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- (71) **Applicant:** CLEANLOGIX LLC [US/US]; 26074 Avenue Hall, Unit 6, Santa Clarita, CA 91355 (US).
- (72) **Inventors; and**
- (71) **Applicants (for US only):** JACKSON, David [US/US]; 26074 Avenue Hall, Unit 6, Santa Clarita, CA 91355 (US).  
MARIAN, Liviu [US/US]; 26074 Avenue Hall, Unit 6, Santa Clarita, CA 91355 (US).  
SOTO, Felipe [US/US]; 26074 Avenue Hall, Unit 6, Santa Clarita, CA 91355 (US).  
LEE, John [US/US]; 26074 Avenue Hall, Unit 6, Santa Clarita, CA 91355 (US).
- (74) **Agent:** HONG, David; Law Office of David Hong, Post Office Box 2111, Santa Clarita, CA 91386-2111 (US).
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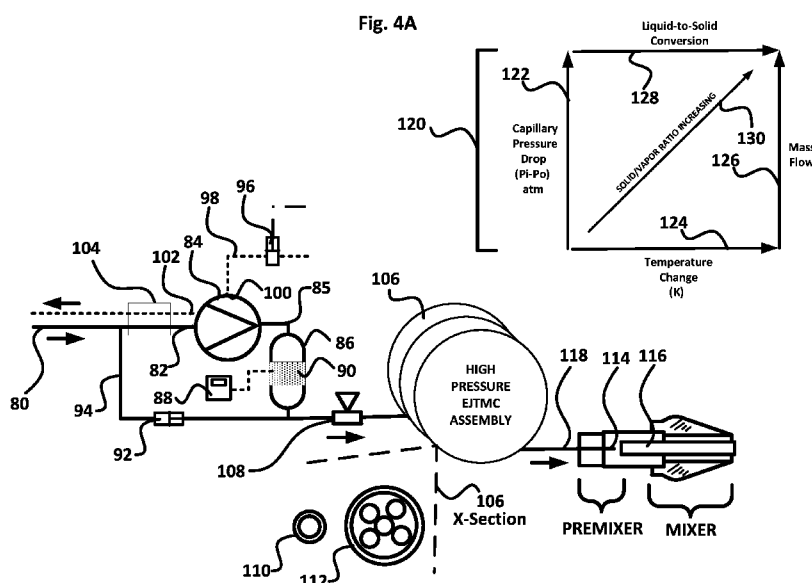
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(54) **Title:** METHOD AND APPARATUS FOR FORMING AND REGULATING A CO<sub>2</sub> COMPOSITE SPRAY



(57) **Abstract:** A method and apparatus is disclosed for the production, delivery and control of microscopic quantities of minute solid carbon dioxide (CO<sub>2</sub>) particles having uniform density and distribution for use in a CO<sub>2</sub> Composite Spray process, which employs compression of liquid carbon dioxide to form a supersaturated liquid, which is then condensed via micro-capillaries into minute and highly energetic solid carbon dioxide particles, which are injected into a propellant gas stream.

PCT Patent Application:

**METHOD AND APPARATUS FOR FORMING AND REGULATING A CO<sub>2</sub>  
COMPOSITE SPRAY**

Inventors:

**JACKSON, David; MARIAN, Liviu; SOTO, Felipe; LEE, John**

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**CROSS REFERENCE**

This application claims the benefit of United States Provisional Patent Applications 61/836,635 (filed 18 June 2013) and 61/836,636 (filed 18 June 2013), which are all incorporated by reference.

**TECHNICAL FIELD and BACKGROUND ART**

The present invention relates to a method and apparatus for producing, controlling and projecting a dense fluid spray, and specifically to carbon dioxide (CO<sub>2</sub>) solid-gas composite sprays such as the CO<sub>2</sub> Composite Spray™, a Trademark of CleanLogix LLC, used for precision cleaning, cooling and machining applications. More particularly, the present invention is an improved CO<sub>2</sub> Composite Spray cleaning method and apparatus.

Cleaning delicate surfaces with a strong spray stream consisting of sub-micron sized solid carbon dioxide particles propelled by gaseous carbon dioxide was first proposed by S. A. Hoenig (see "The application of dry ice to the removal of particulates from optical apparatus, spacecraft, semiconductor wafers and equipment used in contaminant free manufacturing processes", September 1985). The theory describing solid/gas carbon dioxide spray causes it to fall under the category of surface preparation and cleaning techniques in the form of a spray stream. The energy available in any spray stream can best be described by the sum of the kinetic energy of each solid component in the stream as defined in the following equation ( $KE = \frac{1}{2} MV^2$ ) where: KE=kinetic energy available in the stream; M=mass per unit solid in the stream; and V=velocity of the solid in the stream.

The advantage solid/gas carbon dioxide spray has over gaseous sprays is that the mass term of the equation is increased significantly with the introduction of the solid carbon dioxide particles which in turn increases the kinetic energy available in the stream. The solid/gas carbon dioxide spray stream, with a nozzle exit velocity much lower than a gaseous spray stream, will remove contaminants the gaseous spray stream will not. In fact, the solid/gas carbon dioxide spray stream will remove contaminants that the gaseous spray stream is unable to remove at any

nozzle exit velocity.

Following the initial efforts by S. A. Hoenig, referenced above, various efforts were directed to developing methods and apparatus capable of creating a spray stream of a mixture of frozen particles and a delivery gas, as well as the spray stream of solid/gas carbon dioxide. Most were merely capable of producing carbon dioxide solids in a carbon dioxide gaseous spray with no particular effort having been made to optimize the cleaning capability of the system. Only a slight improvement in cleaning over purely gaseous sprays was achieved by the earliest systems. Also, the carbon dioxide available at the time was not very pure or, if it was, it was very expensive. The impure carbon dioxide could not get pristine surfaces clean without leaving behind an undesirable residue, and the pure but expensive carbon dioxide was cost prohibitive, necessitating the development of dense fluid purification and delivery systems.

In the late 1980's researchers at Hughes Aircraft Company began working to investigate and develop new cleaning techniques for optical surfaces. These researchers knew from prior experience that critical optical surfaces, such as vapor deposited gold coatings and pristine polished silicon, will adversely change when any physical contact occurs. The researchers at Hughes were able to improve upon the solid/gas carbon dioxide spray cleaning technology by designing equipment that was much better than the early designs; however, the Hughes Aircraft equipment was extremely expensive.

In the late 1980's and early 1990's other companies, encouraged after seeing the results achieved by Hughes and a few other entities, began developing and marketing solid/gas carbon dioxide spray cleaning equipment. These prior efforts are exemplified by U.S. Pat. Nos. 4,806,171 issued Feb. 21, 1989 to W. H. Whitlock et al; No. 4,962,891, issued Oct. 16, 1990 to L. M. Layden; No. 5,125,979, issued Jun. 30, 1992 to E. A. Swain et al; No. 5,315,793 issued May 31, 1994 to R. V. Peterson; No. 5,354,384, issued Oct. 11, 1994 to J. D. Sneed et al; No. 5,364,474, issued Nov. 15, 1994 to J. F. Williford, Jr.; No. 5,390,450, issued Feb. 21, 1995 to L. N. Goenka; No. 5,409,418, issued Apr. 25, 1995 to K. Krone-Schmidt et al; and No. 5,558,110 issued Sep. 24, 1998 to J. F. Williford, Jr.

Conventional cryogenic spray cleaning processes thus described have traditionally employed supersonic de Laval-type (convergent-divergent) spray nozzles. The main disadvantage of de Laval cryogenic spray nozzles is that there is an unbalancing effect at the nozzle exit of the fluid stream. The surrounding fluid (ambient atmosphere) tends to drag the nozzle fluid stream, causing the flow stream to diverge rapidly upon discharge from the nozzle exit. This causes the liquid droplets or sublimable solid particles to expand quickly, resulting in

a significant loss of cleaning agent (solid particles) through plume expansion or the production of numerous and small solid particles, which generally requires the spray nozzle to be placed in close proximity to a substrate surface to be effective. The de Laval CO<sub>2</sub> spray nozzles produce a two-phase aerosol (CO<sub>2</sub>(g)-CO<sub>2</sub>(l)) through a rapid Joule-Thomson expansion process which wastes liquid carbon dioxide and spray cleaning energy is chiefly controlled only by changing the distance between the nozzle exit and the surface, or the liquid CO<sub>2</sub> feed pressure (see Bowen '128 described herein). However this is counterproductive because the carbon dioxide aerosol particles are shrinking in size, quantity and velocity, all of which adversely affects spray cleaning control and efficiency. Another shortcoming common to conventional cryogenic spray techniques utilizing de Laval spray nozzle designs is the intrusion and entrainment of atmospheric contaminants into the cryogenic particle flow stream. The most important aspect of these is atmospheric moisture condensation in the spray plume. Wet atmosphere entrained within the cold spray plume boundary is delivered to the surface along with the cleaning spray particles which complicates the cleaning process. Wetness is caused by the lack of effective shielding of the sublimating particle stream from the ambient atmosphere and insufficient heat capacity within the spray boundary to prevent condensation.

To overcome these constraints, improved CO<sub>2</sub> spray cleaning and cooling techniques were developed in the late 1990's and early 2000's by the first named inventor comprising unique carbon dioxide (CO<sub>2</sub>) "composite" sprays (CO<sub>2</sub> Composite Spray™, a trademark of CleanLogix LLC) used in cleaning, cooling and lubrication applications. A CO<sub>2</sub> Composite Spray is used today in a number of industrial applications ranging from the removal of submicron particles from hard disk drive component during an assembly operation to the removal of heat from cutting tools and substrates during a precision machining operation.

Examples of more recent conventional apparatuses and methods developed by the first named inventor of the present invention for generating and using a CO<sub>2</sub> Composite Spray are described in U.S. Patent Nos. 5,725,154, 7,293,570, and 7,451,941. These include coaxial CO<sub>2</sub> spray cleaning apparatus ('154), sequentially segmented flexible capillary condenser assembly ('570), and flexible enhanced Joule-Thomson capillary in a coaxial spray delivery apparatus and method ('941).

CO<sub>2</sub> Composite Sprays employ Coaxial or Coaxial-Coanda two-phase composite spray nozzle designs with so-called "capillary condensation" processes to convert saturated liquid CO<sub>2</sub>

into solid CO<sub>2</sub> particles. A CO<sub>2</sub> Composite Spray uses a compressed fluid to accelerate controlled amounts of solid CO<sub>2</sub> particles (cleaning or cooling agent) of controllable size, density, concentration, heat capacity and kinetic energy. Compressed gases, also termed dense fluids, are gases compressed above standard temperature and pressure conditions, and may even be compressed to liquid-like densities as well. Examples of dense fluids include compressed air, nitrogen, hydrogen, oxygen, ozone, and carbon dioxide. Compressed gases exhibit a range of solubility chemistry – behaving as both solvents and solutes – depending upon pressure and temperature, and depending upon the cohesion chemistry of the solvent-solute system (reference: Handbook of Solubility Parameters and other Cohesion Parameters, A.F. Barton, CRC Press, 1983). Dense fluids are uniquely employed in a CO<sub>2</sub> Composite Spray as propellant, cleaning, and cooling fluids. For example, a basic CO<sub>2</sub> Composite Spray system compresses CO<sub>2</sub> into a saturated liquid CO<sub>2</sub>. Liquid CO<sub>2</sub> is then condensed into microscopic solid CO<sub>2</sub> particles. Solid CO<sub>2</sub> particles are sized and injected into a temperature- and pressure-regulated dense fluid or compressed gas such as clean-dry-air, N<sub>2</sub>, Ar, or CO<sub>2</sub> and directed at a substrate using various applicator and spray nozzle configurations. The primary function of a propellant gas – also described herein as a “Dense Fluid Propellant Gas” - is to catapult microscopic solid CO<sub>2</sub> particles into a surface with sufficient energy to produce a highly dense liquid CO<sub>2</sub> at the contacting interface – forming a liquid (or so-called dense fluid) “splat”. The combination of energetic solid particle impacts and dense fluid splats provide significant acoustic cavitation, shear stress, and fluorocarbon-like chemistry – and depending upon dense fluid propellant gas temperature and pressure, and CO<sub>2</sub> particle concentration and additives – provides infinitely-adjustable cleaning and cooling spray compositions.

To make solid carbon dioxide particles, a capillary condenser assembly comprising an elongated segment (or sequential segments) of thermally-insulating polyetheretherketone (PEEK) capillary tubing is used. A capillary condenser assembly provides a simple and efficient means for subcooling (boiling) and condensing liquid carbon dioxide into a low velocity but dense mass of solid-phase particles. Varying the length and internal diameter(s) of the capillary condenser, including stepping, produces particles having different particle size distribution ranges and density. Once formed, CO<sub>2</sub> particles are injected and vortically mixed into a heated dense fluid propellant gas such as nitrogen, clean-dry air, or CO<sub>2</sub> gas, any of which may be optionally ionized, which flows coaxially with the capillary condenser assembly. Thus the gaseous propellant pressure and temperature and particle generation are independently and

variably controlled to produce a specific type of spray composition and energy for a particular cleaning application. A coaxial or coaxial-Coanda spray nozzle is used to integrate the two streams. In accordance with Bernoulli and/or Coanda flow stream principles the solid CO<sub>2</sub> particles are accelerated variably in a range from subsonic to near-sonic velocities.

5 It is known by those skilled in the art that very small amounts of CO<sub>2</sub> particles will perform a lot of cleaning or cooling work. This is a “less is more” process and chemistry paradigm. However, much of the CO<sub>2</sub> used within a conventional CO<sub>2</sub> cleaning spray is excessive and lean sprays produced by same tend to be spongy (gas-filled). It is understood that a leaner (less particle dense and uniform spray) using more densely compacted particles will  
10 produce cleaner surfaces (or cooler surfaces) faster. In this regard, there has been much work to minimize CO<sub>2</sub> usage, to improve spray particle uniformity, and to maximize spray work. However, up to this point achieving this goal has been illusive with numerous and varied constraints. First the production of very small amounts CO<sub>2</sub> particles must be consistent and efficient. Second small amounts of dimensionally small CO<sub>2</sub> particles must be delivered under  
15 high velocity propellant mass flow to the surface under energetic conditions needed for efficient cleaning (or cooling) action. Heretofore it has not been possible to achieve high cleaning (or cooling) effectiveness while efficiently generating ultra-small quantities of uniformly distributed CO<sub>2</sub> particles within a CO<sub>2</sub> Composite Spray as well as more conventional de Laval spray schemes. For example, in the late 1990’s, Bowen introduced a high pressure CO<sub>2</sub> snow spray  
20 apparatus, described under U.S. Patent No. 5,853,128. In U.S. Patent No. 5853128, liquid carbon dioxide is first compressed to between 2,000 psi and 5,000 psi and forced through a de Laval expansion nozzle to improve liquid-to-solid conversion and to increase particle velocity for improved cleaning performance. The principal drawback of this approach is a significant amount of CO<sub>2</sub> is used, between 15 and 50 pounds of CO<sub>2</sub> per hour per nozzle or more, to  
25 increase spray cleaning effectiveness.

Another significant drawback is that the rapid condensation through a nozzle expansion means produces a very cold and dense spray that lacks particle size and spray density uniformity. Adjunct means such as hot gas shrouds or jets, environmental processing chambers, and even mechanical spray screens (i.e., U.S. Patent 8,454,409, Bowers et al) must be employed  
30 to produce a uniformly distributed CO<sub>2</sub> gas-particle spray. Although fluid pressure may be attenuated through the expansion nozzle, upwards or downwards, with the conventional nozzle expansion means, for example the aforementioned ‘128 invention, to control the mass flow of

the resulting treatment stream, the particle size distribution, fluid temperature and spray power of the resulting treatment stream are not independently adjustable and utilize significant amounts of liquid CO<sub>2</sub> to produce a suitable mass of treatment particles.

Moreover, newer composite spray methods and apparatuses by the first name inventor of the present invention described in U.S. Patent Numbers '154, '570 and '941 herein have not heretofore been successful in achieving precise CO<sub>2</sub> particle generation and flow control at very low flow rates. For example micrometering saturated liquid CO<sub>2</sub> into and through a capillary condenser below 3 to 5 pounds CO<sub>2</sub> per hour produces significant sputtering (or choking) and/or particle loss (sublimation) during transport to the coaxial mixing and acceleration nozzle.

Compounding this problem, conventional CO<sub>2</sub> Composite Sprays employ a liquid CO<sub>2</sub> supply scheme that controls liquid CO<sub>2</sub> supply pressure, temperature and density within a very broad pressure and temperature range along the saturation line.

For example, conventional capillary condensers having internal diameters (ID) of 0.020, 0.030 and 0.080 inches, or sequential segments comprising all three diameters, cannot be effectively metered using saturated liquid CO<sub>2</sub> injection and an 18-turn micrometering valve. An 18-turn metering valve used to control saturated liquid CO<sub>2</sub> capillary injection in the range between 0.1 to 2 turns, representing a flow orifice adjustment range of between approximately 0.001 and 0.004 inches, results in clogging, sputtering, choking and sinusoidal-like spray fluctuations due to the saturated liquid CO<sub>2</sub> boiling (cooling, pressure dropping and expansion) within the metering valve body and internal capillary segments. This problem is greatly worsened using shorter segments of these capillaries, for example using a 0.030 ID capillary with a capillary condenser loop segment shorter than 36 inches in length. Using smaller capillary ID's such as 0.020 inch or smaller and stepped configurations starting with same such as described under U.S. Patent '570 in combination with metered saturated liquid carbon dioxide introduces more capillary pressure through restriction which improve flowability but significantly diminishes the amount of CO<sub>2</sub> particle generation (particle spray density) and mass flow control. For these reasons capillaries smaller than 0.020 inch, and in particular small capillaries have lengths longer than a couple of feet, have not been preferred in commercial CO<sub>2</sub> Composite Spray cleaning applications.

All of these constraints result in downstream particle injection fluctuations from the capillary condenser and within the coaxial propellant gas mixing nozzle – resulting in cleaning or cooling spray composition fluctuations in the lower saturated liquid CO<sub>2</sub> injection ranges of between 0.1 and 3 pounds per hour per nozzle. Although the fluctuations do diminish as the

liquid CO<sub>2</sub> injection rate is increased, which is wasteful, it is common to have spray instability below capillary injection rates of 3 to 5 pounds CO<sub>2</sub> per hour using a 0.030 inch ID capillary condenser, for example.

CO<sub>2</sub> Composite Spray fluctuations are problematic for applications requiring precise process control – for example fixed precision cleaning rates or cooling rates. A reactive control scheme is employed in conventional CO<sub>2</sub> Composite Spray applications to minimize, but cannot eliminate, spray fluctuations. A reactive control scheme compensates for upstream fluctuations in saturated liquid CO<sub>2</sub> supply pressure, temperature and density, as well as capillary condenser fluxes discussed above, which in turn dampens spray fluctuations caused by variable capillary CO<sub>2</sub> particle-gas production rates during injection into the heated propellant gas. A reactive control scheme controls a CO<sub>2</sub> Composite Spray composition by monitoring and controlling the composite spray mixing temperature (cold CO<sub>2</sub> particles mixed with hot propellant gas). A certain amount of particles plus a certain amount of heated propellant gas produce a certain mixing temperature. Typically the propellant pressure, temperature and flow rate are held somewhat constant and the saturated liquid CO<sub>2</sub> injection rate into the capillary condenser is adjusted to maintain the mixing temperature between an upper control limit (UCL) and a lower control limit (LCL). For example, typically the capillary injection flow rate is maintained between 5 to 8 pounds liquid CO<sub>2</sub> per hour for a coaxial spray equipped with a 0.030 inch ID capillary to achieve optimal spray stability control. The problem with reactive control is that the spray mixing temperature must be measured at a distance downstream from the nozzle exit to assure a fully mixed composite spray. This involves an off-line and time-delayed temperature measurement and metering valve adjustment period. Moreover this procedure is not real-time and is basically always drifting out of control above or below the UCL and LCL set points. Finally, the PC or PLC, software and automated temperature measurement and mechanical valve controls needed for this reactive control scheme add significant cost and complexity to a CO<sub>2</sub> Composite Spray system.

The prior art has relied on various CO<sub>2</sub> spray generation, monitoring and control schemes. The cleaning sprays produced by the prior art habitually drift during use, and variably produce either too lean or too rich CO<sub>2</sub> cleaning sprays. Conventional CO<sub>2</sub> treatment sprays must be re-calibrated frequently through either by-eye manual adjustments or automatic adjustment using temperature-based spray composition measurements in combination with servo-controlled metering valves.

As such there is a present need for generating and delivering a continuously stable, more

powerful, and ultra-lean (particle density) CO<sub>2</sub> Composite Spray. Moreover, CO<sub>2</sub> spray technology is needed that can provide the following characteristics and benefits:

1. Ultra-lean CO<sub>2</sub> spray compositions with more numerous submicron particles;
2. A faster and more stable spray adjustment;
- 5 3. Higher spray cleaning power (or cooling capacity);
4. Faster cleaning (or cooling) rates;
5. A lower spray cost;
6. A lower energy usage; and
7. Automated monitoring and control of the CO<sub>2</sub> Composite Spray.

## 10 SUMMARY OF THE INVENTION

A spray apparatus for producing and regulating a stream of propellant gas and carbon dioxide comprising: the carbon dioxide in a first state, which is a saturated liquid; compressing the carbon dioxide in the first state to form a second state, which is super-saturated at a density greater than 0.9 g/ml; said compression is adjusted using a high pressure pump; a condensation  
15 of the carbon dioxide in the second state within a micro-capillary tube to form a third state, which is a microscopic solid; said propellant gas and said carbon dioxide in the third state are mixed to form the stream of the propellant gas and the carbon dioxide; said carbon dioxide mixing rate is adjusted using a high pressure pump; and whereby the stream is used to treat a substrate surface.

20 In one preferred embodiment, the micro-capillary is at least one high-pressure capillary tube for receiving supersaturated carbon dioxide; the micro-capillary has a length of from 6 inches to 20 feet, an outer diameter of from 0.020 inch to 0.125 inch, and an inner diameter of from 25 micron to 0.010 inch; the micro-capillary comprises one or more capillaries in a parallel  
25 flow arrangement having a length of from 6 inches to 20 feet, an outer diameter of from 0.020 inch to 0.125 inch, and an inner diameter of from 25 micron to 0.010 inch; the micro-capillary comprises polyetheretherketone or stainless steel high pressure capillary tubes; the carbon dioxide in the first state is compressed to super-saturation using the high pressure pump; the high pressure pump compresses the carbon dioxide in the first state into the micro-capillary to form the carbon dioxide in the second state, which is supersaturated; the supersaturated carbon  
30 dioxide is compressed within the micro-capillary to a pressure between 900 psi and 10,000 psi; the supersaturated carbon dioxide is compressed to a pressure between 1,000 psi and 5,000 psi; the supersaturated carbon dioxide is thermally controlled at a temperature between 5 degrees C and 40 degrees C; the supersaturated carbon dioxide is thermally controlled at a temperature

between 10 degrees C and 25 degrees C.

In one preferred embodiment, the propellant gas is clean dry air, nitrogen, argon or carbon dioxide; the propellant gas is thermally controlled at a temperature between 5 degrees C and 250 degrees C; the propellant gas and the carbon dioxide in a third state are mixed coaxially; the propellant gas and the carbon dioxide in a third state are mixed using an adjustable expansion tube for receiving the carbon dioxide in a third state produced by the pressurized micro-capillary; the saturated carbon dioxide is at a pressure between 500 psi and 900 psi; the saturated carbon dioxide is at a temperature between 5 degrees C and 40 degrees C; the supersaturated carbon dioxide is a liquid or a supercritical fluid; the treatment spray generates a shear stress on the substrate surface at between 10 kPa and 100 MPa; the treatment spray produces a temperature on the substrate surface between -40 degrees C and 200 degrees C; the injection rate of the carbon dioxide in the third state is between 0.1 lbs per hour and 20 lbs per hour.

In one preferred embodiment, the stream of the propellant gas and the carbon dioxide is a spray plume and is analyzed in real-time using a photometric device; the spray plume has a geometry, which has a width, a height, a length, a composition or a CO<sub>2</sub> particle density; the geometry of the spray plume is adjusted using a propellant gas pressure, a propellant gas temperature, an additive concentration, or CO<sub>2</sub> particle concentration changes; the photometric device uses a light source to transmit a light beam perpendicular to the spray plume from a first position to a second position; the first position to the second position defines the length of the spray plume; the photometric device uses a light receptor mounted perpendicular to the spray plume; the light receptor captures the attenuated light beam as it passes through or is reflected from the spray plume; the photometric device is connected to a computing device; the computing device is connected to an adjustable CO<sub>2</sub> Composite Spray generator; the computing device analyzes the change in the light beam, when passing through the spray plume or being reflected from the spray plume; the computing device adjusts propellant gas pressure, propellant gas temperature, additive injection rate, or supersaturated CO<sub>2</sub> injection rate of said adjustable CO<sub>2</sub> Composite Spray generator to regulate said geometry to maintain a characteristic of the spray plume; the light source includes halogen light, deuterium light, Laser light or LED light; the light source operates in the ultraviolet, visible or infrared region; the light receptor includes photodiode detector, radiance detector or UV-VIS-IR spectrophotometer; the light receptor measures light absorption, light reflection or light florescence; the computing device calculates a light attenuation profile index value for a spray plume geometry; the light attenuation profile

index value changes with CO<sub>2</sub> particle density and particle size, propellant temperature and pressure, organic and inorganic additives, or water vapor content within the spray plume; the spray plume geometry is controlled in real-time based on the light attenuation profile index; at least one light source or at least one light receptor is used; the spray plume is moved from a first position to a second position perpendicular to said spray plume; the light source and light receptor are moved from a first position to a second position perpendicular to said spray plume; a metrological instrument is used to correlate spray plume geometry to a spray plume performance metric; the metrological instrument comprises a substrate surface temperature measurement system, a OSEE surface measurement system, a FTIR surface analysis system, an impact shear stress measurement system or a particle counting system; the spray plume performance metric comprises cooling capacity, impact particle shear stress, contamination removal rate, surface finish, or surface cleanliness level.

It is an object of the present invention to provide an improved CO<sub>2</sub> Composite Spray cleaning system; a further object of the present invention is to provide an improved capillary condenser process and apparatus operating under supersaturation or supercritical conditions at pressures greater than 900 psi, and preferably in the range between 1000 and 5000 psi, or more, and at a temperature of between 70 degrees F and 100 degrees F regardless of the pressure and temperature of the saturated liquid carbon dioxide in a supply line; another object of the present invention is to use high capillary fluid pressure and adjustment thereof to provide precise mass flow control in the range between near-zero to 3 pounds CO<sub>2</sub> per capillary condenser element; another object of the present invention is to provide an improved CO<sub>2</sub> Composite Spray composition control using one or more high pressure micro-capillaries in a parallel-flow bundle to provide an adjustable mass flow range with high pressure-regulated flow control; another object of the present invention is to provide a method and apparatus for CO<sub>2</sub> Composite Spray capable of removing contaminants such as particles, residues and heat from delicate surfaces without damage to the surface using minuscule amounts of microscopic solids at very low composite spray pressures and propellant flow rates; another object of the invention is to provide a CO<sub>2</sub> Composite Spray system capable of capillary condensation and injection pressures of up to as high as 10,000 psi for increasing the production and injection velocity of the solid carbon dioxide particles, thus decreasing coaxial propellant velocity drag and increasing the available kinetic energy in the CO<sub>2</sub> Composite Spray stream to enable removal of strongly adhered contaminants by carbon dioxide spraying without damage to the surface being sprayed; another object of the present invention is to provide a means for monitoring and controlling the particle

density of the CO<sub>2</sub> Composite Spray produced by the present invention. Light-based metrological tool is used to measure spray geometry and feed certain information into a computer controller to make adjustments to maintain or change particle injection; an object of the present invention is to provide a robust method and apparatus for real-time compositional and structural analysis of a CO<sub>2</sub> Composite Spray; a further object of the invention is to provide a compositional and structural analysis method using ultraviolet, visible, and/or near-infrared light-based radiance and/or photometric measurements; another object of the invention is to provide a method for determining the density of particles of solid carbon dioxide entrained in a propellant gas and determining the changes in CO<sub>2</sub> particle density therein; another object of the invention is to provide a method for determining the quantity of gaseous, liquid or solid inorganic and organic additives contained or entrained in a CO<sub>2</sub> Composite Spray; another object of the invention is to provide a method for analyzing single or multiple CO<sub>2</sub> Composite Sprays; another object of the invention is to provide a method for analyzing the composition and structure of a CO<sub>2</sub> Composite Spray in an in-line or longitudinal direction and in a perpendicular direction; another object of the present invention is to provide a novel method for conveniently adjusting the particle size of minute amounts of CO<sub>2</sub> particles, produced during high pressure micro-capillary condensation; and another object of the present invention is to provide energy efficient low-volume methods and apparatuses using Vortex and Peltier technologies for condensing and delivery small volumes of saturated liquid CO<sub>2</sub> from CO<sub>2</sub> gas for use in the high pressure micro-capillary condensing system.

Briefly, the present invention uses one or more high-pressure joule-Thomson micro-capillary condensers to efficiently produce microscopic amounts of solid CO<sub>2</sub> particles from a supersaturated liquid CO<sub>2</sub> which are then mixed into and accelerated to near-sonic velocities using a heated clean dry gas propellant gas. High pressure micro-capillary condenser assembly is used herein as both a mass control device and a liquid-to-solid condenser device.

One or more micro-capillaries are used within the same capillary condenser assembly under supersaturation pressure conditions to achieve precision pressure-regulated mass control while allowing for changes in incremental changes in mass flow range. The result is significantly more precise control with ultra-low usages of liquid CO<sub>2</sub> than achieved today using a conventional CO<sub>2</sub> spray technologies, including the CO<sub>2</sub> Composite Spray which typically ranges between 3 and 15 pounds of CO<sub>2</sub> per spray nozzle per hour.

To achieve precise control at very low mass flows, the present invention utilizes a significantly greater capillary fluid pressure (supersaturated liquid carbon dioxide) than the

conventional saturated gas-liquid capillary fluid feed pressures used in a conventional CO<sub>2</sub> Composite Spray, which ranges between 750 psi and 900 psi.

The present invention has the additional advantage of significantly improving and maintaining low CO<sub>2</sub> particle mass flows to near-zero flow rates using significantly less propellant mass flow to controllably accelerate microscopic amounts of particles to near-sonic velocities.

The present invention increases spray stream particle densities and coaxial propellant injection velocities in the range between 0.1 pounds per hour and 1.5 pounds per hour, or more, per micro-capillary using supersaturated liquid CO<sub>2</sub> per capillary condenser at a controlled fluid feed pressure of between 900 psi and 10,000 psi and at temperatures of between 10 degrees C and 38 degrees C, and preferably at a pressure range of between 1000 psi and 5,000 psi and at temperatures of between 20 degrees C and 30 degrees C (for supersaturated liquid CO<sub>2</sub>).

Micro-capillaries may be “bundled” in a parallel-flow arrangement to increase mass flow without degrading pressure-regulated flow control. For example, combining one or more high pressure micro-capillaries having an internal diameter (ID) of 0.005 inch in a parallel-flow bundled assembly allows for increasing the pressure-regulated mass flow range linearly and incrementally. For example: 0.5 to 1.5 pounds per hour using one (1) 0.005 inch ID capillary, 12 inch length, 1000-1500 psi injection control range; 1.0 to 3 pounds per hour using two (2) 0.005 inch ID capillaries, 12 inch length, 1000-1500 psi injection control range; 1.5 to 6 pounds per hour using three (3) 0.005 inch ID capillaries, 12 inch length, 1000-1500 psi injection control range; and 2.0 to 12 pounds per hour using four (4) 0.005 inch ID capillaries, 12 inch length, 1000-1500 psi injection range, and so on.

Bundled segments may be directly integrated with the propellant mixing portion of the exemplary CO<sub>2</sub> Composite Spray coaxial spray system or more preferably may be transitioned to the propellant mixing portion over a longer distance using a transport capillary having a diameter equal to the sum of the individual internal diameters of the capillary bundle and integrated with a novel CO<sub>2</sub> composite spray nozzle of the present invention.

The present invention utilizes (preferably) a pneumatically controlled hydraulic high pressure pump (electrically actuated piston pump may be used as well) to control both the mass and distribution of a condensed and microscopic mass of uniformly sized and high density solid CO<sub>2</sub> particles. These CO<sub>2</sub> particles are selectively injected into a heated propellant gas, mixed, and accelerated at the substrate being treated, as described in the background and prior art related to the present invention. In this regard, in the prior art adjustments to (and control of)

the CO<sub>2</sub> Composite Spray is typically performed manually based upon visual observation or have been performed automatically using a thermocouple to correlate the CO<sub>2</sub> particle density of the spray at various propellant mass flow pressure/nozzle) and fixed propellant heat capacity (temperature/mass flow) settings. The visual method of control is subjective and produces inconsistencies in both cleaning and cooling performance, and is not a feasible option for on-line or continuous applications requiring automatic control and consistent performance. The thermodynamic control method provides automatic analysis and control vis-à-vis automated pressure and mass flow regulators, but is slow and provides only mixing temperature information for the spray composition, irrespective of all of the adjustable variables inherent in a CO<sub>2</sub> Composite Spray. The conventional analysis and control methods do not provide information about the physical or chemical form or profile of a CO<sub>2</sub> Composite Spray – which relates to mass flow rates, pressures, temperatures, CO<sub>2</sub> particle size distribution, and chemical or physical additives which may be contained or entrained within the spray plume. In the present invention, spectroscopic analysis using UV, VIS, NIR light, and which may include specialized spectroscopic techniques such as Raman analysis, is used to assess both the chemical and physical characteristics of a CO<sub>2</sub> Composite Spray to optimize its performance in cleaning, machining, and cooling operations.

Measurements may be based upon light absorption, reflection or emission phenomenon. For example, ozonation is used as an additive within a CO<sub>2</sub> Composite Spray and its spray concentration is roughly estimated from ozone production and metering control techniques, which can vary significantly. The present invention can simultaneously determine the CO<sub>2</sub> particle concentration (physical) and ozone concentration (chemical) within the plume directly.

In the present invention, CO<sub>2</sub> particle density is ascertained based on physical light obscuration (light blocking/rejection) as well as light absorption in the 2 micron infrared wavelength region. Oxygen and ozone absorb the UV region, and water vapor absorbs in the near-IR region. Similarly and not shown, other chemical or physical additives which absorb or obscure light can be monitored and controlled using the present invention. A suitable light source is coupled with a suitable spectrophotometer or a simple radiance (or gross light transmission) or light intensity measurement device is used in the present invention to determine various physical and chemical aspects of a dynamic CO<sub>2</sub> Composite Spray using light absorbance, fluorescence, reflectance, transmission, or Raman measurement. A wide-spectrum light source such as deuterium, tungsten or halogen (215 nm – 2500 nm) or more specific spectrum sources such as LED or Laser may be used, including monochromatic radiation, near

monochromatic radiation, continuous spectra and band spectra light sources. Simple radiometric or more complex photometric measurement techniques may be employed in the present invention, dependent upon the amount of information needed to properly assess the physical and chemical characteristics of a particular CO<sub>2</sub> Composite Spray.

5           An exemplary light measurement scheme uses spectroscopic light. Spectroscopic light is passed through the spray plume body to assess the chemistry, density and/or physical shape of the CO<sub>2</sub> Composite Spray. A simple radiance measurement may be used in the present invention to determine apparent spray density at a particular and representative portion of a spray plume. This information is used to characterize or profile the CO<sub>2</sub> spray plume for  
10   quality, performance, real-time dynamic control. Examining the shape of a spray plume, its profile, is another and more accurate means for contrasting and comparing the plume shape of a CO<sub>2</sub> Composite Spray. As an example, the area under a representative portion of a curve representing a profile (radiance or photometric values) may be determined by integrating the curve function using two representative measurement boundary values (% transmission,  
15   %absorption, intensity etc.).

          In the present invention, wide-spectrum light transmission measurements are used to differentiate CO<sub>2</sub> Composite Sprays having varying CO<sub>2</sub> particle densities and chemical additive concentrations, which are not possible to discriminate visually. The power of light transmission measurements to discriminate similar spray plumes is demonstrated by the different transmission  
20   intensities measured for spray compositions having similar CO<sub>2</sub> particle densities. The ability to discriminate CO<sub>2</sub> Composite Sprays makes this technique very useful for quality assurance (QA) or quality control (QC) operations to ensure consistent spray characteristics and spray performance in a particular application.

Other objects and advantages of the present invention will become apparent from the following  
25   description and accompanying drawings.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

          The accompanying drawings, which are incorporated into and form a part of the disclosure, illustrate prior art or an embodiment of the invention and, together with the description, serve to explain the principles of the invention.

30           Figure 1 illustrates schematically the prior art enhanced Joule-Thomson capillary condensation technique and constraints regarding saturated liquid CO<sub>2</sub> mass flow and particle

density control.

Figure 2 schematically illustrates an embodiment of the present invention comparing and contrasting the highly variable saturated liquid CO<sub>2</sub> density as compared to a supersaturated liquid CO<sub>2</sub> feedstock used in the present invention.

5        Figure 3 illustrates an embodiment of the present invention for using supersaturated liquid CO<sub>2</sub> hydraulic pressure in combination with a micro-capillary or capillary bundle to control mass flow.

10        Figure 4A schematically illustrates an embodiment of the present invention comprising an exemplary system to produce a supersaturated liquid CO<sub>2</sub> and produce particles therefrom using a high-pressure enhanced Joule-Thomson micro-capillary apparatus. Figure 4B schematically illustrates an embodiment of the present invention comprising an exemplary expansion-propulsion nozzle for precisely adjusting the size of minute CO<sub>2</sub> particles prior to injection into a propellant gas stream.

15        Figure 5 schematically illustrates the differences between a saturated liquid CO<sub>2</sub>, supersaturated liquid CO<sub>2</sub>, and supercritical CO<sub>2</sub> using a phase diagram.

Figure 6 illustrates schematically the present invention using the high-pressure enhanced Joule-Thomson micro-capillary condensation technique using supersaturated liquid CO<sub>2</sub> mass flow control and high pressure micro-capillary condensation as a proactive control scheme for providing improved ultra-low mass flow and particle density control.

20        Figure 7 schematically illustrates an embodiment of the present invention comprising an exemplary Vortex-based condensing system to produce a supply of saturated liquid CO<sub>2</sub> feedstock for use in the present invention.

25        Figure 8 schematically illustrates an embodiment of the present invention comprising an exemplary Peltier-based condensing system to produce a supply of saturated liquid CO<sub>2</sub> feedstock for use in the present invention.

30        Figure 9A schematically illustrates the experimental apparatus and method for demonstrating the adjustable range of spray energy using the present invention. Figure 9B provides experimental evidence demonstrating the spray power of the present invention. Figure 9C provides experimental evidence demonstrating the spray performance of the present invention. Figure 9D is a picture of the prior art CO<sub>2</sub> Composite Spray in normal light. Figure 9E is a picture of the CO<sub>2</sub> Composite Spray of the present invention in normal light. Figure 9F is a picture of the CO<sub>2</sub> Composite Spray of the present invention under illumination.

Figure 10 is a graph showing the relationship between spray mixing temperature and

capillary pressure.

Figure 11 illustrates exemplary absorption profiles for various chemistries common to a CO<sub>2</sub> Composite Spray.

Figure 12 illustrates schematically the apparatus embodiments of a light-based compositional and structural analysis system for profiling a CO<sub>2</sub> Composite Spray.

Figure 13 illustrates schematically the use of radiance and photometric spray plume data to establish an upper control limit (UCL) and lower control limit (LCL) for compositional elements such as CO<sub>2</sub> particle density, additive concentration, and water content.

Figure 14 schematically illustrates exemplary spray profiles derived from radiance measurements of a CO<sub>2</sub> Composite Spray.

Figure 15 schematically illustrates the computation of a spray profile metric – area under the profile curve - used for quickly analyzing and controlling a CO<sub>2</sub> Composite Spray.

Figure 16 schematically illustrates the measurement of a CO<sub>2</sub> Composite Spray plume in both longitudinal and perpendicular directions.

Figure 17 schematically illustrates the exemplary system for measurement of a CO<sub>2</sub> Composite Spray plume in a perpendicular direction.

The present invention will be best understood from the following description when read in conjunction with the accompanying drawings.

## DETAILED DESCRIPTION OF THE INVENTION

Figure 1 illustrates schematically the prior art enhanced Joule-Thomson capillary condensation technique and constraints regarding saturated liquid CO<sub>2</sub> mass flow and particle density control. Referring to Figure 1, the prior art as discussed herein fails to provide a stable source of saturated liquid CO<sub>2</sub> for capillary condensation processes to produce a consistent and stable supply of CO<sub>2</sub> particles for injection and mixing with a propellant gas, having a constant pressure and temperature. The reasons for this constraint are related to a number of contributing causes including; changes in bulk CO<sub>2</sub> gas supply tank pressures and temperatures during withdraw and usage, changes in environmental temperatures such as factory temperatures and outside storage tank and delivery system temperatures, temperature variations within the CO<sub>2</sub> gas supply lines from source to ceiling or floor to cleaning system, variations in high pressure gas delivery system supply pressures and temperatures, and variations in internal pressure and temperature of refrigerant condenser systems used to condense transported high pressure gas to a cold saturated liquid CO<sub>2</sub> supply.

Even with end-of-line pressure control regulators, ambient temperature and condenser

system fluctuations still result in a pressure and temperature variability, which is somewhat sinusoidal in nature. This results in a highly variable and somewhat unpredictable pressure and temperature swings of a saturated CO<sub>2</sub> feedstock (2) which results in variable liquid density (4), variable capillary boiling densities and resulting variability in particle size and density (6), and upon injection (8) and mixing with a heated propellant gas (10), produce a variable spray composition (12) of CO<sub>2</sub> particles and propellant gas which when projected (14) at a surface produce a variable cleaning (or cooling) rate (16).

The conventional control means involves a reactive scheme (18), whereby the spray is periodically measured – for example by mixing temperature as discussed herein – and the capillary injection rate (20) is adjusted manually or automatically to maintain the CO<sub>2</sub> Composite Spray composition (12) within an acceptable upper control limit (22) and lower control limit (24) over time. The prior art constraints thus described are exacerbated with extremely low liquid CO<sub>2</sub> injection rates and capillary flows (small capillary diameters).

Having thus described various spray control problems associated with conventional CO<sub>2</sub> Composite Sprays using a saturated liquid CO<sub>2</sub> feedstock, Figure 2 schematically illustrates an embodiment of the present invention comparing and contrasting the highly variable saturated liquid CO<sub>2</sub> density as compared to a supersaturated liquid CO<sub>2</sub> feedstock used in the present invention.

The principal constraint with the prior art is a fluctuating saturated liquid CO<sub>2</sub> fluid density. As shown in Figure 2, a graph correlating the capillary injection fluid density (30) with pressure (32) and temperature (34) illustrates the problem clearly. The liquid-vapor saturation boundary line (36) exhibits a density shift (38) of as much as 38% between a saturated liquid CO<sub>2</sub> pressure of between 40 atm and 70 atm and a temperature between 278 deg. K and 304 deg. K. By contrast, and as used in the present invention, a supersaturated boundary line (40) exhibits a density shift (42) of less than 3% between a supersaturated liquid CO<sub>2</sub> pressure of between 70 atm and 680 atm and a temperature between 278 deg. K and 298 deg. K.

The supersaturated liquid CO<sub>2</sub> properties described under Figure 2, and as used in the present invention, uniquely provide both a highly uniform and maximum fluid density over a very broad pressure range as well as a means for precise flow regulation using microscopic capillary condensers, described under Figure 3.

Figure 3 illustrates using supersaturated liquid CO<sub>2</sub> hydraulic pressure in combination with a micro-capillaries or capillary bundles to control CO<sub>2</sub> mass flow and particle density in contrast to an exemplary prior art control scheme using a variable saturated liquid CO<sub>2</sub> supply,

0.030 inch ID capillary, and a 18-turn micrometering valve. Shown in Figure 3, capillary pressure (50) is correlated with CO<sub>2</sub> mass flow (52) for comparing and contrasting flow and mass regulation using an exemplary prior art metering valve control scheme (54) with the capillary pressure metering control (56) method of the present invention. The 18-turn micrometering valve control method (54) is ineffective in the range below 2 to 3 valve rotations, representing an highly unstable and therefore unusable flow control range (58) of between about 0.1 lbs. to 5 lbs. CO<sub>2</sub> per hour using a saturated liquid CO<sub>2</sub> supply of between 750 psi and 900 psi. As such, the prior art method using an optimized 0.030 inch ID Joule-Thomson capillary having a length of about 36 inches with saturated liquid CO<sub>2</sub> injection is suitable only for flow rates above about 5 lbs. CO<sub>2</sub> per hour per capillary (60), and still exhibits some pulsation near this lower injection rate limit. As discussed under Figure 1, the 18-turn metering valve must be adjusted periodically to insure that the capillary particle production rate remains within a predetermined acceptable spray composition control range. Also as discussed herein, using capillaries much small than 0.020 inch ID (to lower flow rate range) with the prior art metering valve flow control means introduces constraints such as lack of precise micro-flow control and fluctuation in particle generation. As such, there is need for enabling more predictable and precise mass and particle flow in the lower ranges between near-zero and 5 lbs. CO<sub>2</sub> per hour per capillary.

The present invention employs a novel capillary pressure metering control method and apparatus. Small capillaries having internal diameters of between 0.001 inch ID and about 0.020 inch ID, and lengths of between about 6 inches to about 36 inches, or more, are used in singular or in parallel bundles to provide both mass flow control and high pressure Joule-Thomson condensation using high pressure-regulated supersaturated liquid CO<sub>2</sub> injection. Using this novel metering method and apparatus, precise and stable control of miniscule amounts of CO<sub>2</sub> flow and particle generation is enabled in the range between near-zero and 5 lbs. per hour per capillary. Now referring to Figure 3, three exemplary capillaries; a 0.001 inch ID capillary (62), a 0.005 inch ID capillary (64), and a 0.010 inch ID capillary (66) having similar lengths. As shown in Figure 3, a 0.001 inch ID capillary (62) produces a very narrow flow range of between approximately 0.1 and 0.3 lbs. per hour over a fluid pressure range of between about 1000 psi and 2000 psi. A 0.005 inch ID capillary (64) produces a very narrow flow range of between approximately 0.5 and 2 lbs. per hour over a fluid pressure range of between about 1000 psi and 2000 psi. A 0.010 inch ID capillary (66) produces a very narrow flow range of between approximately 3 and 5 lbs. per hour over a fluid pressure range of between about 1000 psi and

2000 psi. This clearly illustrates the precision microscopic mass flow range control enabled by the present invention.

In addition, minimum injection pressures are shown under Figure 3 and which are based up a predetermined and controlled supersaturated liquid CO<sub>2</sub> fluid temperature. Minimum injection pressures assure supersaturated liquid CO<sub>2</sub> conditions (highest constant liquid density) upon injection into a capillary or capillary bundle. Exemplary minimum injection pressures include, for example, about 900 psi for fluid temperatures of about 10 degrees C (68), about 1000 psi for fluid temperatures of about 20 degrees C (70), and about 1200 psi for fluid temperatures of about 30 degrees C (72).

Moreover, parallel bundles of capillaries may be used to further extend the pressure-regulated mass control range thus described to 15 lbs. CO<sub>2</sub> per hour, or more, discussed under Figure 4A.

Figure 4A schematically illustrates an embodiment of the present invention comprising an exemplary system to produce a supersaturated liquid CO<sub>2</sub> and with which to produce particles therefrom using a high-pressure enhanced Joule-Thomson micro-capillary assembly. The method and apparatus of Figure 4A significantly improves the condensation process and conversion efficiency as compared to the prior art Enhanced Joule Thompson Capillary (EJTC) condenser methods and apparatuses of U.S. Patent Nos. 5,725,154, 7,293,570, and 7,451,941. The high-pressure Joule-Thomson capillary condensation process herein provides improved production, control and injection of CO<sub>2</sub>, particularly at very low flow rates, into heated propellant gas for cleaning and cooling applications. For example, the method and apparatus of U.S. Patent '941, Fig. 1a (2), may be replaced with the improved method and apparatus of Figure 4A.

Now referring to Figure 4A, a suitable supply or feedstock of saturated liquid CO<sub>2</sub>, contained and flowed through a supply tube (80), and typically having a variable vapor pressure of about between 750 psi and 1000 psi and a variable fluid temperature of between 50 degree F and 75 degree F, is introduced into the inlet (82) of an exemplary air-driven hydraulic pressure amplifier (84). This may include for example a cylinder supply of liquid CO<sub>2</sub>, a refrigerant-condensed CO<sub>2</sub> from a source of gaseous CO<sub>2</sub>, and novel low-volume Vortex- and Peltier-based condenser systems described under Figures 7 and 8 herein. The saturated liquid CO<sub>2</sub> is compressed to a supersaturation pressure of between 1,000 psi and 10,000 psi and compressed into a supply of supersaturated liquid CO<sub>2</sub> and stored using a fluidly-connected (85) storage system comprising an insulated and temperature controlled high-pressure cylinder (86).

Exemplary high pressure liquid pumps (84) suitable for use with the present invention include air-driven and air-regulated hydraulic amplifiers and boosters Haskel Pump Models numbers MS-7, MS-12, MS-21, AAD-5, AAD-7 and/or DSF-B15, available from Haskel International Inc, Burbank California. However other brands and types of air, electric or hydraulically driven pumps capable of pressurizing CO<sub>2</sub> gas or saturated liquid CO<sub>2</sub> into a supersaturated liquid CO<sub>2</sub> feedstock are suitable for practicing the present invention.

Thermally-insulated cylinders (86) may include simple high pressure pipe or ported sample cylinders having internal volumes adequate to ballast a feedstock supply of supersaturated liquid CO<sub>2</sub> without undue thermal changes in the fluid during use. Storage volumes and heating loads may be calculated based upon downstream capillary condenser demand (lbs. CO<sub>2</sub>/hour). Thermal control is provided, for example, using a digital temperature controller (88) and a heating element wrapped or bolted about the storage cylinder (86), all of which is wrapped in a suitable thermal insulation media. Supersaturated fluid temperature is preferably controlled at a temperature of about 70 degrees F, or a few degrees above ambient temperature to insure stability with respect to the surrounding environment. This insures a stable and consistent supersaturated liquid CO<sub>2</sub> density.

However, for longer micro-capillary condenser lengths of 20 feet or more it may be useful to feed the capillary segment or capillary bundle condenser assembly described herein using supercritical CO<sub>2</sub> at a temperature of about 88 degrees F, or higher, and at a much higher injection pressure of 2,500 psi or more. The combination of zero surface tension, extremely low viscosity, and high fluid density enables a more gradient condensation process within longer, smaller capillary condensers. Supercritical CO<sub>2</sub> injection uniquely transitions the feedstock through three stages of cooling, condensation, and crystallization: supercritical→liquid→solid, providing a much larger pressure and temperature gradient for longer capillary condensers.

A spring-loaded pressure relief valve or automated gate valve (92) may be used to maintain a constant pressure within the storage cylinder (86), allowing excess fluid volume to relieve and return (94) to the saturated (or supercritical) feedstock supply line (80).

The exemplary air-driven hydraulic booster pump (84) is controlled using a manual or automatic air drive system. Using a manually-adjustable or automated digital pressure regulator (96), compressed air (100) is regulated between 20 psi and 150 psi and fed (98) into the air drive section of the pump (84). Pump drive air-regulation correlates roughly linearly to compressed fluid output pressure, and depending upon the pump selected, will control CO<sub>2</sub> fluid pressures between 900 psi and 10,000 psi. Upon drive air compression and expansion from the air drive

exhaust section (102) of the pump (84), the expanding drive air cools significantly in accordance with Joule-Thomson expansion cooling principles. This cooling capacity may be used in the present invention within a countercurrent intercooler assembly such as a tube-tube heat exchanger (104) to cool and densify the saturated liquid CO<sub>2</sub> feedstock contained in the supply  
5 line (80).

Following the generation of a supply of supersaturated liquid CO<sub>2</sub> (or supercritical CO<sub>2</sub>), the supersaturated fluid is metered using a micro-capillary segment or micro-capillary condenser bundle (106), called a High-Pressure Enhanced Joule Thomson Micro-Capillary condenser assembly (or abbreviated as EJTMC assembly herein). Turning the metering on and off is  
10 accomplished using an automated valve (108), for example a Series 9 or 99 pulse valve available from Parker Hannifin, Fairfield, NJ, which is fluidly connected in-line between the storage cylinder (86) and the EJTMC assembly (106).

The EJTMC assembly comprises a capillary loop having a length of between 6 inches and 30 feet, or more, and internal diameters preferably between 0.001 inch and 0.015 inch,  
15 called micro-capillaries herein. As shown in Figure 4A, micro-capillaries may be “bundled” in a parallel-flow arrangement to increase mass flow without degrading pressure-regulated flow control. For example, a single micro-capillary (110) having an 0.005 inch ID capillary, at 12 inch length, will provide a precision flowrate of about 0.5 to 1.5 pounds per hour between an injection pressure range of 1000-1500 psi. In another example, a bundled micro-capillary  
20 assembly (112) comprising four (4) 0.005 inch ID capillaries, 12 inch length, will provide a precision flowrate of about 2 to 12 pounds per hour within the injection pressure range of between 1000-1500 psi.

Single EJTMC micro-capillary or bundled EJTMC assemblies (106) are fluidly connected (114) via a coaxial premixer (i.e., micro-capillary fed coaxially within a portion of the  
25 dense fluid propellant tube) and into a dense fluid propellant mixer assembly (116) of the exemplary CO<sub>2</sub> Composite Spray coaxial spray system, for example as described under Figure 2a of U.S. Patent ‘941, or alternatively may be transitioned to and fluidly connected to said propellant mixing portion over a longer distance using a transport capillary segment (118) having a diameter equal to the sum of the individual internal diameters of the capillary bundle.  
30 Preferably, single EJTMC micro-capillary or bundled EJTMC assemblies are fluidly connected to the exemplary expansion, positioning and mixing spray nozzle described under Figure 4B herein.

Regarding the exemplary capillary bundle-to-transport capillary transition method thus

described, it is important not to expand the micro-capillary fluids quickly using a segmented and expanding capillary apparatus such as taught in U.S. Patent '570, as this will cause clogging and sputtering, among other undesirable effects. Given the small internal diameters of capillaries used in the present invention, a gradual pressure drop along a uniform capillary condenser

5 volume is preferred to allow the microscopic quantity of supersaturated liquid carbon dioxide to gradually boil, cool and condense into a free-flowing and uniformly dispersed mixture of uniformly sized microscopic CO<sub>2</sub> solid particles and CO<sub>2</sub> vapor. For example a high-pressure capillary bundle containing four (4) 0.005 inch ID capillaries in parallel (having an ID sum of  $d_1+d_2+d_3+d_4 = 0.020$  inch) may be affixed to a 0.020 inch ID transport capillary segment thus

10 forming a uniform capillary bundle-to-transport capillary volume transition. Thus the capillary bundle serves as both a high-pressure injector and flow restrictor; a novel Joule-Thomson throttle. By contrast, incremental and sequential capillary volume change as used in U.S. Patent '570 (Fig. 2) uses a segmented sequence of serially-connected capillaries having increasing internal diameters ( $d$ ) of  $d_1 < d_2 < d_3 < d_4$  and so on which produces abrupt volume increases for

15 rapid expansion and condensation of saturated liquid carbon dioxide first into a mass of small crystals ( $d_1$ ) which then coalesce and grow along each expansion step ( $d_2, d_3$  and  $d_4$ ) into an aerosol containing fewer particles (low density) but having a much larger average particle size. The crystal growth process of U.S. Patent '570 is analogous to a snowball gathering size and mass as it rolls downhill or the coalescence of freezing microscopic rain droplets into large hail

20 on their downward descent from the upper atmosphere. Such a particle growth technique is undesirable in the present invention as it causes excessive particle growth and results in low and non-uniform particle distributions or densities within a CO<sub>2</sub> Composite Spray.

By contrast, the present invention overcomes this constraint by preventing abrupt pressure drops and excessive expansion cooling immediately following high-pressure

25 supersaturated liquid CO<sub>2</sub> capillary injection. Supersaturated liquid CO<sub>2</sub> boils (cools) gradually and uniformly within and along a capillary segment under very high pressure gradients. There is no sputtering or clogging and mass flow (microscopic particle generation) is controlled using a combination of variably-controlled high fluid pressure and micro-capillary bundles.

Referring to the graphical relationship chart (120) under Figure 4A, a high pressure,

30 supersaturated liquid CO<sub>2</sub> (or supercritical CO<sub>2</sub>) condensation process using an EJTC micro-capillary system thus described increases capillary pressure drop (122), increases capillary temperature drop (124), controls capillary mass flow (126), and all of which increases Joule-Thomson cooling and condensation processes (128). As such the method and apparatus of

Figure 4A increases the production of microscopic and minute solids (130).

By contrast, the CO<sub>2</sub> Composite Sprays discussed in the prior art - which employ one or more capillaries having internal diameters of, for example, 0.020, 0.030, 0.040, 0.060, and 0.080 inch  
5 in combination with a micrometering valve and using saturated liquid carbon dioxide - cannot provide precision mass control (and production of uniform microscopic CO<sub>2</sub> particles) and linearity through the entire mass flow range from near-zero flows to the maximum flows. Using capillaries with internal diameters below 0.020 inches does produce a smaller mass flow of smaller particles, but also produces inconsistent particle flows (i.e., increased pulsing,  
10 sputtering and sublimation losses) when expanded into larger diameter capillary segments. For example, smaller mass flows comprising smaller-sized CO<sub>2</sub> particles are more susceptible to heating and sublimation within the longer or stepped capillary transitions present in the prior art (i.e., U.S. Patent '570). As such, much of the cleaning or cooling agent (solid CO<sub>2</sub> particles) is destroyed (sublimated) in transit and prior to introduction with the propellant gas, which itself  
15 further sublimates a portion of the surviving CO<sub>2</sub> particle population prior to impacting surfaces under spray treatment.

Having thus described the preferred embodiments of the high-pressure EJTMC condenser assembly for producing minute amounts of microscopic CO<sub>2</sub> crystals, Figure 4B schematically illustrates a dense fluid particle-propellant mixing and spray delivery nozzle (also  
20 referred to as a “mixer”) embodiment of the present invention. The present embodiment provides several useful functions in the present invention. In a first aspect of the present embodiment, CO<sub>2</sub> micro-crystals (and cold dense vapor) produced by the EJTMC apparatus and process of Figure 4A are modified further to increase particle size through an adjustable (in-situ) super-cooling and crystal-growth process. In a second aspect of the present embodiment, the  
25 pressure and flow of the CO<sub>2</sub> particle stream are mechanically balanced with the pressure and flow rate of a propellant gas stream to optimize CO<sub>2</sub> particle acceleration and particle conservation (i.e., avoid excessive turbulent mixing). In a third aspect of the present embodiment, the CO<sub>2</sub> particle stream is injected within the spray nozzle body (and into the propellant gas stream) through a precise mechanical alignment of both the internal coaxial and  
30 longitudinal orientations.

The EJTMC apparatus and process described under Figure 4A produces a very small amount of relatively high-pressure, fast-moving, and ultra-fine CO<sub>2</sub> particles – also termed “microseeds” – entrained in cold CO<sub>2</sub> vapor, which is discharged at the terminal end of the high-

pressure EJTMC condenser assembly (Figure 4A (106)). CO<sub>2</sub> microseeds produced by the present invention are grown (crystallized) into a useful size within a short and small-volume expansion tube. Following this, grown crystals and residual CO<sub>2</sub> vapor are injected coaxially at a precise location within the propellant stream, and with pressure balancing and precise

5 coaxially injection within the mixing zone of the spray nozzle. The cold micro-particle and vapor mixture is injected into an adjustable expansion micro-chamber, whereupon the cold CO<sub>2</sub> microseeds accumulate particle mass according to the following mechanism – rapid pressure and temperature drop during sudden expansion cause dense cold vapor to condense onto the solid phase microseeds as a cold boiling liquid film, which then condenses further to a frozen solid

10 surface layer. The expansion-cooling-condensing process occurs within a very short traverse and rather small expansion volume. The expansion volume determines the amount of crystal growth, and the particles grow layer-upon-layer until finally injected into and mixed with the propellant stream at the terminal end of the expansion tube. Additionally, the higher pressure, low-flow CO<sub>2</sub> microseeds and vapor discharged from the EJTMC condenser assembly (Figure

15 4A (106)) and expanded mixture of CO<sub>2</sub> microseeds and vapor produced by the expansion chamber must be balanced with the relatively high-flow, lower pressure propellant gas within the spray nozzle assembly to eliminate turbulence. In this regard, the expansion tube assembly of the present embodiment provides the capability of mechanically adjusting (or balancing) the pressures and flows between the two streams during mixing.

20 Now referring to Figure 4B, minute amounts of CO<sub>2</sub> microseeds and dense cold CO<sub>2</sub> vapor as depicted by the small arrow (496) - flowing within a moveable or position-adjustable capillary segment (500) as depicted by the double arrow (501) - is selectively coalesced and condensed as depicted by a larger arrow (498) at various positions within and along the longitudinal traverse of a thermally-insulated (optional) rigid expansion tube (502), which may

25 be grounded to dissipate electrostatic discharge build-up during the expansion process. The adjustable expansion tube assembly (502) may be constructed for example using full or partial heat-shrinkable Teflon insulation (504) covering a stainless capillary tube (506). The stainless capillary tube (506) has a slightly larger inside diameter (508) as compared to the outside diameter of the capillary injection tube (510). Given this arrangement, the inner capillary tube

30 (500) may be selectively re-positioned anywhere along the interior within the rigid expansion tube (506). An elastomeric nut and flangeless ferrule sealing assembly (512), for example, may be used to secure the capillary segment (500) to the expansion tube (502). The moveable capillary segment (500) and rigid expansion tube (506) thus forms an adjustable and

microscopic expansion volume (514) therein, designated as “V1”. The rigid expansion tube (506) itself is positioned within the throat (516) of an outer coaxial propellant nozzle (518) near the discharge position (520) of the propellant nozzle – thus forming an adjustable particle-propellant mixing volume (522) therein, designated as “V2”. An elastomeric nut and flangeless ferrule sealing assembly (not shown), for example, may be used to secure and the expansion nozzle assembly (502) to the propellant nozzle assembly (524). A dense fluid propellant gas (525) such as clean dry air, nitrogen, or carbon dioxide is heated between about 60 degrees F to about 300 degrees F and flows coaxially (526) over the optionally insulated rigid expansion tube assembly (502), mixes with and accelerates the expanded CO<sub>2</sub> particles from the nozzle exit (520).

Figures 4B-I and 4B-II describe the operation of the novel expansion apparatus described under Figure 4B. The moveable capillary segment (500) may be positioned anywhere from the terminal end (Figure 4B-I, 528) of the rigid expansion tube (506) to the inlet portion (Figure 4B-II, 530) of same. The length of the rigid expansion tube (506) is preferably constructed to be between about 0.5 inches to 8 inches in length with inside diameters of between about 0.0625 inches to 0.250 inches to accommodate moveable capillary segments having slightly smaller outside diameters – for example from about 0.06 inches to 0.20 inches. Other combinations (i.e., lengths and diameters) of capillary segment (500) and expansion tube (506) may be used which meet the adjustability requirements discussed herein. A larger expansion volume – V1 (Figure 4B, 514) – produces larger CO<sub>2</sub> crystals (Figure 4B-II, 532). A smaller expansion volume – V1 (Figure 4B, 514) – produces smaller particles (Figure 4B-I, 534). As such, and using the present embodiment, the particle size is adjustable from fine (small V1) to coarse (large V1) using a simple moveable tube-within-tube expansion device as described. The present embodiment also serves as a precision particle-into-propellant injection-alignment tube. The mixing volume – V2 (Figure 4B, 522) – and propellant gas (Figure 4B, 525) flowrate (pressure) are balanced – via in-situ adjustment of the expansion tube (Figure 4B, 506) within the nozzle throat (Figure 4B, 516) to accommodate the differences between expanded fluid pressure-flow and dense fluid propellant gas pressure-flow.

The CO<sub>2</sub> particle growth methods of the prior art and developed by the first named inventor are not suitable for use with the present invention. The following discussion compares and contrasts the novel particle size adjustment apparatus of Figure 4B, Figure 4B-I, and Figure 4B-II to the expansion apparatuses described under U.S. Patent 5,725,154 (‘154) and U.S. Patent 7,134,946 (‘946).

The apparatus of '154 moves a propellant nozzle body ('154, Figure 10, (14)) over an inner fixed-position snow tube ('154, Figure 11, (22)). Further to this, the apparatus described under '154 utilizes a threaded adjustment section ('154, Figure 10, (14)) to provide a CO<sub>2</sub> particle-gas expansion volume change. Threaded adjustment features produce microscopic particles during tuning and thus are not acceptable for precision particle removal applications. In addition, the expansion volume used in '154 utilizes a divergent cavity ('154, Figure 11, (136)), which produces highly non-linear pressure gradients and which is subject to "clogging" or "sputtering" when fully opened (largest expansion volume). By contrast the device of Figure 4B is a cleaner device – utilizing a tube-in-tube adjustment and flangeless ferrule sealing mechanism – and produces a linear volume-pressure gradient during adjustment. Further to this the expansion device provided under Figure 4B has a larger range of particle size control as compared to a divergent expansion cavity of '154.

Now referring to '946, various lengths and increasing diameters ('946, Fig. 6) of flexible PEEK tubing are connected in series to form any variety of expansion tube assembly contained with a propellant tube. The '946 expansion system is cumbersome, cannot be adjusted in-situ, and does not provide precise propellant injection control. Moreover, neither the individual expansion segment volumes nor the terminal positioning of the expansion system are adjustable in-situ within the propellant tube. For example, the CO<sub>2</sub> particle expansion system of '946 (Fig. 6) requires complete disassembly of the coaxial spray applicator device shown in '946 (Fig. 5), removal of the old stepped expansion tube assembly and installation of a new stepped expansion tube assembly, and reassembly of the entire coaxial spray applicator system to accomplish changes in the CO<sub>2</sub> expansion and crystallization process. Still moreover, the entire capillary condenser system must be aligned with the propellant nozzle to balance capillary and dense fluid propellant gas pressures and flows. Moreover, the stepped arrangement of '946 is impractical for use with microscopic amounts of liquid carbon dioxide used in the present invention. The minute amounts of microscopic CO<sub>2</sub> particles generated in the present invention would entirely sublime during the long expansion distance prior to the propellant injection point. Further to this, a separate centering device is required to position the terminating flexible capillary segment of '946 within the terminal end of the spray nozzle.

Figure 5 schematically illustrates the differences between a saturated liquid CO<sub>2</sub>, supersaturated liquid CO<sub>2</sub>, and supercritical CO<sub>2</sub> using a phase diagram. The phase diagram (150) shows the various phases for CO<sub>2</sub> based upon pressure (152) and temperature (154). The vapor-liquid saturation line (156) represents the boiling P-T curve line for a conventional

capillary condenser utilizing gas-saturated liquid CO<sub>2</sub>, typically ranging somewhere along the saturation line (156) between a pressure range of about 750 psi to 875 psi and between a temperature range of about 10 degrees C and 25 degrees C. By contrast, the present invention utilizes high pressure CO<sub>2</sub> fluids - supersaturated liquid (158) or supercritical CO<sub>2</sub> (160) - above the saturation line, typically above the CO<sub>2</sub> critical pressure line (162) of 1070 psi, between a pressure range of about 900 psi to 10,000 psi and between a temperature of about 10 degrees C and 35 degrees C. Supersaturated fluids exhibit a stable, near-maximum liquid density with little variation along a very broad pressure range near room temperature, as discussed under Figure 2 herein. Supercritical fluids when compressed to higher fluid pressures than 2000 psi can exhibit very high liquid-like densities with no surface tension and very low viscosities, and are used in the present invention for injection into very long EJTMC capillary condenser assemblies as discussed under Figure 4A herein.

Figure 6 illustrates schematically the present invention using the high-pressure enhanced Joule-Thomson micro-capillary condensation technique using supersaturated liquid CO<sub>2</sub> mass flow control and high pressure micro-capillary condensation as a proactive control scheme for providing improved ultra-low mass flow and particle density control. Referring to Figure 6, the present invention provide a stable source of supersaturated liquid CO<sub>2</sub> (or supercritical CO<sub>2</sub>) for capillary condensation processes to produce a consistent and stable supply of CO<sub>2</sub> particles for injection and mixing with a propellant gas, having a constant pressure and temperature. The reasons for this stability, and as discussed herein, are related to a number of contributing factors including; elimination of prior art constraints related to changes in bulk CO<sub>2</sub> gas supply tank pressures and temperatures during withdraw and usage, changes in environmental temperatures such as factory temperatures and outside storage tank and delivery system temperatures, temperature variations within the CO<sub>2</sub> gas supply lines from source to ceiling or floor to cleaning system, variations in high pressure gas delivery system supply pressures and temperatures, and variations in internal pressure and temperature of refrigerant condenser systems used to condense transported high pressure gas to a cold saturated liquid CO<sub>2</sub> supply.

This results in a highly stable and predictable supply of liquid CO<sub>2</sub> feedstock (200) which results in constant density (204), constant capillary boiling densities and resulting stability and control of particle size and density (206), and upon injection (208) and mixing with a heated propellant gas (210), produce a stable CO<sub>2</sub> Composite Spray composition (212) of CO<sub>2</sub> particles and propellant gas which when projected (214) at a surface produce a stable cleaning (or cooling) rate (216).

The present invention control means involves a proactive scheme (218), whereby the CO<sub>2</sub> supply is controlled as discussed herein – and the capillary injection pressure (220) is adjusted manually or automatically as needed to produce a different CO<sub>2</sub> Composite Spray particle injection rates and compositions (212). As a result the present invention maintains a much tighter range between an acceptable upper control composition limit (222) and lower control composition limit (224) over time. The prior art constraints are eliminated for extremely low liquid CO<sub>2</sub> injection rates and capillary flows (small capillary diameters).

Having thus described the present invention and its advantages over the prior art, the following detailed discussion illustrates two novel methods and apparatuses under Figures 7 and 8, respectively, for creating a low-volume supply of saturated liquid CO<sub>2</sub> for use with the present invention.

Figure 7 schematically illustrates an embodiment of the present invention comprising an exemplary Vortex-based condensing system to produce a supply of saturated liquid CO<sub>2</sub> feedstock for use in the present invention. Referring to Figure 7, a vortex device (300) is used to create a hot air stream (302) and a cold air stream (304). The cold air stream (304) is fluidly connected to the inlet of an outer insulating tube (306), for example a polyurethane tube, of a tube-in-tube heat exchanger (308) and flows in a countercurrent direction (310) over an inner thermally conductive tube (312), for example a copper tube, which is fluidly connected to source of CO<sub>2</sub> gas (314) flowing through the inner thermally conductive tube (312) at a pressure of between 750 psi and 850 psi. The CO<sub>2</sub> gas flowing through the inner tube (312) condenses (at saturation pressure) into a feedstock of saturated liquid CO<sub>2</sub> (316), along the saturation line of Figure 5 (156) which is fluidly connected to the apparatus of Figure 4A (318); which produces a stable supply of CO<sub>2</sub> particles for injection (319) into a coaxial propellant mixing tube and spray nozzle (324).

As a novel means for improving the efficiency of a Vortex-based condensing technique, the present invention uses a tube-in-tube heat exchanger and flow scheme as described above for the hot fluid (302) produced by the Vortex device (300). The hot air flows countercurrent through a thermally insulative conduit (320) containing an inner thermally conductive conduit (322) flowing a propellant gas. The propellant gas flowing through the conductive conduit (322) is heated and which is supplied to the exemplary coaxial mixing tube and nozzle (324).

The Vortex device as used in the present invention provides both a CO<sub>2</sub> condensing and propellant heating functions, which conserves energy and improves overall system efficiency for small-volume supply systems for use with the present invention. Vortex devices are available

from a number of sources and in a range of cooling (and heating) capacities.

Figure 8 schematically illustrates an embodiment of the present invention comprising an exemplary Peltier-based condensing system to produce a supply of saturated liquid CO<sub>2</sub> feedstock for use in the present invention. Referring to Figure 8, a Peltier device (400) is used to create a hot side (402) and a cold side (404). The cold side (404) is mated with a tube-in-shell heat exchanger (408) which contains an inner thermally conductive tube (412), for example a copper tube, which is fluidly connected to source of CO<sub>2</sub> gas (414) flowing through the inner thermally conductive tube (412) at a pressure of between 750 psi and 850 psi. The CO<sub>2</sub> gas (414) flowing through the inner tube (412) condenses (at saturation pressure) into a feedstock of saturated liquid CO<sub>2</sub> (416), along the saturation line of Figure 5 (156) which is fluidly connected to the apparatus of Figure 4A (418); which produces a stable supply of CO<sub>2</sub> particles for injection (419) into a coaxial propellant mixing tube and spray nozzle (424).

As a novel means for improving the efficiency of a Peltier-based condensing technique, the present invention uses a tube-in-shell heat exchanger and flow scheme as described above for the hot side (402) produced by the Peltier device (400). The hot side is mated to a tube-in-shell heat exchanger (430) which contains an inner thermally conductive tube (432), for example a copper tube, which is fluidly connected to source of propellant gas (434). The propellant gas (434) flowing through the conductive tube (432) is heated, producing a heated propellant gas (435), which is supplied to the exemplary coaxial mixing tube and nozzle (424).

The Peltier device as used in the present invention provides both a CO<sub>2</sub> condensing and propellant heating functions, which conserves energy and improves overall system efficiency for small-volume supply systems for use with the present invention. Peltier devices are available from a number of sources and in a range of cooling (and heating) capacities.

## EXPERIMENTAL 1

Having thus described the preferred and exemplary embodiments of the present invention with regards to CO<sub>2</sub> particle generation, the following discussion by reference to Figures 9A, 9B, 9C, 9D, 9E and 9F details experimental testing, results, and analysis comparing and contrasting the performance characteristics between the present invention with the prior art – specifically prior-art and first-generation spray cleaning system described and operated under U.S. Patent 5,725,154 (U.S. Patent ‘154) and prior-art and second-generation spray cleaning system described and operated under U.S. Patent 7,451,941 (U.S. Patent ‘941) spray system scheme modified with a stepped capillary system described under U.S. Patent 7,293,570 (U.S. Patent ‘570). All CO<sub>2</sub> composite spray cleaning systems tested under operated under equivalent

dense fluid propellant gas pressure and temperature conditions.

Test Apparatus and Conditions for the Present Invention:

A commercial CO<sub>2</sub> composite spray system called the PowerSno™ CO<sub>2</sub> composite spray cleaning system, Model PS6000, manufactured by CleanLogix LLC, Santa Clarita, California, described under U.S. Patent 7,451,941 (U.S. Patent ‘941) was modified using the present invention. The system modifications comprised the apparatus of Figure 4A (high pressure capillary condenser assembly) and Figure 4B (spray nozzle). The modified spray system was set-up and operated using key process test parameters as described under Table 1. The CO<sub>2</sub> “microseeds” produced by an 0.008 inch ID EJTMC assembly of Figure 4A (106), 12 inches in length, were fed into the adjustable spray nozzle of Figure 4B and expanded into a coarse particle feed stream using an exemplary expansion chamber - 6 inch long x 0.0625 inch ID expansion chamber of Figure 4B (514) – prior to injection into (and mixing with) the propellant gas stream of Figure 4B (525).

**Table 1 – Experimental Test Parameters for Present Invention**

| Key Test Parameters                                | Values                                                        |
|----------------------------------------------------|---------------------------------------------------------------|
| Dense Fluid Propellant Gas                         | Clean Dry Air (-40 Degree F Dew Point)                        |
| Dense Fluid Propellant Gas Temperature             | 200 degrees C                                                 |
| Dense Fluid Propellant Gas Flow Rate<br>(Pressure) | 1.7 scfm (at 100 psi)                                         |
| EJTMC Segment Length                               | 12 inches                                                     |
| EJTMC Segment Internal Diameter                    | 0.008 inches (expanded into coarse particles)                 |
| EJTMC Feed Pressure and Temperature                | 1200 psi/15 degrees C (Super-saturated Liq. CO <sub>2</sub> ) |
| CO <sub>2</sub> Mass Flow through EJTMC Assembly   | 1.25 lbs/hour                                                 |
| CO <sub>2</sub> Particle Type (Fine/Coarse)        | Coarse (Expanded High Pressure Micro-Spray)                   |

Test Apparatus and Conditions for Prior Art:

The apparatus used to demonstrate the spray performance of a first-generation spray system (U.S. Patent 5,725,154 (U.S. Patent ‘154)) comprised a MicroSno™ CO<sub>2</sub> spray cleaning system, Model MS6000, manufactured by Deflex Corporation, Santa Clarita, California, using a

single segment of 36 inch long 0.030 inch internal diameter (0.0625 inch outside diameter) PEEK coaxial CO<sub>2</sub> condenser capillary. As shown under Table 2, the key test parameters used for dense fluid propellant gas type, temperature, and pressure were equivalent to the test conditions used with present invention and used the capillary condensation and nozzle mixing scheme of U.S. Patent '154.

**Table 2 – Experimental Test Parameters for U.S. Patent '154**

| Key Test Parameters                                  | Values                                                   |
|------------------------------------------------------|----------------------------------------------------------|
| Dense Fluid Propellant Gas                           | Clean Dry Air (-40 Degree F Dew Point)                   |
| Dense Fluid Propellant Gas Temperature               | 200 degrees C                                            |
| Dense Fluid Propellant Gas Flow Rate<br>(Pressure)   | 3.2 scfm (at 100 psi)                                    |
| Capillary Segment Length                             | 36 inches                                                |
| Capillary Segment Internal Diameter                  | 0.030 inches                                             |
| Capillary Feed Pressure and Temperature              | 800 psi/15 degrees C (Saturated Liquid CO <sub>2</sub> ) |
| CO <sub>2</sub> Mass Flow through Capillary Assembly | 10 lbs/hour (Lean Spray)                                 |
| CO <sub>2</sub> Particle Type (Fine/Coarse)          | Fine                                                     |

The apparatus used to demonstrate the spray performance of a second-generation spray system - U.S. Patent 7,451,941 (U.S. Patent '941) spray system scheme modified with U.S. Patent 7,293,570 (U.S. Patent '570) - comprised a PowerSno™ CO<sub>2</sub> composite spray cleaning system, Model PS6000, manufactured by CleanLogix LLC, Santa Clarita, California, using a "stepped" Enhanced Joule-Thomson Capillary (EJTC) condenser system comprising a 30 inch segment of 0.030 inch internal diameter (0.0625 inch outside diameter) PEEK tubing connected to a 30 inch segment of 0.070 inch internal diameter (0.125 inch outside diameter) PEEK capillary tube. As shown under Table 3, the key test parameters used for dense fluid propellant gas type, temperature, and pressure were equivalent to the test conditions used with present invention and used the capillary condensation and nozzle mixing schemes of U.S. Patent '941 (EJTC condenser-nozzle-spray scheme) and U.S. Patent '570 (stepped capillary scheme), respectively.

**Table 3 – Experimental Test Parameters for U.S. Patents '570/'941**

| Key Test Parameters | Values |
|---------------------|--------|
|---------------------|--------|

|                                                    |                                                          |
|----------------------------------------------------|----------------------------------------------------------|
| Dense Fluid Propellant Gas                         | Clean Dry Air (-40 Degree F Dew Point)                   |
| Dense Fluid Propellant Gas Temperature             | 200 degrees C                                            |
| Dense Fluid Propellant Gas Flow Rate<br>(Pressure) | 3.2 scfm (at 100 psi)                                    |
| EJTC Segment Length                                | 60 inches                                                |
| EJTC Segment Internal Diameters (Stepped)          | 0.030 inch to 0.070 inch                                 |
| EJTC Feed Pressure and Temperature                 | 800 psi/15 degrees C (Saturated Liquid CO <sub>2</sub> ) |
| CO <sub>2</sub> Mass Flow through EJTC Assembly    | 10 lbs/hour (Lean Spray)                                 |
| CO <sub>2</sub> Particle Type (Fine/Coarse)        | Coarse (Stepped Expansion)                               |

#### Spray Power Test Apparatus and Method:

The present invention and prior art systems - U.S. Patent '154 (first-generation spray) and U.S. Patents '570/'941 (second-generation spray) - were tested to determine the maximum achievable spray impact stress, under identical propellant gas pressures and temperatures. Referring to Figure 9A, the present invention including a prior-art PowerSno™ Model PS600 CO<sub>2</sub> spray system modified with the apparatus of Figure 4A (600) and Figure 4B (602) (spray nozzle) was positioned with the spray nozzle 2 inches (604) from a 2" rectangular piece of FujiFilm™ Mylar micro-encapsulated contact pressure test film (606) – a available from Tekscan, Boston, MA - taped to a sheet metal supporting base plate (608). Various types of FujiFilm impact stress films are available from Tekscan with pressure ranges from 0.1 MPa to 130 MPa. Again referring to Figure 9A, the initial test used the PowerSno modifications of Figure 4A (600) and Figure 4B (602) to produce a CO<sub>2</sub> composite spray (610), and using the spray test parameters listed under Table 1 (coarse particle stream), which was directed at the test film (606) at an impact angle of approximately 90° for approximately 60 seconds to achieve complete film color development. Spray impact stresses are indicated on the pressure-sensitive film, as color variations on the impacted film ranging from colorless, to faint pink, and to dark red (highest impact stress). It is noteworthy that the spray impact testing using the present invention almost immediately physically damaged a FujiFilm HS high-pressure film (50-100 MPa range) surface – producing a dark red color at the perimeter of the spray (612), indicating a shear stress of approximately 80 MPa, and completely etching away the Mylar film entirely at the center of the spray (614), indicating a shear stress of greater than 100 MPa. This damage required moving the spray head across the test film very rapidly to complete the 60 second

exposure cycle, producing lighter reddish color development pattern (616). FujiFilm pressure test films, ranging from low pressure ranges to high pressures ranges, are supplied film color-to-pressure correlation charts. Using the FujiFilm HS high pressure film chart (618), the spray testing for the present invention indicates a maximum impact pressure of between 80 MPa (620) at the spray perimeter to as high as 100 MPa at center of the spray, and even higher based on the physical damage to the film (622). As such, the reliable film pressure measurements accepted under this experiment for comparison and discussion of results are considered very conservative, and more than likely exceed the maximum shear stress value reported herein significantly.

Subsequently, the identical spray impact test procedure was performed using the prior art CO<sub>2</sub> spray systems – ‘U.S. Patent ‘154 and U.S. Patents ‘570/’941 – and using the spray test conditions listed under Table 2 and Table 3, respectively. These spray tests necessitated the use of lower pressure films - FujiFilm LS (10-50 MPa range) for ‘570/’941 and LW (2.5-10 MPa range) for ‘154 - due to the lower impact stresses produced by both prior art systems. It is noteworthy that neither of the prior art systems physically damaged the pressure-sensitive Mylar film surfaces during spray impact tests.

#### Results:

The spray impact tests revealed both expected and unexpected results. Referring to Figure 9B, as expected the coarse particle-laden spray stream produced by the prior art second-generation U.S. Patents ‘570/’941 CO<sub>2</sub> spray system using a stepped capillary scheme yielded impact shear stresses of about 500% greater than the single capillary system used in the first-generation U.S. Patent ‘154 CO<sub>2</sub> spray system test. U.S. Patents ‘570/’941 system (0.030/0/070 stepped capillary) yielded a peak shear stress of about 60 MPa (700) and the U.S. Patent ‘154 system (0.030 capillary) achieved a peak shear stress of about 10 MPa (702), using the key spray process conditions listed under Table 3 and Table 2, respectively.

The coarse particle-laden spray stream produced by the present invention using the high-pressure micro-capillary condensation process and expansion processes of Figure 4A and Figure 4B, respectively, yielded a peak impact shear stress of (at least) 80 MPa (704) – 700% greater than the single capillary system used in the U.S. Patent ‘154 spray test and more than 33% greater than the stepped capillary enhancement used in the U.S. Patent ‘570/’941 process. Most notably the present invention uses much smaller particles (practically invisible to the unaided eye) and approximately 88% less CO<sub>2</sub> usage, indicative of a much more energetic spray process with superior CO<sub>2</sub> economy. Spray testing experiments were also performed to determine the range for the present invention. This was accomplished by adjusting the expansion volume

(V1) of the exemplary spray nozzle of Figure 4B to provide a minimum expansion volume and a maximum volume therein. Energetic microscopic particle streams produced shear stresses less than 2 MPa (at 100 psi propellant pressure) to at least 80 MPa.

Discussion of Results:

5           The directed performance goals for the present invention were to produce adequate cleaning power while using only very small quantities of CO<sub>2</sub>. As such, the actual spray impact results for the present invention under Figure 9B (704) were quite unexpected and appear counterintuitive. The spray test experiments were repeated several times to confirm the results reported herein. Referring again to Figure 9B, the expected result was that smaller and fewer  
10       particles (i.e., microseeds) produced by the present invention would produce spray impacts which would be less than U.S. Patents '570/'941 (700), or possibly even less than U.S. Patent '154 (702). This initial logic and expectation seemed appropriate given the spray power dependency established between the two prior art systems, which is based on particle size (assuming all of key spray parameters are maintained somewhat the same).

15           Quite remarkably the present invention produces a range of spray impact stresses – from less than U.S. Patent '154 (as expected) for ultrafine particles being produced to greater than U.S. Patents '570/'941 for coarser particles (not expected) – and demonstrated this adjustable spray power range using 80%+ less CO<sub>2</sub> than the prior art spray systems.

          The significant performance of the present invention is demonstrated aptly by comparing  
20       the spray performance ratios between the three spray systems tested. A performance ratio (PR) is calculated as maximum shear stress (MPa) divided by CO<sub>2</sub> usage (lbs/hour). Now referring to Figure 9C, the first-generation CO<sub>2</sub> composite spray system, U.S. Patent '154, using a 0.030 inch capillary condenser is considered a benchmark, and has a performance ratio value of 10 MPa divided by 10 lbs/hour or a PR=1 (800). The performance ratio of the U.S. Patents  
25       '570/'941 spray system using a stepped .030/.070 inch capillary condenser gives a maximum performance ratio of PR=6 (802) or 5x greater than U.S. Patent '154. The present invention produces a PR=64 (804), which is 64x greater than U.S. Patent '154 spray system and 11x greater than the U.S. Patents '570/'941 spray system.

          Possible explanations for the enhanced performance of the present invention are offered  
30       as follows by contrast to prior art CO<sub>2</sub> sprays. High-pressure capillary injection of microseeds into the small expansion chamber of Figure 4B (514) produces smaller and harder CO<sub>2</sub> particles which have a higher density, and which move at much higher velocity which produces more energetic surface impacts. Evidence for this supposition is a rather loud jet crackling sound

present during particle expansion (i.e., maximum V1), which is not present in the prior art tested herein. Jet noise crackle arises in supersonic jet flows (Reference: Quantifying crackle-inducing acoustic shock-structures emitted by a fully-expanded Mach 3 jet, Baars et al, AIAA Journal, May 27-29, 2013).

5           Another factor is surface impact density. More numerous and smaller particles increase contact area at the substrate surface interface. High frequency energetic impacts produce higher outflow velocities for the resulting splat and the production of higher unload stresses.

          Related to this, and possibly one of the most critical factors is CO<sub>2</sub> composite spray geometry. CO<sub>2</sub> composite spray abnormalities present in the prior art, and already discussed  
10       herein, include spray pulsing and spray particle density fluctuations. These defects are primarily caused by changing pressure and temperature conditions in the saturated liquid CO<sub>2</sub> during injection into the capillary condenser assembly. Another spray abnormality present in the prior art is spray swirling or rotation. Spray rotation occurs following mixing of the CO<sub>2</sub> particles from the capillary condenser (regardless of type) into the propellant gas. The variations between  
15       particle-propellant gas velocities, densities and temperatures result in vortexing, thermal flux and drag – all of which results in what is observed as a rotating spray stream – so-called Kelvin-Helmholtz instability. These abnormalities result in reduced spray cleaning or cooling energy available to the surface being treated. Referring to Figure 9D, the prior art spray (900) produces a pulsating and swirling particle-gas stream (902) that is visible to the un-aided eye in normal  
20       room light.

          The present invention resolves the prior art spray defects using high-pressure micro-capillary condensation coupled with pressure-balancing within an adjustable nozzle assembly. Referring to Figure 9E, the present invention produces a steady-state non-swirling jet stream (904) which is barely perceptible to an un-aided eye in normal room light (906) and without  
25       illumination (908). Moreover, and referring to Figure 9F, the CO<sub>2</sub> composite spray (910) produced by the present invention is actually quite dense - populated with innumerable hard, fast-moving microscopic CO<sub>2</sub> particles when illuminated with a bright white light (912). Moreover, the present invention demonstrates and confirms fluid stream balancing, evidenced by a lack of swirling within the spray stream. It is believed the supercritical fluid pressure  
30       conditions used in the present invention produce a micronizing effect, similar to the RESS (Rapid Expansion of Supercritical Solutions) process, wherein the highly compressed CO<sub>2</sub> fluid is rapidly expanded to produce more numerous microscopic crystals of solid carbon dioxide which have very high surface area, higher density and higher trajectory velocities (i.e., less drag)

as compared to the prior art. As such, the experimental results demonstrated in the present invention are indicative of high frequency, high energy, and closely-packed surface impacts with minimized propellant-particle mixing turbulence.

## EXPERIMENTAL 2

5 An experiment was performed to determine the relationship between spray mixing temperature of a CO<sub>2</sub> Composite Spray with the variation in micro-capillary pressure of within the EJTMC assembly.

### Spray Power Test Apparatus and Method:

10 The present invention was tested to determine the changes in composite spray mixing temperature for an exemplary high pressure micro-capillary while maintaining a fixed mixing propellant gas (clean dry air) pressure, flow rate and temperature. The test apparatus for the present experiment comprised a prior-art PowerSno™ Model PS6000 CO<sub>2</sub> spray system modified with the apparatus of Figure 4A and Figure 4B. The mixing spray nozzle of Figure 4B was positioned 0.25 inches from a K-Type thermocouple connected to a digital thermometer -

15 Omega Model CL23A, Omega Engineering. The EJTMC high-pressure condenser of Figure 4A (106) comprised a 12 inch long micro-capillary having an internal diameter of 0.008 inches positioned coaxially (and adjustably) within the spray nozzle apparatus of Figure 4B. The coaxial CO<sub>2</sub> spray assembly thus described was operated with a propellant gas flow fixed at a pressure of 70 psi at a fixed temperature of 20 Degrees C, and a propellant gas flow rate of about

20 2 scfm. Liquid CO<sub>2</sub> supply pressure to the micro-capillary EJTMC assembly was adjusted within the range stepwise from 0 psi (no injection) to 2000 psi. The mixed spray temperature was measured and recorded for each supersaturated injection pressure step.

### Results:

25 Reproducible spray mixing temperatures for several micro-capillary pressure values are summarized under Table 4.

**Table 4 – Experimental Test Parameters for Present Invention**

| <b>Micro-Capillary<br/>Pressure<br/>(PSI)</b> | <b>Mixing Temperature<br/>(Deg. C)</b> |
|-----------------------------------------------|----------------------------------------|
| <b>0</b>                                      | <b>20</b>                              |
| <b>900</b>                                    | <b>5.4</b>                             |

|             |             |
|-------------|-------------|
| <b>1000</b> | <b>4.1</b>  |
| <b>1100</b> | <b>3.9</b>  |
| <b>1200</b> | <b>2.1</b>  |
| <b>1500</b> | <b>-0.3</b> |
| <b>2000</b> | <b>-6</b>   |

#### Discussion of Results:

Referring to Figure 10, the spray temperature-versus-capillary pressure data within the range from 900 psi (1000) to 2000 psi (1002) provides a fairly linear curve (1004). The linear curve can be relied upon within the range tested. Using the test apparatus as configured provides an adjustable spray mix temperature - for example as used within a machining or cooling application - by changing the EJTCM supersaturation pressure in accordance with the curve equation (1006) shown in Figure 10, as an example. Interestingly, the overall mixed spray pressure does not increase appreciably as the capillary pressure is increased, however the number of cooling particles visibly present in the mixed composite spray increases. This is indicative of enhanced Joule-Tompson cooling, and conversion of liquid to solid, due to an increase in the pressure drop (and temperature drop) within the micro-capillary assembly.

Having thus described the preferred embodiments of generating an enhanced CO<sub>2</sub> particle spray described herein by reference to Figure 1 through Figure 10, the following discussion by reference to Figure 11 through Figure 17 describes the preferred embodiments for monitoring and controlling a CO<sub>2</sub> Composite Spray generated by the present invention using a source of coherent or incoherent light, a light detector, and a computing device integrated with a CO<sub>2</sub> Composite Spray generator.

Figure 11 illustrates exemplary absorption profiles for various chemistries common to a CO<sub>2</sub> Composite Spray. Common chemistries found within a CO<sub>2</sub> Composite Spray include air (nitrogen, oxygen), carbon dioxide, and water vapor (purposely injected or condensed from the atmosphere). As shown in the Figure 11, each compound has a unique absorption fingerprint or profile – carbon dioxide absorbs in the infrared region (2002), oxygen and ozone absorb in the ultraviolet region (2004), and water vapor absorbs in the visible to infrared region (2006). An overlay of carbon dioxide, oxygen/ozone and water demonstrates a significant amount of absorption from the ultraviolet to infrared region (2008). The present invention provides various light-based means for differentiating the components of a CO<sub>2</sub> Composite Spray, and using this information to adjust (and maintain) individual components for optimal spray performance in

cleaning, cooling and machining operations.

Figure 12 illustrates schematically the apparatus embodiments of a light-based compositional and structural analysis system for profiling a CO<sub>2</sub> Composite Spray. Referring to Figure 12, a CO<sub>2</sub> Composite Spray nozzle and plume (2010) is positioned between a beam of light (2012), derived from any number of light sources (2014) including wide spectrum deuterium, tungsten, and/or halogen, operating in the range of between 200 nm and 2500 nm, as well as more specific light spectra sources derived from LED or Laser. Transmitted light (2016) which has been passed through one or more portions of the spray plume (2010) is piped into a photometric analyzer or light detector (2018). Exemplary detectors (2010) suitable for practicing the present invention include various spectrophotometers available from Ocean Optics, Dunedin, FL and photodiode-based light detectors available from Gigahertz-Optik, Newburyport, MA. Various types of analysis can be performed on the transmitted light (2016), and which is dependent upon the type of light source (2014) and detector (2018). Exemplary analytical techniques include absorbance, fluorescence, reflectance, transmission, and Raman measurements. The various analyses produce a data set in the form of electrical values (2020) which can be normalized and processed to form a fingerprint or profile for a given CO<sub>2</sub> Composite Spray having a certain CO<sub>2</sub> particle size distribution, particle density (particles-in-propellant), additive scheme, pressure and temperature. For example, one or more measurements can be made along the spray plume longitudinally (2022) at different positions along the traverse or perpendicularly (2023) facing the spray plume to determine the chemical and physical aspects (and changes thereof), including both chemical content and structural information, from the nozzle exit to a predetermined distance along its trajectory (longitudinal plume measurements) or from side-to-side (perpendicular plume measurements) at a certain distance from the nozzle exit.

Figure 13 illustrates schematically the use of radiance and photometric spray plume data to establish an upper control limit (UCL) and lower control limit (LCL) for compositional elements such as CO<sub>2</sub> particle density, additive concentration, and water content using the exemplary system described under Figure 12. Now referring to Figure 13, a library of profiles derived from the analytical data (2030) can be established for different CO<sub>2</sub> Composite Sprays and used for adjusting or maintaining same during the application of the spray within a cleaning, cooling or machining operation. Upper control limits (2032) and lower control limits (2034) can be established and which can be used by an operator or automatic controls to maintain various spray components within acceptable limits. Such a quality control-assurance scheme is

extremely useful, for example, in precision particle cleaning applications where there is a direct correlation between the cleaning rates (submicron particle removal rate) and multi-variant CO<sub>2</sub> particle density, particle size, spray pressure, and spray temperature.

Figure 14 schematically illustrates exemplary spray profiles derived from radiance measurements of a CO<sub>2</sub> Composite Spray. As shown in Figure 14, a spray profile can be established using the apparatus of Figure 12, and for example using a wide-spectrum light source such as a halogen light and photodiode detector to measure light transmission changes through the spray plume. Employing the analytical apparatus of Figure 12 upon one or more predetermined points along the spray plume produces a fingerprint or profile, which is dependent upon multiple spray composition variables including CO<sub>2</sub> particle density, particle size distribution, propellant pressure and mixing temperature, additives and additive concentrations. Correlating the percent (%) light transmission level (2040) at various positions (2042) along the spray plume produces a unique spray profile (P) for each unique CO<sub>2</sub> Composite Spray composition. Exemplary spray profiles include a lean spray profile (2044), a rich spray profile (2046), and an optimal spray profile (2048), possessing the optimum composition for a particular spray application.

Optimal spray profiles derived from the present invention can be further analyzed to determine a fingerprint value for a particular CO<sub>2</sub> Composite Spray composition. Figure 15 schematically illustrates the computation of a spray profile metric derived from the area under the optimal profile curve. This value is termed a Spray Profile Index (or "SPI") herein and is useful for quickly assessing and controlling a CO<sub>2</sub> Composite Spray. Basically two spray positions (2050) representing representative profile of the optimum CO<sub>2</sub> Composite Spray plume and having unique normalized radiance or photometric data values (2052), are used to integrate the optimal curve equation (2054) to produce a unique SPI value (2056).

The present invention is used to characterize the composition and structure of a CO<sub>2</sub> Composite spray using both perpendicular and longitudinal spray plume analysis. As shown in Figure 16, longitudinal measurements (2060) comprise analyzing the reflective, absorption, or fluorescence properties of light as viewed into the spray plume (2062) moving past the detector, or transmitted light gathering device (2064). Perpendicular measurements (2066) comprise analyzing the reflective, absorption, or fluorescence properties of light as viewed into the spray plume (2068) moving toward the detector, or transmitted light gathering device (2070).

Longitudinal spray plume measurements generally produce radiance or photometric profiles (2072) characterized by a maximum absorption level (2074) near the nozzle exit to a

minimum absorption level (2076) downrange of the nozzle exit for normalized radiance or photometric values (2078) plotted against various longitudinal measurement locations (2080). Longitudinal spray plume analysis is used for determining the length of the spray plume as well as its diameter at various points along the traverse. In addition, longitudinal spray plume analysis is used for correlating various longitudinal spray profiles with particle density, particle size distribution, particle velocity, pressure, and temperature.

Perpendicular spray plume measurements generally produce radiance or photometric profiles (2082) characterized by a maximum absorption level (2084) near the center of the spray plume and minimum absorption levels (2086) at the perimeters of the spray plume for normalized radiance or photometric values (2088) plotted against various perpendicular measurement locations (2090). Perpendicular spray plume analysis is used for determining the diameter of the spray plume at various distances from the nozzle exit, including determining the alignment or positioning of the CO<sub>2</sub> particle injection capillary within the coaxial spray nozzle. In addition, perpendicular spray plume analysis is used for correlating various perpendicular spray profiles with particle density, particle size distribution, particle velocity, pressure, and temperature.

As discussed herein, the prior art does not teach a capability to dynamically monitor, control, and change a CO<sub>2</sub> Composite Spray in real-time during the application of same to treat a substrate using a photometric method, for example during the application of a CO<sub>2</sub> Composite Spray to provide precision cooling during a machining process or a precision spray cleaning process.

In a first example, a substrate being machined can be monitored during the application of a CO<sub>2</sub> Composite Spray plume using an infrared (IR) sensor to monitor substrate heating during the machining process and then making adjustments to the spray plume to change cooling capacity and cleaning effects (i.e., spray force). However this is a reactive approach - the machined substrate is already either too hot or too cold – and the spray plume is being adjusted after-the-fact. Such reactive control schemes do not characterize the treatment spray plume characteristics in real-time as a means for dynamically controlling or changing conditions, for example treatment plume heat capacity, in relation to a particular set of key process variables such as machining path, machining speed, machining feed rate, depth of cut, type of cutting tool or coating, or composition for substrate being machined. An improved approach, and an aspect of the present invention, is to examine, correlate, and control the treatment spray plume composition in relation to the key process variables of the machining process – thus changes are

being made in real-time in anticipation of changes in machining process based on pre-determined machining command outputs (i.e., M-Codes) to the CO<sub>2</sub> Composite Spray generator. For example, during a machining process pre-determined spray plume profiles can be developed possessing the proper force, chemistry, and heat capacity dynamically during the machining process – with the present invention monitoring and controlling those profiles in real-time. As such, an IR sensor may be used as a quality control (i.e., heat management) measurement tool to correlate spray composition profiles developed using the present invention to machining processes and/or machining heat.

As another example, during a precision spray cleaning process it is critical to maintain precise spray plume composition to provide spray cleaning consistency during a given spray treatment time. Any change in treatment spray composition during the application of the treatment spray introduces variability in surface cleaning quality on the substrates being treated. This has been a challenge up to this point. A current method is to over-process the substrate due to known spray control variances and then analyze the treated (cleaned in this case) substrate surface afterward using, for example, a photoemission analyzer (i.e., OSEE monitor), impact shear stress films, or surface particle analyzer (i.e., SurfScan device). Another method is to analyze the treatment spray off-line using thermometry to make gross adjustments to the spray composition, for example CO<sub>2</sub> particle injection rate, and return the treatment spray back on-line to the cleaning process. This is disruptive to the precision cleaning processes, introducing unnecessary Takt time, and introduces unnecessary variance in surface cleaning quality level. As such, it is a key aspect of the present invention to monitor the spray plume in real time and maintain a constant composition to insure consistent cleaning process. Moreover, the present invention can make dynamic changes to same as needed to accommodate the precision cleaning process using the novel light-based monitoring, analysis, and control scheme described herein. Exemplary analytical techniques as described above may be correlated with spray plume index values or profiles to optimize precision cleaning processes for a particular type of substrate, surface contaminant (i.e., particles, residues, and heat), and processing time – providing real-time statistical process control (SPC).

An exemplary system for analyzing and controlling the characteristics of a CO<sub>2</sub> Composite Spray is given in Figure 17. The exemplary system shown is used to dynamically characterize a CO<sub>2</sub> Composite Spray plume and make adjustments to same as needed to maintain a pre-determined composition or to dynamically change in real-time spray plume characteristics including pressure, temperature, CO<sub>2</sub> particle density, or additive chemistry in

response to (or based upon), for example, an input outside the system which is examining the substrate surface being treated with the spray plume, before, during or after substrate treatment using same. Outside analytical inputs, for example, a surface analyzer such as OSEE (Optically Stimulated Electron Emission) surface analyzer, particle measurement system, acoustic vibration measurement device, or IR thermometer may be used in the present invention to correlate treatment spray plume profiles to the precision cleaning or machining processes for which they are being applied to optimize removal or control of process contaminations - residues, particles or heat.

Now referring to Figure 17, an exemplary spray system for use with the present embodiment comprises an adjustable CO<sub>2</sub> Composite Spray generator system (2100), CO<sub>2</sub> spray delivery line (2102), and CO<sub>2</sub> spray applicator nozzle assembly (2104). Exemplary adjustable CO<sub>2</sub> Composite Spray generators and applicators suitable for use with the present embodiment are described under U.S. Patent Nos. 5,725,154, 7,451,941, 7,901,540, and 8,021,489, and include the enhanced CO<sub>2</sub> particle generation embodiments of the present invention, for example the methods and apparatuses described under Figure 4A and Figure 4B. These exemplary CO<sub>2</sub> Composite Spray generation and application systems produce a CO<sub>2</sub> Composite Spray or treatment plume (2106) having an adjustable composition comprising propellant gas flow rate, pressure and temperature, CO<sub>2</sub> particle density and particle size distribution, and optional chemical and physical additives. Common to all CO<sub>2</sub> Composite Sprays is the relationship between the characteristics and consistency of the treatment spray plume and its performance within a particular precision cleaning, machining or cooling application. Thus monitoring, maintaining, adjusting same during said application processes is very critical.

As such and again referring to Figure 17, the present embodiment provides a light source (2108) to produce a beam of light (2110) which is passed into a portion of the spray plume along its traverse from a first position (2112) to a second position (2114) to create an attenuated light profile, similar to a fingerprint, of said plume, described under Figure 16. The light source (2108) may be of any variety including laser, LED, or halogen. The light source (2108) may be fixed, moved, or several light sources may be used in an array along the traverse of the treatment spray plume (2106). Alternatively, the spray plume (2106) may be moved backwardly or forwardly from said first position (2112) to said second position (2114) to create a profile. One or more absorbed, reflected or otherwise attenuated light beam(s) (2116) which have been passed through the treatment spray plume (2106) is received by one or more light collector(s) or reflector(s) (2118) connected vis-à-vis one or more sensor cable(s) (2120) to one or more

amplifier(s) (2122), which convert the attenuated light beam(s) into a current or voltage signal(s) which are distributed using one or more cable(s) (2124) into a computer processor (2126). The computer processor may be any variety including industrial computer with analog input card and software or a process logic controller (PLC) and software to perform the plume profile analysis and computation as described under Figure 16. Alternatively, said sensor cable(s) (2120) and amplifier(s) (2122) may be substituted with a fiber optic sensor, fiber optic cable, and spectrophotometer (all not shown) to provide a chemical analysis of the treatment plume using wavelength-specific absorbance, fluorescence, or Raman spectroscopic analysis. The computer processor and software (2126) analyzes the spray plume, performing for example analysis as described under Figure 16, and making adjustments as required to the CO<sub>2</sub> Composite Spray generator (2100) to maintain (or change) a particular treatment plume characteristic. Such adjustments can be performed using an suitable digital output device with the computer processor (2126) which is connected vis-à-vis a control cable (2128) to the CO<sub>2</sub> Composite Spray generator (2100) to make such adjustments – for example changing propellant pressure and temperature, CO<sub>2</sub> particle injection rate, and additives as necessary to maintain or change treatment plume characteristics for a particular cleaning or machining application.

For example, with regards the enhanced CO<sub>2</sub> particle generation and injection process of the present invention, said computer processor (2126) can increase or decrease pump pressure (Fig. 4A, 84) to increase or decrease, respectively, the production rate of microscopic CO<sub>2</sub> particles within the high pressure EJTC assembly (Fig. 4A, 106), and subsequent injection mass flow into the exemplary mixing nozzle assembly comprising a CO<sub>2</sub> particle-propellant gas premixer and mixer assembly as shown under Figure 4A. A pressure sensor (not shown) and optional temperature sensor (not shown) located on the discharge side of the pump (Fig. 4A, 85), would provide supersaturated carbon dioxide (liquid or supercritical) pressure and temperature measurements as inputs into the computer processor (2126) for correlation of EJTC fluid injection pressure and temperature, with changes in CO<sub>2</sub> Composite Spray plume particle density.

Such adjustments are necessary to either maintain a certain treatment plume characteristic or adjust same to accommodate necessary changes in the application. For example, a change in propellant pressure from a higher spray pressure level to a lower spray pressure level and maintained for a more sensitive portion of a substrate surface being cleaned, or an increase in CO<sub>2</sub> particle injection rate may be required to increase the heat capacity of the treatment spray to better manage higher machining heat at a certain stage of a machining

operation. As such external analytical measurement techniques may be used in conjunction with the present invention to correlate the spray plume profile to a particular performance characteristic. Again referring to Figure 17, for example an infrared (IR) sensor (2130) and IR beam (2132) can be used to create a computer look-up table correlating a range of substrate (2134) surface temperatures versus spray plume (2106) profiles. Substrate (2134) surface temperatures can be fed (2136) from the IR sensor (2130) and fed (2138) into a thermocouple input card (not shown) within the computer processor (2126). Other types of external analytical measurement techniques such as OSEE may be used to correlate quantitative cleaning process performance (i.e., apparent cleaning rates) to treatment plume profiles.

Having thus described the preferred aspects of the light-based monitoring and control embodiment, the following discussion illustrates various uses of the present embodiment.

### **Examples of Use**

As described under Figure 11, each compound has a unique absorption fingerprint or profile – carbon dioxide absorbs in the infrared region (2002), oxygen and ozone absorb in the ultraviolet region (2004), and water vapor absorbs in the visible to infrared region (2006). An overlay of carbon dioxide, oxygen/ozone and water demonstrates a significant amount of absorption from the ultraviolet to infrared region (2008). The light-based analytical apparatus and methods described herein under Figures 12, 13, 14 and 15 are used for differentiating the components of a CO<sub>2</sub> Composite Spray.

#### **Determining Ozone Concentration in a CO<sub>2</sub> Composite Spray**

Ozone is used within a CO<sub>2</sub> Composite Spray to enhance cleaning and machining performance through both oxidation and oxygenation mechanisms, and is the subject of several co-pending provisional patent applications by the first named inventor of the present invention. Knowledge and control of ozone and oxygen levels within a CO<sub>2</sub> Composite Spray is important for both process optimization and quality assurance. Referring to Figure 11, ozone absorbs (Fig. 11, (2004)) strongly in the UV region between 200 nm and 300 nm and between 500 nm and 650nm. Analyzing UV absorption characteristics within or near these regions using the apparatus described under Figure 12 produces an absorption profile which can be correlated using the SPI calculation technique described under Figure 15 to various ozone concentrations within a CO<sub>2</sub> Composite Spray.

#### **Determining CO<sub>2</sub> Particle Density in a CO<sub>2</sub> Composite Spray**

CO<sub>2</sub> Composite Spray particle size and density is a critical factor in the performance of the spray functions within a cleaning or machining operation. For example, a very lean (low

CO<sub>2</sub> particle density) and a very high temperature (high propellant gas temperature and/or mass flow rate) spray composition is desirable for precision cleaning operations. A very coarse (large size) and rich (high density) particle stream entrained in a cooler propellant gas flow is more desirable for heat extraction, cooling or machining applications. As such it is important to understand and control the physical composition – particle size and density - of a CO<sub>2</sub> Composite Spray. Carbon dioxide solids entrained in a CO<sub>2</sub> Composite Spray absorb both visible and infrared radiation. As such, two light-based analytical methods are available to determine particle concentration – [1] Visible light absorbance and [2] near-infrared radiation absorption. Referring to Figure 11, carbon dioxide absorbs (Fig. 11, (2002)) strongly in the near-infrared region at approximately 2000 nm. Analyzing NIR absorption characteristics at this wavelength employing the apparatus described under Figure 12 and using a spectrophotometer produces an absorption profile which can be correlated using the SPI calculation technique described under Figure 15 to various carbon dioxide concentrations within a CO<sub>2</sub> Composite Spray. The SPI value will account for both CO<sub>2</sub> solid and vapor concentrations combined. Alternatively, a photodiode detector allows for the selective measurement of light attenuation or obscuration. Light radiance SPI values selectively describe CO<sub>2</sub> particle concentrations as well as changes in particle size.

#### **Determining Dryness of a CO<sub>2</sub> Composite Spray**

CO<sub>2</sub> Composite Spray dryness (i.e., presence of condensed water droplets) is a critical factor in the performance of the spray function within a cleaning or machining operation. For example, an ultra-dry CO<sub>2</sub> Composite Spray is representative of a very lean (low CO<sub>2</sub> particle density) and high temperature (high propellant gas temperature and/or mass flow rate) spray profile. An ultra-dry CO<sub>2</sub> Composite Spray is desirable in precision cleaning applications to prevent the condensation of atmospheric water vapor (and entrained organic and inorganic particles and residues) into the CO<sub>2</sub> Composite Spray. Referring to Figure 11, water vapor absorbs (Fig. 11, (2006)) strongly in the visible to near-infrared region between 800 nm and 2000 nm. Analyzing the visible to NIR absorption characteristics at this range employing the apparatus described under Figure 12 and using a spectrophotometer produces an absorption profile which can be correlated using the SPI calculation technique described under Figure 15 to various water vapor concentrations within a CO<sub>2</sub> Composite Spray, related to CO<sub>2</sub> particle density and particle size, propellant temperature and mass flow, and atmospheric humidity. The SPI value thus calculated accounts for condensable water vapor concentrations within various CO<sub>2</sub> Composite Spray compositions.

A method and apparatus is disclosed for the production, delivery and control of microscopic quantities of minute solid carbon dioxide (CO<sub>2</sub>) particles having uniform density and distribution for use in a CO<sub>2</sub> Composite Spray process. The pressure of a near- or saturated liquid carbon dioxide within a capillary condenser assembly is selectively compressed to a density greater than 0.9 mg/L using a high pressure pump to form a supersaturated liquid (or supercritical) CO<sub>2</sub> feedstock having a controlled and optimal liquid CO<sub>2</sub> density and temperature. A high pressure micro-capillary condenser assembly is used to efficiently convert precise quantities of supersaturated liquid CO<sub>2</sub> at ultra-low flow rates into a uniform mass, density and distribution of minute and highly energetic solid carbon dioxide particles. Said solid carbon dioxide particles are selectively injected into a propellant gas stream by adjusting injection pump pressure to form a CO<sub>2</sub> Composite Spray having variable particle density. Said spray composition is monitored and adjusted in real-time using a novel photometric means. A light beam is passed through a portion of the CO<sub>2</sub> Composite Spray stream, during which the transmitted light is collected using a detector and analyzed using a computer processing device. Light sources include wide-spectrum and specific wavelengths such as halogen, deuterium, Laser and LED, and operate in the ultraviolet, visible and infrared region. Detectors include simple photodiode detectors for measuring radiance or intensity, and more sophisticated analytical spectrophotometers. Computer processing devices include a personal computer or process logic controller. Light absorption, reflection and/or florescence data are correlated with CO<sub>2</sub> particle density and particle size, spray plume length, organic and inorganic spray additives, and water vapor content. The treatment spray geometry may be correlated with various metrological instruments and methods and is used to optimize and control a CO<sub>2</sub> Composite Spray in precision cleaning, machining, and cooling processes.

As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which can be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure. Further, the terms and phrases used herein are not intended to be limiting; but rather, to provide an understandable description of the invention. The terms "a" or "an", as used herein, are defined as: one or more than one. The term plurality, as used herein, is defined as: two or more than two. The term another, as used herein, is defined as at least a second or more. The terms including and/or having, as used herein, are

defined as comprising (i.e., open language). The term coupled, as used herein, is defined as connected, although not necessarily directly, and not necessarily mechanically.

Any element in a claim that does not explicitly state “means for” performing a specific function, or “step for” performing a specific function, is not be interpreted as a “means” or  
5 “step” clause as specified in 35 U.S.C. Sec. 112, Paragraph 6. In particular, the use of “step of” in the claims herein is not intended to invoke the provisions of 35 U.S.C. Sec. 112, Paragraph 6. All cited and referenced patents, patent applications and literature are all incorporated by reference in entirety.

What is claimed is:

1. A spray apparatus for producing and regulating a stream of propellant gas and carbon dioxide comprising:

the carbon dioxide in a first state, which is a saturated liquid;

5 compressing the carbon dioxide in the first state to form a second state, which is super-saturated at a density greater than 0.9 g/ml;

said compression is adjusted using a high pressure pump;

a condensation of the carbon dioxide in the second state within a micro-capillary tube to form a third state, which is a microscopic solid;

10 said propellant gas and said carbon dioxide in the third state are mixed to form the stream of the propellant gas and the carbon dioxide;

said carbon dioxide mixing rate is adjusted using a high pressure pump; and

whereby the stream is used to treat a substrate surface.

2. The apparatus of claim 1 wherein the micro-capillary is at least one high-pressure capillary  
15 tube for receiving supersaturated carbon dioxide.

3. The apparatus of claim 2 wherein the micro-capillary has a length of from 6 inches to 20 feet, an outer diameter of from 0.020 inch to 0.125 inch, and an inner diameter of from 25 micron to 0.010 inch.

4. The apparatus of claim 2 wherein the micro-capillary comprises one or more capillaries in a  
20 parallel flow arrangement having a length of from 6 inches to 20 feet, an outer diameter of from 0.020 inch to 0.125 inch, and an inner diameter of from 25 micron to 0.010 inch.

5. The apparatus of claim 2 wherein the micro-capillary comprises polyetheretherketone or stainless steel high pressure capillary tubes.

6. The apparatus of claim 1 wherein the carbon dioxide in the first state is compressed to super-  
25 saturation using the high pressure pump.

7. The apparatus of claim 6 wherein the high pressure pump compresses the carbon dioxide in the first state into the micro-capillary to form the carbon dioxide in the second state, which is supersaturated.

8. The apparatus of claim 7 wherein the supersaturated carbon dioxide is compressed within the  
30 micro-capillary to a pressure between 900 psi and 10,000 psi.

9. The apparatus of claim 8 wherein the supersaturated carbon dioxide is compressed to a pressure between 1,000 psi and 5,000 psi.

10. The apparatus of claim 7 wherein the supersaturated carbon dioxide is thermally controlled

at a temperature between 5 degrees C and 40 degrees C.

11. The apparatus of claim 10 wherein the supersaturated carbon dioxide is thermally controlled at a temperature between 10 degrees C and 25 degrees C.

12. The apparatus of claim 1 wherein the propellant gas is clean dry air, nitrogen, argon or  
5 carbon dioxide.

13. The apparatus of claim 12 wherein the propellant gas is thermally controlled at a temperature between 5 degrees C and 250 degrees C.

14. The apparatus of claim 1 wherein the propellant gas and the carbon dioxide in the third state are mixed coaxially.

10 15. The apparatus of claim 1 wherein the propellant gas and the carbon dioxide in the third state are mixed using an adjustable expansion tube for receiving the carbon dioxide in the third state produced by the pressurized micro-capillary.

16. The apparatus of Claim 1 wherein the saturated carbon dioxide is at a pressure between 500 psi and 900 psi.

15 17. The apparatus of Claim 1 wherein the saturated carbon dioxide is at a temperature between 5 degrees C and 40 degrees C.

18. The apparatus of Claim 1 wherein the supersaturated carbon dioxide is liquid or supercritical fluid.

19. The apparatus of claim 1 wherein the treatment spray generates a shear stress on the  
20 substrate surface at between 10 kPa and 100 MPa.

20. The apparatus of claim 1 wherein the treatment spray produces a temperature on the substrate surface between -40 degrees C and 200 degrees C.

21. The apparatus of claim 1 wherein injection rate of the carbon dioxide in the third state is between 0.1 lbs per hour and 20 lbs per hour.

25 22. The apparatus of claim 1 wherein the stream of the propellant gas and the carbon dioxide is a spray plume and is analyzed in real-time using a photometric device.

23. The apparatus of claim 22 wherein the spray plume has a geometry, which has a width, a height, a length, a composition or a CO<sub>2</sub> particle density.

24. The apparatus of claim 23 wherein the geometry of the spray plume is adjusted using a  
30 propellant gas pressure, a propellant gas temperature, an additive concentration, or CO<sub>2</sub> particle concentration changes.

25. The apparatus of claim 22 wherein said photometric device uses a light source to transmit a light beam perpendicular to the spray plume from a first position to a second position.

26. The apparatus of claim 25 wherein the first position to the second position defines the length of the spray plume.
27. The apparatus of claim 22 wherein the photometric device uses a light receptor mounted perpendicular to the spray plume.
- 5 28. The apparatus of claim 27 wherein the light receptor captures the attenuated light beam as it passes through or is reflected from the spray plume.
29. The apparatus of claim 22 wherein the photometric device is connected to a computing device.
30. The apparatus of claim 29 wherein the computing device is connected to an adjustable CO<sub>2</sub>  
10 Composite Spray generator.
31. The apparatus of claim 29 wherein the computing device analyzes change in the light beam, when passing through the spray plume or being reflected from the spray plume.
32. The apparatus of claim 30 wherein the computing device adjusts propellant gas pressure, propellant gas temperature, additive injection rate, or supersaturated CO<sub>2</sub> injection rate of said  
15 adjustable CO<sub>2</sub> Composite Spray generator to regulate said geometry to maintain a characteristic of the spray plume.
33. The apparatus of claim 25 wherein the light source includes halogen light, deuterium light, Laser light or LED light.
34. The apparatus of claim 25 wherein said light source operates in the ultraviolet, visible or  
20 infrared region.
35. The apparatus of claim 27 wherein said light receptor includes photodiode detector, radiance detector or UV-VIS-IR spectrophotometer.
36. The apparatus of claim 27 wherein said light receptor measures light absorption, light reflection or light florescence.
- 25 37. The apparatus of claim 29 wherein said computing device calculates a light attenuation profile index value for a spray plume geometry.
38. The apparatus of claim 37 wherein the light attenuation profile index value changes with CO<sub>2</sub> particle density and particle size, propellant temperature and pressure, organic and inorganic additives, or water vapor content within the spray plume.
- 30 39. The apparatus of claim 37 wherein the spray plume geometry is controlled in real-time based on the light attenuation profile index.
40. The apparatus of claim 25 wherein at least one light source is used.
41. The apparatus of claim 27 wherein at least one light receptor is used.

42. The apparatus of claim 25 wherein the spray plume is moved from a first position to a second position perpendicular to said spray plume.

43. The apparatus of claim 25 wherein the light source and the light receptor are moved from a first position to a second position perpendicular to said spray plume.

5 44. The apparatus of claim 22 wherein a metrological instrument is used to correlate spray plume geometry to a spray plume performance metric.

45. The apparatus of claim 44 wherein said metrological instrument comprises a substrate surface temperature measurement system, an OSEE surface measurement system, a FTIR surface analysis system, an impact shear stress measurement system or a particle counting  
10 system.

46. The apparatus of claim 44 wherein the spray plume performance metric comprises cooling capacity, impact particle shear stress, contamination removal rate, surface finish, or surface cleanliness level.

Fig. 1  
PRIOR ART

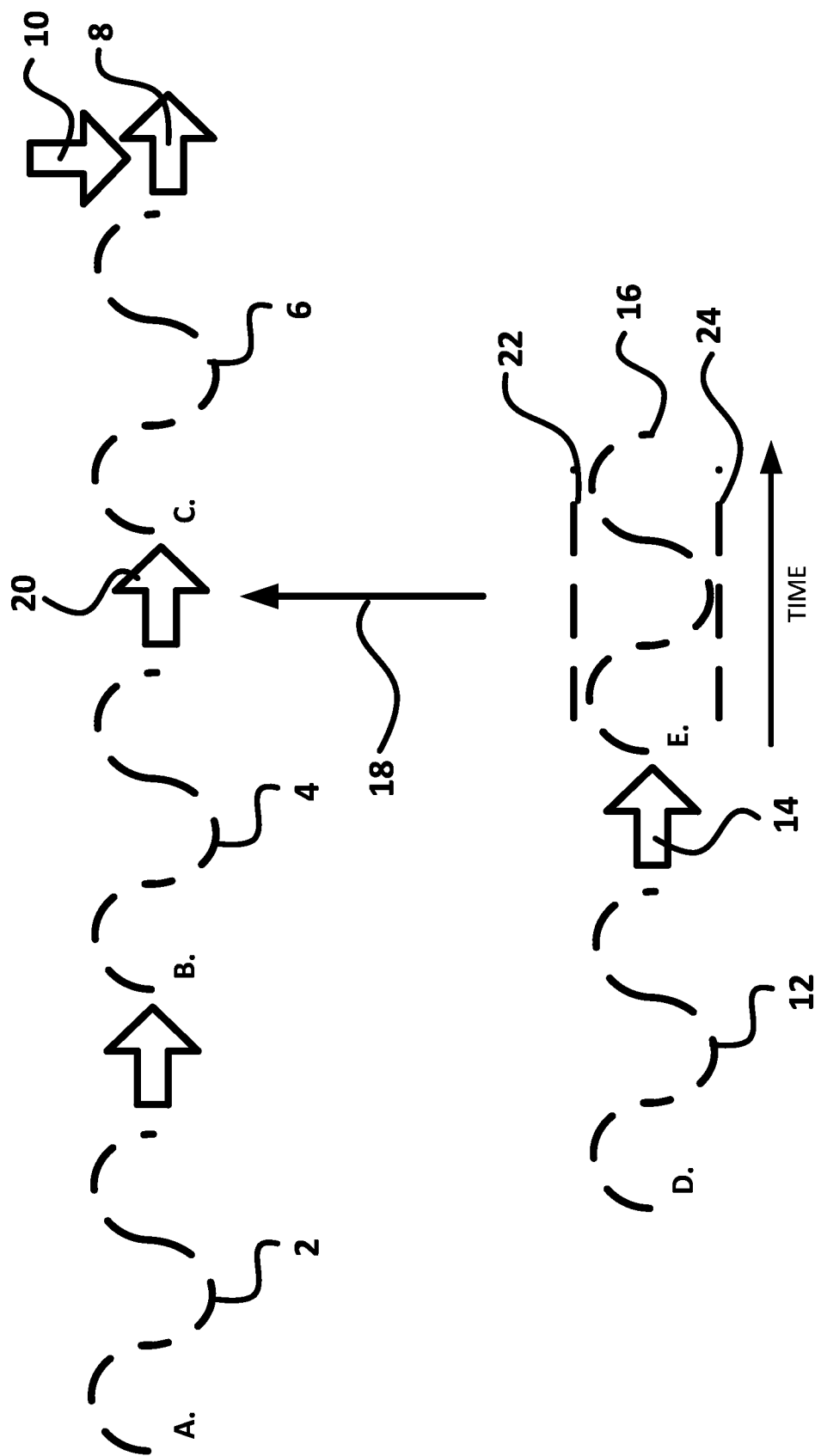


Fig. 2

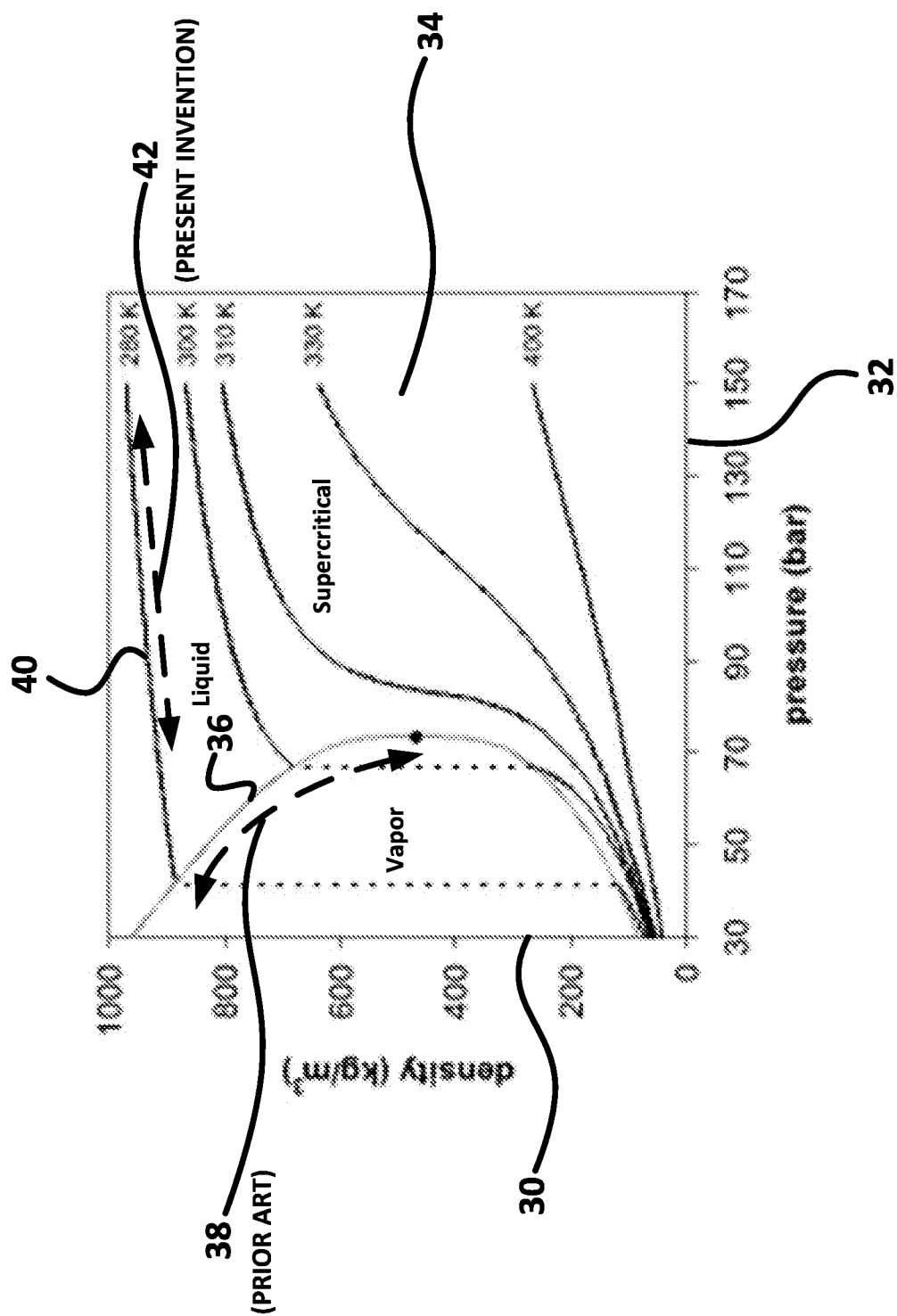


Fig. 3

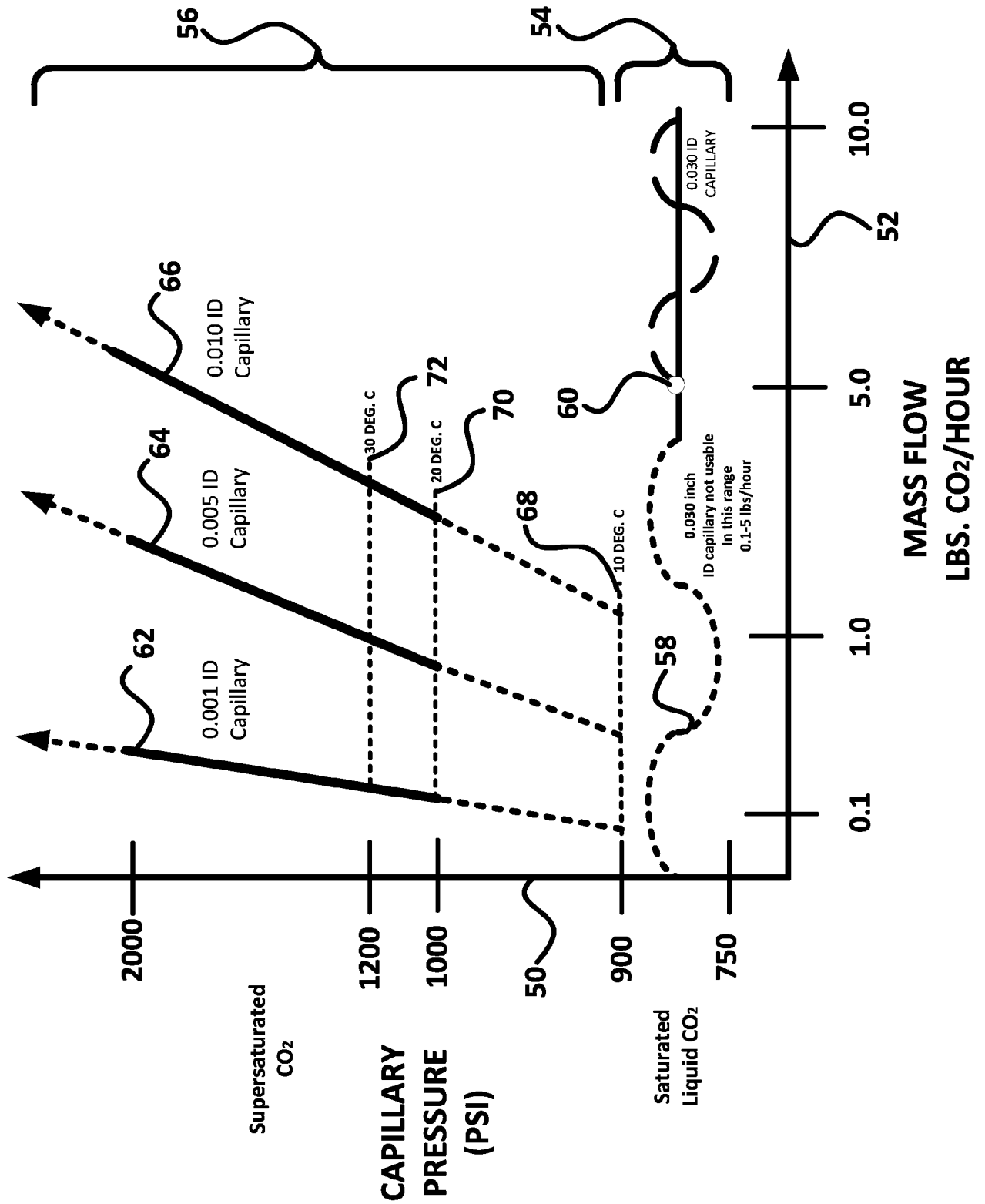
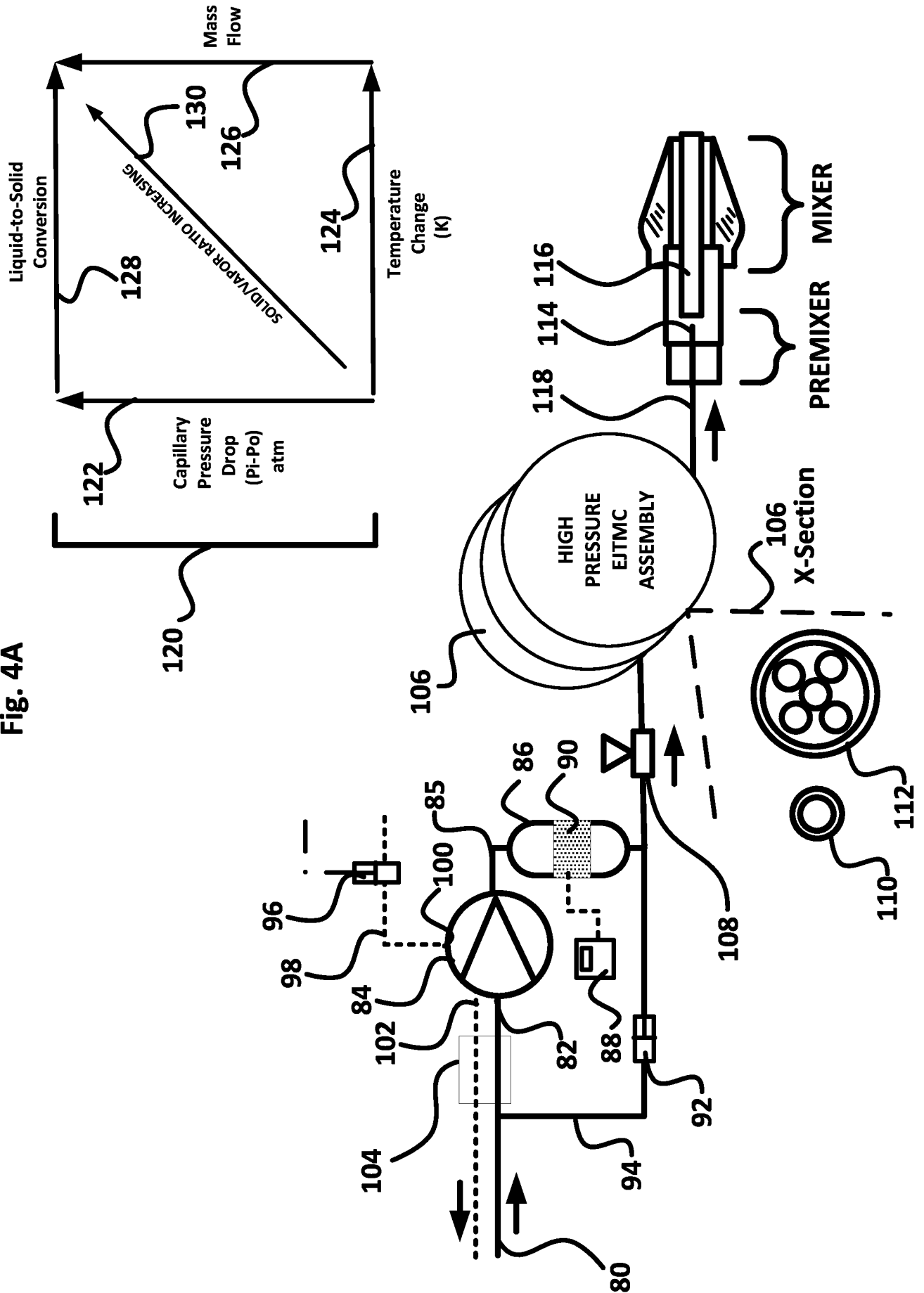
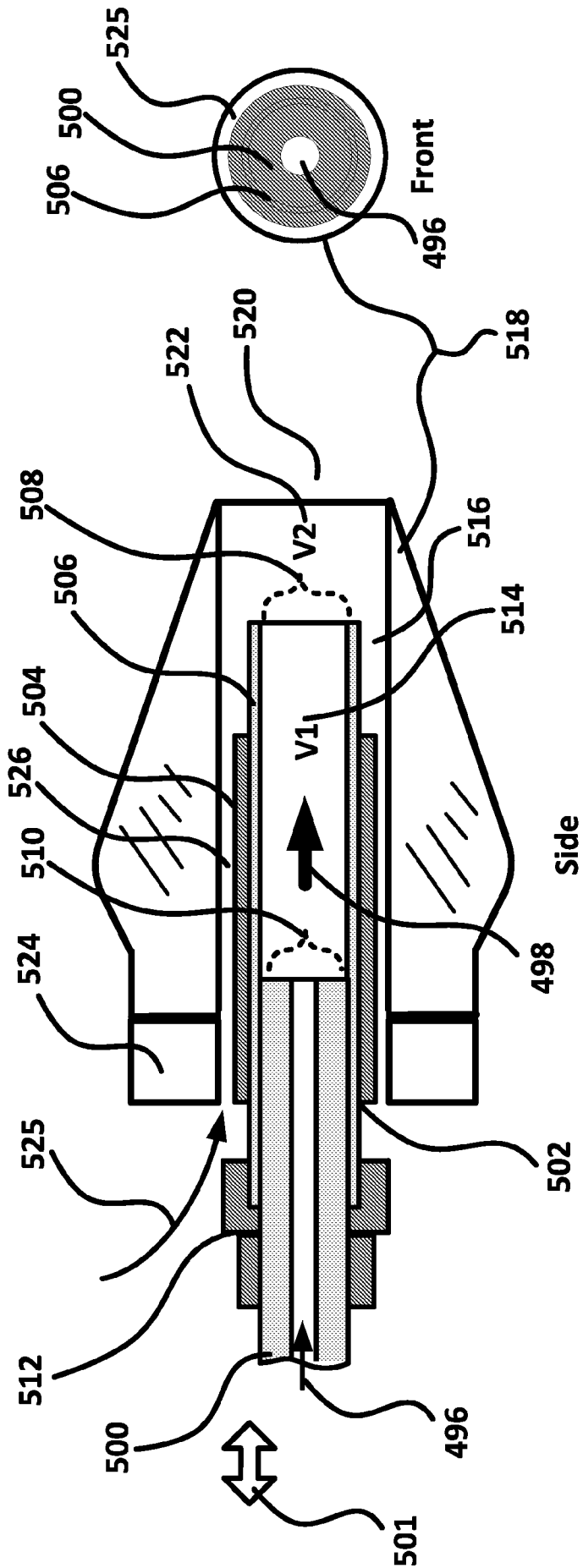


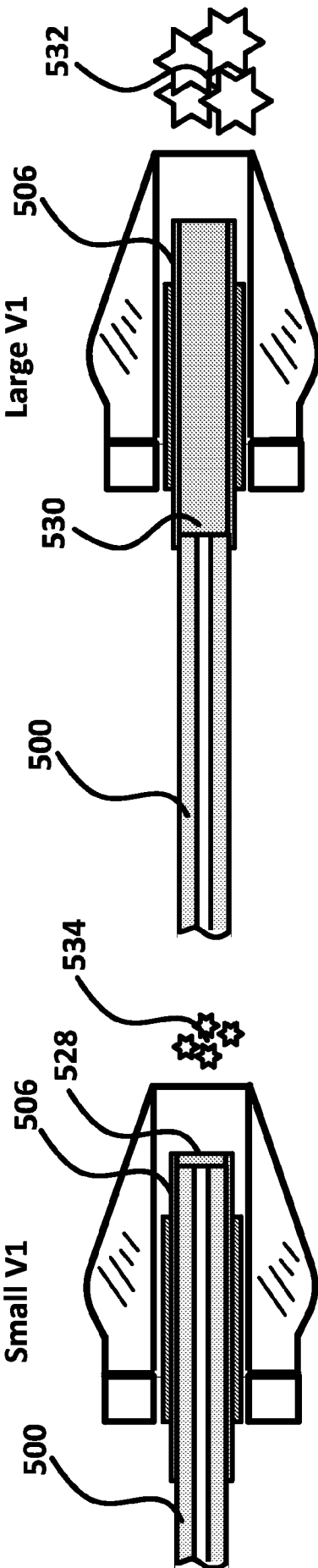
Fig. 4A



**Fig. 4B**



**Fig. 4B-I**  
**Small v1**



**Fig. 4B-II**  
**Large V1**

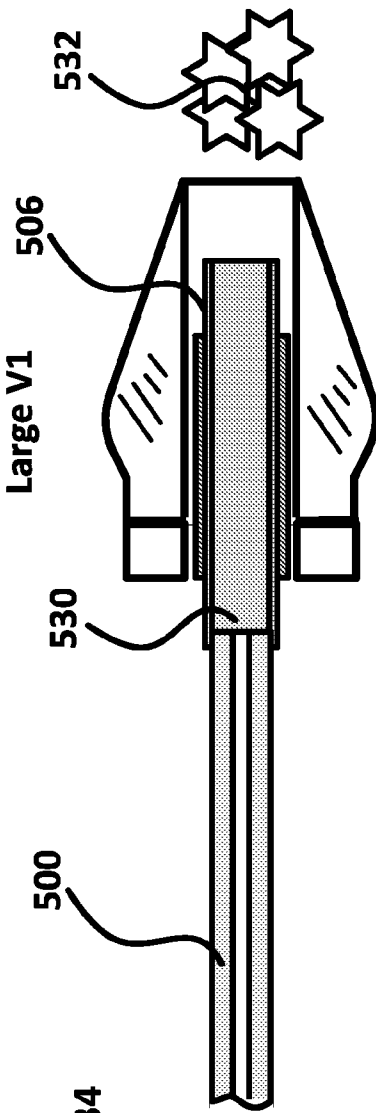


Fig. 5

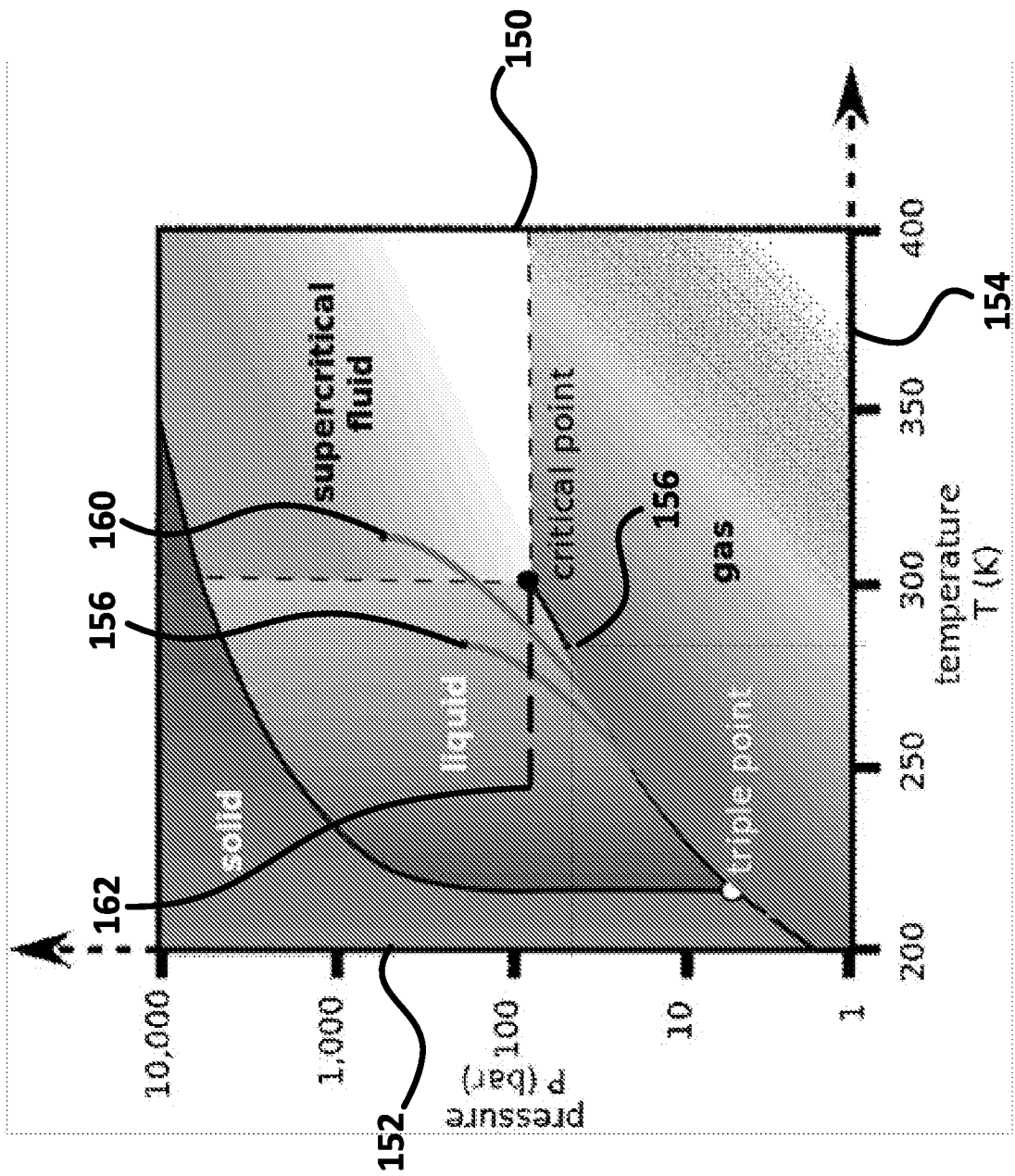
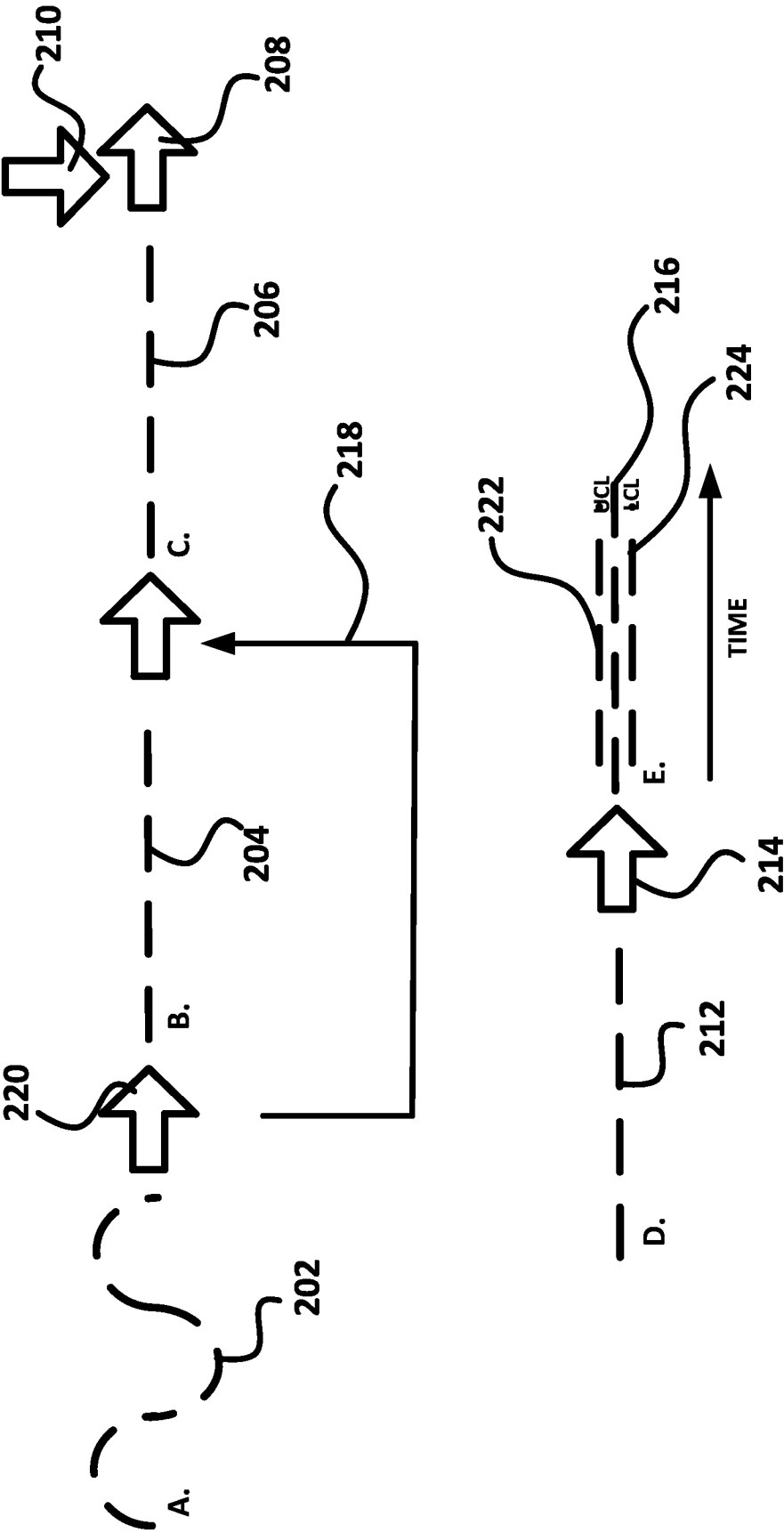


Fig. 6  
PRESENT INVENTION



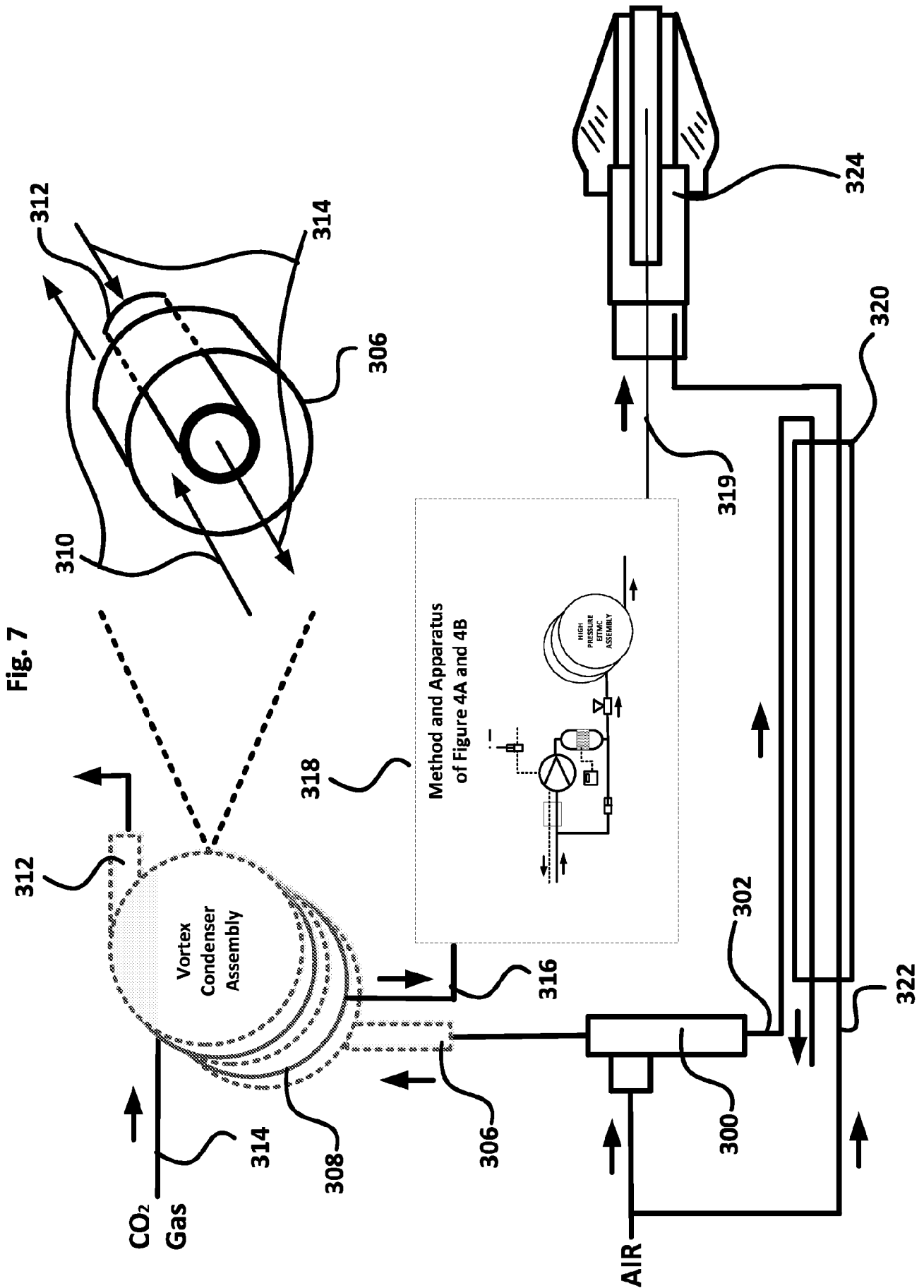
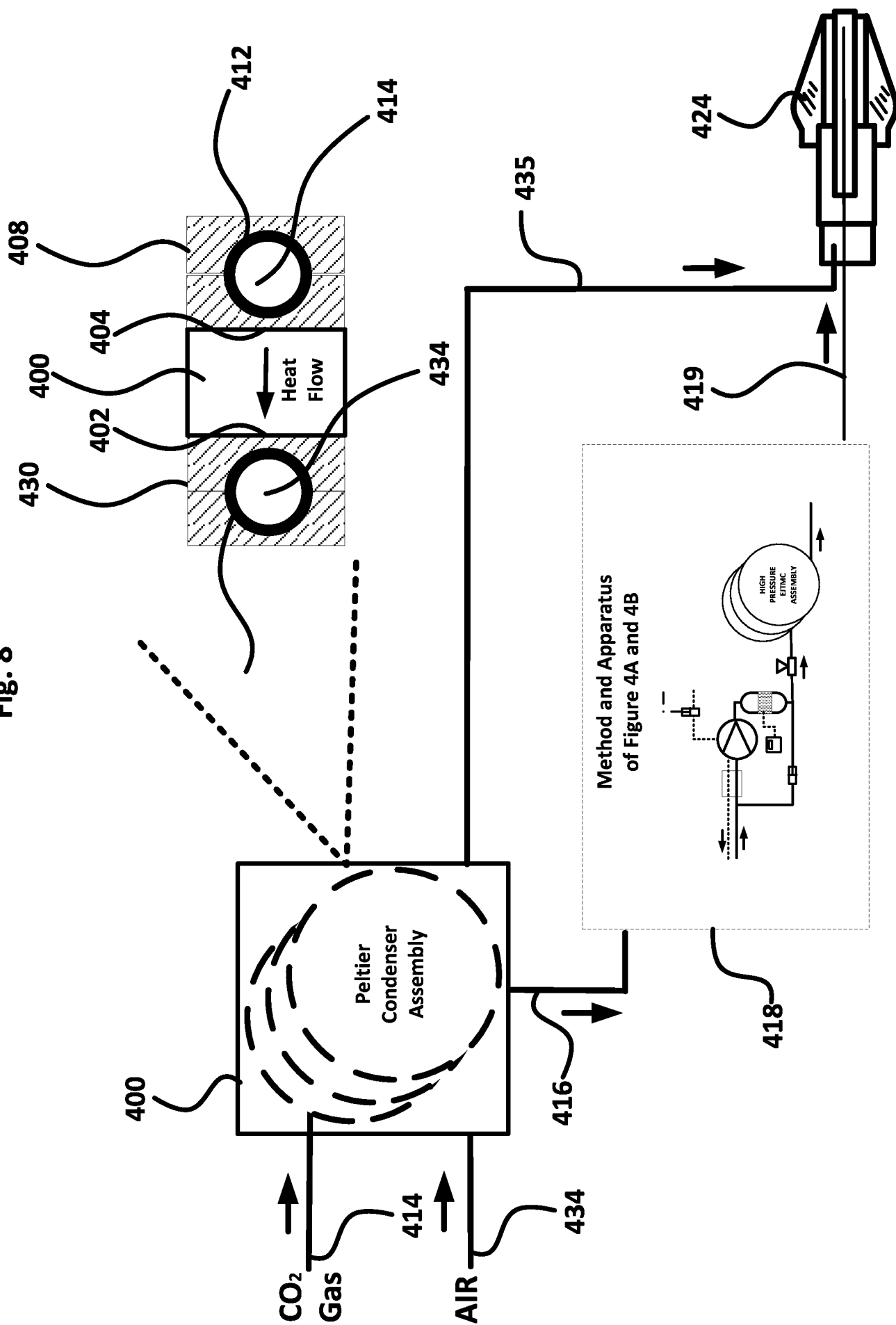


Fig. 8



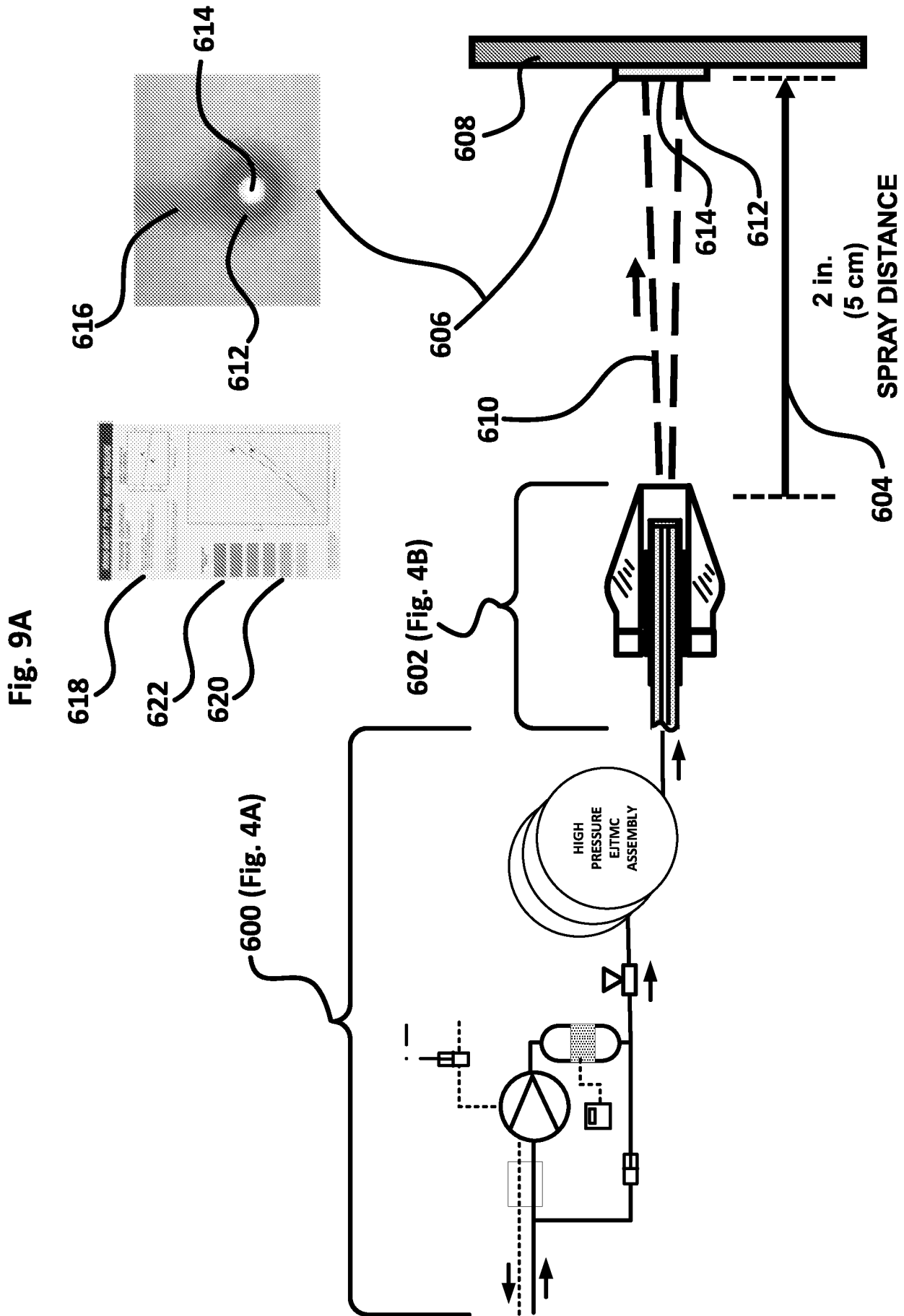


Fig. 9B

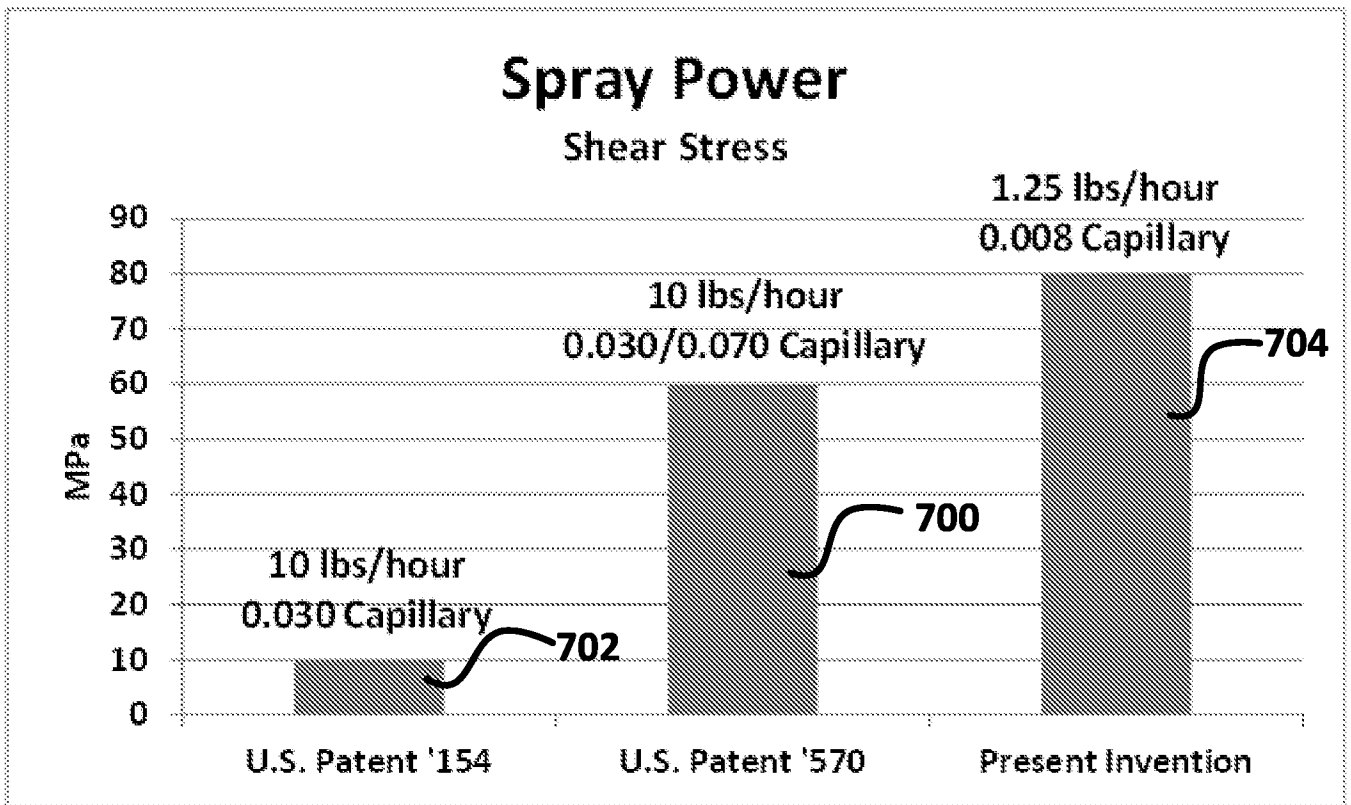
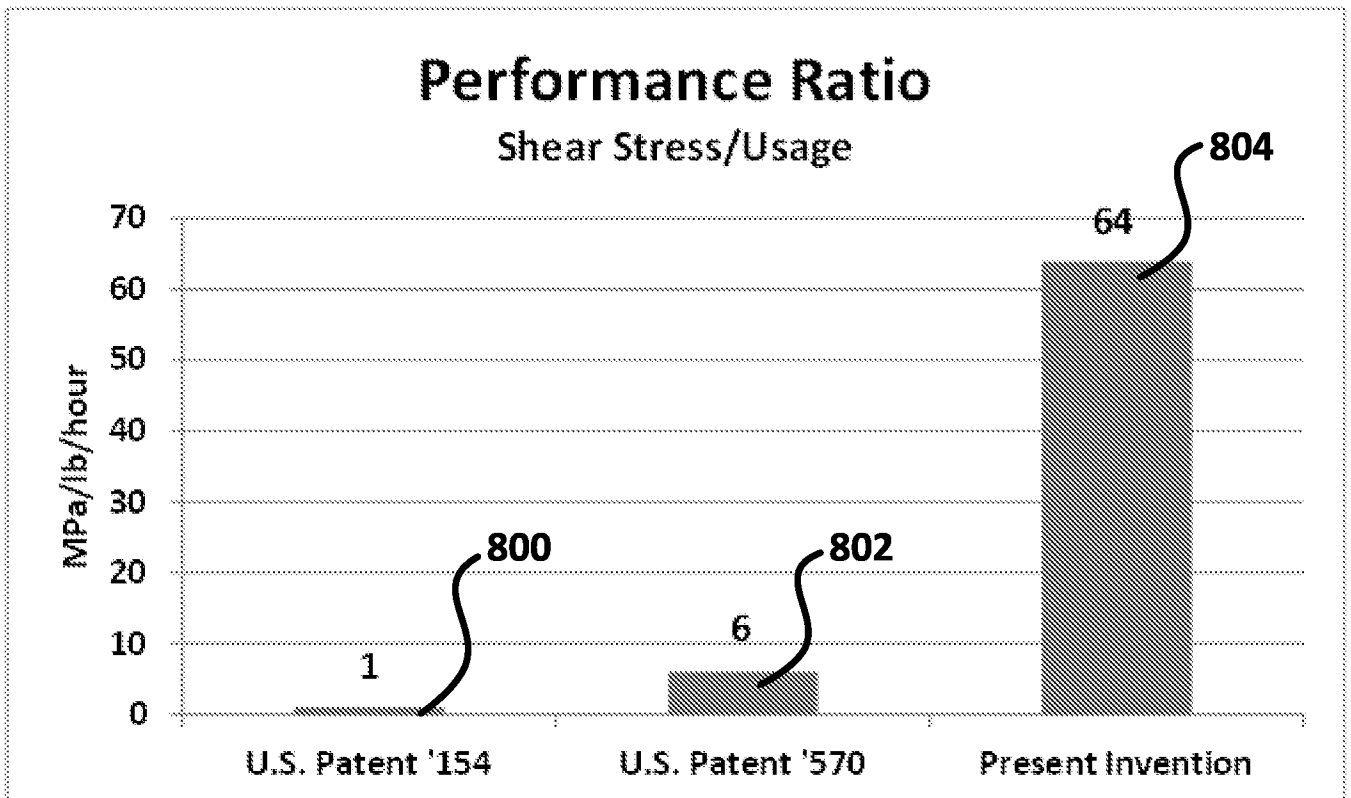
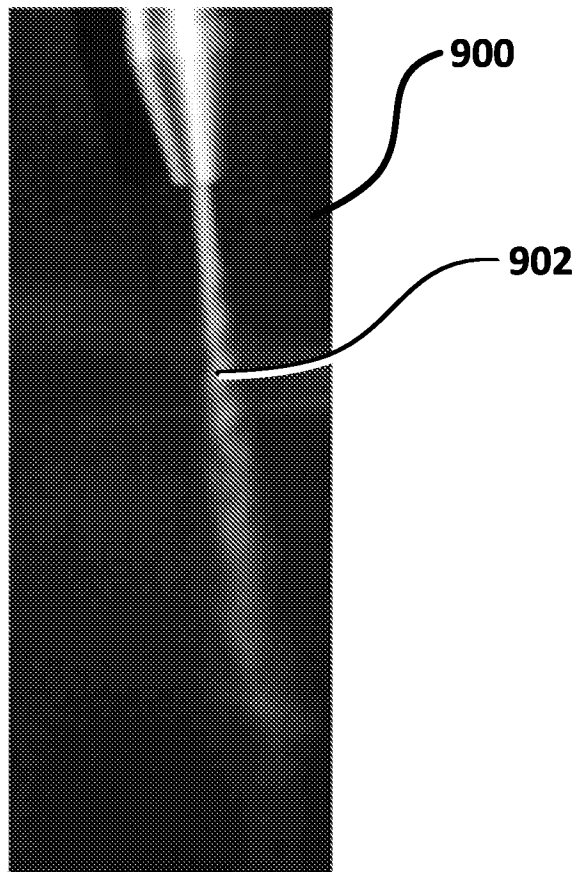


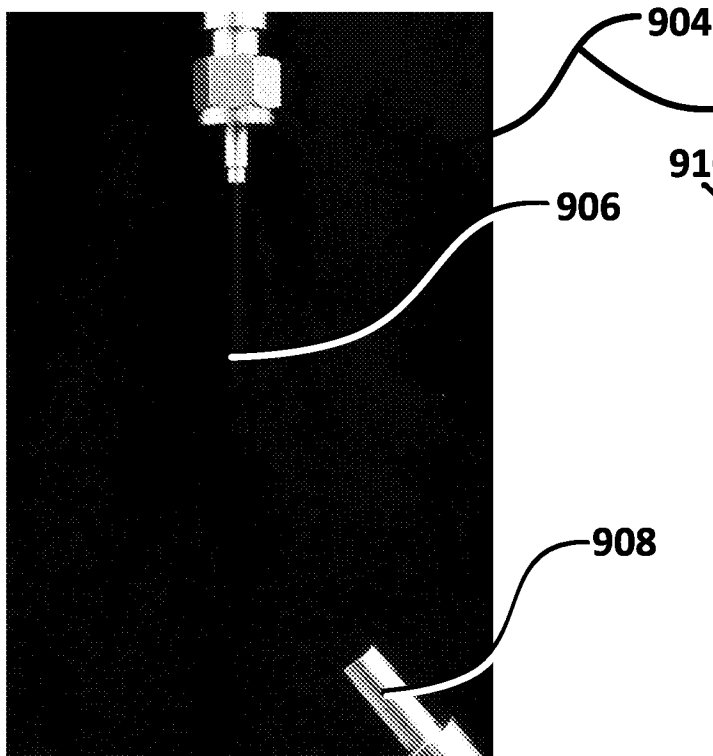
Fig. 9C



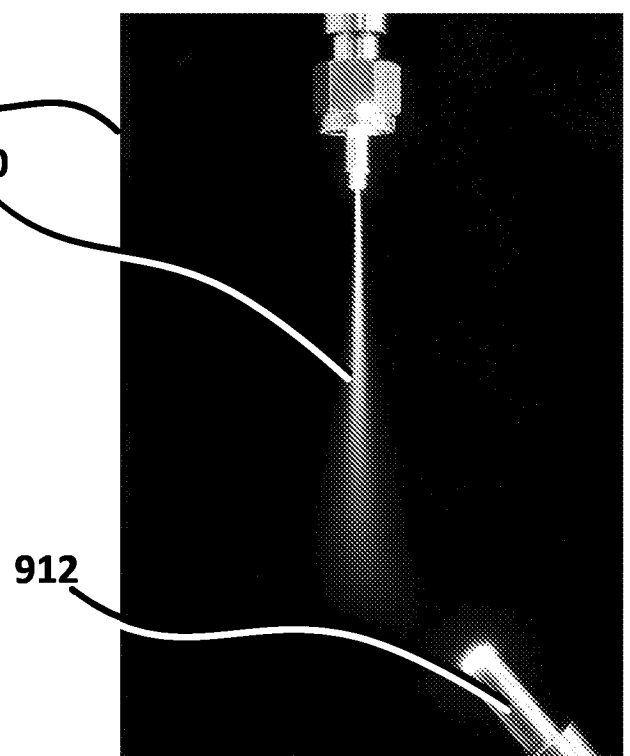
**Fig. 9D**  
**PRIOR ART**



**Fig. 9E**  
**PRESENT INVENTION**



**Fig. 9F**  
**PRESENT INVENTION**



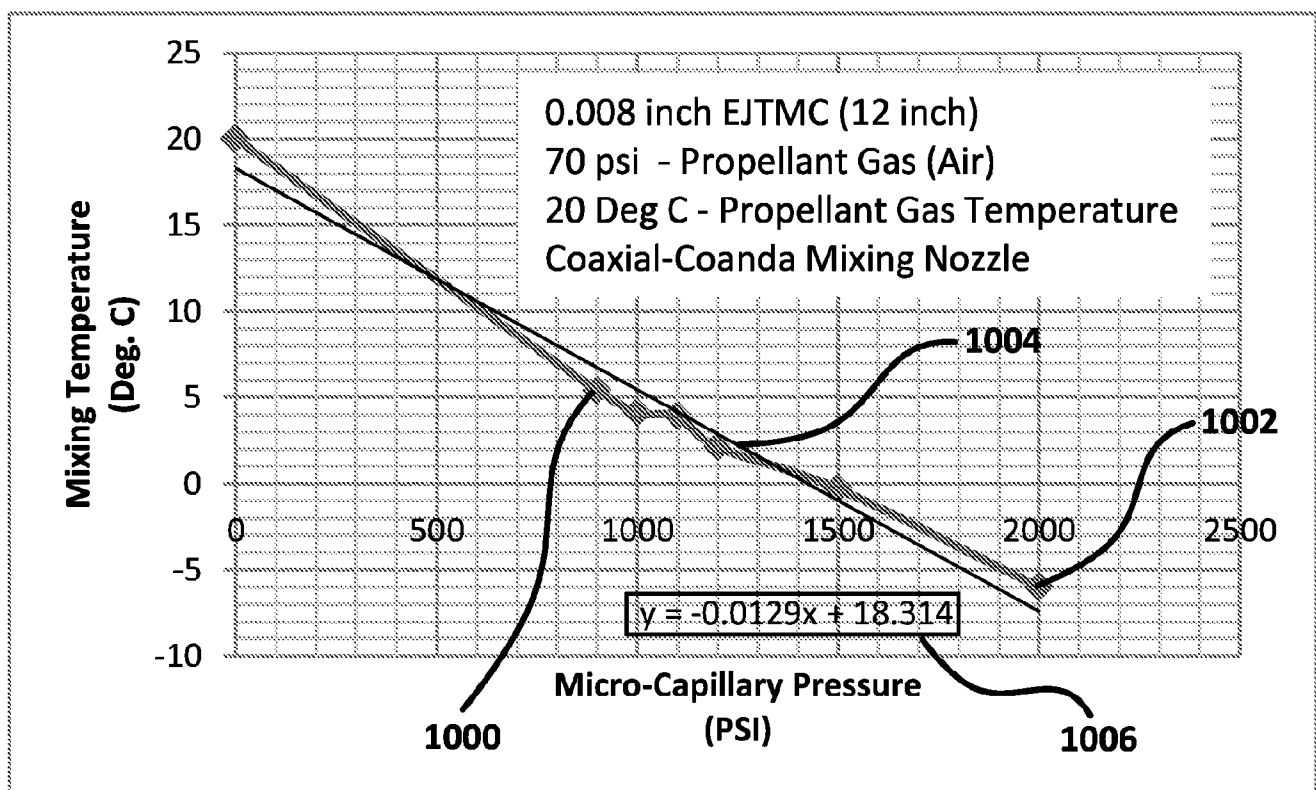
**Fig. 10**

Fig. 11

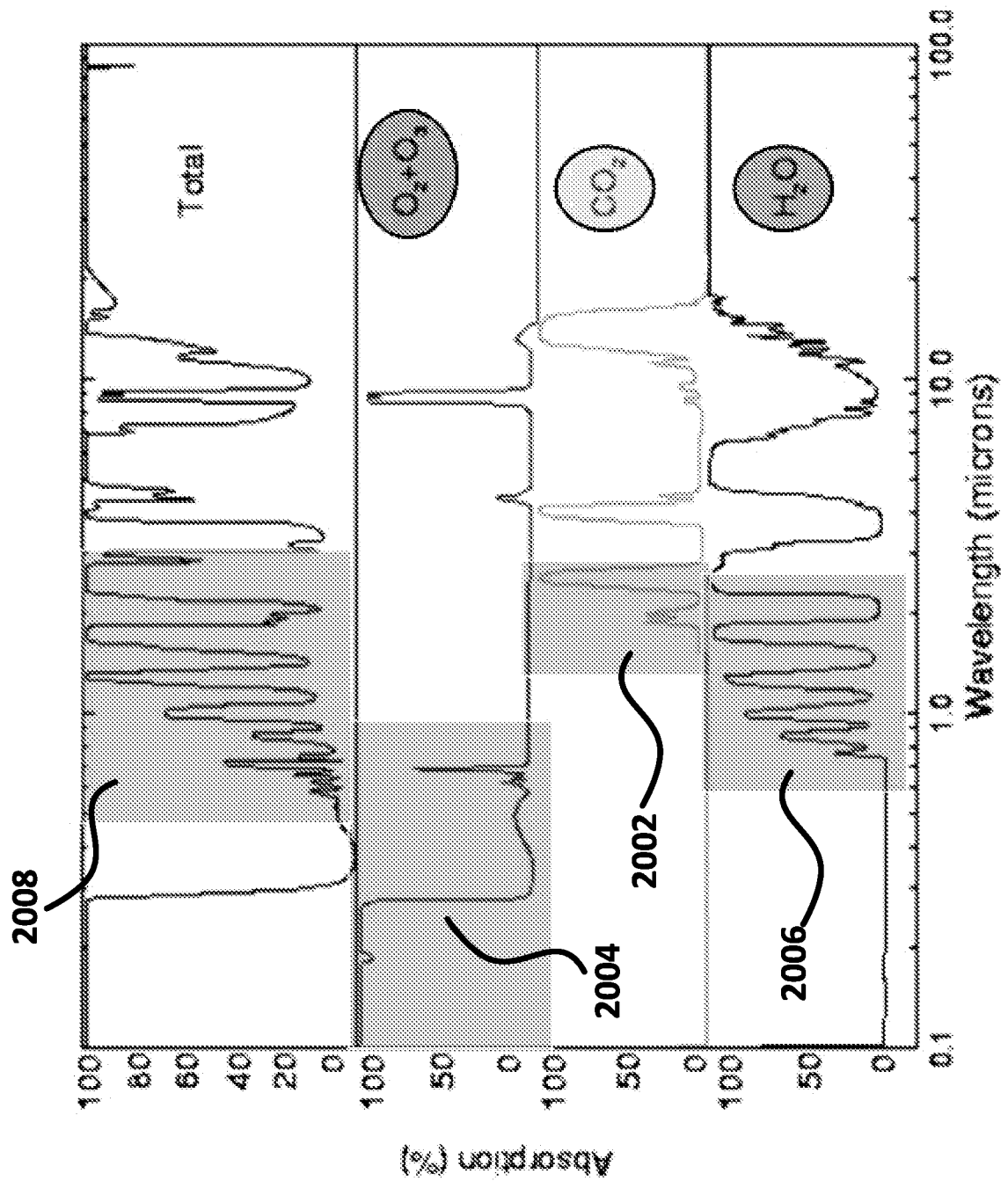


Fig. 12

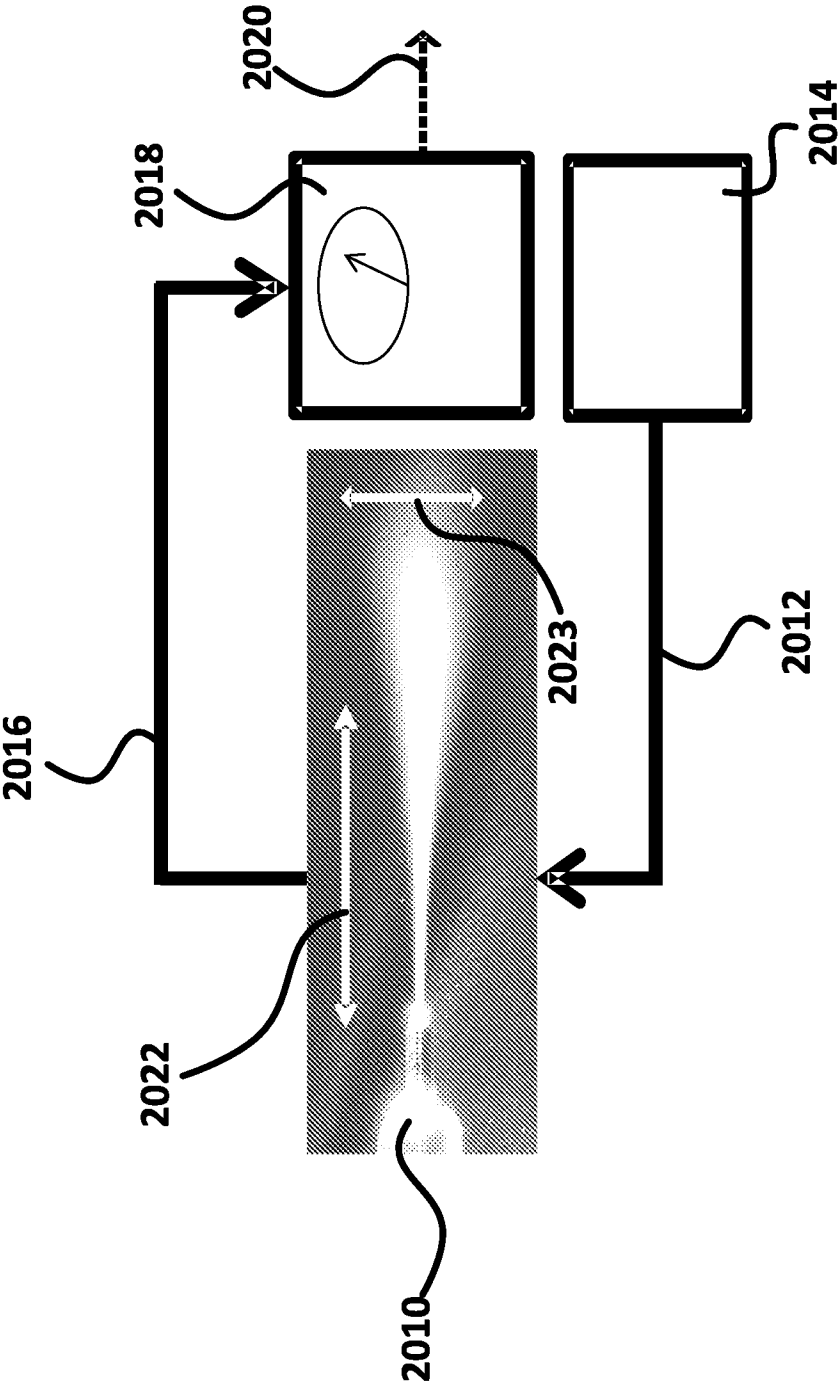


Fig. 13

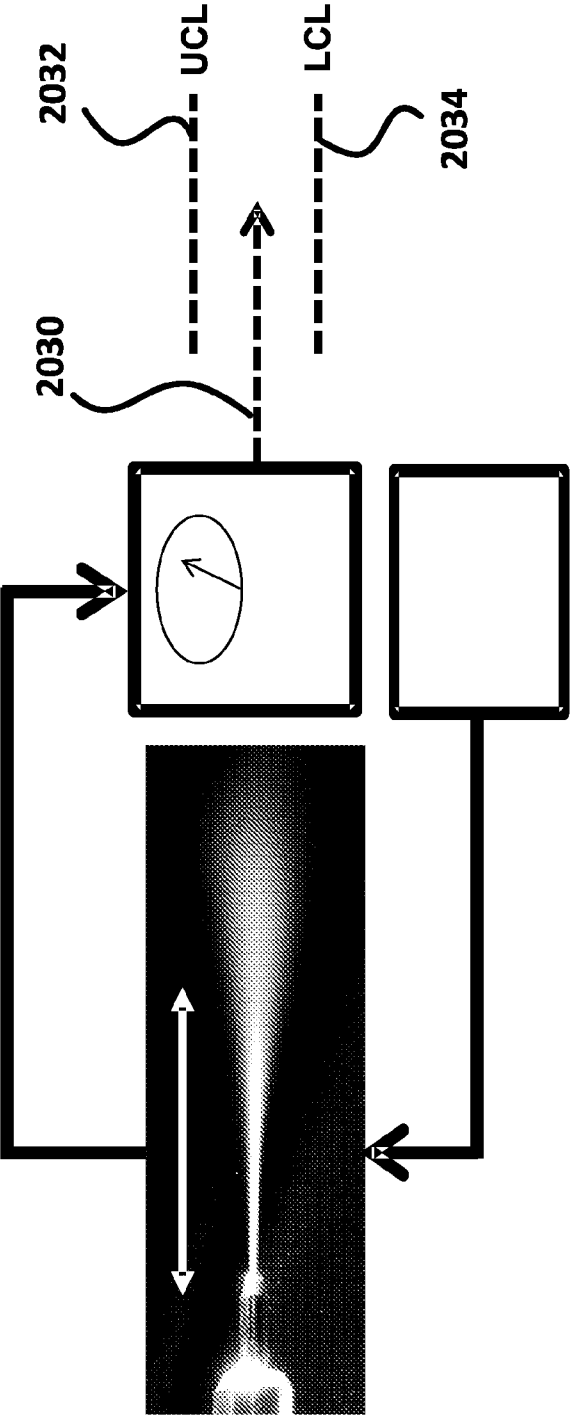


Fig. 14

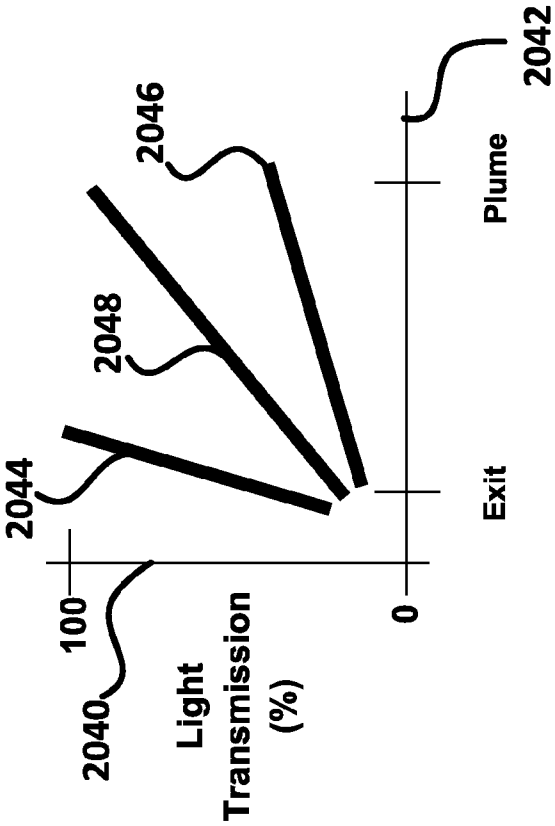


Fig. 15

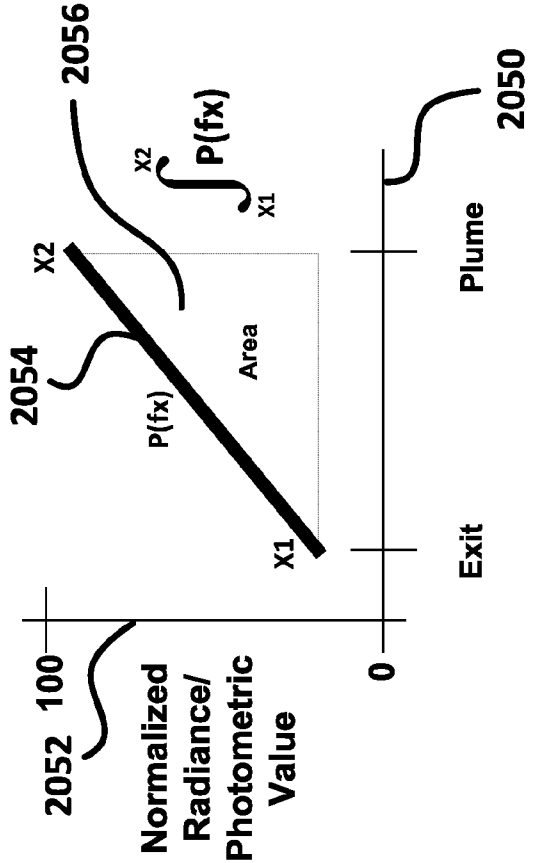


Fig. 16

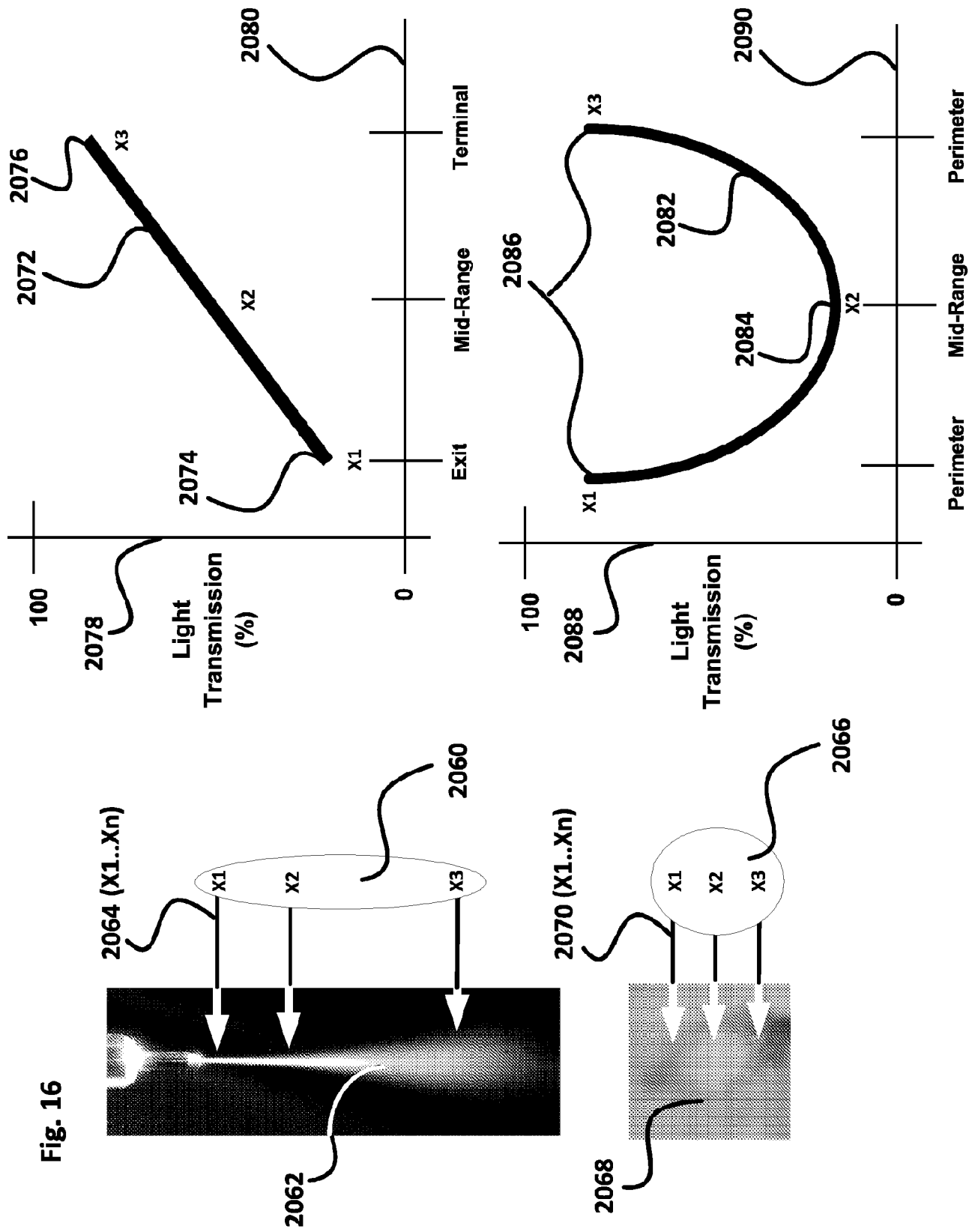


Fig. 17

