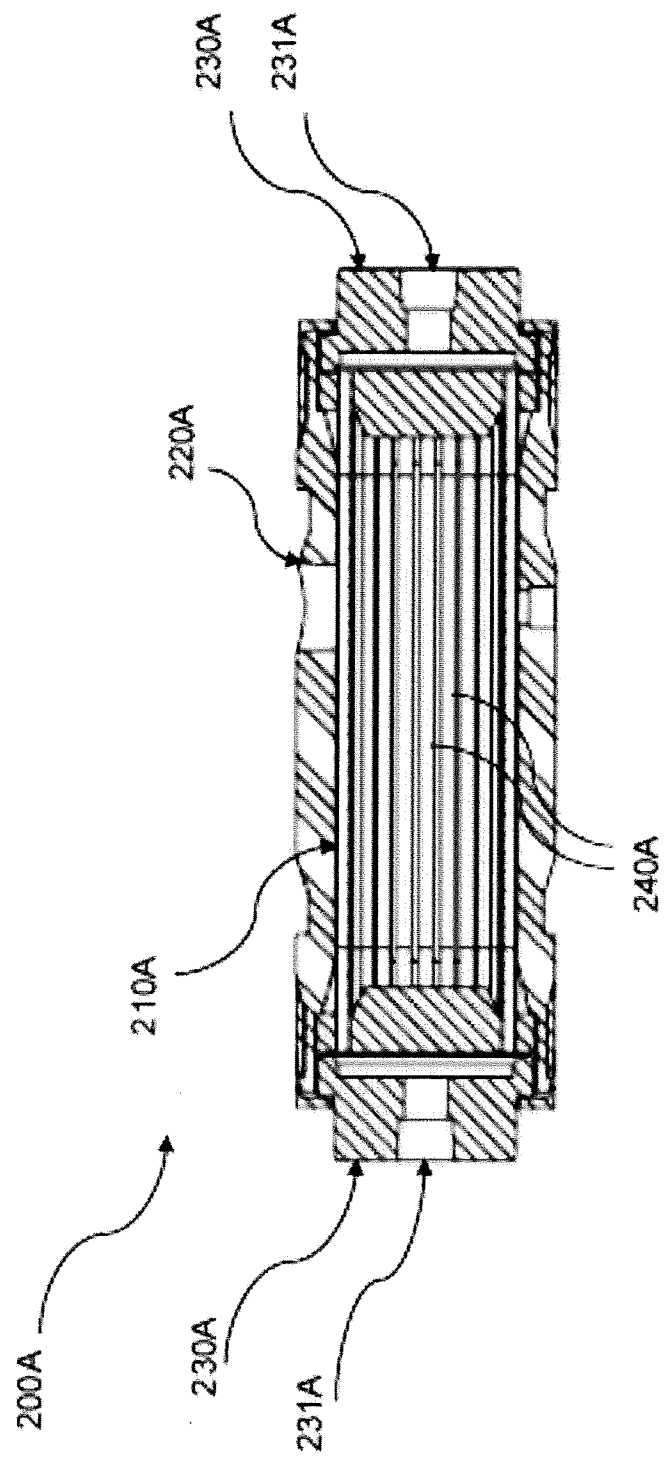


FIGURE 2B

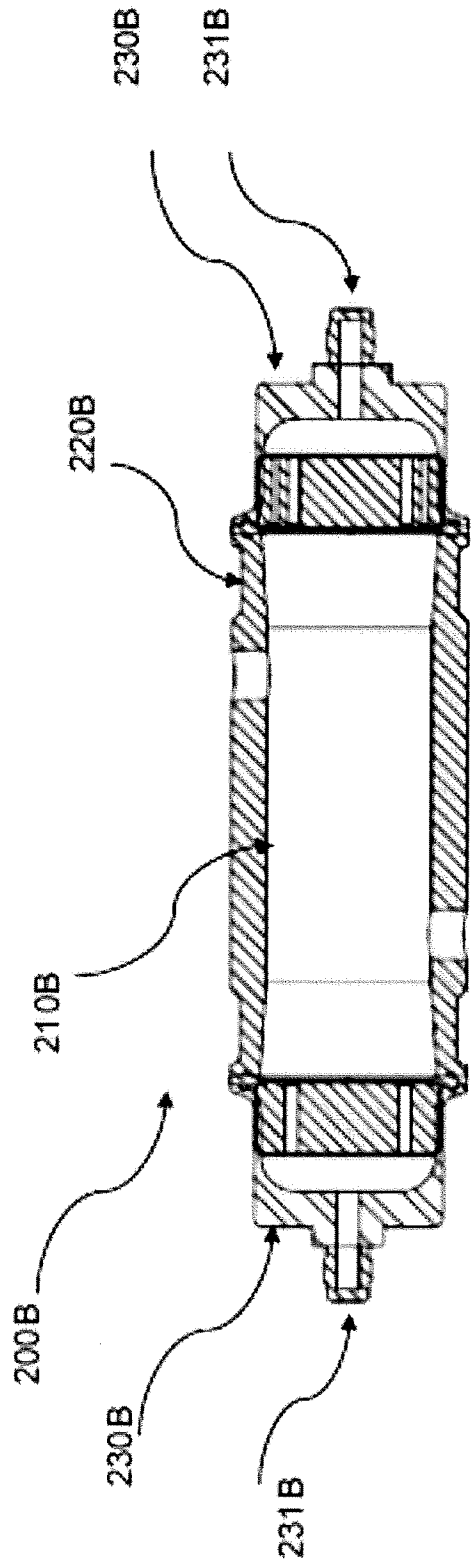


FIGURE 3

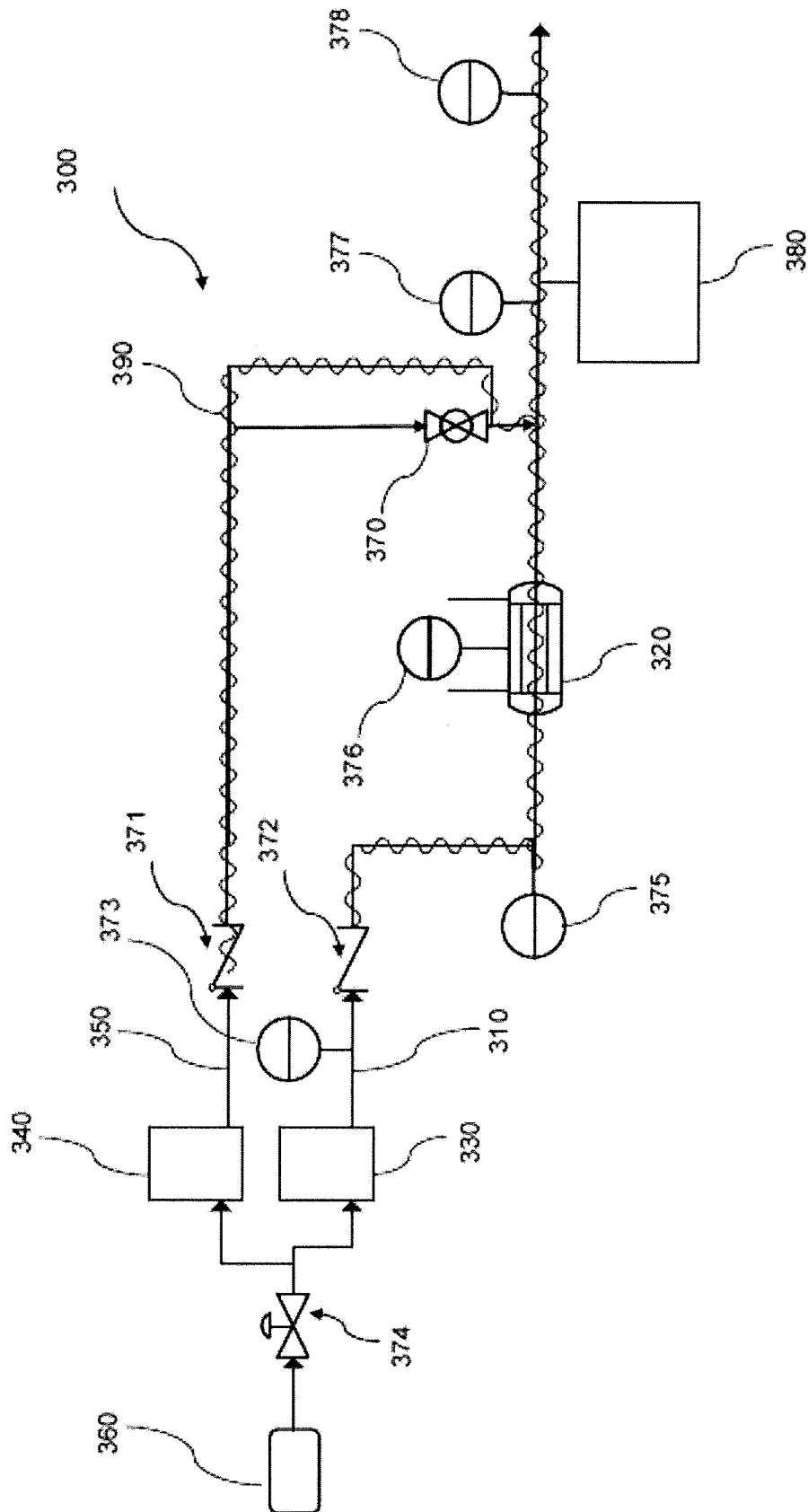


FIGURE 4

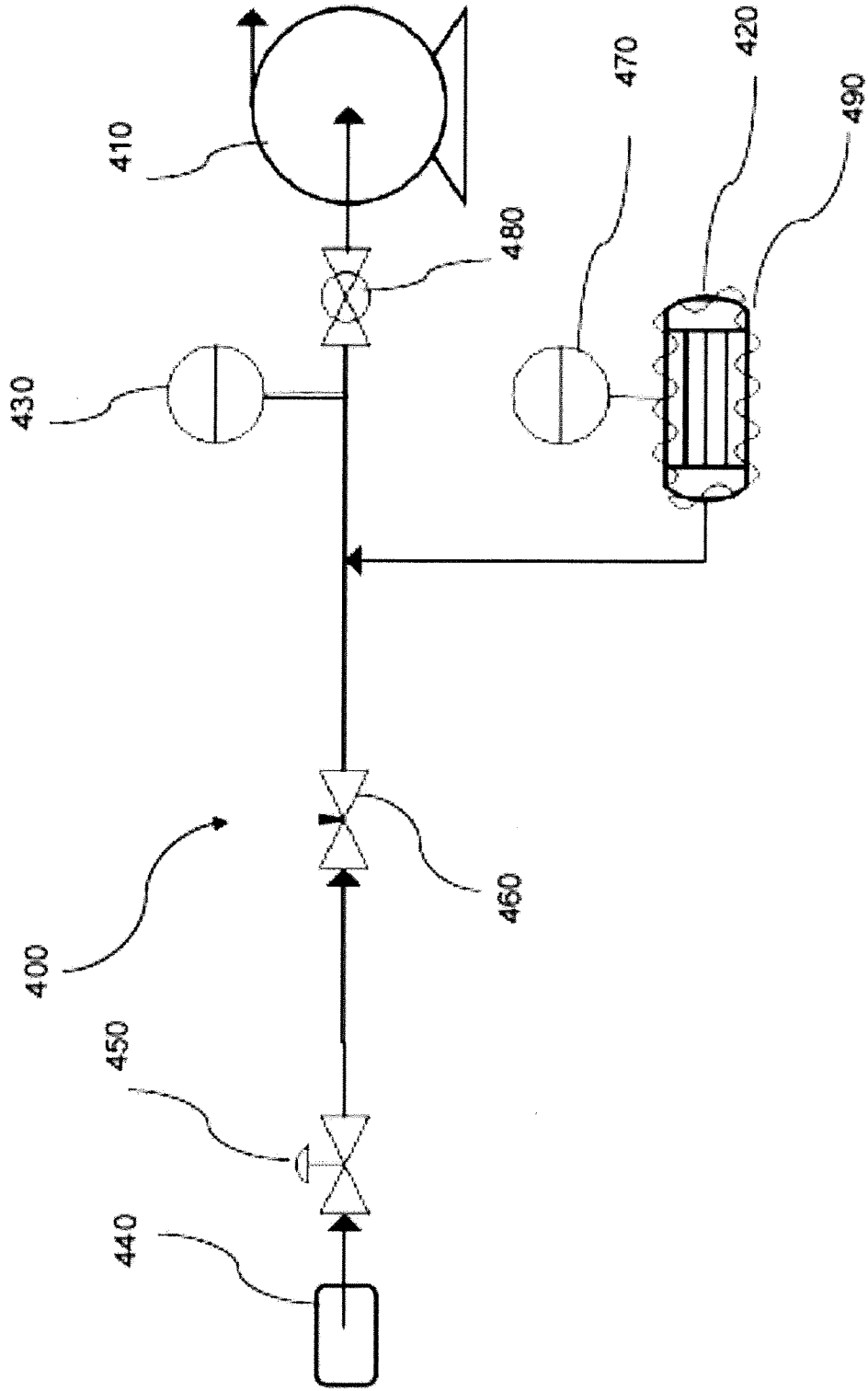


FIGURE 5

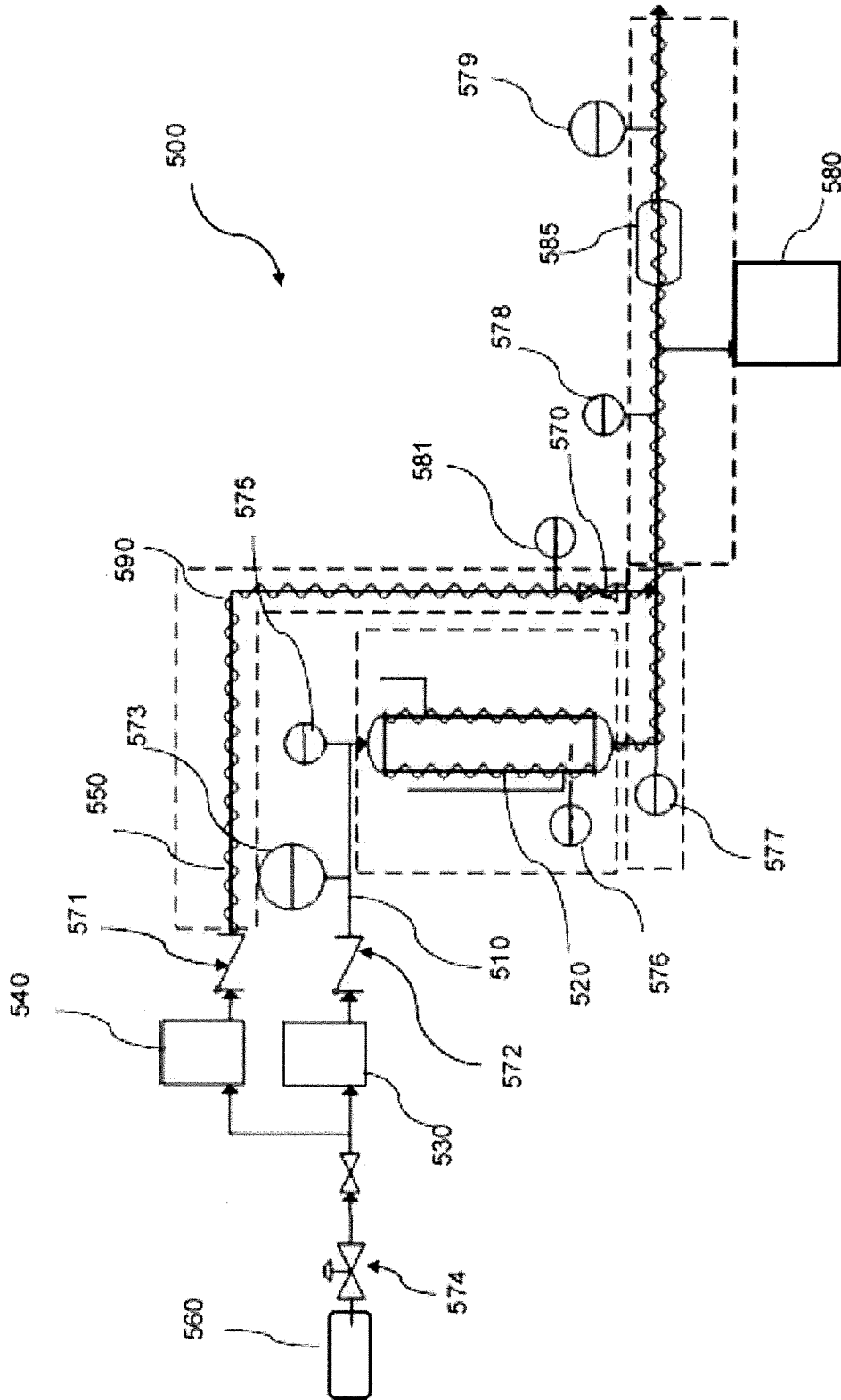


FIGURE 6

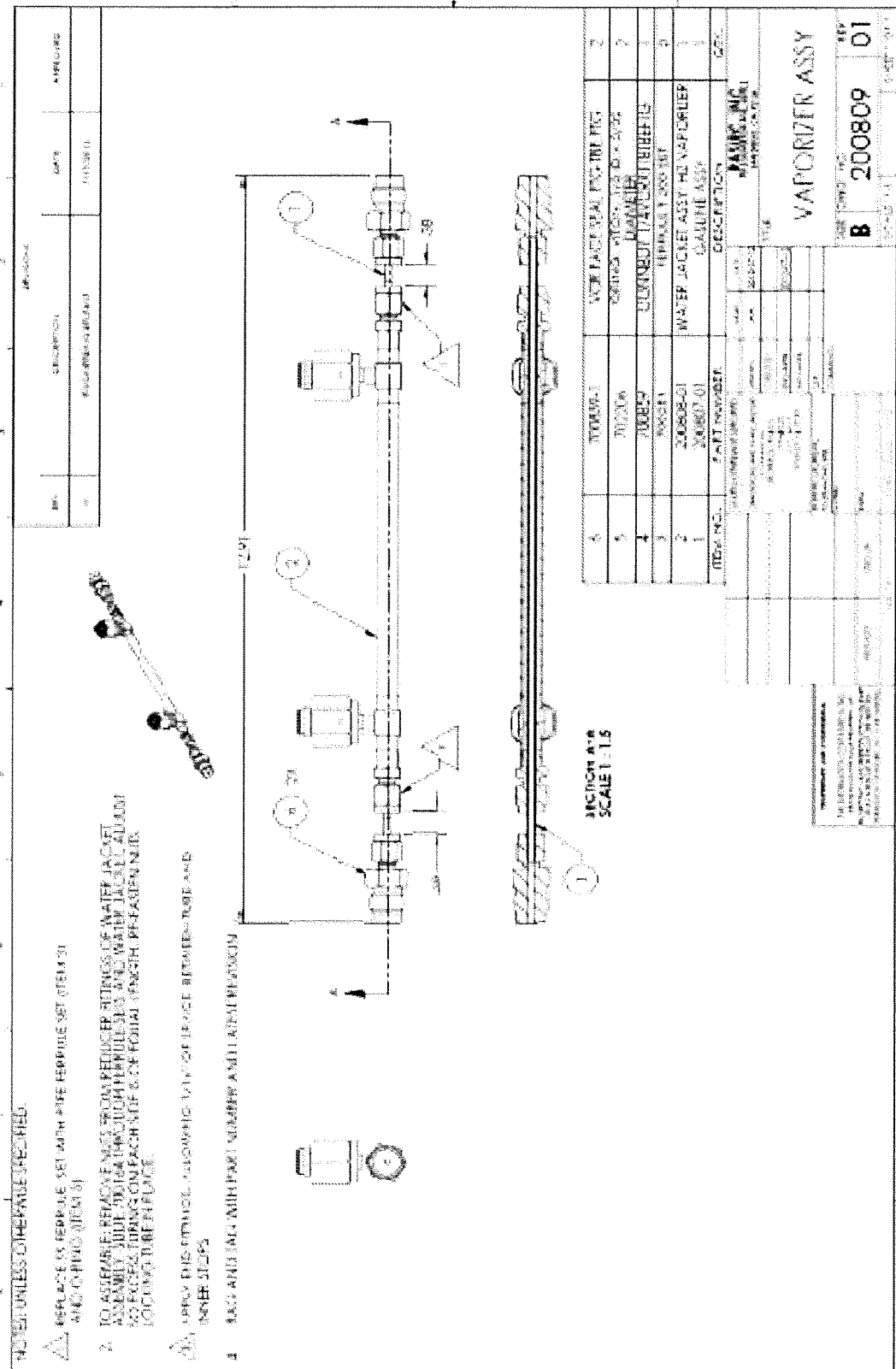


FIGURE 7

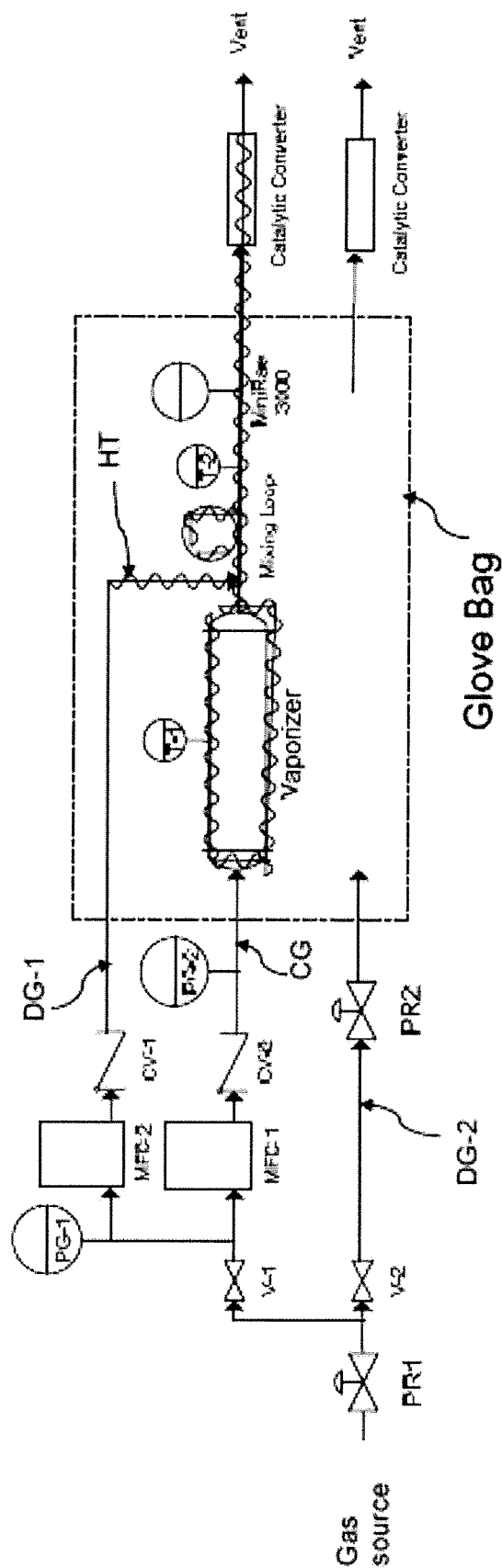


FIGURE 8

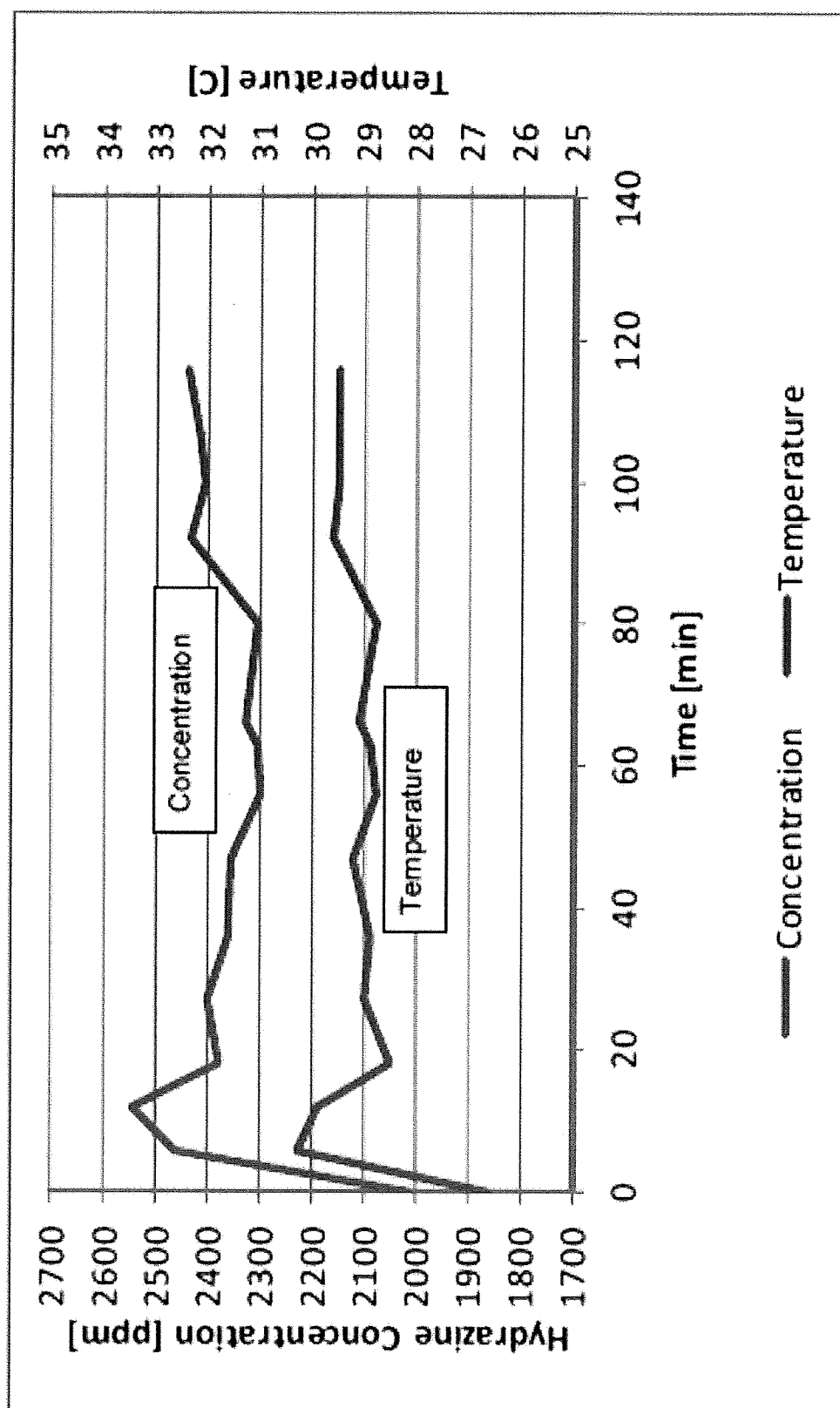


FIGURE 9

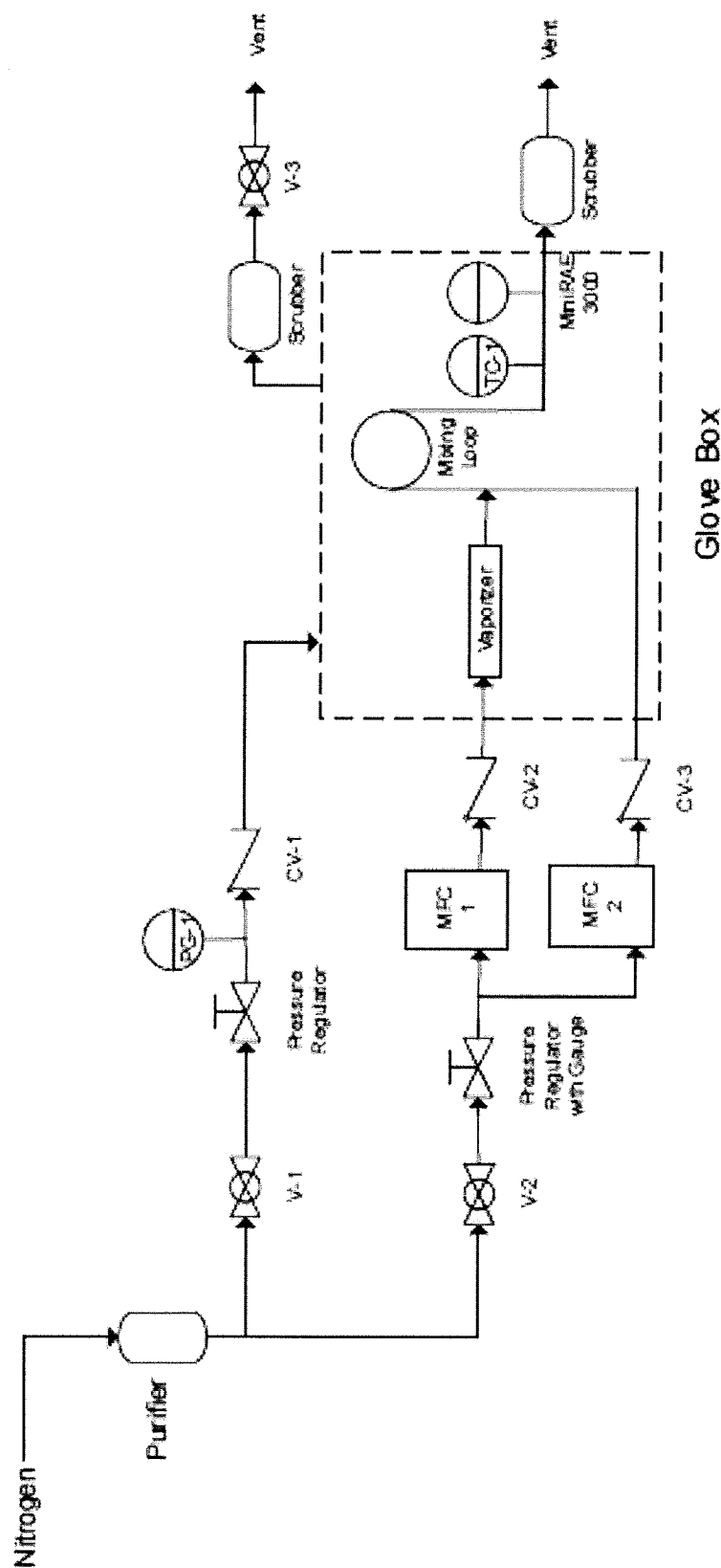


FIGURE 10

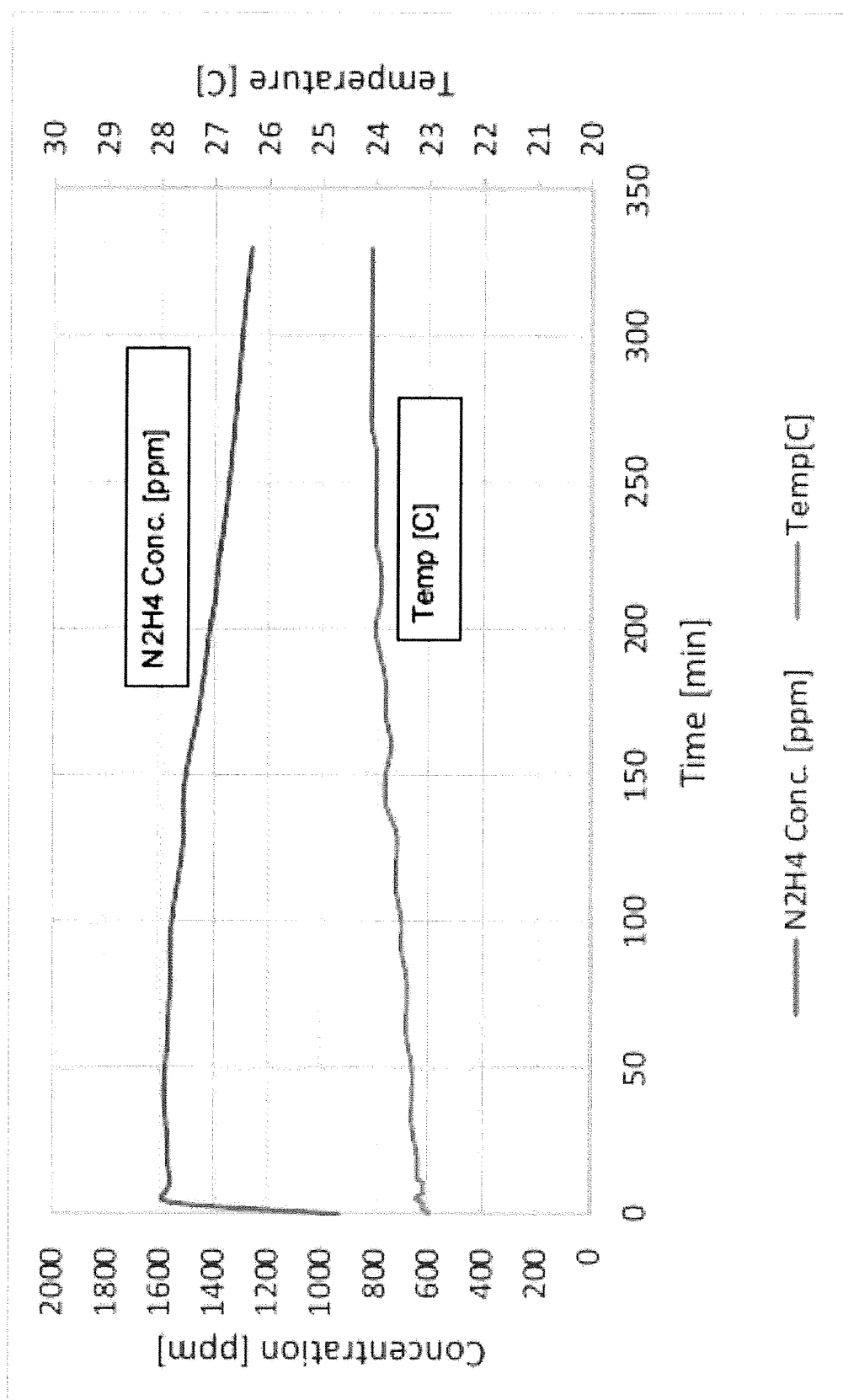


FIGURE 11

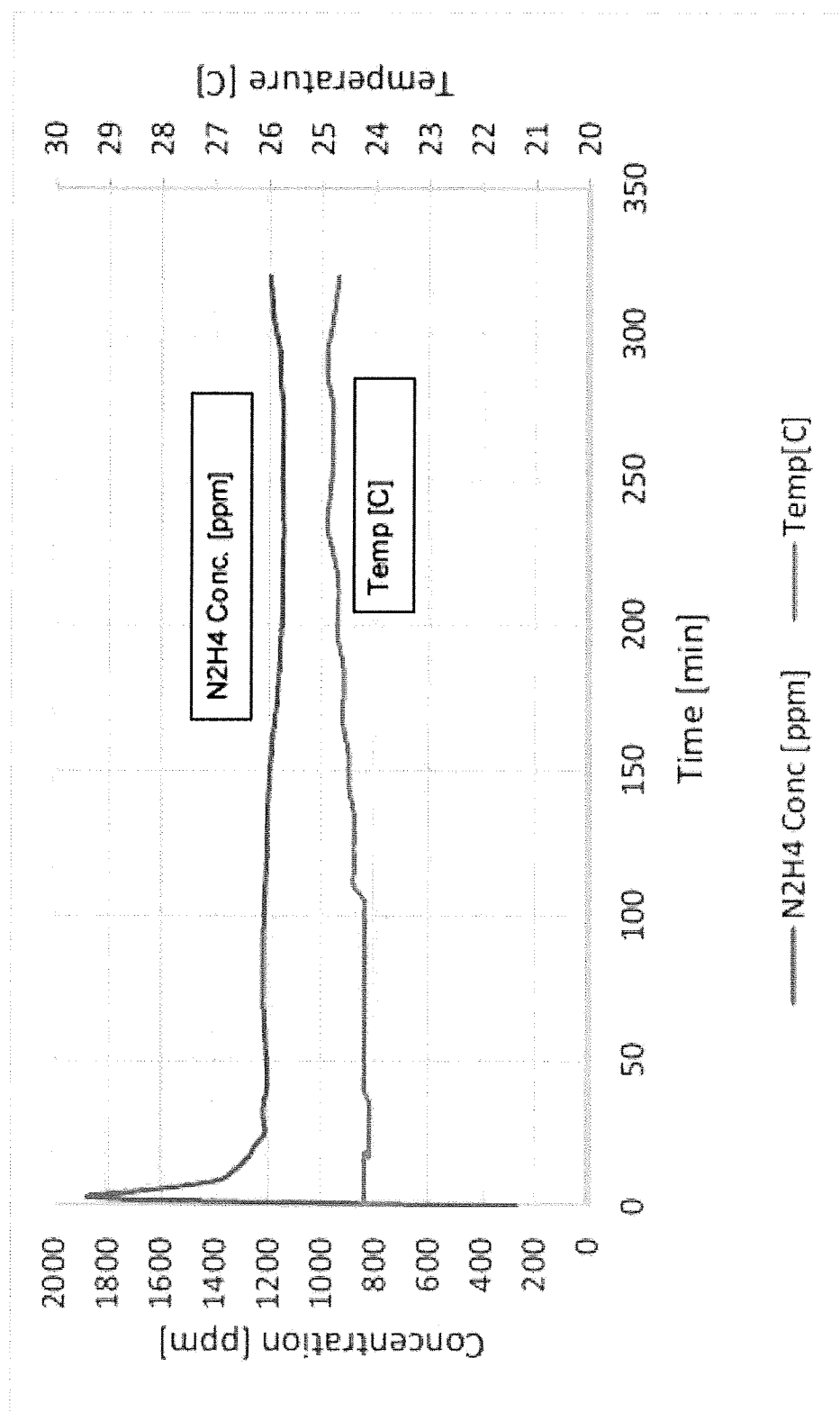


FIGURE 12

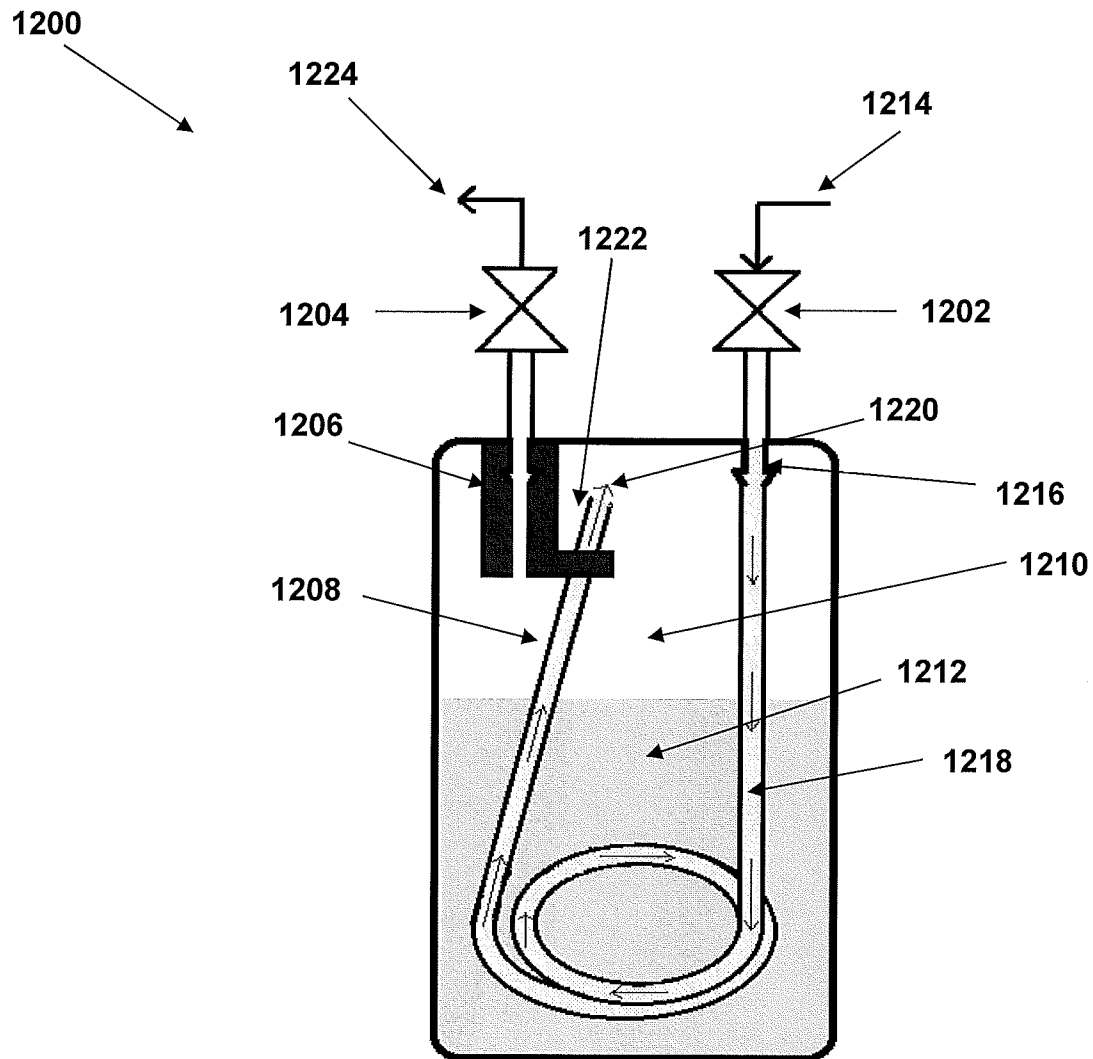
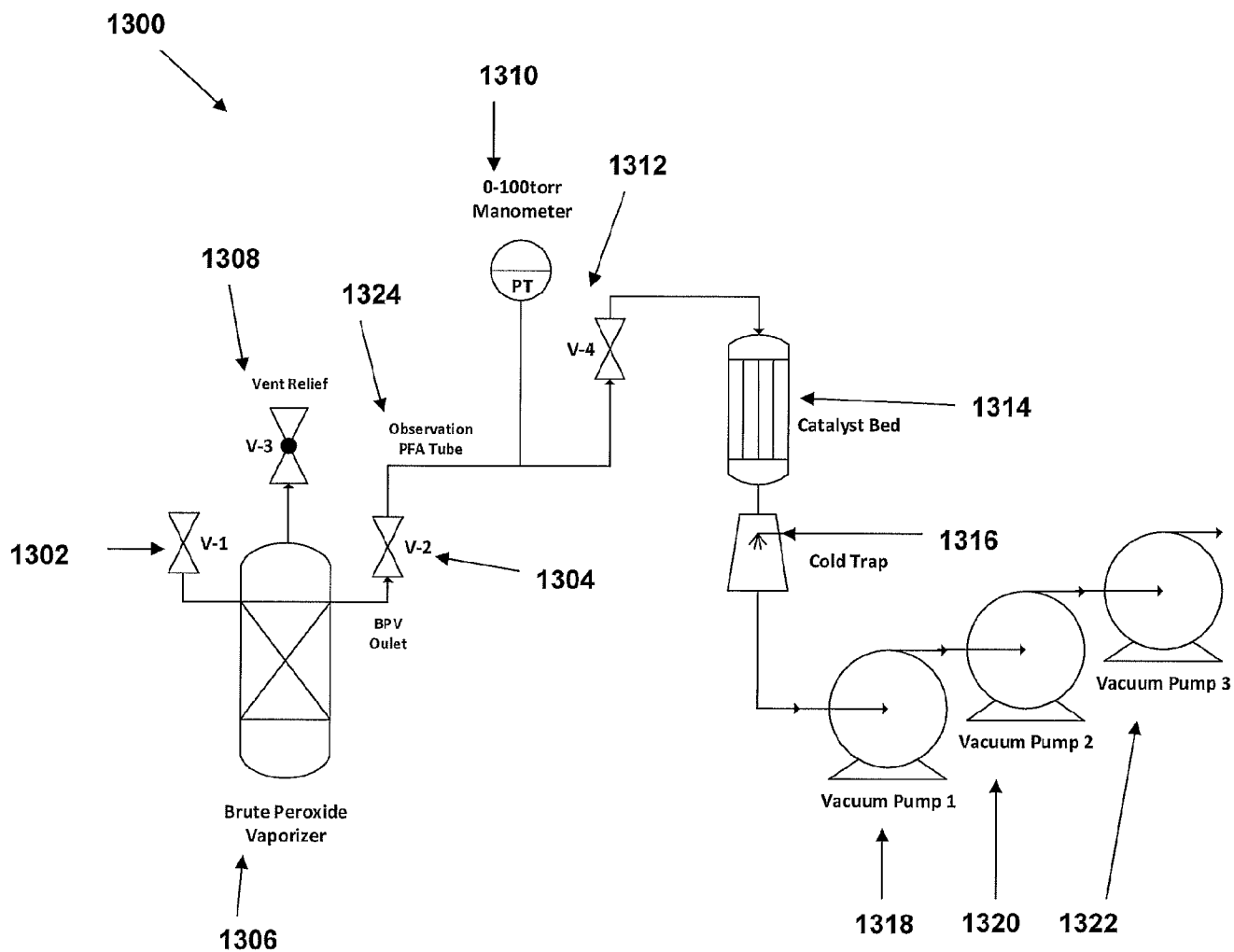


FIGURE 13



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/56887

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/44, B01D 53/77, B01J 20/292, H01G 4/06 (2016.01)

CPC - B01D 53/44, B01D 53/54, B01D 53/78, B01J 20/292, B01J 2219/00051, B01J 2219/00162

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8)- B01D 53/44, B01D 53/77, B01J 20/292, H01G 4/06 (2016.01);

CPC- B01D 53/44, B01D 53/54, B01D 53/78, B01J 20/292, B01J 2219/00051, B01J 2219/00162

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

USPC- 34/364, 34/467, 95/14, 95/19, 95/184, 96/400, 96/401, 96/402, 96/403, 261/129, 261/134, 261/153, 361/311, 361/326;

Patents and NPL (classification, keyword; search terms below)

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

Pub West (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent,

Google Scholar, Free Patents Online; search terms: hydrazine, N2H4, non-aqueous, anhydrous, dehydrate, dessicate, evaporate, vapor, vapour, gas, vacuum, membrane, hydrogen, peroxide, H2O2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2,785,052 A (OSBORG) 12 March 1957 (12.03.1957), col 2, ln 50-61; col 7, ln 28-36; col 7, ln 71 to col 8, ln 40; col 9, ln 32-72; col 10, ln 41-61	1, 2, 27-30
--		
Y		3, 31, 32, 52-56, 59-64, 90-94, 97-102
Y	WO 01/47805 A1 (ATOFINA) 05 July 2001 (05.07.2001), pg 2, ln 14 to pg 3, ln 31; pg 6, ln 4-28	3, 31, 32, 52-56, 59-64, 90-94, 97-102
Y	WO 2013/148262 A1 (RASIRC) 03 October 2013 (03.10.2013), para [010]-[076]	55, 56, 93, 94
Y	US 2002/0144887 A1 (RICARD) 10 October 2002 (10.10.2002), para [0004]-[0032]	1, 3, 27-32, 52-56, 59-64, 90-94, 97-102
Y	US 2,865,714 A (ROBELL) 23 December 1958 (23.12.1958), col 1, ln 53 to col 8, ln 67	1-3, 27-32, 52-56, 59-64, 90-94, 97-102

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

02 February 2016

Date of mailing of the international search report

10 FEB 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No

PCT/US 15/56887

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-26, 33-51, 57, 58, 65-89, 95, 96, and 103-126
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

-- Please See Supplemental Box --

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

Lack of unity: box III

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-3 and 27-32, drawn to a method and chemical delivery system for delivering a hydrazine gas stream.

Group II: Claims 52-56, 59-64, 90-94, and 97-102, drawn to a device and method for providing a process chemical.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group II does not require a method comprising:

- (a) providing a non-aqueous hydrazine solution having a vapor phase comprising an amount of hydrazine vapor;
- (b) contacting a carrier gas or vacuum with the vapor phase; and
- (c) delivering a gas stream comprising anhydrous hydrazine to a critical process or application;

or

a chemical delivery system comprising:

- (a) a non-aqueous hydrazine solution having a vapor phase comprising an amount hydrazine vapor;
- (b) a carrier gas or vacuum in fluid contact with the vapor phase; and
- (c) an apparatus for delivering a gas stream comprising at least one component of the hydrazine solution to a critical process or application, as required by Group I.

Group I does not require a device comprising:

- (a) a housing configured to contain a solution comprising a process chemical to be used in a critical process application;
- (b) a solution comprising a process chemical to be used in a critical process application contained within the housing;
- (c) a head space configured to contain vapor comprising the process chemical in the gas phase;
- (d) an inlet port in fluid communication with the head space and configured to allow a carrier gas to flow into the device through at least one membrane connected to the inlet port, wherein at least a portion of the membrane contacts the solution; and
- (e) an outlet port in fluid communication with the head space and configured to allow a process gas stream comprising the process chemical to flow out of the device;

or

a method comprising:

- (a) providing a solution comprising a process chemical to be used in a critical process application;
- (b) providing a head space in fluid communication with the solution to contain vapor comprising the process chemical in the gas phase, wherein the head space contains at least a portion of at least one membrane that is at least partially in contact with the solution;
- (c) contacting a carrier gas or vacuum with the vapor phase; and
- (d) delivering a gas stream comprising the process chemical to a critical process or application, as required by Group II.

Shared Common Features

The only feature shared by Groups I and II that would otherwise unify the groups is a chemical solution; a carrier gas or vacuum with the vapor phase; and delivering a gas stream to a critical process or application. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by WO 2013/148262 A1 to Alvarez, et al. (hereinafter 'Alvarez').

Alvarez discloses a chemical solution (para [011]); a carrier gas or vacuum with the vapor phase (para [011]); and delivering a gas stream to a critical process or application (para [011]).

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Note: Claims 4-26, 33-51, 57, 58, 65-89, 95, 96, and 103-126 are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).