US 20140237783A1

(19) **United States**

(12) **Patent Application Publication**

(10) **Pub. No.: US 2014/0237783 A1**

(43) **Pub. Date: Aug. 28, 2014**

**Madsen**

(54) **APPLICATION AND ACTIVATION OF DURABLE WATER REPELLANT USING A DENSIFIED FLUID**

(71) Applicant: **CO2Nexus, Inc.**, Denver, CO (US)

(72) Inventor: **Stephen Whitney Madsen**, Arvada, CO (US)

(73) Assignee: **CO2Nexus, Inc.**, Denver, CO (US)

(21) Appl. No.: **14/192,545**

(22) Filed: **Feb. 27, 2014**

**Related U.S. Application Data**

(60) Provisional application No. 61/770,964, filed on Feb. 28, 2013.

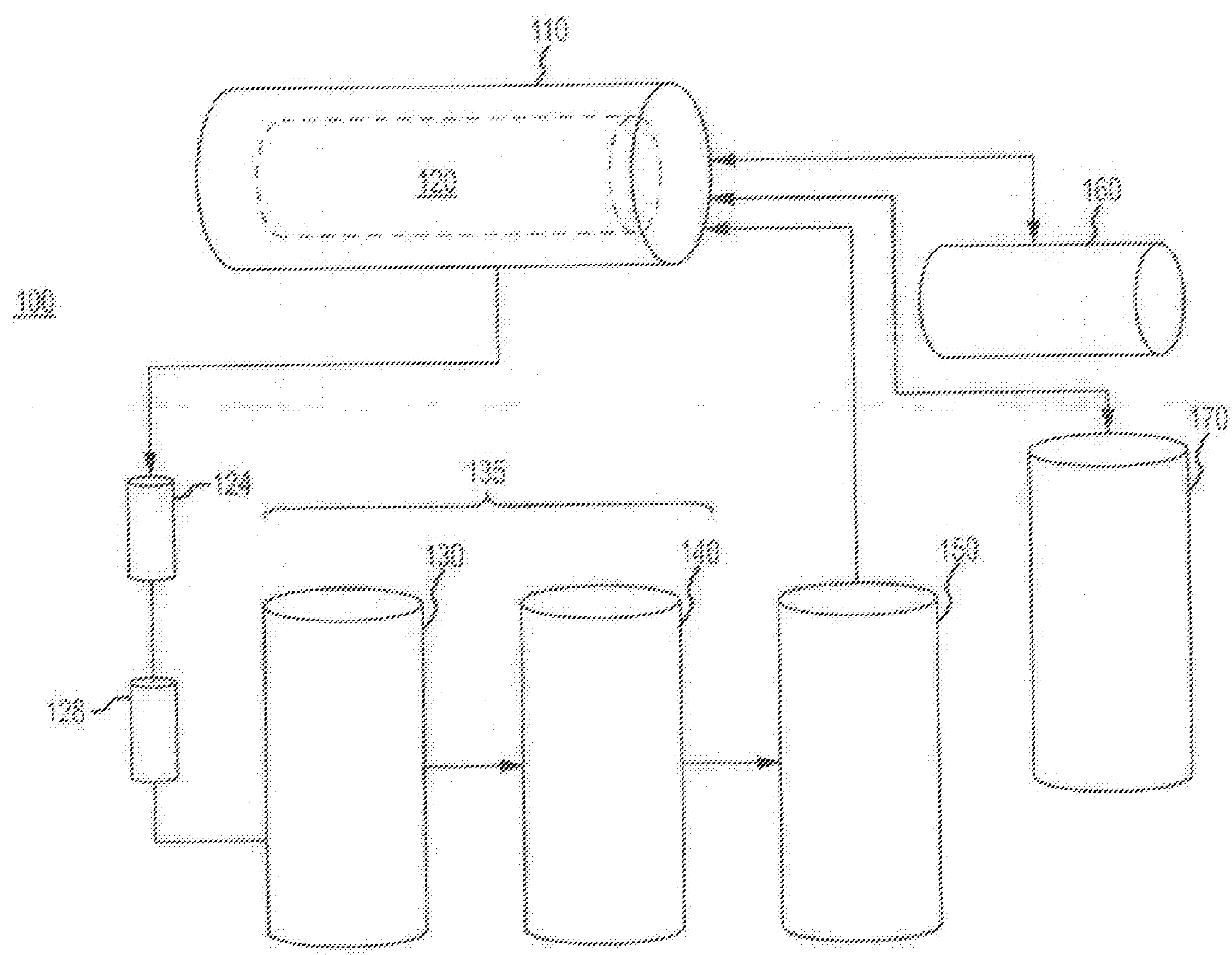
**Publication Classification**

(51) **Int. Cl.**
***D06C 29/00*** (2006.01)

(52) **U.S. Cl.**
CPC .................................... ***D06C 29/00*** (2013.01)
USPC .................................... **28/167**

(57) **ABSTRACT**

A pressurized system using densified fluid can apply and/or activate durable water repellant. Durable water repellant bound to fibers of an article of clothing can be activated by first removing contaminants via a pressurized densified fluid cleaning process and thereafter imputing energy into the durable water repellant via the article's interaction with the densified fluid and its gaseous rinse cycle.



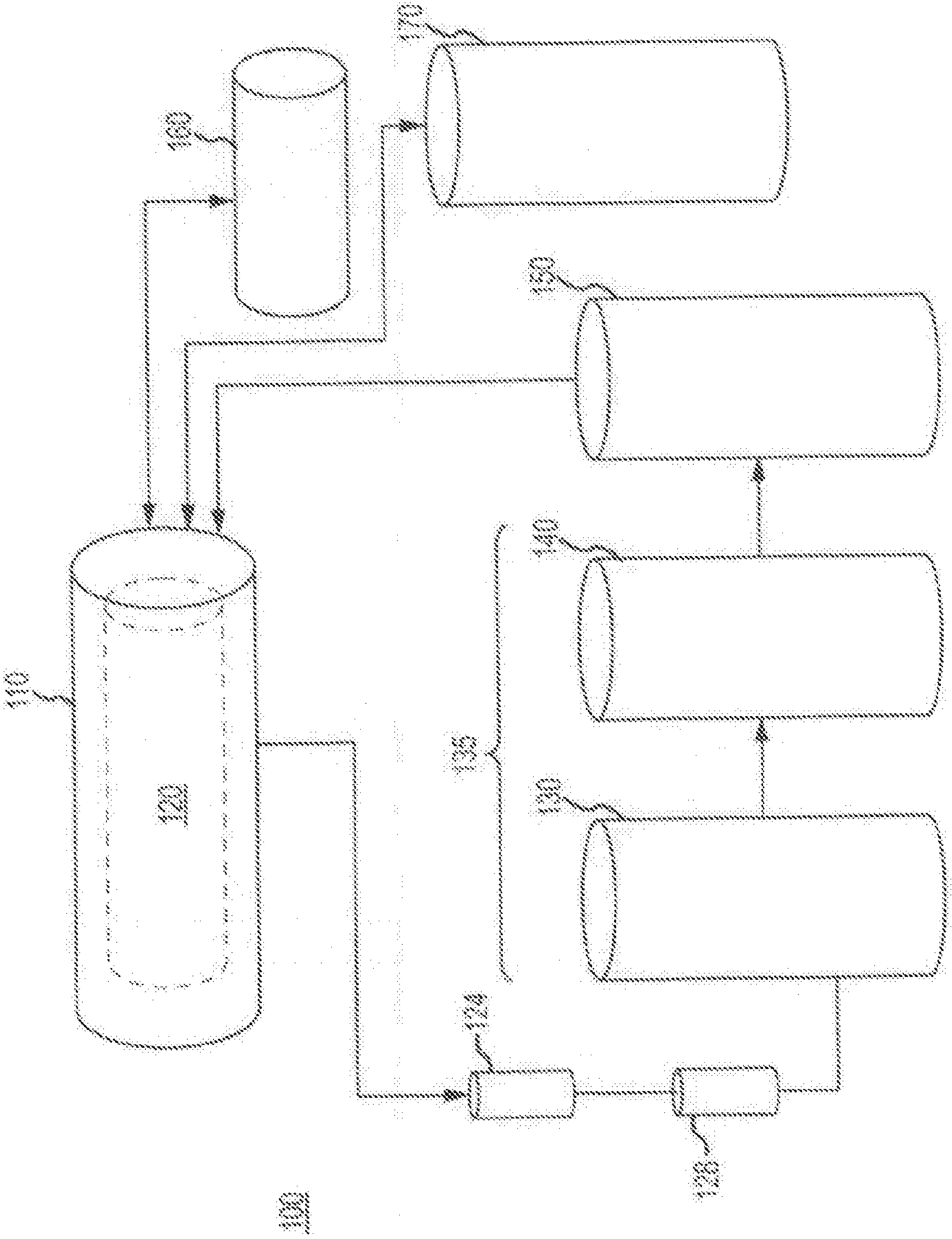
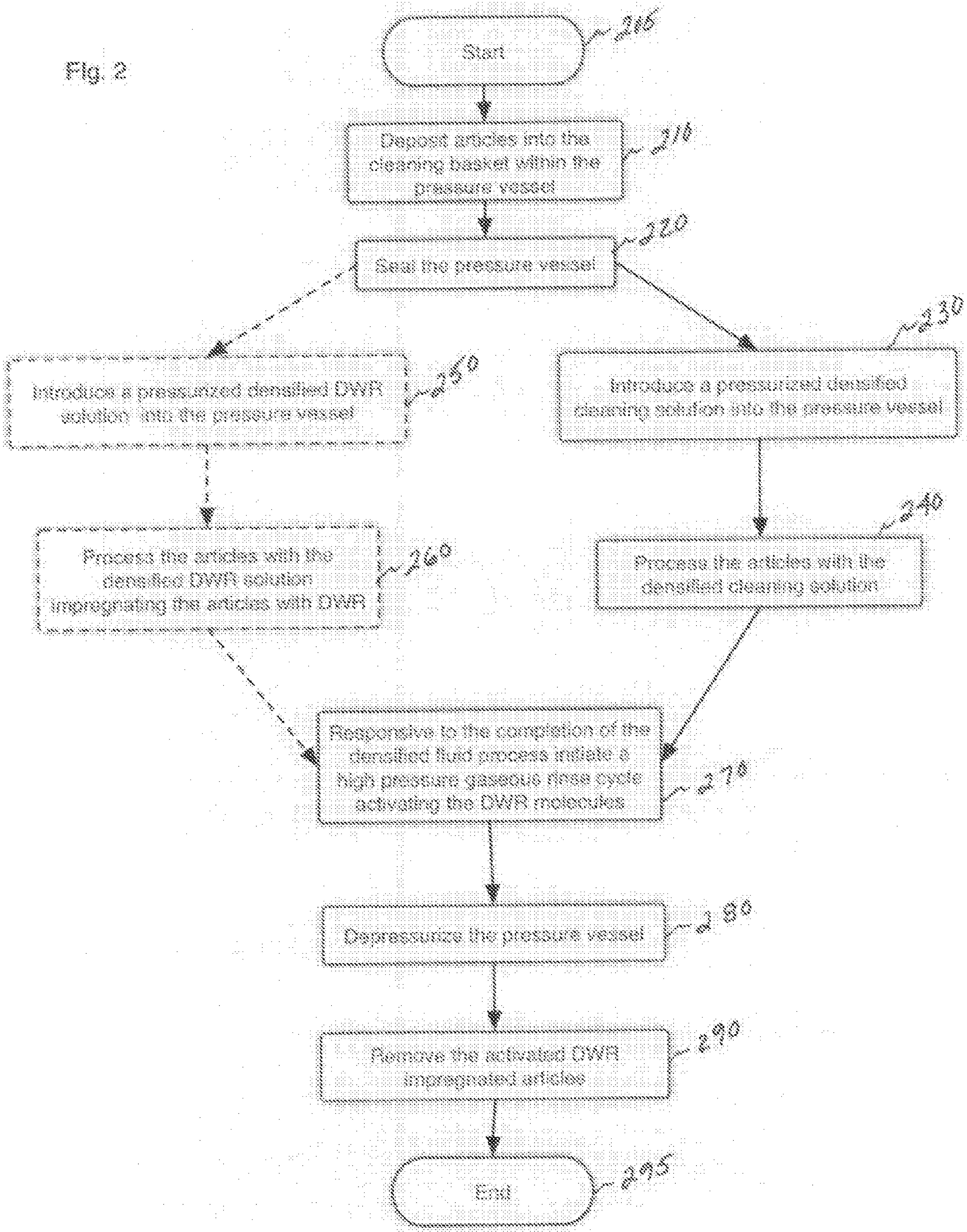



FIG. 1

Fig. 2


Start
200
Deposit articles into the cleaning basket within the pressure vessel
210
Seal the pressure vessel
220
Introduce a pressurized densified DWR solution into the pressure vessel
250
Introduce a pressurized densified cleaning solution into the pressure vessel
230
Process the articles with the densified DWR solution impregnating the articles with DWR
260
Process the articles with the densified cleaning solution
240
Responsive to the completion of the densified fluid process initiate a high pressure gaseous rinse cycle activating the DWR molecules
270
Depressurize the pressure vessel
280
Remove the activated DWR impregnated articles
290
End
295

# APPLICATION AND ACTIVATION OF DURABLE WATER REPELLANT USING A DENSIFIED FLUID

## RELATED APPLICATION

[0001] The present application relates to and claims the benefit of priority to U.S. Provisional Patent Application No. 61/770964 filed 28 Feb. 2013 which is hereby incorporated by reference in its entirety for all purposes as if fully set forth herein.

## BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] Embodiments of the present invention relate, in general, to durable water repellant and more particularly to the application and/or activation of durable water repellant using densified carbon dioxide.

[0004] 2. Relevant Background

[0005] Durable Water Repellent (DWR) is a coating added to fabrics to make them water-resistant (or hydrophobic). The hydrophobic effect is an observed tendency of nonpolar substances to aggregate in an aqueous solution and exclude water molecules. A nonpolar substance possesses an equal sharing of electrons between the two atoms of a diatomic molecule because of the symmetrical arrangement of the electrons. The name hydrophobic, literally meaning "water-fearing," describes the segregation and apparent repulsion between water and nonpolar substances. The hydrophobic effect explains the separation of a mixture of oil and water into its two components, and the beading of water on nonpolar surfaces such as waxy leaves.

[0006] The hydrophobic interaction is mostly an entropic effect originating from the disruption of highly dynamic hydrogen bonds between molecules of liquid water by the nonpolar solute. A hydrocarbon chain or a similar nonpolar region of a big molecule is incapable of forming hydrogen bonds with water and accordingly the introduction of such a non-hydrogen bonding surface into water causes disruption of the hydrogen bonding network between water molecules. In DWR the hydrogen bonds are reoriented tangential to a surface to minimize disruption of the hydrogen bonded 3D network of water molecules and thus creates a water "cage" around the nonpolar surface. The water molecules that form the "cage" (or solvation shell) have restricted mobility. By aggregating such molecules together, nonpolar molecules reduce the surface area exposed to water and minimize their disruptive effect. Thus water cohesion is enhanced.

[0007] The hydrophobic effect can also be quantified by measuring the partition coefficients of non-polar molecules between water and non-polar solvents. The partition coefficients can be transformed to a free energy transfer that includes enthalpic and entropic components. Recall that enthalpy is the measure of total energy of a thermodynamic system while entropy is a measure of disorder or the number of ways that a system may be arranged. The hydrophobic effect is entropy-driven at room temperature because of the reduced mobility of water molecules in the solvation shell of the non-polar solute. However, the enthalpic component of transfer energy is favorable, meaning there is a strengthening of water-water hydrogen bonds in the solvation shell, apparently due to the reduced mobility of water molecules. A solvation shell is a shell of any chemical species that acts as a solvent and surrounds a solute species. When the solvent is water it is often referred to as a hydration shell or hydration sphere. At the higher temperature, when water molecules became more mobile, this energy gain decreases, but so does the entropic component. As a result of such entropy-enthalpy compensation, the hydrophobic effect (as measured by the free energy of transfer) is only weakly temperature-dependent and becomes smaller at a lower temperature.

[0008] Historically, DWR containing long perfluoroalkyl chains have been the chemistry of choice for textile applications. Perfluorinated chemicals are used to incorporate raw materials containing a perfluoroalkyl chain into acrylic or urethane polymer that are used as DWR finishes. The unique water and oil repellency properties of a DWR finish is derived from the perfluoroalkyl chain that is attached to the acrylic or urethane polymer backbone. Most factory-applied treatments of DWR are thus fluoropolymer based. A fluoropolymer is a fluorocarbon-based polymer with multiple strong carbon-fluorine bonds. Fluoropolymers share the properties of fluorocarbons in that they are not as susceptible to the van der Waals force as hydrocarbons. This contributes to their non-stick and friction reducing properties. Also, they are stable due to the stability multiple carbon-fluorine bonds add to a chemical compound. Fluoropolymers may be mechanically characterized as thermosets or thermoplastics. Fluoropolymers can be homopolymers or copolymers and are characterized by a high resistance to solvents, acids, and bases. While the present invention below is described with respect to DWR treatments in general and more specifically toward the use of fluoropolymers, one of reasonable skill in the art will recognize that the innovative techniques and associated apparatus described below are equally applicable to other types of fluorochemicals including perfluorooctane sulfonate (PFOS) and perfluorooctane acid (PFOA). Moreover, the present invention is equally applicable to short chained fluorinated DWR chemistries.

[0009] Silicon is another chemical structure often associated with water repellants. Silicone water repellents or waterproofing agents generally come in two forms. Elastomeric polydimethylsiloxanes describe elastomeric coatings that adhere to a substrate and cure to form a flexible, protective membrane. Penetrating water-repellent chemicals describe reactive silanes and siloxane resins with crosslinkable side chains. These materials have smaller molecular structures, which enable them to penetrate deeply into a substrate with which they chemically bond.

[0010] Silicones have low surface tension, which enables them to spread and soak easily into a substrate's pores. Their highly flexible and mobile siloxane backbone enables the water-repelling methyl groups to orient themselves toward the surface, creating a waterproof "umbrella" similar to fluorine based compounds. Water repellents such as DWR are commonly used in conjunction with waterproof breathable fabrics to prevent the outer layer of fabric from becoming saturated with water. This saturation, called "wetting out," can reduce the garment's breathability (moisture transport through the breathable membrane) and let water through. Without DWR, even a waterproof jacket's exterior would become waterlogged and heavy with the damp fabric sagging and clinging to the wearer. Moreover, DWR does not inhibit breathability since DWR does not "coat" the surface, but rather bonds to the textile fibers leaving the space between the fibers intact.

[0011] Prior methods for factory application of DWR treatments involve applying a solution of a chemical onto the surface of the fabric by spraying or dipping. More recently the chemistry is applied in the vapor phase using Chemical Vapor Deposition (CVD) machinery. Later advances have eliminated per-fluorinated acids, considered to be potentially hazardous to human health by the US Environmental Protection Agency, from the application process.

**[0012]** Durable Water Repellent (DWR) coatings are ubiquitous in many markets; e.g. outdoors apparel, gear, tents, etc. Typically these coatings are applied to a textile or fabric substrate, which then becomes part of a finished product such as a jacket or parka, sleeping bag, footwear or tent, to name just a few examples. At the industrial level, when the fabric or textile is treated, DWR agents are applied via a "wet" chemistry process, and then "activated" or "energized" via heat, again via an industrial process. The "activated" DWR treated fabric then becomes incorporated into a downstream-finished product (e.g. a parka).

**[0013]** There are several problems associated with DWR agents and with the process via which they are applied, "activated," "re-applied", and "re-activated." The first problem is that the fluorocarbons present in DWR are bio-accumulative (i.e. they enter and remain in the bloodstream of those exposed), and they do not degrade in the natural environment. Thus the two main DWR's currently used are considered "likely carcinogens" by the EPA.

**[0014]** Additionally, the process via which they are applied is energy, time and chemically intensive, and creates a problematic secondary waste stream. Moreover, DWR coatings easily degraded, such that after repeated use of a DWR-treated item (e.g. a jacket), and/or several wash and wear cycles, the DWR coating becomes increasingly "de-activated." The usual mechanisms for this de-activation are oils, dirt, and particles that accumulate and interfere with the actual DWR repellency properties at a molecular level. The resulting effect is that water repellency is lessened, which affects marketability, customer satisfaction, and can impact product warranties and/or costs.

**[0015]** There are home-based methods for "re-activating" and "re-coating" finished apparel with a DWR agent, however these suffer from poor performance, poor reliability and involve long, labor and energy intensive steps necessary to "energize" the newly applied DWR, and/or "re-activate" the previously existing DWR. Accordingly, there is a need to provide a means by which to efficiently and effectively restore the DWR properties in DWR treated materials. These and other deficiencies of the prior are addressed by one or more embodiments of the present invention.

**[0016]** Additional advantages and novel features of this invention shall be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following specification or may be learned by the practice of the invention. The advantages of the invention may be realized and attained by means of the instrumentalities, combinations, compositions, and methods particularly pointed out in the appended claims.

## SUMMARY OF THE INVENTION

**[0017]** A system and associated methodology for the application and/or activation of a durable water repellant is hereafter described. One method embodiment for activating durable water repellency includes, depositing within a pressure vessel an article having one or more fibers, wherein the one or more fibers of the article are bound with a durable water repellant. Thereafter the article is processed with a densified fluid to remove contaminants. With the article clean the process continues by energizing the durable water repellant bound to the one or more fibers of the article.

**[0018]** Similarly, durable water repellant can be applied to an article having one or more fibers by depositing it within a pressure vessel and then processing the article with a densified fluid to remove contaminants. In this case, the densified fluid includes durable water repellant in solution that binds to the fibers of the article. Once bound to the fibers the durable water repellant is energized by, in one embodiment, subjecting the article to a high-pressure gaseous rinse cycle.

**[0019]** The present invention further includes, according to another embodiment, a system to activate durable water repellent. Such a system can include a pressure vessel operable to hold a densified fluid at hyper-atmospheric pressure, a storage tank fluidly coupled to the pressure vessel for storing the densified fluid and a distillation system fluidly coupled to the pressure vessel and the storage tank. The distillation system is operable to remove suspended and dissolved contaminants from the densified fluid. Lastly, the system includes an article having one or more fibers in which the fibers of the article are bound with durable water repellant. The interaction between the article and the densified fluid, including the exposure to static electric created during a high pressure gaseous rinse cycle, within the pressure vessel energizes the durable water repellant.

**[0020]** In yet another embodiment of the present invention, durable water repellant can be applied to the fibers of an article using a system that includes a pressure vessel operable to hold a densified fluid at hyper-atmospheric pressure wherein the densified fluid includes durable water repellant in solution. The system can also include a storage tank and a distillation system fluidly coupled to the pressure vessel wherein the distillation system is operable to remove suspended and dissolved contaminants from the densified fluid. Interaction between the article and the densified fluid binds the one or more fibers and concurrently energizes its structure.

**[0021]** The features and advantages described in this disclosure and in the following detailed description are not all-inclusive. Many additional features and advantages will be apparent to one of ordinary skill in the relevant art in view of the drawings, specification, and claims hereof. Moreover, it should be noted that the language used in the specification has been principally selected for readability and instructional purposes and may not have been selected to delineate or circumscribe the inventive subject matter; reference to the claims is necessary to determine such inventive subject matter.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0022]** The aforementioned and other features and objects of the present invention and the manner of attaining them will become more apparent, and the invention itself will be best understood, by reference to the following description of one or more embodiments taken in conjunction with the accompanying drawings, wherein:

**[0023]** FIG. **1** is a high-level depiction of a densified fluid cleaning system according to one embodiment of the present invention; and

**[0024]** FIG. **2** shows a flowchart of one method embodiment for applying and/or activating DWR using a densified cleaning system according to the present invention.

**[0025]** The Figures depict embodiments of the present invention for purposes of illustration only. One skilled in the art will readily recognize from the following discussion that alternative embodiments of the structures and methods illustrated herein may be employed without departing from the principles of the invention described herein.

## DESCRIPTION OF THE INVENTION

**[0026]** DWR works by increasing the contact angle or surface tension created when water contacts a textile or similar surface. Basically, a high contact angle creates a microscopically "spiky" surface that suspends water droplets on the outer fringe of the fabric. The result is that the water droplets keep a rounder shape much like a domed shape bead. The rounder the droplet, the more likely it is to roll off the garment or fabric. A low contact angle conversely allows the water droplet to spread out and cling to the textile and eventually seep in. The molecular chain present in all DWRs can be affected by physical contact (rubbing) and masked by dirt and oils. The result reduces the surface tension and allows the water to flatten out or adhere to the fabric.

**[0027]** The present invention provides a simpler, faster, more effective, and less energy/chemical intensive method for activating DWR present in a textile or fabric substrate. One embodiment of the present invention employs dense phase (e.g. liquid or super critical) Carbon Dioxide ($CO_2$) as the "wet process," specifically via a $CO_2$-based cleaning system in which the item(s) in question are processed.

**[0028]** Mechanisms specific to a $CO_2$ cleaning process employing dense phase $CO_2$ as the principal cleaning/rinsing agent including a high pressure gaseous rinse cycle enables an enhanced DWR chemical structure resulting in an activation and/or application of DWR characteristics.

**[0029]** According to one embodiment of the present invention, a $CO_2$ cleaning methodology includes an enhanced rinsing and distillation process that energizes the molecular bonds present in the DWR components. This is enabled by proper thermodynamic balance (heat transfer such as via refrigeration) accommodated in a system designed with sufficient storage capacity to enable continuous, real time distillation of $CO_2$ to separate contaminants producing pure, uncontaminated $CO_2$ throughout wash & rinse cycle(s). More specifically, the continuous distillation system and $CO_2$ processes of the present invention imputes energy into the DWR fluoropolymer and/or silicon bonds enhancing its hydrophobic characteristics.

**[0030]** Prior, early prototypes of $CO_2$ cleaning systems distilled $CO_2$ in an imprecise and batched manner. Some used partial distillation while others did not distill the fluid at all and rather relied on filtration as the mechanism for cleaning the $CO_2$. Others used a pressure differential for distillation.

**[0031]** The $CO_2$ purification results were poor due to various issues including: poor process flow and valve/piping designs limiting the ability to maintain precise process control and stills that were too small to handle the $CO_2$ volume of the machine. Moreover, the condensing properties of these machines were also too low to achieve the distillation needed to keep the needed volume of $CO_2$ in a clean purified form available throughout the entire cleaning process. The present invention presents a continuous distillation and rinse system that not only produces purified $CO_2$ to assist in cleaning textiles, but also energizes the molecular bonds between the large DWR molecules to further inhibit its ability to bind with hydrogen in a water molecule. As a result, the water molecules form a water cage and bead up on the DWR treated surface.

**[0032]** Another aspect of the present invention that results in an enhanced application and/or activation of DWR is a hi-speed extraction of $CO_2$ and use of advance drive Variable Frequency Drive, (VFD) with precise speed control to accelerate and enhance static electricity generation, throughout the wash/rinse process. This static charge generation through the introduction of a gaseous rinse cycle energizes and activates the DWR. In addition, the added pressure associated with the $CO_2$ cleaning process of the present invention adds additional energy into the DWR treated fabric ultimately enhancing the DWR characteristics. Note that the present invention does not employ heat as a mechanism to "energize" and activate DWR as is applied in the prior art. So, instead of heat, which can ultimately damages the garment, the present invention generates energy (e.g. static electricity) in the $CO_2$ extraction and reclamation cycle that re-aligns the DWR molecules to their most effective configuration. Due to the controlled environment embodied by the present invention the DWR molecules are aligned into their most efficient hydrophobic formation.

**[0033]** According to another embodiment of the present invention, DWR can be applied to pre-constructed garments and/or raw or finished fabrics using techniques presented herein and achieve superior results at the Original Equipment Manufacturer (OEM) level imparting enhanced water repellency properties. Furthermore, embodiments of the present invention can be used to re-apply or re-activate DWR in the secondary market, within the same system, as part of a general re-conditioning or service of garments or other items.

**[0034]** One or more embodiments of the present invention describes a closed system using a continuously cleaned/purified source of and/or super critical $CO_2$ in a cleaning process that approximately lasts 30 minutes. As there is no secondary waste all fluorocarbons and DWR agents are contained within a closed system and water is not used as a cleaning medium. The process includes not only extraction of contaminates that may diminish DWR characteristics as described herein, but reforms (realigns) the DWR chemical structure to its optimal form through the introduction of additional forms of energy such as static electricity and energy exchange as which occurs during decompression. Unlike conventional cleaning and drying processes in which measures are implemented to mitigate the production of static electricity, the present invention employs techniques to enhance the production of static electricity that thereafter energizes the DWR so as to align the poles of the DWR molecules.

**[0035]** Embodiments of the present invention are hereafter described in detail with reference to the accompanying Figures. Although the invention has been described and illustrated with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example and that those skilled in the art can resort to numerous changes in the combination and arrangement of parts without departing from the spirit and scope of the invention.

**[0036]** The following description with reference to the accompanying drawings is provided to assist in a comprehensive understanding of exemplary embodiments of the present invention as defined by the claims and their equivalents. It includes various specific details to assist in that understanding but these are to be regarded as merely exemplary. Accordingly, those of ordinary skill in the art will recognize that various changes and modifications of the embodiments described herein can be made without departing from the scope and spirit of the invention. Also, descriptions of well-known functions and constructions are omitted for clarity and conciseness.

**[0037]** The terms and words used in the following description and claims are not limited to the bibliographical meanings, but are merely used by the inventor(s) to enable a clear and consistent understanding of the invention. Accordingly, it should be apparent to those skilled in the art that the following description of exemplary embodiments of the present invention are provided for illustration purposes only and not for the purpose of limiting the invention as defined by the appended claims and their equivalents.

**[0038]** Durable water repellent (DWR) is a textile finish whose performance attributes (effects) may include water repellency, oil repellency, stain repellency, soil repellency, stain release, soil release, and durability (e.g. to laundering, dry cleaning, abrasion, light exposure, rain, etc.)

**[0039]** Fluoropolymer is a fluorinated polymer made by (co) polymerization of monomers that contain fluorine to create a polymer with fluorine directly bound to carbons of the polymer backbone.

**[0040]** By the term "substantially" it is meant that the recited characteristic, parameter, or value need not be achieved exactly, but that deviations or variations, including for example, tolerances, measurement error, measurement accuracy, limitations and other factors known to those of skill in the art, may occur in amounts that do not preclude the effect the characteristic was intended to provide.

**[0041]** Like numbers refer to like elements throughout. In the figures, the sizes of certain lines, layers, components, elements or features may be exaggerated for clarity.

**[0042]** The terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting of the invention. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. Thus, for example, reference to "a component surface" includes reference to one or more of such surfaces.

**[0043]** As used herein any reference to "one embodiment" or "an embodiment" means that a particular element, feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. The appearances of the phrase "in one embodiment" in various places in the specification are not necessarily all referring to the same embodiment.

**[0044]** As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

**[0045]** Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the specification and relevant art and should not be interpreted in an idealized or overly formal sense unless expressly so defined herein. Well-known functions or constructions may not be described in detail for brevity and/or clarity.

**[0046]** It will be also understood that when an element is referred to as being "on," "attached" to, "connected" to, "coupled" with, "contacting", "mounted" etc., another element, it can be directly on, attached to, connected to, coupled with or contacting the other element or intervening elements may also be present. In contrast, when an element is referred to as being, for example, "directly on," "directly attached" to, "directly connected" to, "directly coupled" with or "directly contacting" another element, there are no intervening elements present. It will also be appreciated by those of skill in the art that references to a structure or feature that is disposed "adjacent" another feature may have portions that overlap or underlie the adjacent feature.

**[0047]** Spatially relative terms, such as "under," "below," "lower," "over," "upper" and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. It will be understood that the spatially relative terms are intended to encompass different orientations of a device in use or operation in addition to the orientation depicted in the figures. For example, if a device in the figures is inverted, elements described as "under" or "beneath" other elements or features would then be oriented "over" the other elements or features. Thus, the exemplary term "under" can encompass both an orientation of "over" and "under". The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly. Similarly, the terms "upwardly," "downwardly," "vertical," "horizontal" and the like are used herein for the purpose of explanation only unless specifically indicated otherwise.

**[0048]** Included in the description are flowcharts depicting examples of the methodology that may be used to activate DWR using $CO_2$. In the following description, it will be understood that each block of the flowchart illustrations, and combinations of blocks in the flowchart illustrations, can be implemented by computer program instructions. These computer program instructions may be loaded onto a computer or other programmable apparatus to produce a machine such that the instructions that executes on the computer or other programmable apparatus create means for implementing the functions specified in the flowchart block or blocks. These computer program instructions may also be stored in a computer-readable memory that can direct a computer or other programmable apparatus to function in a particular manner such that the instructions stored in the computer-readable memory produce an article of manufacture including instruction means that implement the function specified in the flowchart block or blocks. The computer program instructions may also be loaded onto a computer or other programmable apparatus to cause a series of operational steps to be performed in the computer or on the other programmable apparatus to produce a computer implemented process such that the instructions that execute on the computer or other programmable apparatus provide steps for implementing the functions specified in the flowchart block or blocks.

**[0049]** Accordingly, blocks of the flowchart illustrations support combinations of means for performing the specified functions and combinations of steps for performing the specified functions. It will also be understood that each block of the flowchart illustrations, and combinations of blocks in the flowchart illustrations, can be implemented by special purpose hardware-based computer systems that perform the specified functions or steps, or combinations of special purpose hardware and computer instructions.

**[0050]** The hydrogen bond between water molecules is the driving force between two of waters properties: cohesion and adhesion. Cohesion is the ability of water to stick to itself. Cohesion is the driving force behind rain. Water vapor molecules join together until they reach a point in which the combined weight of the molecules cannot be supported by the current atmospheric conditions. Adhesion is the ability of water to stick to other surfaces. This enables water to spread out and form a film. When water comes in contact with these surfaces the adhesive forces are greater than water's cohesive forces. Instead of water sticking together it spreads out.

**[0051]** Water also possesses a high level of surface tension forces. Surface tension is when molecules on the surface of the water are not surrounded by similar molecules on all sides and are thus being pulled only by cohesion forces from molecules in the interior. Surface tension is what causes a water droplet to be round so as to cover the smallest surface area possible. DWR strives to decrease the adhesive forces making water more likely to coalesce.

**[0052]** On a fabric surface, the DWR particle spreads to cover the fabric fibers after it has been applied. The fluoroalkyl chains orient perpendicular to the fabric surface. It can be imagined as microscopic umbrellas connected to the polymer backbone. This myriad of "umbrellas" creates a low surface energy shell on the fabric with a surface energy (adhesive force) lower than that of water or oils. Therefore, when water or oils contact the fabric surface they do not bond with the fluoroaklyl chain preventing the fabric from becoming wet. Water beads up having a high "contact angle." The high surface tension forces of water, along with weak adhesion and high cohesion drives water to form beads that possess minimal contact with the DWR treated surface. The better the treatment, the rounder the beads of water. An optimized DWR finish is designed for a specific fabric based on its fiber type and fabric construction to form an array of microscopic polymer domains on the fabric surface (not a film or coating) with the fluorinated chains erect, perpendicular to the fabric surface and close enough to one another to act like a continuous surface. The image is a plethora of microscopic umbrellas on the surface with the tips touching so that no water or oil can penetrate to the fibers of the fabric. Water or oil cannot spread out, forcing them to bead up, stand up, and slide off the fabric. One skilled in the relevant art will appreciates that silicon based chemistry also orients their methyl groups toward the surface creating a similar array of "umbrellas." These and other chemical structures demonstrating similar characteristics are equally applicable to and contemplated by the present invention.

**[0053]** To create this plethora of microscopic umbrellas, the polymer domains must be correctly aligned. This alignment is driven, in part, by the energy contained within each molecule pole. One or more embodiments of the present invention uses a $CO_2$ cleaning process to impute energy to the DWR molecule resulting in its optimal alignment of the poles and thus produces a water resistant structure. The fluoropolymer associated with most DWR compounds bonds with the individual fiber of a textile. These molecules tend to align themselves into a spiky perpendicular formation reducing the fabric's adhesive forces with respect to water. That is to say, when the fluoropolymer molecules (poles) are energized the umbrellas are all standing up with tips touching. However as time passes, the energy within these molecules can decrease or be compromised by foreign agents such as dirt and oil causes the umbrellas to fall down. As the molecules "lay down" their hydrophobic effect diminishes.

**[0054]** One aspect of the present invention is the ability to apply an initial DWR treatment. The liquid/super critical/gaseous form of $CO_2$ more readily penetrates fabrics than does an aqueous solution. Accordingly, acting as a delivery agent for a fluoropolymer molecule, $CO_2$ can more uniformly and deeply apply a DWR substance than conventional techniques. The DWR substance is placed into a solution with the $CO_2$ and introduced to the untreated fabric during a $CO_2$ cleaning cycle. During the normal cleaning process the DWR substance impregnates the fabric and adheres to the fabric fibers. Depending on concentrations and durations of the cleaning cycle differing degrees of DWR application can be achieved. As one of reasonable skill in the relevant art will appreciate, Silicon based and fluorocarbon based DWR components are equally enhanced by the use of the liquid/super critical/gaseous $CO_2$ delivery systems of the present invention.

**[0055]** According to another embodiment of the present invention and with additional reference to FIG. **1**, DWR molecules within a DWR impregnated fabric are activated (energized) using a densified $CO_2$ cleaning process and apparatus. In one version of the present invention, a cleaning system **100** includes an agitation basket **120** and is enclosed within a pressure vessel **110**. The pressure vessel is coupled to various additional components that may be used to obtain a satisfactory and successful cleaning result using a densified fluid. For example, the pressure vessel **110** can be coupled to a purge tank **160** from which a gaseous form of a densified fluid can be brought to and from the pressure vessel **110** and the cleaning environment. In addition, the pressure vessel **110** can be coupled to one or more storage tanks **170** from which densified fluid can be temporarily stored and supplied to the cleaning process as required.

**[0056]** The $CO_2$ cleaning system of the present invention further includes a distillation system **135** comprised of evaporation **130** and condensation **140** components that converts densified fluid into its gaseous form so as to remove any suspended and dissolved contaminants in the densified fluid that have been eliminated from the soiled articles and then re-condense the gaseous form of the densified fluid back into its liquid form for further use in the cleaning process. As further shown in FIG. **1**, densified fluid collected from the pressure vessel containing various contaminants gained from the soiled articles is passed through a series of mechanical filters **124**, **128** and eventually to an evaporator **130** (distiller) wherein the densified fluid is converted from its densified form to its gaseous form by an change in energy through control of pressure and/or the addition of heat thereby substantially removing any suspended and dissolved contaminants. The now clean gas is then re-condensed into a liquid form in a condenser **140** before being passed to a storage vessel **150** for later use within the pressure vessel.

**[0057]** In another embodiment of the present invention the evaporator **130** of the distillation system **135** includes an internal heat exchanger. The heat exchanger (not shown) can comprise a coil of heating elements arranged for heat transfer to the densified fluid. The energy source from the heating coil can be derived from various media such as but not limited to densified fluid, steam, hot water, electricity, hot air and/or refrigerant. In another embodiment of the present invention steam can be used as source of heat. The heating coil can also be arranged in a boiling vessel in such a way that the coil is submerged in the densified fluid. It is also noted that a spiral or finned coil design increases the heating capacity by maximizing the heating surface although one skilled in the relevant art will recognize that other designs for a heat exchanger could be utilized to achieve the same result.

**[0058]** As one of reasonable skill in the relevant art will appreciate, distillation is a method of separating mixtures based on differences in volatility of components in a boiling liquid mixture. Distillation is a physical separation process and not a chemical reaction. Only when the temperature at which the vapor pressure of the liquid equals the pressure on the liquid do bubbles form without being crushed back into solution. At a basic level, the heating of a volatile mixture of substance A and B (wherein substance A has a lower boiling point) to its boiling point results in a vapor that contains a mixture of A and B. The ratio of A to B in the vapor however will be different than the ratio of A to B in the liquid. In this case the vapor will possess a higher concentration of A since A has a lower boiling point. The vapor can be condensed to a fluid form and the process repeated until liquid of a desired purity of A can be achieved.

**[0059]** The distillation process, gaseous rinse and introduction of static electricity serve to energize the cleaning environment. A portion of this energy is transferred to the molecular structure of the DWR molecules bound to the fabric fibers. These now energized DWR molecules create a perpendicular or spikey orientation with respect to the host fiber which diminishes the fiber/water adhesion force. Said differently, the energized DWR molecules create a water resistant surface by which the cohesive forces of water are greater that the adhesive forces between the fiber and water. The result is that the water beads and ultimately rolls off the fabric.

**[0060]** FIG. **2** presents a flowchart for one methodology for applying DWR to, and/or activating DWR within, an article according to one embodiment of the present invention. The process begins **205** with depositing **210** articles within a cleaning or agitation basket. The basket, located within the pressure vessel, is manipulable to agitate the articles within the pressure vessel to aid in the distribution of the densified solution. The agitation and manipulation of the basket enhances the penetration of the densified solution into the articles for application of the DWR and/or activation of the DWR. One of reasonable skill in the relevant art will appreciate that that the articles deposited within the pressure vessel can be articles of clothing, garment or bulk textiles and fabrics which, subsequent to treatment can then be formed into garments.

**[0061]** With the articles deposited within the basket of the pressure vessel the pressure vessel is sealed **220** and a densified cleaning solution is introduced **230** within the basket. According to one embodiment of the present invention the densified solution is liquefied/gaseous carbon dioxide ($CO_2$). For the purposes of the present application the term fluid and/or densified fluid is used to describe a gaseous, liquid and/or super critical state of a substance or any combination thereof.

**[0062]** Typically a substance can be thought of to exist in three distinct phases. These phases or states are commonly known as solid, liquid, or gas. A phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure. A typical phase diagram has pressure on the Y axis and temperature on the X axis. As one moves across the lines or curves on the graph a substance's phase changes from one to the next. Moreover, the two adjacent phases of a substance can coexist or are in equilibrium on the line separating these regions. The critical point on the graph is a point in the phase diagram in which temperature and pressure are such that the liquid and gaseous phases of the substance are indistinguishable. Beyond this point the temperature and pressure are such that a merged single-phase known as is a super critical fluid exists. The distinction between fluid and gas ceases to exist beyond this point and the substance is referred to as a super critical fluid.

**[0063]** Super critical fluids can diffuse through solids like a gas, and dissolved materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a super critical fluid to be "fine-tuned". Super critical fluids are often used as a substitute for organic solvents in a range of industrial laboratory processes. In general, super critical fluids have properties of both a gas and liquid; super critical fluids (and for that matter densified fluids) can include carbon dioxide, water, methane, ethane, propane, propylene, ethanol, acetone, and ethylene. One significant characteristic of super critical fluids is that there is no surface tension between the liquid/gas phase boundary. By changing the pressure and temperature of the fluid, the properties can be "tuned" to be more liquid or more gas like.

**[0064]** The advantages of super critical fluid extraction (compared with liquid extraction) is that extraction from the textile are relatively rapid because of the low viscosity and high diffusivities. Extraction can be selective to some extent by controlling the density of the medium. Moreover, depressurizing super critical fluid and allowing the super critical fluid to return to a gas phase easily recovers the extracted material. The evaporation process leaves little solid residue behind.

**[0065]** Changes in pressure and temperature can also change the density of a substance such as liquid carbon dioxide. Increasing the pressure always increases the density of a material while increasing the temperature generally decreases the density with some notable exceptions. For example, the density of water increases between its melting point at 0° C. and 4° C. As is commonly know the density of water is greater than that of ice.

**[0066]** The effect of pressure and temperature on the densities of liquids and solids is small. The compressibility for a typical liquid or solid is 10−6 bar-1 (1 bar=0.1 MPa) and a typical thermal expansivity is 10−5:K−1. This roughly translates into needing around ten thousand times more atmospheric pressure to reduce the volume of a substance by one percent. A one percent expansion of volume typically requires a temperature increase on the order of thousands of degrees Celsius. So while the change in density of a liquid is substantially insignificant, the point at which it transitions from a liquid to a gas can be significantly impacted by both pressure and temperature. Therefore, a densified fluid (gaseous, liquid or super critical) comprises, for the purposes of this application, a substance or solution that, based on temperature or pressure, varies between gaseous, liquid and a super critical state. One of reasonable skill in the art will recognize that a densified fluid will, in its liquid state, be coexistent with a gaseous form of the fluid in areas having a free surface such as, for example, the pressure vessel.

**[0067]** With the pressure vessel pressurized to hyper-atmospheric pressure and the articles within introduced to a densified cleaning solution, the articles are processed **240** within the basket and within the densified solution to remove any contaminants, oil, soil, dirt or other impurities that might alter the DWR's ability. Responsive to the conclusion of the densified fluid process a high pressure gaseous rinse is initiated **270** that can impute additional energy into the articles enclosed within the basket. The gaseous high-pressure rinse generates a substantial amount of static electricity, which activates and energizes the DWR molecules.

**[0068]** With the rinse completed the pressure vessel is depressurized **280** and the activated DWR impregnated articles removed **290** ending the process. The cleaning process using densified solutions not only returns the article to its original condition by removing any soil or contaminants which may impede existing DWR characteristics, it energizes the DWR molecules aligning their structure to form a more cohesive and effective resistance to water adhesion.

**[0069]** The densified cleaning system **100** can also be used to apply DWR components to articles, garments, textiles and the like. As with the prior methodology the untreated articles are deposited **210** within the basket of a pressure vessel. The pressure vessel is sealed **220** and the cleaning process begins.

**[0070]** Rather than simply introducing a densified cleaning solution to remove any contaminants and impurities from the articles, a pressurized densified DWR solution can be introduced **250** into the pressure vessel. As the solution cleans the article **260**, the DWR component binds with the fibers of the textile so that upon completion of the cleaning process, the articles within are impregnated with the DWR molecules. One of reasonable skill in the relevant art will appreciate that the time during which the articles are subjected to the DWR densified solution as well as the DWR concentration, pressure of the vessel and temperature of the environment may vary so as to arrive at an optimal and desired DWR impregnation result.

**[0071]** The DWR characteristics are again enhanced through the use of a high-pressure gaseous rinse cycle **270** that energizes and activates the DWR molecules that remain bound to the fibers of the articles within the basket of the pressure vessel. Upon completion of the rinse the pressure vessel is depressurized **280** with the newly impregnated and activated DWR articles being removed **290**.

**[0072]** These and other implementation methodologies for applying and activating DWR components can be successfully utilized by the densified cleaning system **100** of the present invention. These implementation methodologies and the specifics of their application within the context of the present invention will be readily apparent to one of ordinary skill in the relevant art in light of this specification.

**[0073]** Although the invention has been described and illustrated with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example and that numerous changes in the combination and arrangement of parts can be resorted to by those skilled in the art without departing from the spirit and scope of the invention, as hereinafter claimed.

**[0074]** While there have been described above the principles of the present invention in conjunction with the application and activation of DWR, it is to be clearly understood that the foregoing description is made only by way of example, and not as a limitation to the scope of the invention. Particularly, it is recognized that the teachings of the foregoing disclosure will suggest other modifications to those persons skilled in the relevant art. Such modifications may involve other features that are already known per se and which may be used instead of or in addition to features already described herein. Although claims have been formulated in this application to particular combinations of features, it should be understood that the scope of the disclosure herein also includes any novel features or any novel combination of features disclosed either explicitly or implicitly or any generalization or modification thereof which would be apparent to persons skilled in the relevant art, whether or not such relates to the same invention as presently claimed in any claim and whether or not it mitigates any or all of the same technical problems as confronted by the present invention. The Applicant hereby reserves the right to formulate new claims to such features and/or combinations of such features during the prosecution of the present application or of any further application derived therefrom.

**1**. A method for activating durable water repellency, the method comprising:

depositing within a pressure vessel an article having one or more fibers wherein the one or more fibers of the article are bound with a durable water repellant;

processing the article with a densified fluid to remove contaminants; and

energizing the durable water repellant bound to the one or more fibers of the article.

**2**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is a perfluoroalkyl chain.

**3**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is based on fluorine chemistry.

**4**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is based on silicon chemistry.

**5**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is fluoropolymer based.

**6**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is perfluorooctane sulfonate based.

**7**. The method for activating durable water repellency of claim **1**, wherein the durable water repellant is perfluorooctane acid based.

**8**. The method for activating durable water repellency of claim **1**, wherein the densified fluid is super critical carbon dioxide.

**9**. The method for activating durable water repellency of claim **1**, wherein the densified fluid is liquid carbon dioxide.

**10**. The method for activating durable water repellency of claim **1**, wherein processing includes cleaning the article with liquid carbon dioxide.

**11**. The method for activating durable water repellency of claim **1**, wherein energizing includes subjecting the durable water repellant to static electricity.

**12**. The method for activating durable water repellency of claim **1**, wherein energizing includes subjecting the article to a pressurized gaseous rinse cycle imparting energy to the durable water repellant.

**13**. The method for activating durable water repellency of claim **1**, wherein energizing includes transferring energy from the densified fluid to the durable water repellent.

**14**. The method for activating durable water repellency of claim **1**, wherein energizing includes transferring energy from a gaseous rinse cycle to the durable water repellant.

**15**. A method for durable water repellant application, the method comprising:

depositing within a pressure vessel an article having one or more fibers;

processing the article with a densified fluid to remove contaminants wherein the densified fluid includes a durable water repellant; and

energizing the durable water repellant bound to the one or more fibers of the article.

**16**. The method for durable water repellant application according to claim **15**, wherein processing includes binding the durable water repellant with the one or more fibers of the article.

**17**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is a perfluoroalkyl chain.

**18**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is based on fluorine chemistry.

**19**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is based on silicon chemistry.

**20**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is fluoropolymer based.

**21**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is perfluorooctane sulfonate based.

**22**. The method for durable water repellant application according to claim **15**, wherein the durable water repellant is perfluorooctane acid based.

**23**. The method for durable water repellant application according to claim **15**, wherein the densified fluid is super critical carbon dioxide.

**24**. The method for durable water repellant application according to claim **15**, wherein the densified fluid is a super critical fluid.

**25**. The method for durable water repellant application according to claim **15**, wherein processing includes cleaning the article with liquid carbon dioxide.

**26**. The method for durable water repellant application according to claim **15**, wherein energizing includes subjecting the durable water repellant to static electricity.

**27**. The method for durable water repellant application according to claim **15**, wherein energizing includes subjecting the article to a pressurized gaseous rinse cycle imparting energy to the durable water repellant.

**28**. The method for durable water repellant application according to claim **15**, wherein energizing includes transferring energy from the densified fluid to the durable water repellent.

**29**. The method for durable water repellant application according to claim **15**, wherein energizing includes transferring energy from a gaseous rinse cycle to the durable water repellant.

**30**. A durable water repellant activation system, the system comprising:

a pressure vessel operable to hold a densified fluid at hyper-atmospheric pressure;

a storage tank fluidly coupled to the pressure vessel for storing the densified fluid;

a distillation system fluidly coupled to the pressure vessel and the storage tank wherein the distillation system is operable to remove suspended and dissolved contaminants from the densified fluid; and

an article having one or more fibers wherein the one or more fibers of the article are bound with a durable water repellant and wherein interaction between the article and the densified fluid within the pressure vessel energizes the durable water repellant.

**31**. The durable water repellant activation system of claim **30**, wherein the distillation system is operable to rinse the article using high-pressure gas.

**32**. The durable water repellant activation system of claim **31**, wherein rinsing the article with high-pressure gas energizes the durable water repellant.

**33**. The durable water repellant activation system of claim **30**, wherein static electricity generated by the pressure vessel energizes the durable water repellant.

**34**. The durable water repellant activation system of claim **30**, wherein the durable water repellant is a perfluoroalkyl chain.

**35**. The durable water repellant activation system of claim **30**, wherein the durable water repellant is fluoropolymer based.

**36**. The durable water repellant activation system of claim **30**, wherein the densified fluid is carbon dioxide.

**37**. The durable water repellant activation system of claim **30**, further comprising an agitation basket within the pressure vessel and operable manipulate the article within the pressure vessel.

**38**. A durable water repellant application system, the system comprising:

a pressure vessel operable to hold a densified fluid at hyper-atmospheric pressure wherein the densified fluid includes a durable water repellant in solution;

a storage tank fluidly coupled to the pressure vessel for storing the densified fluid;

a distillation system fluidly coupled to the pressure vessel and the storage tank wherein the distillation system is operable to remove suspended and dissolved contaminants from the densified fluid; and

an article having one or more fibers wherein the one or more fibers of the article bind with the durable water repellant and wherein interaction between the article and the densified fluid within the pressure vessel energizes the durable water repellant bound to the one or more fibers.

**39**. The durable water repellant application system of claim **38**, further comprising an agitation basket within the pressure vessel and operable manipulate the article within the pressure vessel.

**40**. The durable water repellant application system of claim **38**, wherein the distillation system is operable to rinse the article using high-pressure gas.

**41**. The durable water repellant application system of claim **40**, wherein rinsing the article with high-pressure gas energizes the durable water repellant.

**42**. The durable water repellant application system of claim **38**, wherein static electricity generated by the pressure vessel energizes the durable water repellant.

**43**. The durable water repellant application system of claim **38**, wherein the durable water repellant is a perfluoroalkyl chain.

**44**. The durable water repellant application system of claim **38**, wherein the durable water repellant is fluoropolymer based.

**45**. The durable water repellant application system of claim **38**, wherein the densified fluid is carbon dioxide.

* * * * *