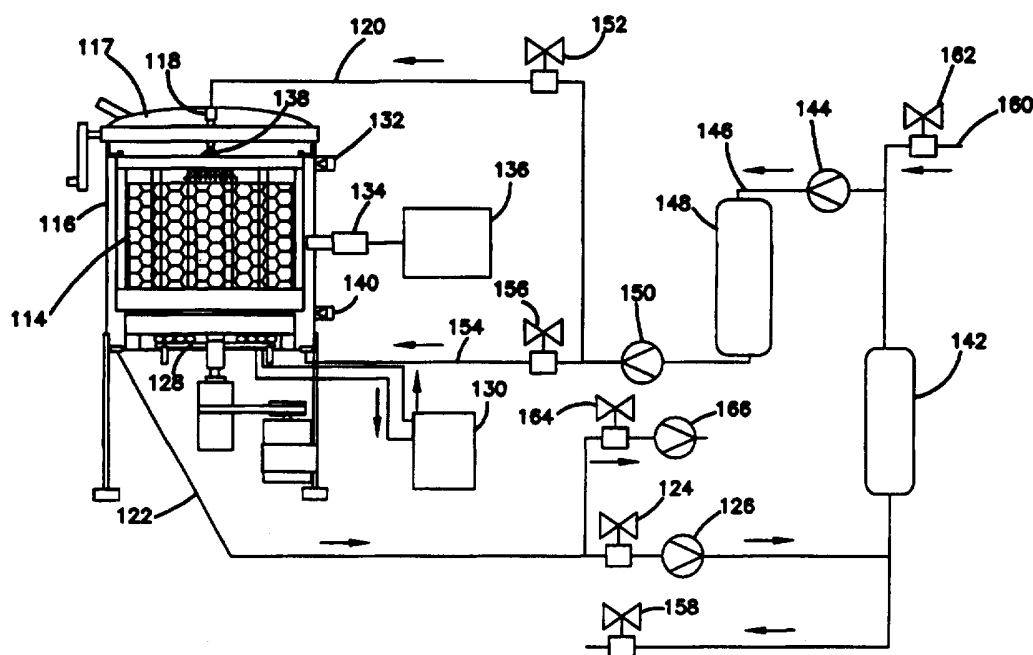




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(54) Title: DENSE FLUID CENTRIFUGAL SEPARATION PROCESS AND APPARATUS



(57) Abstract

An apparatus and process is disclosed herein for removing two or more substances from a particular substrate by placing the substrate with the substances such as contaminants in a dense fluid centrifuge apparatus (116) within a pressure vessel. By changing the composition of the particular dense fluid between a solvent state and a non-solvent state via varying the temperature of the dense fluid between a temperature below a critical temperature and a temperature above the critical temperature and a pressure below the critical pressure and a pressure above the critical pressure. By uniformly rotating the substrate in the dense fluid, centrifugal and shearing forces are produced separating the substances from the substrate.

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DENSE FLUID CENTRIFUGAL SEPARATION PROCESS AND APPARATUS

Field of the Invention

The present invention relates generally to the use of liquified, supercritical and heavy gases, hereafter described as dense fluids, for cleaning substrates. More particularly, the present invention relates to a process of using centrifugal energy in combination with dense fluids or dense fluid mixtures to clean a variety
5 of inorganic and organic substrates, including biomaterials, metalworks, ceramics, and glasses. Moreover, this invention relates to preparation of substrates more uniformly for subsequent materials engineering process for deposition or impregnation of both external surfaces and interstices of said materials with chemical or physical agents to provide long-term preservation or
10 enhanced material performance characteristics.

Background of the Invention

Conventional substrate preparation processes (i.e., cleaning, sterilizing, separations) such as precision cleaning, sterilization, or preservation processes
15 using hazardous organic solvents, toxic gases, radiation, and topical biocides are currently being re-evaluated due to problems with environmental pollution, toxicity, inefficiency, or poor performance. The use of toxic, carcinogenic, or mutagenic substances to achieve cleaning or sterility have been shown to be deleterious to the environment, pose significant health threats, require strict
20 control, and create hazardous waste disposal problems. Also, conventional cleaning processes may damage or alter material performance properties. For example, steam autoclaving may greatly accelerate oxide growth on titanium biomaterials (Lausmaa *et al.*, "Accelerated Oxide Growth on Titanium Implants During Autoclaving caused by Fluorine Contamination" *Biomaterials* 6 January
25 1985) and must be carefully controlled.

In some cases, the cleaning or sterilizing media chemically reacts with interstitial material residues to form harmful by-products. For example, toxic by-products or residual media left in biomaterials, such as implants, following

conventional cleaning and ethylene oxide gas sterilization have been shown to adversely impact the performance of those implants. (Scherer *et al.*, "Hazards Related to Gas Sterilized Materials," *Laryng. Rhinol. Otol.* 65 1986.)

Finally, conventional substrate preparation processes are often performed
5 as separate operations, involving immersion of, or application of topical
sterilants, disinfectants, and other chemical agents. For example, several
physical and chemical sterilization methods are used in industry. These methods
include gamma radiation treatment (Baquey *et al.*, "Radiosterilization of
Albuminated Polyester Prostheses" *Biomaterials* 8 1987), ultraviolet radiation,
10 steam autoclaving, dry heat, and toxic gas sterilization (Peczar *et al.*
Microbiology McGraw-Hill Publishers, 1977, pp 425-423).

Biomedical, aerospace, high energy, high vacuum substrates are
fabricated from different types of materials, having various internal and external
geometries and compositions. These may be assembled into biomedical devices
15 such as medical implants, valves, or artificial joints, or they may be surgical aids
such as sponges, guide-wires, and clips, and may be contaminated with more
than one type of inorganic, organic, or biological contaminant. These highly
complex materials require pre-cleaning and sterilization processes prior to use in
critical environments such as the human body. Often, assembled devices must be
20 disassembled to accommodate conventional cleaning and sterilization processes.

Polymeric substrates used in surgical applications, or biomaterials, must
be free of interstitial organic and inorganic residues and microbiological
contaminants to provide maximum biologic adhesiveness (cellular adhesion) and
no biologic reactivity (biocompatibility). These polymers must be capable of
25 performing their intended function over prolonged periods in contact with living
tissue and body fluids. This is a highly specialized environment of great
biochemical complexity. The principal medical uses of polymers include:
structural materials, joint replacements, dental materials, medical devices
(including tubing for transport of biofluids both inside and outside the body),
30 adhesives, and sutures. The residual monomers, oils, plasticizers, dyes,
pigments, and other additives can produce harmful side effects such as toxic

chemical release through bioreaction, infection, swelling, or complete implant device rejection.

Because conventional substrate cleaning and sterilization processes are performed as independent procedures, often the sterilization procedure re-
5 contaminates the material with residues or adversely affects the physical properties and subsequent performance of the materials (Doundoulakis "Surface Analysis of Titanium after Sterilization Role in Implant-Tissue Interface and Bioadhesion" *J. Prosthetic Dentistry* 58 Number 4, October 1987).

10 Additionally, conventional cleaning and sterilization (chemical and biological separations) processes are effective only on external surfaces of composite or intricately arranged substrates and provide little or no internal cleaning and sterilization capability. For example, with the deposition or implant processes disclosed in U.S. Patent No. 5,213,619 (Jackson), it is imperative that both external and internal surfaces be both chemically and biologically clean
15 prior to application of physical or chemical agents to preclude premature material degradation or other undesirable end-product performance characteristics.

Conventional substrate preparation processes rely on methods employing hazardous organic cleaning solvents such as isopropyl alcohol in U.S. Patent No. 4,710,233 (Hohmann *et al.*), chlorinated hydrocarbons, and other toxic and
20 flammable compounds. These conventional cleaning agents and processes are generally not chemically compatible with organic materials such as spices and herbs (perishables), only clean or sterilize external surfaces, and do not provide a means of extending the cleanliness of the material once following processing. Additionally, the referenced patent teaching applies primarily to metal tools, and
25 it does not consider the removal of sterilizing agent from foodstuffs.

The use of supercritical fluids as washing agents is disclosed in U.S. Patent No. 4,944,837 (Nishikawa *et al.*). There is disclosed a material washed in a supercritical atmosphere to prepare the material for resist stripping using a supercritical fluid or an admixture solvent.

30 These nonenergized monophasic supercritical fluids exhibit drawbacks in that they are poor cleaning solvents for many typical contaminant removal or chemical agent implant applications. Initially, a contaminant or chemical agent

must be provided in the proper solvent environment in order to be transported. This may involve employing one or more dense fluids, different fluid states (liquid and supercritical) and chemical agent admixtures which are based upon knowledge of the solubility chemistries of the targeted contaminants or the chemical agents. Secondly, our research shows that most often high energy inducements such as those used in this invention are required to effectively solubilize, transport or implant contaminants or chemical agents, respectively. Finally, Nishikawa '837 does not disclose altering the chemical or physical characteristics of the bulk material for utilization in critical environments where different bulk (internal and external surface) properties such as long-term preservation, improved ductility, or decreased conductivity would be required.

Centrifugation is applied in many processes to separate contaminants from substrates. Examples include removing particulates from air, particles from oil, sediment in water, and liquids from solids, wherein the air, oil, water, and solid are considered the substrates in these processes respectively. These conventional centrifugal separations exhibit drawbacks. Initially, phase and density differences of the substrate and contaminant system are fixed. Separation efficiency is predominantly dependent upon the rotational velocities, thermal energy, and time. The temperature of the entire system (substrate/contaminate) is uniform and tends to enhance separation slightly with increase. Centrifugal and shearing forces, if present together, are usually proportional and dependent upon one another. As a result, separation efficiency for a conventional system tends to be constant. Finally, solubility chemistry of the separation media (substrate) remains constant.

To optimize a conventional centrifugal separation requires controlling temperature, rotational velocity, and contact time. Generally, high temperature, high rotational velocity, and long substrate contact time improves the separation in conventional centrifugal separations, almost without exception. Moreover, adjunct shearing forces produced by the movement of the substrate (i.e., oils, water, air, solid) upon the contaminants is relatively fixed, so that a "fixed" range of contaminants is removed in a conventional substrate/contaminate system.

Applicant has disclosed the use of centrifugation in prior patent No. 5,344,493 issued September 6, 1994 for a "Cleaning Process Using Microwave Energy and Centrifugation in Combination with Dense Fluids". The process described therein advantageously maintains a substrate bearing polar
5 contaminants at a temperature at which liquified dense fluid is near-supercritical by flowing dense fluid through an environment. It primarily irradiates the substrate with microwave energy to raise localized temperatures above the critical, thus creating microenvironments of supercritical fluid, resulting in multi-phasing due to simultaneous localized heating and cooling. Usually the substrate
10 is non-metallic and the dense fluid is non-absorbent of the microwave energy. In addition, the substrate is retained within a rotatable bracket and spun at constant speed during the cleaning process, to migrate contaminants outwardly under centrifugal force. While this process is advantageous over prior art systems, the separation effects are based upon heating of polar microwave-responsive
15 contaminants, and the process does not facilitate cleaning of metal substrates in a much shorter time interval, or separation of very small particulates. The present invention uses a number of separate fluid dynamics, chemical, phasic, and mechanical effects in cumulative fashion to materially increase efficiency and reduce cleaning times under a wide variety of conditions.

20

Summary of the Invention

The present invention overcomes the drawbacks of the prior art by providing a separation process and apparatus using dense fluids to simultaneously dissolve, entrain, or otherwise capture and mobilize substances contained in or
25 on a substrate and transport said substances to the outer region of the apparatus device away from the substrate. The term "dense fluid" as used herein means a gas or a mixture of gases compressed to supercritical, liquified, or multi-phased states to achieve liquid-like densities. The method alters the composition of the dense fluid to cause a difference in chemical and physical composition to cause
30 the substance to separate from the dense fluid and substrate due to both solubility (chemical) and density (physical) differences. The present process involves simultaneous multi-phasic transport and separation process within the chamber.

The dense fluids suitable for use in the present process comprise either supercritical or liquified gases and chemical admixtures or agents dissolved in the dense fluid or dense fluid mixtures. Unlike conventional solvents such as water, hexane, isopropyl alcohol, or carbon tetrachloride, dense fluids exhibit unique chemistry such as variable solvency or solubility for a variety of substances, spontaneous wetting action, and powerful penetrating ability.

For the precision cleaning, sterilization, and implantation or deposition exemplifications of the present invention, the dense fluid or dense fluid mixture is chosen to have solubility chemistries, during energizing, which will be compatible with and most effective in dissolving, removing, transporting, implanting, depositing, or chemically degrading the targeted unwanted residues. Solubility parameters or cohesive energy parameters are used in the present invention to provide a method of correlating and predicting the cohesive energy properties of contaminants, substrates, chemical agent solubilities, and dense phase gases or dense fluids. Cohesive energy parameters are used to predict the solubility or maximum solute carrying capacity of a dense fluid or dense fluid admixture for a particular contaminant or contaminants and maximum penetration effect of a dense fluid or dense fluid admixture for complex solid materials and to predict deposition or implantation characteristics for a given chemical agent or chemical agent mixture. Several computational methods exist for calculating cohesive energy values for substrates, chemical agents, and dense fluids (*Handbook of Solubility Parameters and Other Cohesion Parameters* Barton, CRC Press, 1983). These include the Hildebrand, Hansen, and Giddings equations, among others. Subcritical fluid or liquified gas cohesive energy values can be computed using classical Hildebrand calculations based upon readily available vapor pressure data (Hoy "New Values of the Solubility Parameters from Vapor Pressure Data", *J. Paint Technology* 42 Number 541, February, 1970). Finally, cohesive energy values for solid surfaces or materials with higher than liquid densities can be computed based upon readily available surface tension data (L. Jackson, "Surface Characterization Based on Solubility Parameters" *Adhesives Age*, October, 1976).

A second exemplification of the present invention in the employment of centrifugal separation with the unique characteristics and separation capabilities using dense fluids as a separation media exposed to centrifugal force.

Generalized formulae describing the relationships between conventional

5 centrifugal and shearing forces are specified below, respectively:

Centrifugal Energy (Eq. 1):

10
$$F_c = (D/2)(\omega^2)(1/g), \text{ where}$$

F_c = Centrifugal force

D = Diameter of centrifuge

ω = radial velocity

g = gravitational acceleration

15

Shearing Energy (Eq. 2):

$$F_s = (C)(\sigma)(V^2/2)(A), \text{ where}$$

20

F_s = Shear force (or drag force)

C = Coefficient of drag

σ = Density of fluid

V = Velocity of fluid (squared)

A =

25

projected area of contaminate being removed from substrate

Separation efficiency (F_r), the resultant of F_c and F_s acting on a substrate-substance system, in a conventional centrifugal separator improves as a function of increased variation between the densities of the substrate and substances and increased F_c and

30 F_s .

Unlike conventional centrifugal separations, the present invention allows users to simultaneously control fluid density (σ), temperature (T), pressure (P), fluid velocity (V), coefficient of drag (C), resulting in independent control of solvent solubility (δ), centrifugal force (F_c), and shearing force (F_s), and resulting separation

35 efficiencies (F_r).

Brief Description of the Drawings

The present invention will be described with reference to the accompanying drawings, wherein like reference numerals identify corresponding or like components.

5 In the drawings:

Fig. 1 is a graph showing the enhancement effect of systems and methods in accordance with the invention over conventional dense fluid separation processes with respect to particle size versus rotational velocity;

10 Fig. 2 is a graph showing the enhancement effect of systems and methods in accordance with the over conventional dense fluid separation processes with respect to percent removal versus process time;

Fig. 3a is a phase diagram for dense carbon dioxide with a separation boundary described in relation to liquid, gas, and supercritical phases;

15 Fig. 3b is a diagram showing the differences between conventional dense fluid and DFC separation mechanisms with related phase diagrams showing phase transition boundaries;

Fig. 4 is a diagram showing normal and inverted dense fluid centrifugal process energy components;

20 Fig. 5a is a diagram showing the 2-dimensional relationship between centrifugal and shearing energy components in a conventional centrifugal separation system;

Fig. 5b is a diagram showing the 3-dimensional relationship between solubility chemistry, centrifugal, and (dense fluid) shearing energy components in a dense fluid centrifugal separation system;

25 Figs. 6a-c are diagrams showing the drum cage, bearing assembly, and drive connection device, respectively, for use in an exemplary dense fluid centrifuge device in accordance with the invention;

Fig. 7 is a diagram showing a complete dense fluid centrifugal separation apparatus with various exemplary design features;

30 Figs. 8a-f are diagrams showing an exemplary inverter device and mechanism for inverting the substrates in a separation apparatus in accordance with the invention;

Fig. 9 is a diagram showing exemplary dense fluid centrifugal separation apparatus with associated dense fluid supply, delivery, and recycle subsystems; and

Fig. 10 is a flowchart of steps employed in an exemplary dense fluid centrifugal separation process.

5

Detailed Description of the Invention

Fig. 1, in the upper left-hand portion, shows the performance characteristics of static dense fluid cleaning systems that remove particulate matter down to approximately 25 μm , depicted as Region A. By contrast, dense fluid centrifugation, shown as Region B, extends the particle removal range to below 25 μm . Table I below gives the performance data for equivalent coupons cleaned with a conventional (mixed) dense fluid extraction and enhanced extraction using the dense fluid centrifugation process under equivalent temperature and pressure conditions.

15

Table I

SIZE RANGE (μm^1)	Number of Particles/Square Foot		
	A ²	B ³	
0.5 - 1	2,500	200	92%
1 - 10	295	25	INCREASED
10 - 25	100	1	SEPARATION
25 - 50	75	1	
50 - 100	10	0	
>100	0	0	

25

¹ A - Conventional Dense Fluid Particle Separation

² B - Dense Fluid Centrifugal Particle Separation

³ μm - Micrometer, Micron, 1×10^{-6} Meters

30

Conventional dense fluid cleaning systems described in the Jackson patent No. 5,213,619 referenced above rely on natural fluid diffusion and fluid transport

mechanisms, and subsequent discharge of dissolved or entrained substances from the separation chamber to effect separation of the substance (considered contaminates in this case) from substrate. In this related art, the dense fluid generally acts only upon the contaminate and the contaminate must be removed from the chamber to prevent "fall-out" or recontamination of the substrate.

By contrast, dense fluid centrifugation of the invention acts upon the entire system, including the substrate, contaminate, and the dense fluid cleaning media. The apparatus of the present invention separates the heavy (contaminated dense fluid) fluid to the outer chamber walls from the lighter (clean dense fluid) at the center of the chamber (location of substrates being processed). By changing the fluid properties of the dense carbon dioxide (CO₂), dissolved and entrained contaminates contained in the heavy dense fluid separate within the chamber and flow to the bottom of the chamber for periodic discharge. This concentration and discharge mechanism is a unique characteristic for this innovative separation process and is extremely effective when cleaning grossly contaminated substrates such as machined metal products. This effect is shown in Fig. 2. As shown in the Fig. 2, better than 90% of the gross oils (Curve A) are removed from the substrate (machined connector pins in this case) using the dense fluid centrifuge as compared to the less than 10% using conventional dense fluid (Curve B) over the same time period of approximately 5 minutes.

The gases most suitable for use in the present invention include inorganics such as CO₂, xenon, nitrous oxide, sulfur hexafluoride and mixtures thereof. Organic gases such as hydrocarbons (i.e., butane, pentane) may also be used in the present invention in certain separations, however organic gases may degrade into hazardous by-products in high-energy environments (acoustics, microwaves) and, therefore, are not suitable for use in these embodiments of the present invention. Preferably, the suitable gas or gas mixture is preconditioned to remove gaseous impurities such as hydrocarbons, moisture, and microscopic particulates having diameters of 0.2 micrometers or larger.

Dense CO₂ is the preferred dense fluid for use in practicing the present process as both the substrate preparation and chemical agent carrier solvent since it is non-toxic and inexpensive. The critical temperature of CO₂ is 305° Kelvin

(°K, 32°C) and the critical pressure is 72.9 atmospheres (atm) (75 kilograms per square centimeter). The solute carrying capacity, or cleaning qualities of CO₂ can be modified by changing its physical and chemical makeup, while remaining at or above its critical pressure. Increasing the temperature of dense phase CO₂ from 5 298°K (25°C) to 350°K (77°C) at the critical pressure for CO₂ (73 atm) changes the dense fluid internal energy content from approximately 22 MPa^{1/2} to approximately 8 MPa^{1/2}. This solvent energy change is accompanied by a change in dense fluid state from liquid phase to supercritical phase once the critical 10 temperature of 305°K (32°C) is reached. This change in internal cohesive energy is accompanied by an overall change in the dipole-dipole solubility properties (solvent spectrum) of dense phase CO₂ excluding hydrogen bonding and polar energy contributions of which dense phase CO₂ has none.

Alternatively, blends of nitrous oxide-CO₂, xenon-CO₂ and argon-CO₂ provide enhanced solute carrying capability by changing or shifting the solubility 15 chemistry range hence contaminant or chemical agent selectivity range.

Referring to Fig. 3a, methods in accordance with the present invention operate in the near-supercritical region whereby separations are achieved within the chamber by changing phase from liquid state to heavy vapor state and from supercritical state to heavy vapor state and from liquid state to supercritical state, 20 and vice-versa for each transition, with only minimal temperature and pressure changes. The present process involves making minute physical changes of Δ24 atm and Δ12°K in the dense fluid or dense fluid mixture to cause phase transitions and centrifugal separations based upon density and phase differences. The invention utilizes the "interphase region" where dramatic differences in solubility, viscosity, 25 and density shifts occur between all phases involved. A substance dissolves or entrains in a solvent state, separates from the substrate, re-precipitates in a heavy gas or vapor state, and separates from the vapor state in one continuous process using a single volume of dense fluid media. This rapid substance separation mechanism and small temperature and pressure shifts required to achieve efficient 30 separation is in marked contrast with the Phase Shifting process as previously disclosed by Jackson. A comparison between the "ex situ" conventional Jackson

process (U.S. Patent 5,013,366) and the present "in situ" DFC separation process is shown in Fig. 3b.

Referring to Fig. 4a, center 2 of the chamber contains substrate 4 containing a substance rotating with shearing force 6 with dense fluid 8 rotating with shearing force 10. The entire system is experiencing centrifugal force 12 which reaches a maximum at outer region 14 of the system.

Referring to Fig. 4b, center 16 of the chamber contains substrate 18 containing a substance which is stationary with shearing force 20 which is equivalent to a drag force created by dense fluid 22 rotating with shearing force 24. The entire system is experiencing centrifugal force 26 which reaches a maximum at outer region 28 of the system.

Figs. 4a and 4b show the separation forces present during dense fluid centrifugation with a substrate centrifuging in the centrifuge chamber (Fig. 4a) and also with the substrate held stationary in the center of the centrifuge chamber (Fig. 4b).

Figs. 5a and 5b compare the differences between conventional centrifugal separations with dense fluid centrifugal separations. Fig. 5a shows the 2-dimensional relationship that exists in a conventional centrifugal separation system with regard to centrifugal and shearing forces (for liquid-liquid and liquid-solid phases). Fig. 5b shows the 3-dimensional relationship that uniquely exists in dense fluid centrifugal separations showing the added dimension of solubility chemistry.

Many centrifugal processes and devices are unique. In fact, many centrifugal extraction processes are the subject of issued United States patents. For example, the Podbielniak centrifugal extractor and process, U.S. Patent No. 2,044,996, uses special staging and low volume extraction compartments providing improved separations and yields. In the Quadronics Centrifugal Extractor (U.S. Patent 3,114,707, Doyle *et al.*), special flow control techniques are employed within the centrifuge to improve separations. Other patents have been issued for different centrifugal processes including U.S. Patent 2,036,924 and 3,108,953. In all of these patents, the temperature, contact time (feed rates), and rotational velocities are the predominant control factors.

The dense fluid centrifugation process, of the present invention, affords separation control capabilities that are not found with these prior centrifugal designs.

Mixing systems employ various mechanical methods to uniformly disperse various substances - solid-gas, liquid-solid, liquid-gas so that all substances are present in relatively equal concentrations in one mixed phase. This is accomplished through diffusive, convective, or mechanical shearing mechanisms.

For example, the Weiskoph (2,845,045) and Polatsee (2,437,968) patents teach conventional mixing and agitating mechanisms and devices. The Weiskoph patent employs a mixing blade (Fig. 5) to mix the washing fluid to disperse the cleaning agent and articles being processed. The Polatsee patent teaches the use of a drum (Fig. 1, 31) that rotates while a mixing blade (Fig. 1, 76) agitates the cleaning media with the articles being processed in the drum. Both of these examples illustrate the conventional art of mixing the cleaning media and articles (substrates) to optimize cleaning. Typically in these separation processes, the dirty cleaning media is discarded and replaced with clean media in successive washing cycles to achieve the desired separation. This technique is also common in dense fluid extraction processes as taught by Jackson and others.

Conventional dense fluid extraction/separation systems employ mechanical mixers, paddles, or blades to insure rapid equilibrium between the dense fluid, substrate, and substances. For example, Jackson (5,215,592) teaches the use, in a Photochemical Dense Fluid Extraction, of a paddle wheel mixing blade to uniformly mix substrate and dense fluid media during processing. However, only simple geometric substrates are effectively processed in this manner. This technique is inefficient when used on complex and bulky substrates such as a lot of rivets, connector pins, coffee beans, and most other commercial separation product applications. Mixing the fluid about a large quantity or mass of uniform substrate cleans only the outer substrates. The substrates contained at the center of the mass transfer dissolved contaminants through slow diffusive and convective mechanisms. The mixture must be removed from the chamber and replaced with clean dense fluid to continue the separation process. In addition, particles and insoluble residues that are trapped deep inside the mass cannot be mobilized and mixed into solution. All conventional dense fluid separations suffer from this technical problem.

Centrifugal systems, according to Chemical Engineer's Handbook, Section 18-73 (Separations), consist of employing centrifugal force to enhance separation according to differences in density between any two or more substances - solid-gas, liquid-solid, liquid-gas, so that substances are separated into distinct phases. Separation efficiency is increased several hundredfold over conventional separations such as gravity settling, phase transition, filtration, and momentum transfer mechanisms.

The present dense fluid centrifugation process does not have the inherent separation limitations of conventional mixed systems discussed above and have more capability than conventional centrifugal treatments.

A brief overview of the process of the present invention is as follows:

Starting condition:

Substrate containing one or more substances is contained at the center of a centrifugal separation chamber.

15 Sequence 1:

Substances contained on or in substrate contained in a dense fluid solvent state (i.e., liquid or supercritical fluid phase) dissolved or entrained in the dense fluid.

Sequence 2:

20 Substances precipitate during dense fluid phase change from solvent state (liquid or supercritical fluid phase) to non-solvent state (heavy gas phase).

Sequence 3:

Substances separate from heavy gas phase and substrate under centrifugal energy.

25 Sequences 1 through 3 is repeated as required to achieve complete separation but without exchanging the contents of the chamber.

End-result:

The separation (i.e., fractionated, cleaned, sterilized) substrate is contained in the center of the chamber and the substances are concentrated in the outer region of the chamber and finally removed during a final depressurization sequence.

30

Exemplary Dense Fluid Centrifuge Apparatus:

Figs. 6a, 6b, and 6c show portions of an exemplary dense fluid centrifuge assembly consisting of a centrifuge drum subassembly (Fig. 6a), a dry-film lubricated bearing system (Fig. 6b), and a drive connection device (Fig. 6c).

5 Referring to Fig. 6a, the drum consists of aluminum or stainless steel and comprises several posts 30 bounded by upper rigid ring assembly 32 and lower circular drum mounting plate 34. A basket or substrate or shearing cage (not shown in Fig. 6a) is placed in the area bounded by the posts. The lower drum mounting plate contains several bolt holes 36 through which bolts 38 connect the drum assembly to an
10 exemplary bearing system (Fig. 6b) using springs 40 through bolt holes 42.

The bearing system comprises outer stationary race subassembly 44 and inner rotating race subassembly 46 with ball bearings 48 and separator (not shown) providing interfacial rotation. The bearing assembly is mounted to the center of the bottom of the cleaning chamber (not shown) using bolts 50 which pass through holes
15 52 in the outer bearing race 44, employing standoffs 54.

The exemplary drive connection device (Fig. 6c) comprises a cylindrical bottom 56 which has a machined rectangular upper connecting section 58. Upper connection section 58 inserts into a mating female slot 60 which has been machined into the center of the inner race (16) of the bearing assembly. The bottom section
20 (26) of the drive connection device attaches to an external motor drive. A suitable centrifuge drive motor (not shown in Figs. 6b and 6c) is affixed to the outside bottom center of the centrifugal separation chamber and includes a drive shaft that extends up into the chamber. The drive motor shaft is coupled to a drive connection device which is inserted into the inner race, producing rotation of the drum cage and
25 contents.

Fig. 7 shows the exemplary dense fluid centrifuge separation chamber complete with the exemplary centrifuge assembly showing other exemplary machine design features. The exemplary centrifuge system has a chamber 62, quick opening closure 64 with handle 66, and a suitable open/close mechanism 68 designed to
30 withstand pressures and temperatures used in the system. The exemplary centrifugal separator has several ports including bottom inlet port 70, bottom exhaust port 72, upper level sensor port 74, lower level sensor port 76, acoustic horn port 78,

microwave adaptor port 80, and upper inlet port/sprayer assembly 82. The exemplary separation chamber contains a centrifuge assembly consisting of drum cage 84 which is attached to inner bearing race 86 using spring-loaded bolt connections 88. The bearing assembly shown has outer race 90 which is attached
5 to the bottom of the cleaning chamber using bolts and standoffs 92. The exemplary centrifugal separation chamber also contains heat exchange assembly 94 with inlet 96 and outlet 98 ports for circulating thermalant or coolant using a separate temperature control system (not shown). Also shown in the figure is the drive connection device 100 and drum seal assembly 102 which prevents small substrates
10 contained within a basket (not shown) or within cage 84 from getting down between the drum cage and the chamber wall and also contains a connection for insertion and lock-down of a centrifuge inverter assembly (not shown). Finally, as shown in the arrowed figure 104, the exemplary centrifugal separation machine is mounted so that it can be operated in any orientation from the vertical axis to the horizontal axis.

15 Operation of the machine to rotate parts within a basket about a horizontal axis has particular advantage for a number of applications. When the central axis is horizontal the parts can be tumbled within the basket during rotation. This constantly changes the orientation of the parts with respect to the dense fluid environment and each other, exposing different surfaces at different times and
20 enhancing the access of the dense fluid to internal cavities and corners. A large quantity of small pins, for example, can be cleaned more rapidly in this manner than by any other known technique.

Figs. 8a-8f show an exemplary dense fluid centrifuge inverter assembly and mechanism. Referring to Figs. 8a, 8b, and 8c, the inverter allows for the fixturing
25 of substrates within the dense fluid centrifuge cage. This allows for centrifugal separation of stationary substrates in accordance with the processes described herein. As shown in Fig. 8a, the inverter is constructed to be similar to but smaller than drum cage 108 to allow for the insertion of the inverter into the drum cage as shown in Figs. 8b and 8c. The inverter bolts into the drum seal assembly (Fig. 7, 102
30 which allows the drum cage 108 to rotate freely about the inverter 106. Referring to Figs. 8d, 8e, and 8f, once the inverter is inserted and locked in, a suitable basket 110 containing substrates is inserted into the inverter 106. Once inserted, the drum

cage 108 rotates and creates centrifugal and shearing forces which are then translated to the inverter containing the basket containing the substrates being processed. Also shown in Figs. 8d, 8e, and 8f are centrifuging baffles 112 which are attached (at least 4) to the drum cage to assist with centrifuging the dense fluid
5 about the inverter and contents. This is helpful in maintaining uniform flow about the inverter.

Exemplary Dense Fluid Centrifugal Separation Process:

Referring to Figs. 9 and 10, the following exemplary dense fluid centrifugal
10 Separation Process involves four interphasic transitions Supercritical-Gas, Gas - Liquid, Liquid - Gas, and Gas - Liquid (called a SGLGL DFC Separation Scheme).

While multiple phase transitioning sequences are possible using dense fluid centrifugal separation, any sequence should preferably terminate with the liquid phase so that separated substances, concentrated in the outer chamber region during
15 successive transitions, are flushed out of the apparatus during final draining and depressurization operations.

The process of the present invention is applicable for removing one or more substances from one or more substrates. The substrates are placed within basket or fixture 114 within centrifugal chamber 116. The substrates are rotated in a
20 clockwise or counter clockwise direction at a uniform g-force of greater than 1 x g. During the process the direction of rotation may be changed from clockwise to counter clockwise or counter clockwise to clockwise as desired. Changing the direction of the centrifugation increases the scouring action of the cleaning process (increases fluid shear) and the separation efficiency with a reduction of at least 50%
25 in the separation time. The shear action affects both sides of the substrate.

A dense fluid, in either a liquid state or a super critical state, is introduced into the centrifuge. The density, centrifugal force, vortex action, shear action and/or chemistry of the dense fluid to enhance the cleaning process. At the end of the cleaning process the dense fluid is withdrawn from the dense fluid centrifuge and
30 the rotation of the substrates is stopped.

The present invention is effective in removing small particles (20 microns or less) and insoluble residues from the surfaces of the substrates and keeps them

away from the clean surface by taking advantage of "g-force zones" which are created as a result of the centrifugal process. The g-force within the centrifuge increase with an increase in the radius (distance from the center of rotation). Therefore, the g-force is greatest at the outer wall of the centrifuge. In contrast, 5 conventional cleaning systems only mix the substrates to be cleaned with the cleaning fluids and, as a result, do not provide the fluid shear necessary to remove small particles or chemical residues trapped deep within the relatively large mass of the substrate.

One application of the dense fluid centrifuge of the present invention is 10 provided, in detail, below:

Step 1. A substrate (not shown) containing one or more substances is placed in dense fluid centrifugal chamber 116 using suitable fixture 114.

Step 2. Chamber door 117 is closed.

Step 3. The substrate containing the substances is centrifuged in a 15 clockwise (or counter clockwise) direction using the centrifugal drive system described herein and shown in the figure to produce a g-force of between 10 and 3,000 x g and to produce associated fluid shearing forces which are at a tangent to the substrate and oppose the rotation of the centrifuge or substrate.

Step 4. The chamber is fluidized with supercritical CO₂ at 82 atm and 20 32°C through the spray head 118 and through the inlet line 120.

Step 5. The pressure of the supercritical fluid is lowered to just below the critical pressure (68 atm) through exhaust line 122 via valve 124 and pump 126. The temperature is maintained above the critical temperature (32°C) using internal temperature control coolant/thermalant coils 128 coupled to external recycling 25 thermal control unit 130.

Step 6. The temperature of the chamber is decreased below the critical temperature (30°C) and an associated pressure of approximately 66 atm, using the temperature control system.

Step 7. The centrifuge is reversed in direction and the temperature of 30 the liquid CO₂ is raised to just above the critical temperature 32°C.

Using the internal temperature control provided by coolant/thermalant coils 128 coupled to external recycling thermal control unit 130, the associated pressure remains below the critical pressure (approximately 68 atm).

5 This causes a phase change from liquid state to heavy gas state, causing the substances to separate to the outer walls of the cleaning chamber. Refer to Fig. 3a and associated discussions herein describing the forces present that cause physiochemical separation.

Step 8. The temperature of the heavy gas is lowered to below the critical temperature using the internal temperature control coolant/thermalant coils 10 132 coupled to external recycling thermal control unit 128 with an associated pressure of approximately 66 atm.

Steps 5 through 8 may be repeated one or more times during the dense fluid centrifugation separation process to achieve optimum results. During each interphasic transition, centrifugal separation is occurring.

15 Step 9. The chamber is drained completely through drain line 122 and substances and dense fluid are recovered using an external separation and recovery unit.

Step 10. The centrifuge system is stopped and the substrate is recovered from the separation chamber.

20 The above dense fluid centrifugation process is exemplary only. The present invention is uniquely useful in that several types of dense fluid centrifugal treatments can be performed using the three interphasic transitions: Supercritical-Gas and Liquid-Gas and Supercritical-Liquid. For example, the following dense fluid centrifugation separation processes have been developed for the following
25 applications:

Separation Scheme A: Supercritical-Gas-Liquid (SGL)

- Removing oil from inside silicone substrates
- Cleaning optical assemblies
- 30 - Removing plasticizer from polymer

Separation Scheme B: Liquid-Gas-Liquid (LG)

- Removing oils from machined metal

Separation Scheme C: Supercritical-Liquid-Gas-Liquid (SLGL)

- 5 - Removing oils from glass capillary tubes

Exemplary Dense Fluid Centrifugal Separation Process for Use in Degreasing Oily Metallic Parts:

The substrates are loaded into the dense fluid centrifuge as described above.

- 10 The centrifuge is then rotated in a clockwise direction to 800 rpm and the chamber is fluidized with dense CO₂.

- The speed of the centrifuge is then alternately slowed to 500 rpm and sped-up to 800 rpm several times per minute. The centrifuge is then stopped and accelerated in the counter clockwise direction to a speed of 800 rpm. The speed of
- 15 the centrifuge is then alternately slowed to 500 rpm and sped-up to 800 rpm several times per minute, in the counter clockwise direction. The clockwise/counter clockwise centrifugation described above are repeated, during which the pressure within the dense fluid chamber is reduced to thereby reduce the density of the fluid, which remains in the liquid phase, from 0.9 to 0.6 g/ml. This step removes both
 - 20 soluble and insoluble substances (oils) from the substrates and transfers them to the walls of the chamber.

The centrifuge is finally accelerated to 800 rpm, to force all soluble and insoluble substances to the chamber wall and the dense fluid centrifuge chamber is emptied. The walls of the chamber can be flushed to remove insoluble substances.

- 25 As described above, the substance may be separated by entrainment, not solubilization as required by conventional dense fluid systems. Also since the material is not solubilized, but is removed from the "solvent" the amount of substance which can be removed from the substrate is greater than in processes where the substance would have to be dissolved and would be expected to saturate
- 30 the solvent. The centrifuge is emptied under centrifugation which inhibits redeposition of the substance on the substrate, thus leading to a more efficient cleaning process.

In this embodiment of the invention changing rotational velocities and direction changes fluid shear angles, relative velocities, centrifugal forces and fluid shear (turbulence). It should be noted that other parameters, such as the density of the dense fluid, can also be changed to enhance cleaning of the substrate.

- 5 Maximizing the difference between the density of the dense fluid and the substance, in a single phase (liquid or supercritical) during centrifugation greatly enhances the *in situ* dense fluid separation of substance-dense fluid-substrate.

Alternative Exemplary Dense Fluid Centrifugal Separation Process for Use in

10 Degreasing Oily Metallic Parts:

Oily metallic parts are placed in the centrifuge chamber and the centrifuge is accelerated to 800 rpm and the chamber is fluidized to 82 atm at 30°C with CO₂. The speed of the centrifuge is then alternately slowed to 500 rpm and sped-up to 800 rpm several times per minute. The centrifuge is then stopped and accelerated

15 in the counter clockwise direction to a speed of 800 rpm. The speed of the centrifuge is then alternately slowed to 500 rpm and sped-up to 800 rpm several times per minute, in the counter clockwise direction. The clockwise/counter clockwise centrifugation described above are repeated, during which time the chamber is de-pressurized, incrementally over several minutes to 54 atm at 20°C.

- 20 During this process the phase of the dense fluid does not change but significant changes in density and viscosity occur. This dense fluid centrifugation technique enhances separations by removing substances from the solute and depositing them at the chamber wall (the high g-force zone).

Table II illustrates the density changes which occur during dense fluid

25 centrifugation.

Table II

Elapsed time (min.)	Sequence description	Fluid density (g/ml)	Substance density (g/ml)	Δ density (%)	Cleaning action
5 1	Start of dense fluid phase fill sequence	0.02	0.85	98	Physical
2	Start of dense fluid phase cleaning sequence	0.9	0.85	6	Chemical/physical
4	End of dense fluid phase cleaning sequence	0.5	0.86	41	Chemical/physical
10	End of dense fluid phase drain sequence	0.02	0.85	98	Physical

10 The physiochemical shift during the initial filling procedures produces a large surface drag (fluid shear) which enhances the separation of the substance from the substrate. Shifting from a liquid phase to a heavy vapor phase at the end of the process produces another significant density shift which aids in cleaning.

15 Alternative Example (External Energy Input):

As one alternative example of the present invention, a dense fluid/substrate/substance energizing system is employed to enhance separation under centrifugal treatment. Referring to Fig. 9, an acoustic energizing device as taught by Jackson (5,213,619) is used to enhance separation following Step 6 above.

20 Following filling the chamber with dense fluid, the dense fluid centrifuge is stopped and acoustic energy of a frequency of 20 KHz and an energy input of between 500 to 2,000 watts is introduced via an acoustic horn 134 and generator 136 mounted through the wall of the separation chamber. Acoustic waves are maintained for between 3 and 5 minutes in either a pulsed or continuous cycling mode, whereupon
 25 the acoustic generator is turned off and the centrifugal separation is resumed at Step 7 above.

Alternative Example (Centrifugal Spray Separation):

30 As another alternative example to the present invention and during overhead spray filling of the chamber under Step 4 above, the dense fluid (liquid in this case) is removed from the chamber simultaneously through the drain line 122 and returned

to the chamber via the spray head 138 through inlet line 140. This example is useful for recycling a small amount of liquid CO₂ in the centrifugal spray separation process to remove gross substrate surface contamination prior to complete filling, phase transition, and draining sequences in subsequent steps (i.e., a gross cleaning
5 procedure). The small amount of liquid CO₂ used during this sequence can also be removed from the chamber completely and recycled using a separate fluid recycling unit prior to initiating the above follow-on sequences or it may be the only step performed.

10 Alternative Example (Stationary Substrate Centrifugal Treatment):

As yet another alternative example of the practice of this invention, the substrate being processed according to the above process and examples is processed in a stationary position using the centrifuge inverter assembly described herein. The same processes may be performed as described above except that in this example
15 the substrate remains stationary in the center as the dense fluid centrifuges about it. This example is useful for extremely heavy substrate loadings or in situations where irregularly shaped substrates create an extreme imbalance condition when centrifuged.

20 Fluid Conservation (External Dense Fluid/Substance Recovery):

Another aspect of the present invention, also shown in Fig. 9, is an exemplary simple dense fluid and substance recovery and reuse scheme. Dense fluid containing dissolved and entrained substances are pumped from centrifugal cleaning chamber 116 through drain line 122 and exhaust valve 124 using a suitable
25 pump 126 and into separator vessel 142. The mixture of dense fluid and substances contained in separator vessel 142 is separated through expansion into gas phase (light fraction) and liquid and solid phases (heavy fraction). The light fraction is pumped using pump 144 through transfer line 146 and recompressed to liquid state in a secondary clean fluid storage vessel 148. The separated and recycled dense
30 fluid can be pumped back to the centrifugal separation chamber via pump 150 and through the overhead spray feed line 120 through inlet valve 152 or to a bottom filling line 154 through a second inlet valve 156. The solid and liquid substances

can be recovered from the separator vessel 142 through an exhaust valve 158. Liquid CO₂ is supplied through line 160 and valve 162 for initial system changing or replenishment operations.

5 Centrifugal Thermal Vacuum Post Treatment:

As an alternative feature of the present invention and also shown schematically in Fig. 9 is a centrifugal thermal vacuum (CTV) treatment process. Following centrifugal separation sequences and Step 9 described above with regard to Fig. 10, a vacuum pressure of between 1×10^{-2} and 1×10^{-4} Torr (0.1 atm) is pulled
10 through exhaust line 122 through a valve 164 and vacuum pump 166 for 15 to 60 minutes. The internal temperature of the chamber can be adjusted to between 30° and 100°C during this operation to facilitate volatilization of trace gas or residues using the internal heat exchange coils 128 and temperature control system 130. This treatment is useful for degassing polymeric substrates and for removing trace
15 volatile residues left behind following centrifugal dense fluid treatments above. Following CTV treatment, the chamber pressure is returned to ambient.

Implanting Process:

Another feature of the present invention is that the implanting (coating or
20 impregnation) treatment process as taught by Jackson (5,213,619) can be used in conjunction with during or following this process and using the device described herein. The present device and process produce a much more uniformly coated substrate when used in conjunction with the older Jackson technique.

A specific example of use of the dense fluid centrifugal separation process
25 is directed to cleaning of a hydraulic manifold to meet the following requirements: Clean to meet non-volatile residue level of 1 mg/ft² and a particle level of no more than 1 particle greater than 25 microns per sq/ft² of sampled surface area.

Process:

The manifold is cleaned in one continuous process in accordance with the
30 following process description:

The precision machined hydraulic manifold containing oily residues and gross particulates is placed in the centrifuge chamber using a suitable loading

basket. The centrifuge drive is activated and the manifold contained within the basket is spun at a velocity of approximately 100 rpm. The machine is pressurized to about 58 atm with gaseous CO₂ to an operating pressure that exceeds 58 atm but is less than the critical pressure (P_c) of the dense fluid. The temperature of the internal cavity is maintained between 20°C (293°K) and 30°C (303°K), in any case below the critical temperature (T_c) of the dense fluid using the inner-wall mounted heat exchanger. As the internal cavity pressure approaches approximately 58 atm, liquid CO₂ (dense fluid) is maintained in the feed line and begins to flow through the spray head.

The rotating manifold impacts the dense fluid as it sprays down onto the structure from the sprayer head and fills the chamber. There is a corresponding rise in internal pressure from 58 atm to approximately 65 atm as the gas in the upper section of the cavity is compressed and dissolved into the liquid CO₂. This action rapidly removes surface contaminants from the manifold and moves them to the outer wall under centrifugal force. After filling the cavity with dense fluid, the centrifuge is momentarily stopped and acoustic energy is transmitted into the vessel through a titanium horn as taught by Jackson U.S. Patent Number 5,213,619. The acoustic energy is turned off and centrifuge is turned back on in the opposite direction. Following this, the dirty fluid is removed from the chamber through the exhaust port. This action causes the dirty CO₂ to "snap off" the manifold surfaces as the liquid CO₂ recedes under centrifugal force and simultaneous drainage.

Following the liquid CO₂ spray and acoustic centrifugation separation sequence above, the cavity is filled with clean supercritical CO₂. This is accomplished by adjusting the internal temperature to 32°C (306°K) using the internal heat exchanger and pressurizing the chamber to approximately 82 atm with CO₂. The manifold is rotated at 300 rpm during this operation. The manifold is centrifugally cleaned in supercritical CO₂ for several minutes following which the pressure is allowed to drop to below 73 atms (critical pressure) but the temperature is maintained above 32°C (critical temperature) to effect a change from supercritical to heavy vapor phase (first phase change). Following this the temperature is reduced to 29°C causing the heavy vapor to condense to liquid state (second phase change). Following this, the liquid CO₂ is pumped from the chamber carrying away

precipitated substances contained on the outer walls of the chamber. The centrifuge is maintained at 300 rpm during this draining operation to prevent re-deposition of contaminating substances on the substrate. Following drainage, the chamber is evacuated to a pressure of approximately 1×10^{-2} Torr at 30°C and held for 15
5 minutes.

Following this sequence, the centrifuge is stopped and the chamber is returned to ambient by opening the exhaust port to allow clean filtered CO_2 gas to return the internal pressure to ambient (1 atm). The chamber door is opened and the precision cleaned manifold is removed from the chamber.

10 The present invention therefore can be seen to define a dynamic separation process that uniquely changes the phases of both dense fluid and substance simultaneously under the action of centrifugal and shearing forces to separate the substance from both the substrate and the dense carrier fluid simultaneously within the same chamber and operation. Only one chamber volume (or less) of dense fluid
15 is typically required to completely separate the substrate and substances.

While particular exemplifications of the present invention have been shown and described, those skilled in the art will be aware that changes and modifications may be made without departing from this invention in its broader aspects. For example, any configuration of trays, baskets or racks can be used in the dense fluid
20 centrifuge, the process of the invention can be used in combination with ionic and non-ionic surfactants, chelating agents, reducing agents, oxidizing agents, precipitating agents, co-solvents, deodorizers and combinations thereof, which can be incorporated into the process prior to or during the dense fluid centrifugation.

Ionic surfactants suitable for use in the present invention include ether amines
25 at concentration of about 0.1 to 2% (v/v). These ionic surfactants are particularly useful for metal cleaning. Non-ionic surfactants suitable for use in the present invention include alkylaryl polyether alcohols at concentration of about 0.1 to 2% (v/v). These non-ionic surfactants are particularly useful for electronic substrate cleaning. Reducing agents suitable for use in the present invention include
30 dimethyldithiocarbamates at concentration of about 0.1 to 5% (v/v). These reducing agents are particularly useful for cleaning metal ions from substrates. Co-solvents suitable for use in the present invention include naphthenic and paraffinic oils at

concentration of about 1 to 5% (v/v) and silicone oils at a concentration of about 1 to 5% (v/v). These co-solvents surfactants are particularly useful for metal cleaning and cleaning medical devices, respectively. Oxidizing agents suitable for use in the present invention include ozone (<1% v/v) and hydrogen peroxide at a concentration of about 5% (v/v). These oxidizing agents are particularly useful for cleaning medical devices, textiles, optic (H₂O₂) and dry sterilization. When ozone is used, it is injected into the dense fluid centrifuge chamber at 55 atm and 20°C, producing supercritical ozone (sc-O₃). Deodorizing agents suitable for use in the present invention include chlorophyll at concentration of about 1 to 5% (w/v). These deodorizing agents are particularly useful for textile cleaning and deodorizing. A mixture of supercritical O₃ (sc-O₃) and liquid CO₂ (l-CO₂) is a powerful cleaning and disinfecting agent and is useful with a variety of substrates.

A mixture of sc-O₃ and l-CO₂ can be prepared, *in situ*, by pressurizing a vessel with a mixture of CO₂ and 2 to 10% (v/v) O₂ at a temperature of between about 10 to 30°C, pressure of between about 55 to 150 atm or at a temperature and pressure above the critical point for O₃ and below the critical temperature for CO₂, where the interphasic constants for sc-O₃ and l-CO₂ are >12°C and >55 atm and <30°C and >73 atm, respectively. A suitable internal ionizer comprising at least two electrodes having a potential difference of between 1,000 to 2,000 volts (DC) is used to create supercritical ozone from the oxygen gas phase dissolved in the liquid carbon dioxide phase. The mixture of O₂ and l-CO₂ acts as a dielectric medium between the electrodes which allows for the silent discharge ionization of oxygen to occur.

In an alternative *in situ* procedure 2.45 GHz microwave energy is used with an activated carbon substrate to generate an electrical discharge. Sc-O₃ generation is proportional with time.

In an *ex situ* generation, and O₃ generator is a separate high pressure unit capable of generating a concentrated mixture of l-CO₂ and sc-O₃ which is injected into the cleaning chamber, which is filled with l-CO₂.

The process can also be used in combination with a variety of physical agents to enhance separation of substances from substrates and include microwave energy

(polymeric extraction), acoustic energy (inorganic removal) and electrostatic energy (particle agglomeration) as set forth in Table III.

Table III

	Microwave DFC	Acoustic DFC	Electrostatic DFC
5 Features	Microwave absorbing substances/substrates in a relatively non-absorbing dense fluid extraction environment to improve mass transfer at dense fluid/ substrate interface	Cavity solid surface/liquid interface to improve mass transfer at dense fluid/substrate interface	Stress and charges interfaces cause improved mass transfer and particle agglomeration at dense fluid/ substrate interface
General Application	Non-metallic extractions	Inorganic substance separation	Used as electronic "flypaper" in outer separation zone of dense fluid centrifuge
Limitations	Not suitable for use with metallic substrates	Short range and can be erosive	Short range effects in dielectrics

10 The dense fluid centrifugation process of the present invention is normally performed at temperatures of from 0°C to 100°C, pressures of 1 atm to 300 atm, densities from 0.002 to 1.0 g/ml, solubilities from 8 MPa^{1/2} to 22 MPa^{1/2} and rotational velocities (fluid and/or substrate) from 10 rpm to 2,500 rpm in either clockwise, counter clockwise or alternately clockwise and counter clockwise, other
 15 ranges can be used depending on the type of dense fluid/mixture used. While the process of the present invention normally uses CO₂; nitrous oxide, xenon, sulfur hexafluoride and hydrocarbon gases and mixtures thereof are also useful. Also, during the fill stage of the process a spraying action of produced is useful as a pretreatment such as oil washing to remove insoluble debris and residues or for
 20 post-treatments such as coating substrates with antioxidants, rust inhibitors, fire retardants or disinfectants.

Use of Acoustic Energy and DFC for Cleaning Extruded Silicone Tubes

25 Extruded silicone tubes, such as cerebral drainage tubes, are placed in a chamber and the chamber and tubes are fluidized to 100 atm and 30°C in I-CO₂ and rotated at 100 to 500 x g in a clockwise direction for several minutes. The chamber is then stopped and acoustic energy is applied in a pulse mode (on for 20 seconds

and off for 5 seconds). During the acoustic treatment the temperate is allowed to rise above the critical temperature of 32°C or is maintained below the critical temperature using an internal refrigeration coil. The chamber is then rotated in a counter clockwise direction to remove particles and materials.

5 The process steps described above are repeated as required to completely clean the tubes. At the end of the cleaning process the rotation of the chamber is maintained while the chamber is emptied. The chamber is then stopped and the chamber is de-pressurized to ambient pressure.

10 In other cleaning applications the acoustic treatment, which heats the substrate and the process medium, can be replaced with a microwave treatment which heats only the substrate.

 In use the apparatus of the present invention draws dirty fluids away from the substrates to the perimeter of the centrifuge where they drained to a drain tank to prevent redeposition on the substrates.

15 The aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of this invention.

WHAT IS CLAIMED IS:

1. The method of removing contaminants from the surfaces of parts using dense fluids, comprising the steps of:
 - spinning the parts within an open but confining enclosure located within an enclosed volume;
 - 5 establishing a dense fluid environment within the enclosed volume;
 - subjecting the parts to fluid shear forces; and
 - varying the pressure and temperature of the dense fluid to change the phase of the dense fluid between solvent and non-solvent states.
- 10 2. The method as set forth in claim 1 above, wherein the phases are cycled between at least two of the supercritical, gas and liquid states.
3. The method as set forth in claim 2 above, wherein the cycling terminates with the liquid phase and the method includes the further steps of
15 depressurizing the enclosed volume and thereafter draining the fluid.
4. The method as set forth in claim 1 above, wherein the dense fluid is carbon dioxide and the pressure is varied in the range of about 58 to 82 atmospheres and the temperature is varied in the range of about 30° to about 100° Celsius.
20
5. The method as set forth in claim 1 above, wherein the parts are spun at a rate and radius to impart about 10 x g to about 3,000 x g.
6. The method as set forth in claim 1 above, wherein the method
25 includes the further step of impacting the parts with agitating wave energy.
7. A method of cleaning hydrocarbon materials adhering to part surfaces comprising the steps of:
 - subjecting the parts to high speed rotation within an enclosed volume;

cycling a dense fluid through solvent and non-solvent phases within the volume as the parts are rotated; and

extracting the dense fluid from the enclosed volume after contaminants have been substantially cleaned.

5

8. The method set forth in claim 7 above, wherein the axis of rotation is substantially horizontal and the rate of rotation permits tumbling of parts within the enclosed volume.

10 9. The method of removing trace contaminants from the surfaces of parts using dense fluids comprising the steps of:

subjecting the parts to fluid shear forces;

concurrently impacting the parts with wave energy; and

concurrently cycling the dense fluid through at least two different

15 fluid phases.

10. A process for removing one or more substances from a chosen substrate comprising the steps of:

20 placing said substrate containing said substances in a dense fluid centrifuge apparatus contained in a pressure vessel;

introducing a chosen dense fluid into the pressure vessel;

25 changing the composition of the chosen dense fluid between solvent state and non-solvent state by varying the temperature of dense fluid between a temperature below said critical temperature and a temperature above said critical temperature and a pressure below said critical pressure and a pressure above said critical pressure; and

uniformly rotating said substrate containing said substances in said changed dense fluid to produce centrifugal and shearing forces effective to separate the substance from the substrate.

30

11. The process as defined in claim 10 wherein said changing step includes varying said pressure from 1 atm to 300 atm.

12. The process as defined in claim 10 wherein said changing step includes varying said temperature of dense fluid from 298° to 310° Kelvin.

13. The process as defined in claim 10 wherein said uniformly rotating
5 step includes phase transition from solvent state to non-solvent state to effect separations to produce centrifugal and shearing forces within a dense fluid centrifugal chamber.

14. The process as defined in claim 10 wherein said uniformly rotating
10 step includes centrifugation speeds ranging from 100 to 2,000 revolutions per minute; and pulsing said centrifugal rotation continuously while reversing direction to provide alternative shearing angles and forces.

15

15. The process as defined in claim 10 wherein said uniformly rotating step includes centrifugal forces ranging from 5 to 3,000 x g.

16. The process as defined in claim 10 wherein said placing step includes
20 holding the substrate stationary using a centrifuge inverter assembly while the entire dense fluid is centrifuged about the substrate.

17. The process as defined in claim 10 wherein said changing step
25 includes a chosen dense fluid selected from a group consisting of nitrous oxide, carbon dioxide, xenon, sulfur hexafluoride, hydrocarbon gases and mixtures thereof.

18. The process as defined in claim 10 wherein said placing step for the substrate includes selecting the substrate from a group consisting of metallics, inorganics, organics, biomaterials, plants and animal products.

30

19. The process as defined in claim 10 wherein said placing step includes the substances chosen from a group consisting of inorganics, organics, residues, oils, ionics, non-ionics, and particles.

5 20. The process as defined in claim 10 wherein said uniformly rotating step continues for a time period varying between 5 and 120 minutes for substance separation from the substrate.

10 21. The process as defined in claim 10 wherein said changing step includes adding gas modifiers to the chosen dense fluid consisting of one or more substances selected from the group of alcohols, terpenes, surfactants, detergents and oils.

15 22. The process as defined in claim 10 wherein said uniformly rotating step includes introducing adjunct energizing processes in combination with dense fluid centrifugation to enhance substance separation which processes include acoustics, microwaves, and electrostatics.

20 23. The process as defined in claim 10 wherein said changing step includes maintaining a temperature of between 30° and 100°C and a pressure of between 1×10^{-2} and 1×10^{-4} Torr used in combination with centrifugation as a post treatment thermal vacuum cleaning process for enhancing the separation of substances from polymeric or porous substances and as a precision cleaning post-treatment.

25

24. A dense fluid centrifugal separation apparatus for removing contaminating substances from a particular substrate, the combination comprising:
a pressure vessel;
a dense fluid centrifuge within said pressure vessel;
30 a dense fluid contained within said dense fluid centrifuge;
means for changing the composition of said dense fluid between a solvent state and a non-solvent state;

said changing means including means for varying the temperature of said dense fluid between a temperature below a critical temperature and a temperature above said critical temperature and for varying pressure below a critical pressure and a pressure above said critical pressure; and

5 rotating means within said dense fluid centrifuge supporting the substrate in said dense fluid for generating centrifugal and shearing forces to produce separation of the substances from the substrate.

25. A cleaning system for contaminated parts comprising:
10 means defining a boundary establishing a partially penetrable part containing opening;
a stationary housing encompassing the boundary barrier to define circumferential space therebetween;
means for introducing a dense fluid into the interior of the housing;
15 flow interrupting means disposed about the boundary barrier within the circumferential space; and
means coupled to the boundary barrier through the housing for rotating the boundary barrier and parts contained therein.

20 26. A cleaning system as set forth in claim 25 above, further including means coupled to the housing for varying the dense fluid pressure, and means coupled to the housing for varying the dense fluid temperature.

27. A cleaning system as set forth in claim 25 above, further including
25 means for injecting wave energy into the housing interior and boundary barrier to impinge on the parts.

28. A cleaning system as set forth in claim 25 above, wherein the means for rotating the boundary barrier and parts is bidirectional.

30

29. A cleaning system as set forth in claim 25 above, wherein the system further includes coupling means between the boundary barrier and means for

rotating that is disengageable from the boundary barrier to allow removal of the boundary barrier and contained parts.

30. A cleaning system as set forth in claim 25 above, further including
5 mounting means coupled to support the housing, and comprising means for orienting the housing about substantially orthogonal axes.

31. Apparatus for cleaning parts having surface oils, using dense fluids, the apparatus comprising:

10 a parts cage substantially concentric about a central axis, the parts cage having apertures therein sized to retain parts in the interior;

a housing encompassing the parts cage and defining an enclosed volume, the housing being substantially concentric with the central axis and being spaced from the outer periphery of the parts cage;

15 disengageable coupling means in the housing along the central axis for supporting and rotating the parts cage;

drive means exterior to the housing and coupled to the coupling means for rotating the parts cage within the housing;

20 means for introducing dense fluid into the enclosed volume;

means coupled to the housing for changing the phase of the dense fluid therein; and

means disposed between the parts cage and the housing for impeding circumferential dense fluid flow as the parts cage is rotated.

25 32. A process for removing a contaminant from a substrate comprising: placing the substrate in a dense fluid centrifuge;

rotating the substrate within the dense fluid centrifuge;

contacting the rotating substrate with a dense fluid;

30 altering a variable parameter wherein the variable parameters are selected from the group consisting of density of the dense fluid, centrifugal force, vortex action of the dense fluid, shear action of the dense fluid, chemistry of the dense fluid and combinations thereof;

removing the dense fluid from the dense fluid centrifuge; and
stopping rotation of the substrate.

33. The process recited in claim 32 wherein the direction of rotation of
5 the substrate is selected from the group consisting of clockwise, counter clockwise,
alternate clockwise and counter clockwise and alternate counter clockwise and
clockwise.

34. The process recited in claim 32 wherein the contaminants to be
10 removed from the substrate are selected from the group consisting of particles of 20
microns and less in size, insoluble residues, oils, stains, waxes, photoresist, drawing
compounds and combinations thereof.

35. The process recited in claim 32 wherein the speed at which the
15 substrates are rotated is varied between about 500 and 800 rpm.

36. The process recited in claim 32 further comprising subjecting the
substrate, which is in contact with the dense fluid, with an external energy source
selected from the group consisting of microwave energy, acoustic energy and
20 electrostatic energy.

37. The process recited in claim 32 wherein the variable parameters are
varied by changing an input selected from the group consisting of temperature of the
dense fluid, pressure of the dense fluid, the direction of centrifugation and
25 combination thereof.

38. The process recited in claim 32 further comprising collecting the
dense fluid removed from the dense fluid centrifuge.

30 39. The process recited in claim 32 wherein the dense fluid is selected
from the group consisting of carbon dioxide, ionic surfactants, non-ionic surfactants,

chelating agents, precipitating agents, ozone, nitrous oxide, xenon, sulfur hexafluoride, hydrocarbon gases and combinations thereof.

40. The process recited in claim 32 further comprising pretreating the
5 substrate, *in situ*, with a cleaning agent prior to contacting the substrate with the dense fluid.

41. The process recited in claim 32 further comprising posttreating the substrate, *in situ*, with a coating after removal of the dense fluid.

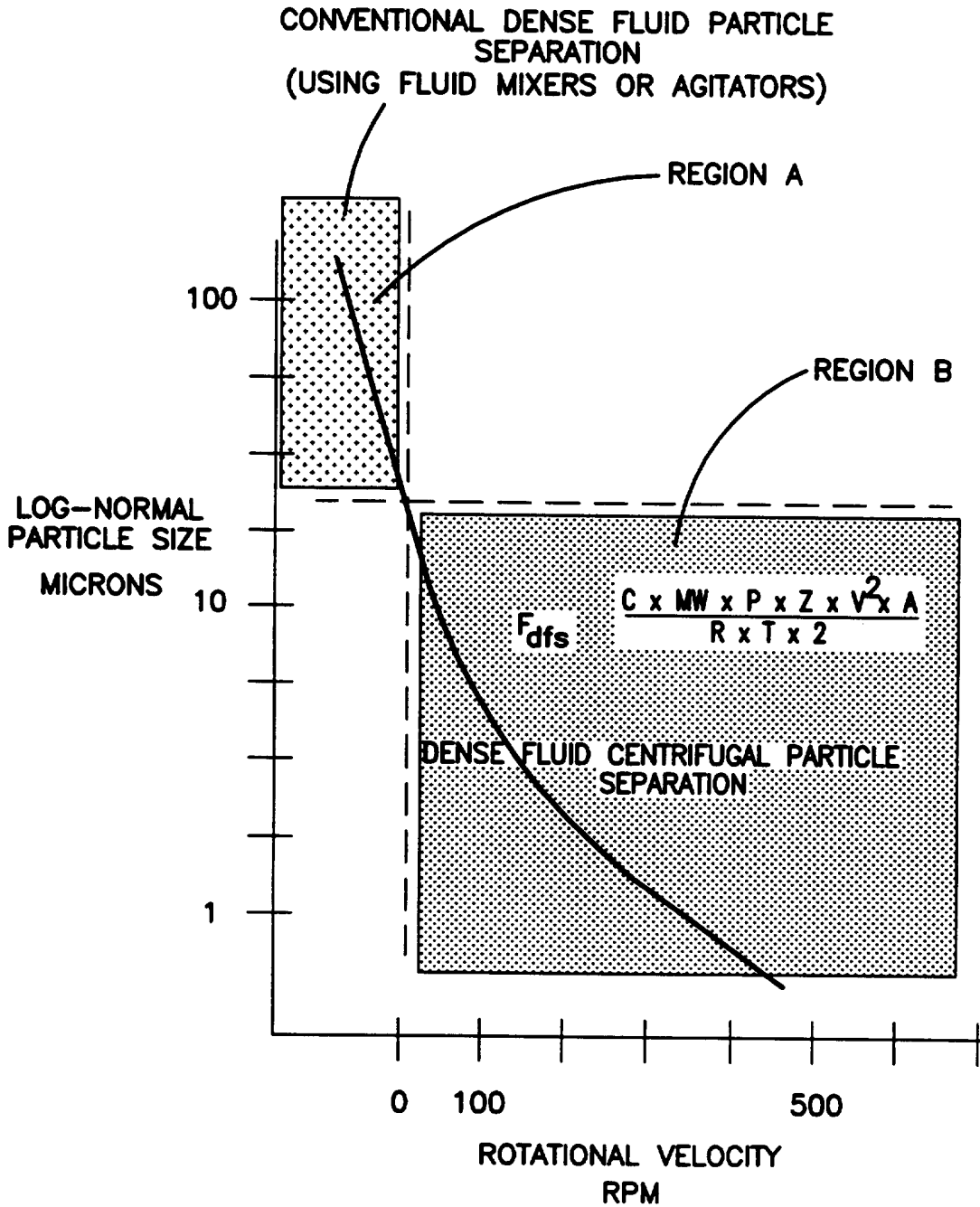


FIG. 1

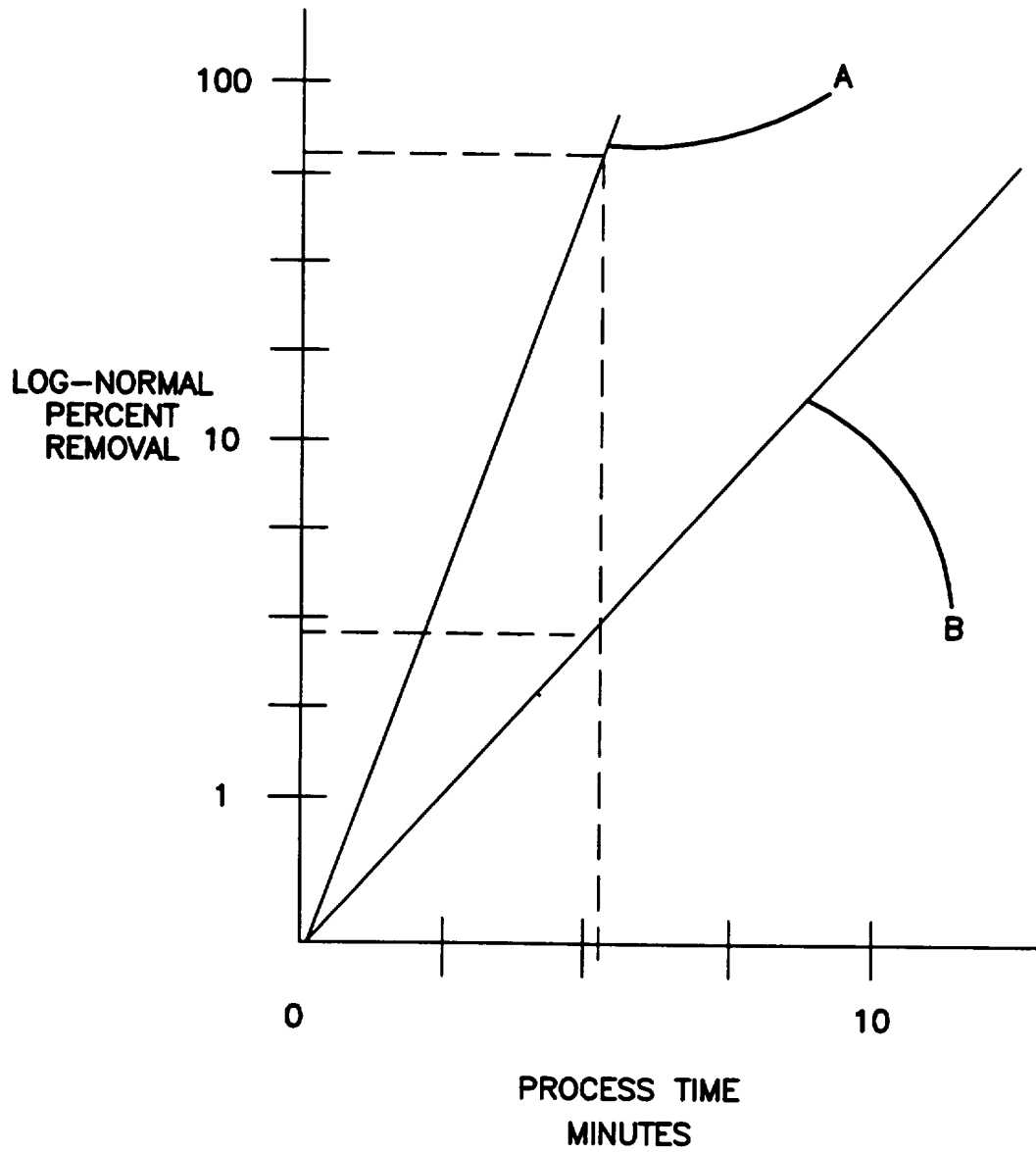


FIG. 2

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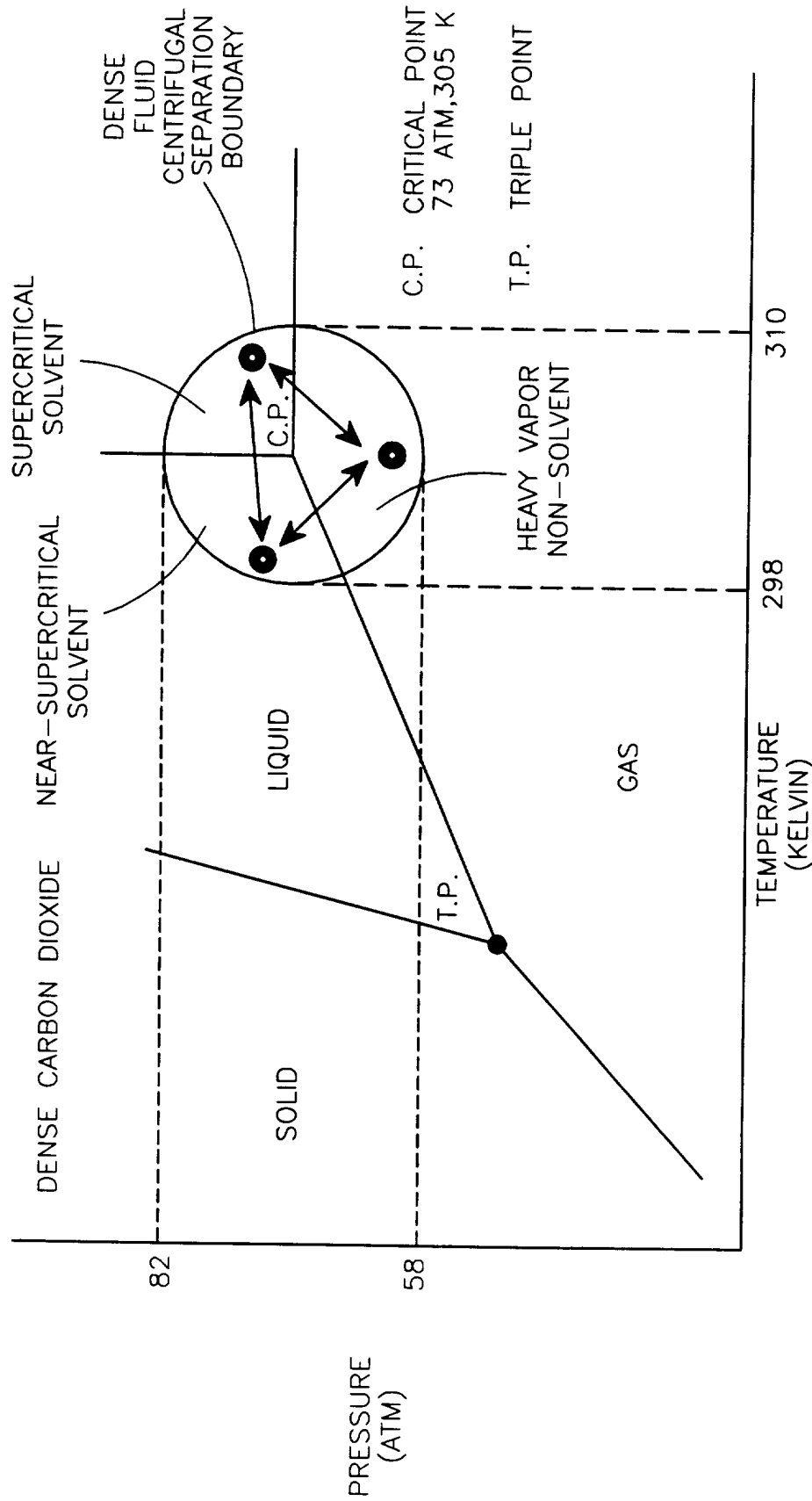
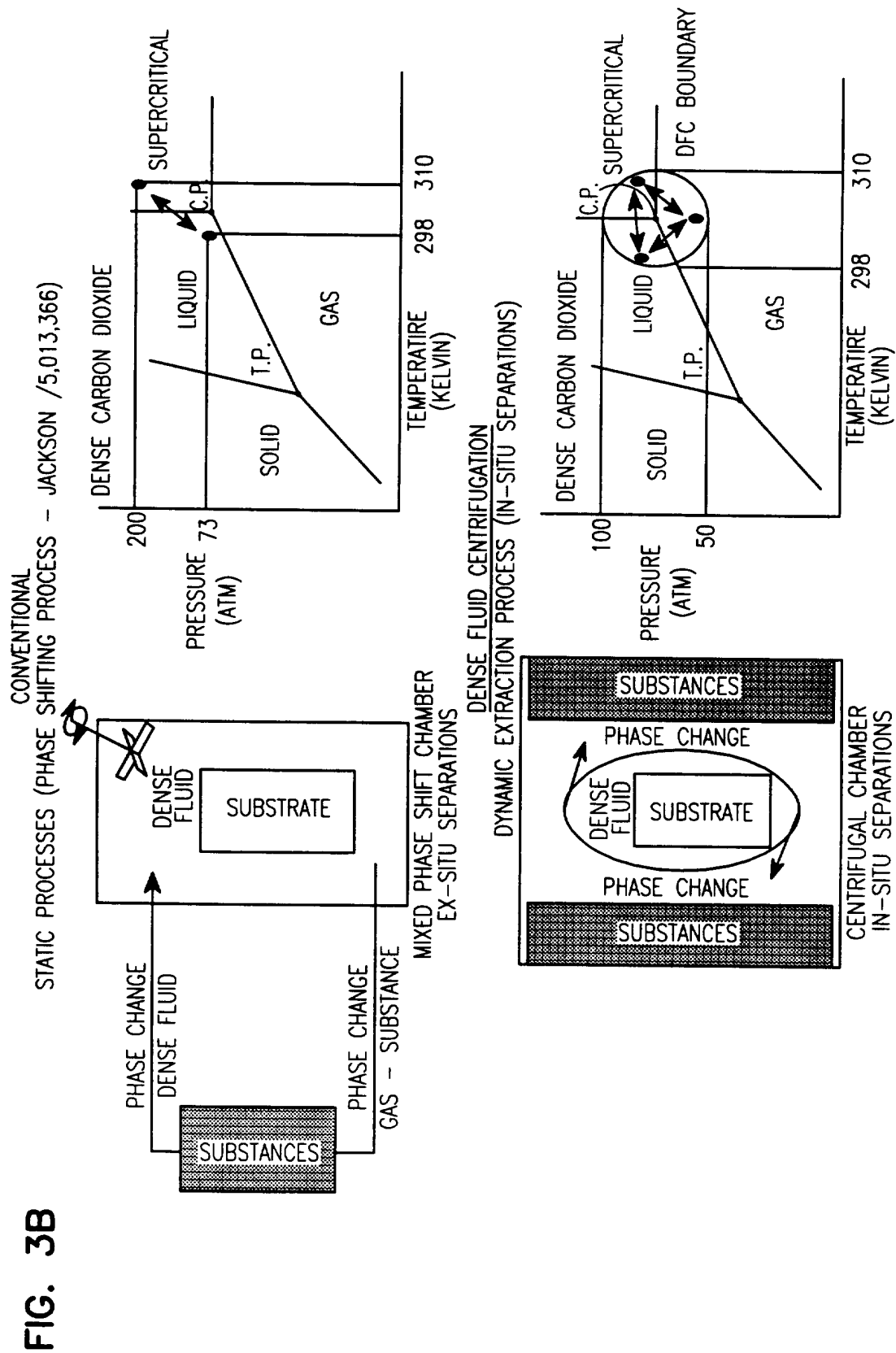


FIG. 3A



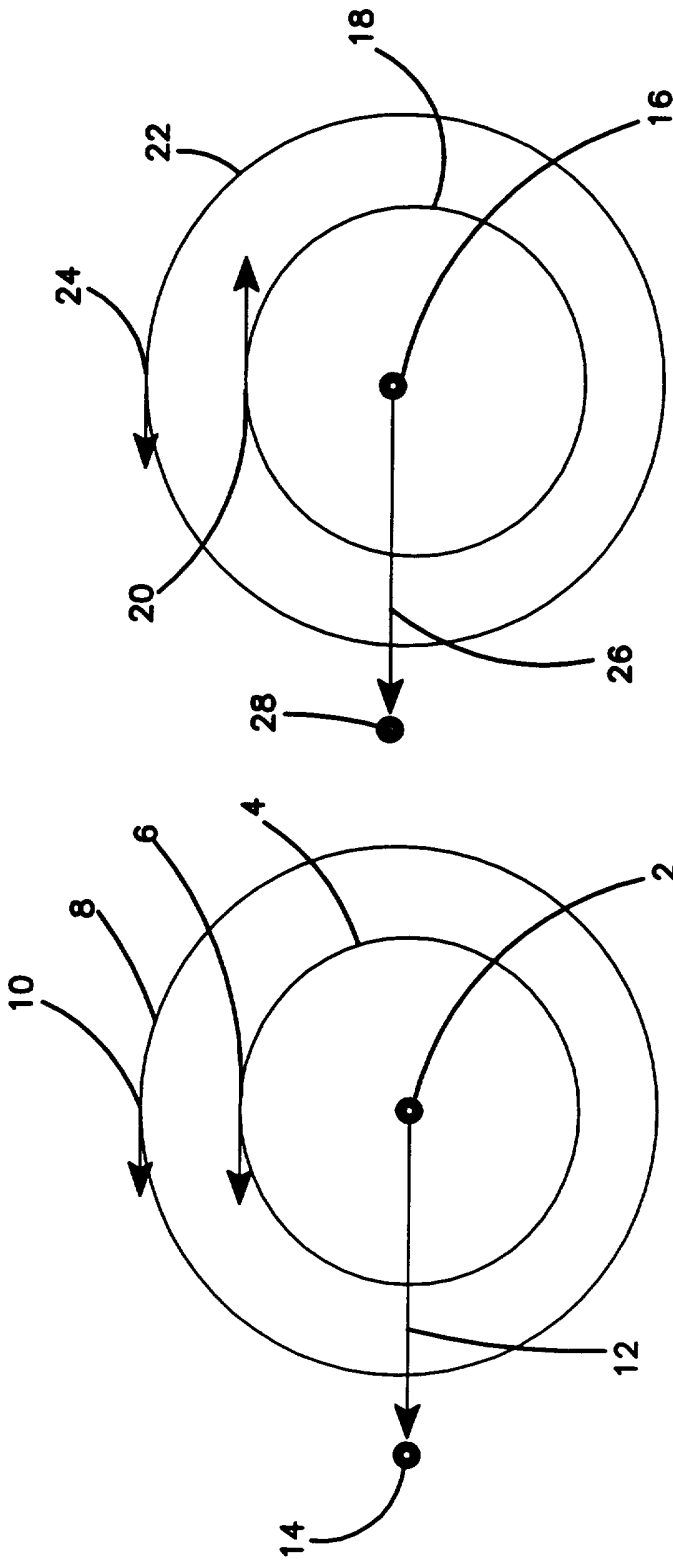


FIG. 4B

FIG. 4A

FIG. 5A
CONVENTIONAL CENTRIFUGAL SEPARATION

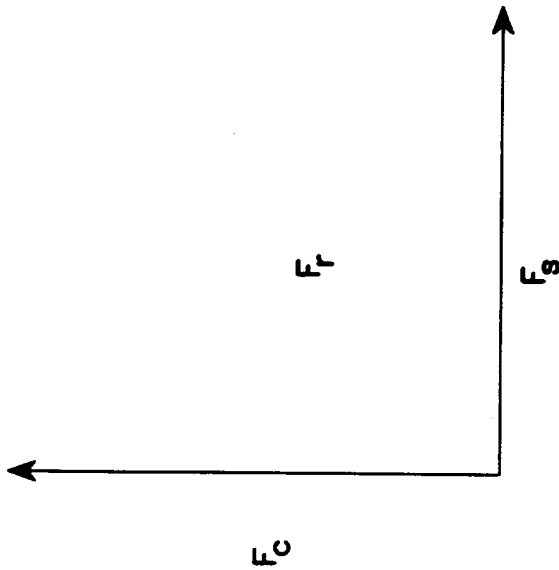
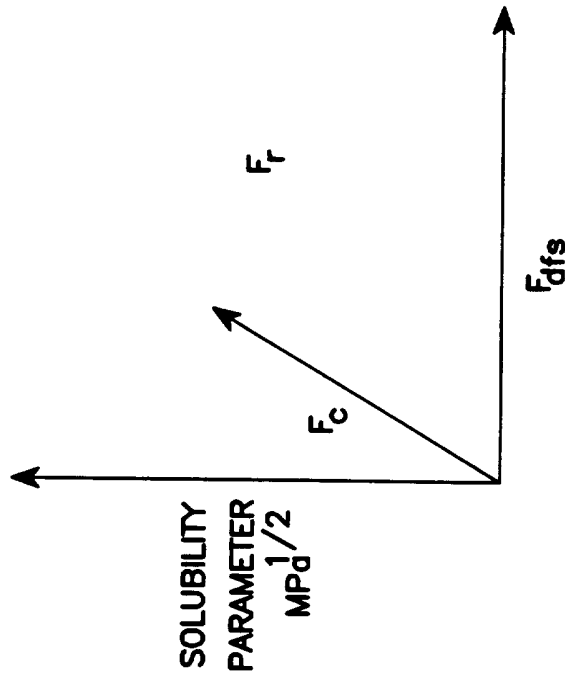


FIG. 5B
DENSE FLUID CENTRIFUGAL SEPARATION



- F_r SEPARATION ENERGY PARAMETER (RESULTANT OF EITHER 2 OR 3 DIMENSIONAL ENERGY PARAMETERS)
- F_c CENTRIFUGAL ENERGY PARAMETER
- F_s SHEARING ENERGY PARAMETER
- F_{dfs} DENSE FLUID SHEARING PARAMETER

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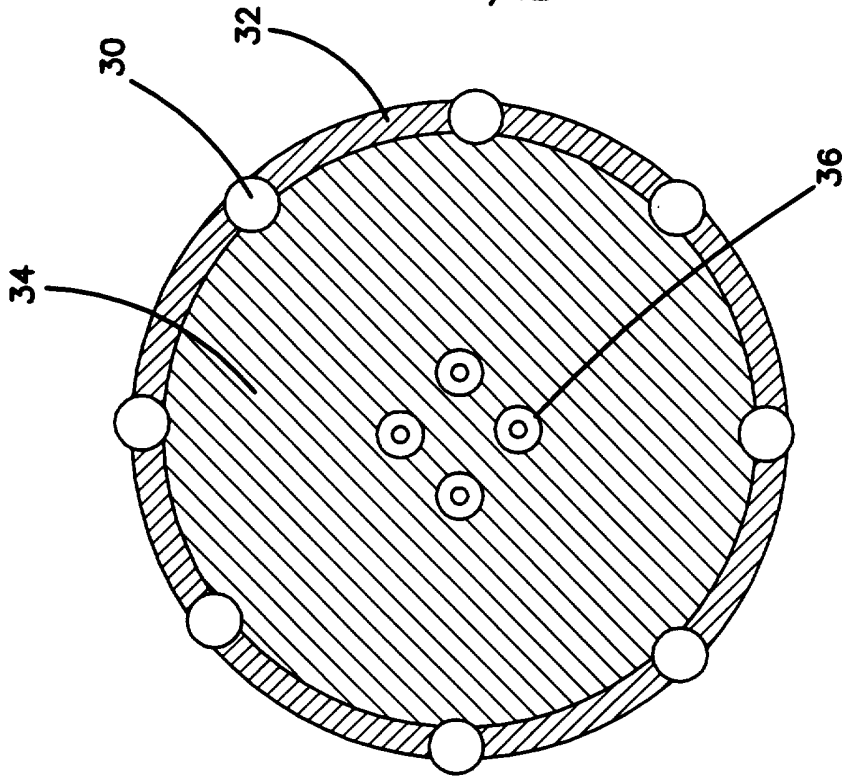


FIG. 6B

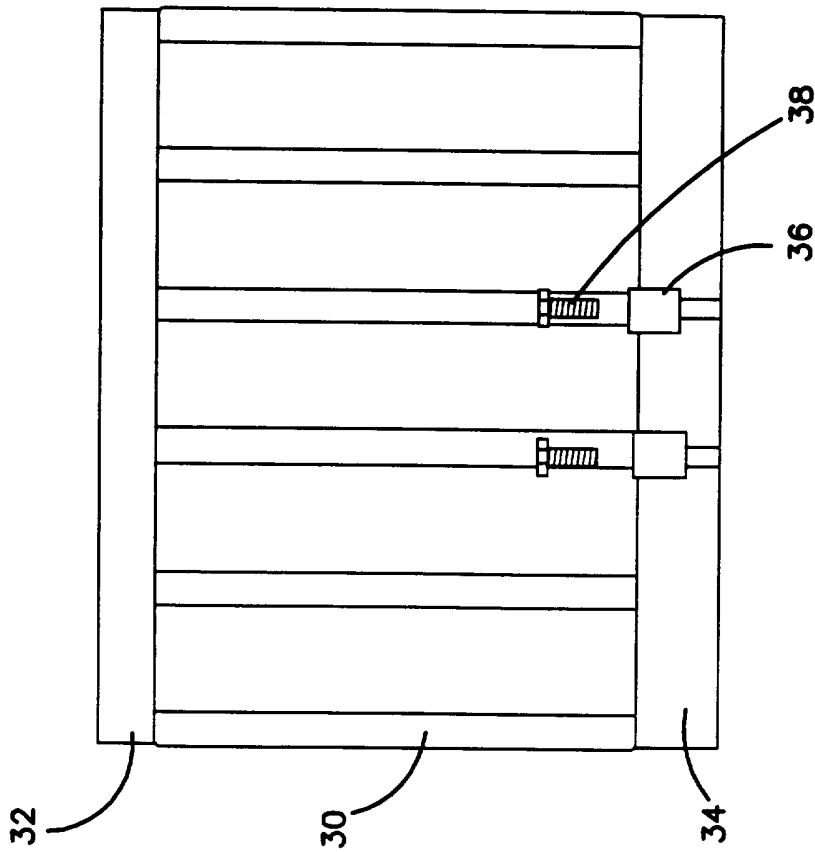


FIG. 6A

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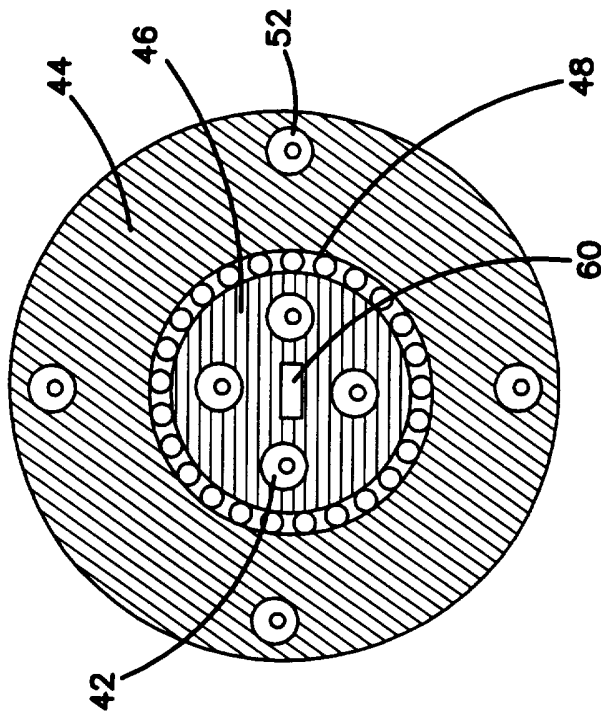


FIG. 6E



FIG. 6F

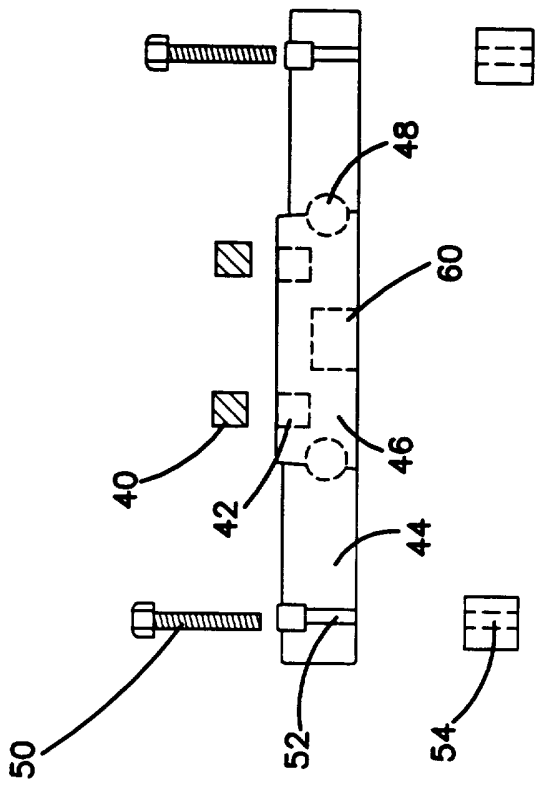


FIG. 6C

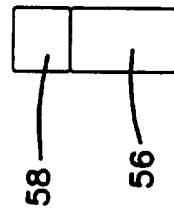


FIG. 6D

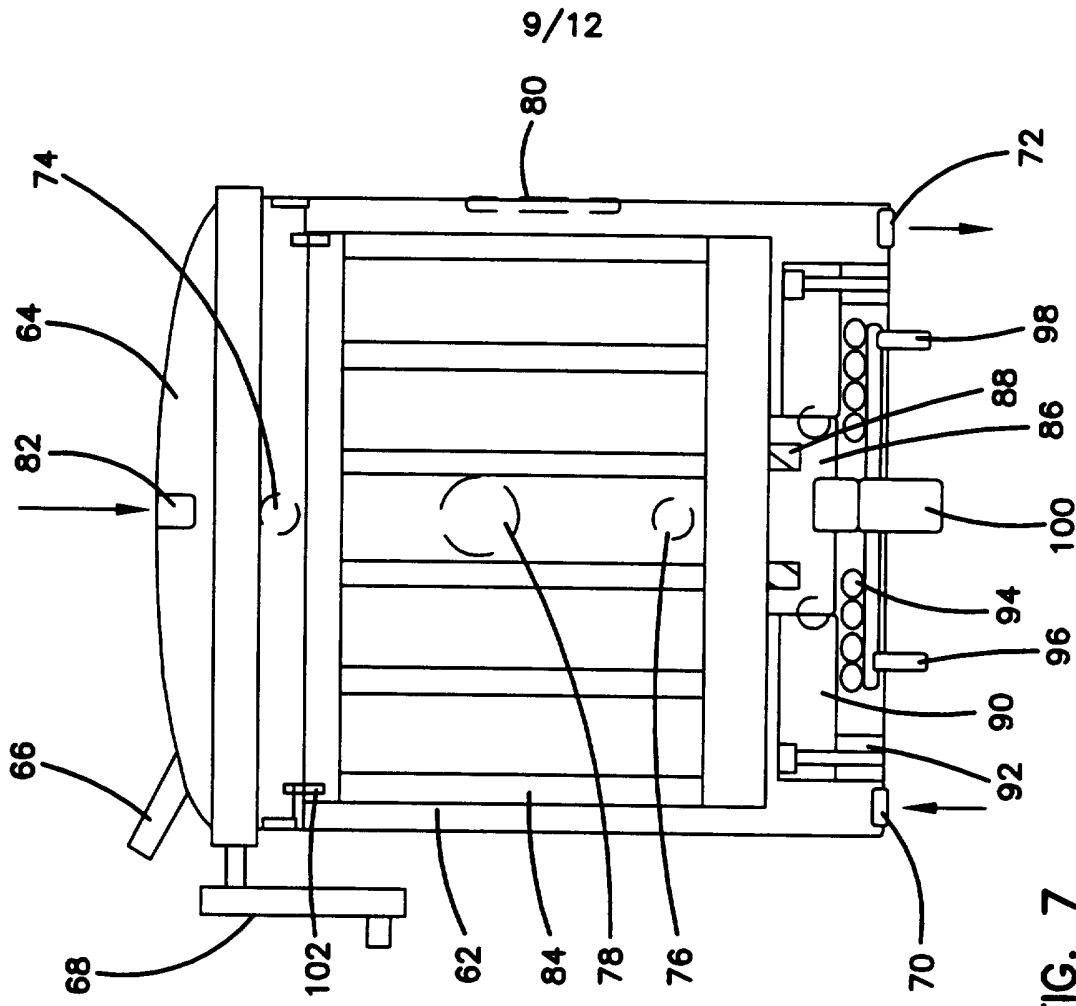
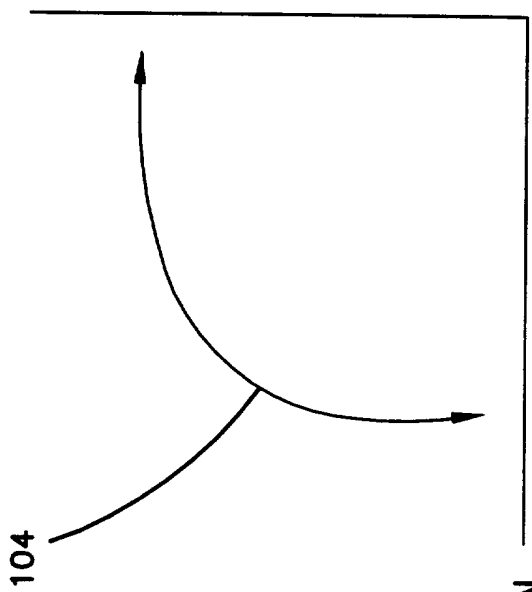


FIG. 7

VERTICAL



HORIZONTAL

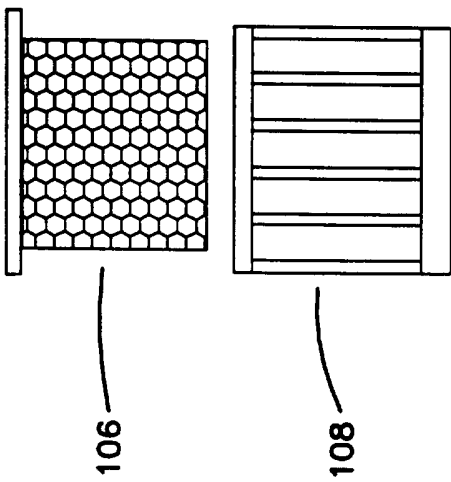


FIG. 8A

INVERTER INSERTION

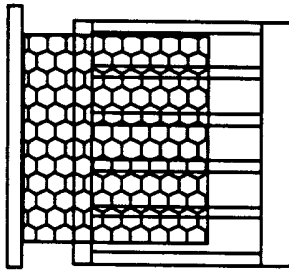


FIG. 8B

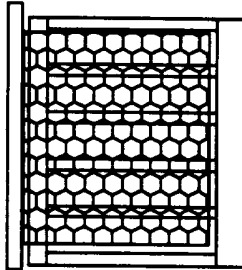
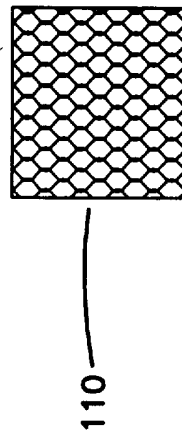


FIG. 8C



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FIG. 8D

BASKET INSERTION

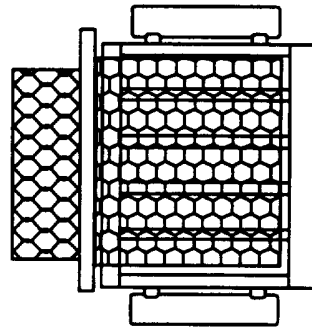


FIG. 8E

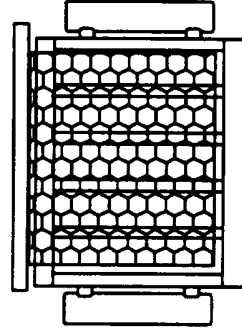
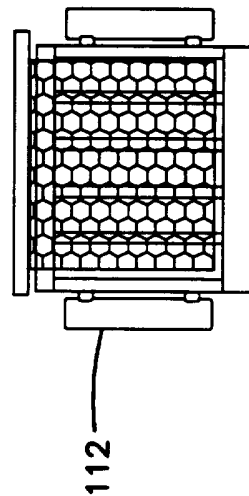


FIG. 8F



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FIG. 8D

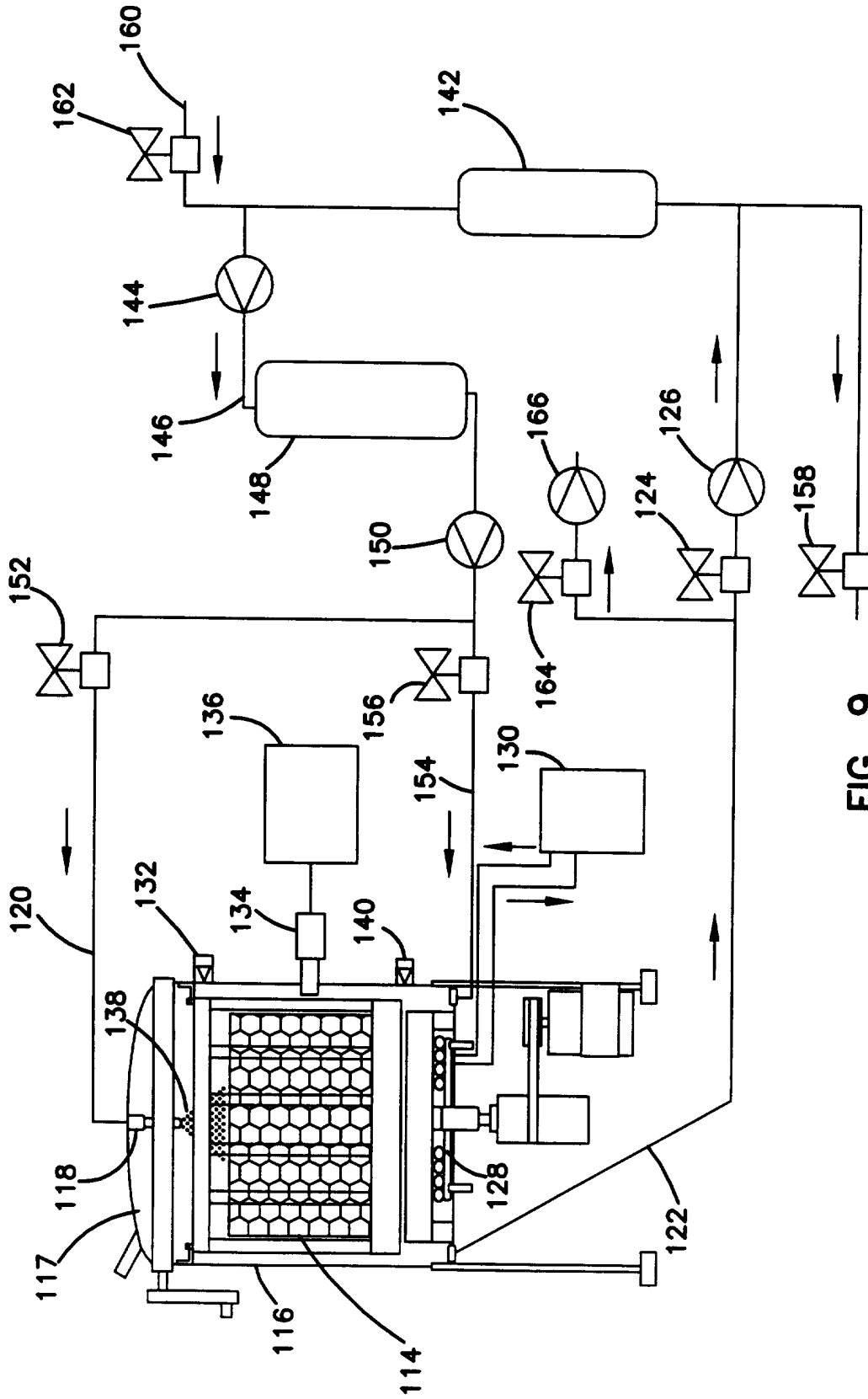


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00048

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :B08B 3/10
US CL :134/105
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 134/105, 153, 148, 198, 111, 162

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,158,100 (TANAKA ET AL.) 27 OCTOBER 1992, see entire document.	1-41
A	US, A, 5,224,503 (THOMPSON ET AL.) 06 JULY 1993, see entire document.	1-41
A	US, A, 5,273,589 (GRISWOLD ET AL.) 28 DECEMBER 1993, see entire document.	1-41
Y	US, A, 5,355,901 (MIELNIK ET AL.) 18 OCTOBER 1994, see entire document.	1-41
Y	US, A, 5,377,708 (BERGMAN ET AL.) 03 JANUARY 1995, see entire document.	1-41
A,P	US, A, 5,456,758 (MENON) 10 OCTOBER 1995, see entire document.	1-41

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search: 13 MAY 1996
Date of mailing of the international search report: 23 MAY 1996

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Facsimile No. (703) 305-3464
Authorized officer: FRANKIE L. STINSON (with signature) for
Telephone No. (703) 308-0861

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00048

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,E	US, A, 5,496,506 (SATO) 05 MARCH 1996, see entire document.	1-41