(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 November 2012 (01.11.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/146304 Al

(51) International Patent Classification:
D06F 35/00 (2006.01) ***D06F 58/20*** (2006.01)

(21) International Application Number:
PCT/EP201 1/056852

(22) International Filing Date:
29 April 201 1 (29.04.201 1)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **ECOLAB USA INC.** [US/US]; 370 Wabasha Street N, St. Paul, Minnesota 55102-1390 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only):* **BEISEMANN, Peter Bruno** [DE/DE]; Haus Gravener StraBe 70, 40764 Langenfeld (DE). **MERZ, Thomas** [DE/DE]; Erikaweg 3a, 40723 Hilden (DE). **POSSMANN, Mario** [DE/DE]; Kaiserstr. 78, 40764 Langenfeld (DE). **WINTER, Johannes Georg** [DE/DE]; Munchner StraBe 89, 82008 Unterhaching (DE). **HEI, Robert D.P.** [US/US]; 2224 30th Avenue, Baldwin, Wisconsin 54002 (US).

(74) Agent: **POLYPATENT;** An den Garten 7, 51491 Overath (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available):* AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available):* ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2012/146304 A1

(54) Title: METHOD FOR APPLYING A LAUNDRY FINISHING AGENT TO LAUNDRY ARTICLES

(57) Abstract: The present invention refers to a method for applying at least one laundry finishing agent to laundry articles, comprising the step of feeding a densified fluid carbon dioxide comprising said laundry finishing agent into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

METHOD FOR APPLYING A LAUNDRY FINISHING AGENT TO LAUNDRY ARTICLES

The invention relates to a method for applying laundry finishing agents to laundry articles.

Background of the invention

The desirability of adding a fragrance to laundry during the cleaning process has been recognized for decades. A vast array of scented fabric conditioners are available on the market today. These products combine perfumes with softening and conditioning agents to produce laundry that is soft, fresh smelling, static-free, crease-resistant, and easily ironed. In one approach, the conditioners are added during the wash cycle in a washing machine. However, this approach may be wasteful, because much of the perfumes on conditioners in the conditioning compositions do not adhere to the clothes in a washer and are washed away with the waste water. To avoid this waste, fabric conditioners may be added during the drying process in a dryer. As discussed below, this approach has not been entirely satisfactory in imparting a lasting fragrance to freshly laundered articles.

Various methods for adding a fragrance to laundry in a dryer are well known. One of the most common methods employs dryer sheets which are impregnated with conditioning agents and allowed to tumble with the clothes in a dryer. During the drying process, fragrance is imparted to the clothes that come into contact with these dryer sheets. The dryer sheets are typically made of a spongy material and the conditioning agents are chosen such that they melt or flow at conventional dryer operating temperatures. However, these dryer sheets suffer from several drawbacks. Because the conditioning agents are applied through contact between articles of laundry and the sheets, application can be splotchy and uneven. In addition, in order to assure that all articles of laundry come into contact with the sheet, it is necessary for the dryer sheets to be put in the laundry early on in the drying cycle. This can be disadvantageous because any fragrances in the conditioning compositions are likely to volatilize during prolonged exposure to the heat of the drying cycle, leaving little residual fragrance on the textile surface at the end of the drying process. This problem occurs specifically in industrial dryers, such as those used by the hotel industry, which operate at much higher

temperatures than do conventional household dryers. In fact, many industrial dryers work at temperatures hot enough to melt dryer sheets. Finally, the conditioning agents that can be used with dryer sheets are limited because they must be selected from compounds that melt or flow in a fairly specific temperature range. The compositions that meet these criteria are not optimally suited for use as softeners and conditioners.

In other laundry softening or conditioning methods, liquid or solid conditioners are housed in porous containers which are either allowed to tumble freely with the laundry in a dryer or which are attached to the drum of the dryer such that they spin with the laundry. These liquid or solid conditioners are then dispensed through the porous walls of the container during the drying process. As with dryer sheets, these porous containers apply conditioning agents by making direct contact with articles of laundry, which requires prolonged exposure to the laundry during the drying cycle and which may lead to an uneven application of the conditioning agents.

In another method, a fabric softener or conditioner is held in a container within a dryer and hot air is circulated over the container such that the fabric softener or conditioner vaporizes and is carried by the air stream over the laundry. This requires that the softener or conditioner be present during the hottest part of the drying cycle, resulting in the volatilization and loss of volatile fragrant components within the conditioning compositions.

Finally, it is known to spray or sprinkle liquid softeners or conditioners onto either the damp clothes as they enter the dryer, or onto the drum itself before the clothes are placed in the dryer such that the softener or conditioner permeates the laundry as it dries. Unfortunately, the spray nozzles used to apply conditioning compositions frequently dispense the liquids in droplets, rather than a fine mist or vapor which makes it difficult to precisely control the amount and distribution of the liquids as they are applied to laundry.

None of these methods has been entirely successful at imparting a lasting residual fragrance to articles of laundry. Thus, a need exists for a system that is able to impart a fragrance to laundry in a dryer without substantial loss of the fragrance before the completion of the drying process. Such a system would be of

particular value to the hotel industry, where fresh-smelling bath robes, towels, and linens would enhance the comfort of guests and potentially create more repeat customers. Further, the prior art does not provide a simple and cost-effective method to apply laundry finishing agents to laundry articles.

Therefore the object of the present invention was to provide a new method for applying laundry finishing agents to laundry articles.

The present invention provides a method for applying at least one laundry finishing agent to laundry articles, comprising the step of feeding a densified fluid carbon dioxide comprising said laundry finishing agent into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

In the method according to the present invention said laundry finishing agent comes into contact with the laundry articles due to said densified fluid carbon dioxide becoming gaseous. Once the densified fluid carbon dioxide comprising said laundry finishing agent leaves the applicator device with the associated pressure drop, the densified fluid quickly returns to the gaseous phase leaving an effective concentration of the laundry finishing agent which becomes absorbed by the laundry articles. Therefore, the laundry finishing agent when losing its liquid carbon dioxide carrier is released, preferably forming an aerosol, and is thereby dispensed or deposited on and taken up or absorbed by the laundry articles.

With the method according to the present invention laundry finishing agents can be homogenously dispensed onto laundry articles.

It should be noted that the laundry articles do not come into contact with densified fluid carbon dioxide.

In a further preferred embodiment of the method the laundry articles are transported through said chamber (e.g. a steam tunnel or a chamber of an ironer) or are agitated (e.g. in a drier) when feeding said densified fluid carbon dioxide comprising said laundry finishing agent into said chamber containing said laundry articles. Typically the laundry articles are agitated by tumbling them in a drum of a drier, i.e. during the application of said laundry finishing agent to laundry articles by feeding a densified fluid carbon dioxide comprising said laundry finishing agent into a chamber containing laundry articles the laundry articles preferably are

agitated by the rotation of the drier drum in which said laundry articles are placed. The laundry finishing agent may also be applied when laundry articles are processed in a steam tunnel or when subjected to ironing in an ironer.

As used herein the term "chamber" is represented by a container or receptacle, which is closed, but not necessarily sealed. The laundry articles are contained in the chamber itself or within a drum arranged in said chamber. The chamber itself or said drum, respectively, is preferably agitated. An example of a drum within a chamber is a drier drum of a drier for drying laundry articles. Such chambers are normally closed in order to provide the conditions in that way that the laundry finishing agent released from the expanding carbon dioxide is taken up by the laundry articles instead of spreading into and contaminating the surrounding atmosphere. The method may be preferably carried out in a dryer.

If the laundry finishing agent(s) is/are applied during the processing of laundry articles in a steam tunnel, then the "chamber" is represented by the steam tunnel housing, or possibly by a further inner chamber within the steam tunnel. Here the laundry finishing agent is applied when the laundry articles are transported through the chamber, i.e. the steam tunnel.

If the laundry agent(s) is/are applied during ironing of laundry articles by using an ironer, then a chamber is provided in the area of the ironer where the application of the laundry finishing agent is carried out. The installation of a chamber or housing in connection with the ironer, which normally may be operated without any housing, serves the purpose to reduce the contamination of the surrounding atmosphere by the laundry finishing agent(s).

In a further preferred method the gaseous medium contained in said chamber is withdrawn from the chamber. In a still further preferred method the gaseous medium contained in said chamber is withdrawn from the chamber and excess laundry finishing agent comprised in the withdrawn gaseous medium is collected and may be discarded or recycled. These methods serve the purpose to reduce contamination of the surrounding atmosphere by the laundry finishing agent(s), that otherwise may compromise the health of the individuals working in the respective laundry processing facility.

For further reducing the load of laundry finishing agent in the surrounding atmosphere the chamber may be equipped with an exhaust line, in order to remove excess laundry finishing agent which was not absorbed by the laundry articles.

In a preferred method the laundry finishing agent is selected from the group consisting of fragrance, conditioning agent, softening agent, anti-soil-re-deposition agent, soil release agent, ease ironing agent, ease drying agent, antistatic agent, fungistatic, bacteriostatic, hydrophobic agent, oleophobic agent, impregnation material, flame retardant, repellent, scavenger, surfactant, bleaching agent, such as a peracid compound, H_20_2, bleach activator, bleach catalyst, oxidizing agent, optical brightener, chelating agent, builders, radical scavenger such as BHT, paraffin, enzyme and compositions comprising one or more of said agents.

In an alternative embodiment of the present invention the laundry finishing agent may be replaced by a chemical compound having the property to deliver a soil modifying property to soils. The present invention therefore also provides a method for applying at least a chemical compound to laundry articles, comprising the step of feeding a densified fluid carbon dioxide comprising said chemical compound into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous. The present invention therefore provides the means to deliver a soil modifying property to soils. Especially those soils that are only partially removed or difficult to remove with a conventional wash cycle such as cosmetics, makeup, lipstick, non trans-fats and the like. The chemical compound may be selected from the group consisting of penetrants, pre-spotting agents, i.e. pre-treatment agents, HLB modifiers. In a further preferred embodiment of this alternative method the soils are modified by the chemical agent in that way that the soils may be removed in the drying process or in a subsequent wet treatment. Such subsequent wet treatment may either immediately following the drying step or at a later stage once the laundry articles has been used and possibly further soiled.

In a particularly preferred embodiment the laundry finishing agent or the chemical compound having the property to deliver a soil modifying property to soils is having 2 or more carbon atoms, 3 or more carbon atoms, 4 or more carbon

atoms, 5 or more carbon atoms, 6 or more carbon atoms, or is represented by a chemical compound having at least 2 carbon atoms and at least one nitrogen atom, or is represented by a chemical compound having at least one silicon atom, or is represented by a chemical compound having at least one sulfur atom.

In a particularly preferred embodiment the laundry finishing agent is a fragrance. In an alternative preferred embodiment the laundry finishing agent is BHT (butylhydroxyltoluene). In a further alternative preferred embodiment the laundry finishing agent is paraffin. In a further alternative preferred embodiment the laundry finishing agent is a soil release agent.

In addition to the laundry finishing agent additional ingredients may be comprised in the densified fluid carbon dioxide and applied to the laundry finishing agent together with the densified fluid carbon dioxide and the laundry finishing agent, which additional ingredient may be selected from solvent, co-solvent, chelating agent, buffering agent, acidulant, source of alkalinity, rheology modifier or a mixture thereof.

The densified fluid carbon dioxide comprising the laundry finishing agent may also include further compounds, such as another fluid (e.g., water) or gas, co-pressurizing gas or gases or a mixture thereof.

In a further preferred method said densified fluid carbon dioxide comprising said laundry finishing agents is a mixture comprising densified fluid carbon dioxide and said laundry finishing agent. The mixture may further comprise at least one co-solvent such as an alkanol, e.g. ethanol.

In various embodiments, said laundry finishing agent makes up from 0.0001 weight percent of the densified fluid carbon dioxide mixture. In various embodiments said laundry finishing agent will be present in an amount from 0.0001 to 40 weight percent, preferably from 0.0001 to 25 weight percent of the densified fluid carbon dioxide mixture.

In a particularly preferred embodiment the method is carried out after the wet treatment of said laundry articles, said wet treatment comprising the steps of washing, rinsing and drainage. The wet treatment is followed by a drying process. The method according to the present invention may be carried out before, during

or after a drying process of said laundry articles, or during the cool-down cycle of a drying process.

In an alternative embodiment the method is carried out during ironing of the laundry articles in an ironer or during processing the laundry articles in a steam tunnel.

When carrying out the method the pressure within said chamber containing said laundry articles preferably is 1500 hPa, 1200 hPa, 1100 hPa or less. Preferably ambient pressure is applied.

The method according to the present invention preferably is carried out at a temperature of 0°C to 150°C, preferably at a temperature of 10°C to 100°C and further preferred at a temperature of 15°C to 80 °C.

In a further preferred method said densified fluid carbon dioxide comprising said laundry finishing agent is provided in a storage tank prior to the application to the laundry articles. Such storage tank usually is a cylinder. In order to prepare the desired mixture the laundry finishing agent(s) is/are placed in the storage tank which then is filled with densified fluid carbon dioxide. The laundry finishing agent is evenly distributed, dissolved, incorporated, suspended in or otherwise carried by the densified fluid carbon dioxide.

In an alternative embodiment of the method of the present invention said densified fluid carbon dioxide is loaded with said laundry finishing agent by feeding densified fluid carbon dioxide through a cartridge containing said laundry finishing agent, whereby the densified fluid carbon dioxide is taking up the laundry finishing agent, and then immediately is applied to the laundry articles. Such a procedure may be applied in case an unstable component such as a peracid is used. The peracid can be stabilized in dry form with a stabilizer in a cartridge before use. The mixture then is prepared during the dispensing step, by feeding densified fluid cabon dioxide through the cartridge containing the desired agent (such as the peracid) and then immediately dispensed in the chamber containing the laundry articles. In a preferred embodiment the stabilizer may remain in the cartridge. In such a preferred embodiment wherein the stabilizer remains in the cartridge the desired agent (such as the peracid) is selectively extracted from the cartridge.

In a further alternative embodiment of the method of the present invention said densified fluid carbon dioxide is provided continuously and fed via a pipe. In this embodiment the densified fluid carbon dioxide may be loaded by dosing the said laundry finishing agent with a pump into the densified fluid carbon dioxide stream. Therefore, in a preferred method according to the present invention prior to dispensing to said laundry articles said densified fluid carbon dioxide is loaded with said laundry finishing agent by dosing said laundry finishing agent to a stream of densified fluid carbon dioxide, whereby the densified fluid carbon dioxide is taking up the laundry finishing agent. The stream of densified fluid carbon dioxide may be continuous or discontinuous.

Further preferred, the method is carried out in a drier, a steam tunnel or an ironer. The "chamber" corresponds to the drier drum of the drier, to the steam tunnel or to a housing of an ironer in which housing the ironing is carried out by using rollers.

The present invention also provides a method for the wet treatment of laundry articles comprising the steps of washing, rinsing and drainage, wherein after the steps of washing rinsing and drainage a laundry finishing agent is applied to the laundry articles, by bringing laundry articles into contact with a gaseous medium immediately after the gaseous medium has been formed by depressurizing a mixture comprising densified fluid carbon dioxide and said laundry finishing agent.

Preferred embodiments of the method for the wet treatment of laundry articles are defined as described above.

Further, the present invention provides a drier for drying laundry articles, a steam tunnel, an ironer, respectively, adapted for carrying out the method of the present invention. Said drier, steam tunnel or ironer comprises a chamber which is equipped with a supply line for feeding densified fluid carbon dioxide into the chamber and preferably is equipped with an exhaust line for removing gaseous medium from the chamber in order to remove excess laundry finishing agent from the chamber. In preferred embodiments the exhaust line leads to a separator where the laundry finishing agent is collected for the purpose of discarding or recycling.

Typically the densified fluid carbon dioxide comprising laundry finishing agent is stored in a cylinder under a pressure above 55 bar ($5{,}5 \times 10^6$ Pa). For carrying out

the method of the present invention a pipe or hose is arranged for connecting the cylinder with the inner space of the drier. When opening the valve the densified fluid carbon dioxide comprising the laundry finishing agent is released and thereby immediately expanded in its gaseous form. The laundry finishing agent when losing its liquid carbon dioxide carrier is released, preferably forming an aerosol, and is thereby dispensed or deposited on and taken up or absorbed by the laundry articles in the drier.

The drier for drying laundry articles, adapted for carrying out the method of the present invention therefore comprises means for fitting a pipe or hose for transferring the densified fluid carbon dioxide comprising laundry finishing agent from the storage cylinder to the inner space of the drier containing the laundry articles. The skilled person understands that in order to feed densified fluid carbon dioxide from the storage cylinder said storage cylinder must be equipped with a dip tube (ascending pipe), which is immersed in the densified fluid carbon dioxide. This is to avoid that gaseous carbon dioxide in the upper part of the cylinder, which is not containing said laundry finishing agent, is transferred to the chamber.

As mentioned above the densified fluid carbon dioxide may alternatively be loaded with laundry finishing agent or additional ingredient(s) by feeding said densified fluid carbon dioxide through a cartridge containing the respective compound or by dosing the respective compound into the densified fluid carbon dioxide stream, preferably with a pump. In alternative embodiments an ironer or steam tunnel is adapted for carrying out the method of the present invention and therefore comprises means for fitting a pipe or hose for transferring the densified fluid carbon dioxide comprising laundry finishing agent from the storage cylinder to the inner space of the chamber in which the laundry articles are processed.

As mentioned above, the mixture containing densified fluid carbon dioxide, laundry finishing agent and other ingredients may be prepared just prior to use. A laundry finishing agent or additional active ingredient (e.g. peracid or peroxide) which may be unstable in the presence of a carrier such as carbon dioxide if stored for a longer time period, may be stored in a cartridge for example in presence of a stabilizer. Such a cartridge containing an instable ingredient (such as a peracid or peroxide) and a stabilizer can be connected with a pipe through which densified fluid carbon dioxide is fed when the laundry finishing agent shall

be applied to laundry articles. When flowing through the cartridge the densified fluid carbon dioxide takes up all or a part of the ingredient stored in the cartridge, thereby the densified fluid carbon dioxide is loaded with the ingredient stored in the cartridge and the mixture is dispensed and applied to the laundry articles. In a particularly preferred method the densified fluid carbon dioxide when flowing through the cartridge selectively extracts a part of all of the desired agent (laundry finishing agent or additional active ingredient; e.g. peracid or peroxide) contained in the cartridge, thereby the densified fluid carbon dioxide is loaded with the ingredient stored in the cartridge and the mixture is dispensed and applied to the laundry articles, whereas the stabilizer preferably remains in the cartridge.

The present invention also provides a method for the wet treatment of laundry articles comprising the steps of washing, rinsing and drainage, wherein a chemical compound having the property to deliver a soil modifying property to soils is applied to the laundry articles, by feeding a densified fluid carbon dioxide comprising said chemical compound into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

As mentioned above there is a desire to deliver a soil modifying property to soils. There exists a problem of soils that are only partially removed or difficult to remove with a conventional wash cycle such as cosmetics, makeup, lipstick, non trans-fats and the like. For the removal of such tenacious soils a chemical compound which may be selected from the group consisting of penetrants, pre-spotting agents, i.e. pre-treatment agents such as surfactants or surfactant mixtures, HLB modifiers is dispensed onto the respective laundry articles by the above described method, i.e. by bringing said laundry articles into contact with a gaseous medium formed immediately after depressurizing a densified fluid carbon dioxide comprising said chemical compound. In a preferred embodiment the densified fluid carbon dioxide comprising said chemical compound is fed into said chamber comprising said laundry articles before the washing step. This procedure is preferred as the tenacious soils thereby are pre-treated, i.e. pre-incubated with suitable chemical compound, and then removed during a conventional washing step.

In alternative embodiments the chemical compound is applied onto the laundry articles after the washing step, after the rinsing step or after the drainage step, for example before, during or after the drying step. By this method tenacious soils which were not removed by a conventional washing procedure will be removed in a subsequent wet treatment. Such subsequent wet treatment may either immediately follow the drying step or preferably at a later stage once the laundry articles have been in use again and possibly have been further soiled.

Further preferred embodiments as described above in respect to the application of the laundry finishing agent, can also be implemented in the method for applying or dispensing to laundry articles said chemical compound having the property to deliver a soil modifying property to soils.

Detailed description of the invention

The present invention refers to a method for applying at least one laundry finishing agent to laundry articles, comprising the step of feeding a densified fluid carbon dioxide comprising said laundry finishing agent into a chamber containing laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous. Once said densified fluid carbon dioxide becomes gaseous said laundry finishing agent contained or dissolved in the densified fluid carbon dioxide loses its carrier and is thereby homogenously dispensed or deposited onto the laundry articles and becomes absorbed by the laundry articles.

Definitions

As used herein, the term "laundry articles" refers to woven laundry articles as well as to non-woven laundry articles, including clothing, textiles, mattresses, carpets and mops, towels, bed sheets. Exemplary articles of clothing or garments laundered at an industrial laundering facility include robes, uniform shirts, uniform pants, executive shirts, lab coats, aprons, jackets, and shop coats. The reference to textiles includes items or articles that include textiles or fabric. Items or articles that include textiles or fabric can include athletic shoes, accessories, stuffed animals, brushes, mats, hats, gloves, outerwear, tarpaulins, tents, and curtains.

As used herein the term trans-fat refers to unsaturated fat with frans-isomer, whereas non trans-fat refers to unsaturated fat with *c*/s-isomer.

The method of the present invention is particularly useful in connection with industrial laundry where continuous batch washers or wash extractors are used.

In a particularly preferred embodiment the method is applied in connection with the operation of continuous batch washers or wash extractors as well as water extraction devices such as centrifuge or press. After the laundry articles have passed through continuous batch washers or wash extractors and subsequently the water extraction device the laundry articles typically are subjected to drying in driers, removal of knits in steam tunnels or ironing in an ironer.

As used herein, the phrase "densified fluid" refers to a fluid in a critical, subcritical, near critical, or supercritical state. The fluid is carbon dioxide which is a gas at standard conditions of one atmosphere pressure and 0 °C.

As used herein, the phrase "supercritical fluid" refers to a dense gas that is maintained above its critical point, the condition defined by the critical temperature, T_c, and critical pressure, P_c, of the substance, namely of carbon dioxide. The critical point of a pure substance can be represented by the apex of the vapor/liquid equilibrium curve.

Advantageously, in the supercritical region, high compressibility of the fluid allows adjusting properties of the solutions over a wide range, typically by making modest changes in the pressure of the system. As used herein, the phrase "critical point" refers to the transition point at which the liquid and gaseous states of a substance merge into each other and represents the combination of the critical temperature and critical pressure for a substance. The critical pressure is a pressure just sufficient to cause the appearance of two phases at the critical temperature. Critical temperatures and pressures have been reported for numerous organic and inorganic compounds and several elements. Supercritical fluids are typically less viscous and diffuse more readily than liquids. Preferably a densified fluid is at, above, or slightly below its critical point; and minimally a densified fluid is liquefied.

As used herein, the terms "near critical" fluid or "subcritical" fluid refer to a fluid material that is typically below the critical temperature of a supercritical fluid, but remains in a fluid state and denser than a typical gas due to the effects of pressure on the fluid. Preferably a subcritical or near critical fluid is at a

temperature and/or pressure just below its critical point. For example, a subcritical or near critical fluid can be below its critical temperature but above its critical pressure, below its critical pressure but above its critical temperature, or below both its critical temperature and pressure. The terms near critical and subcritical do not refer to materials in their ordinary gaseous or liquid state. Near critical or subcritical fluids require a temperature of at least about 0.5 the critical temperature (T_c), preferably at least about 0.7 T_c and/or a pressure of at least about 0.6 the critical pressure (P_c) preferably at least about 0.7 P_c, more preferably at least about 0.8 P_c. Suitable combinations of critical pressure and temperature include about 0.6-1 0 P_c and/or 0.5-1 0 T_c, about 0.7-4 P_c and/or about 0.7-5 T_c, or about 0.8-3 P_c and/or 0.9-3 T_c. The present invention can also include these quantities not modified by about.

As used herein, the term "non-critical" refers to a composition without the special properties of a near critical, critical, or supercritical fluid. A non-critical substance is typically a normal gas, liquid, or solid, in respect to carbon dioxide a gas.

As used herein, "supercritical fluid carbon dioxide" refers to carbon dioxide that is at or above its critical temperature of 31°C and its critical pressure of 71 atmospheres ($7{,}1 \times 10^6$ Pa), and which can not be condensed into a liquid phase despite the addition of further pressure.

Methods and Compositions Employing Densified Fluids

Near critical, critical, and supercritical densified fluids can be used as a vehicle for laundry finishing agents. The laundry finishing agent is preferably maintained under near critical, critical, or supercritical conditions as a concentrate composition.

For use, the densified fluid carbon dioxide comprising the laundry finishing agent can be directly applied to laundry articles. Preferably, employing a densified fluid as a vehicle for a laundry finishing agent allows applying the laundry finishing agent to laundry articles while the vehicle rapidly evaporates leaving no vehicle residue on the laundry articles.

Preferably, densified fluid carbon dioxide either dissolves, incorporates, suspends or otherwise carries laundry finishing agents employed in the present invention.

Above the critical temperature the fluid carbon dioxide becomes a supercritical fluid attaining the unique properties of a supercritical fluid that seems to have characteristics of both liquid and gas state. At high pressures above the critical point, the resulting supercritical fluid, or "dense gas", will attain densities approaching those of a liquid solvent. These properties are dependent upon the fluid composition, temperature, and pressure. The compressibility of supercritical fluids is greatest just above the critical temperature where small changes in pressure result in large changes in the density of the supercritical fluid. The "liquid-like" behavior of a supercritical fluid at higher pressures results in greatly enhanced solubilizing capabilities compared to those of the subcritical compound, with higher diffusion coefficients and an extended useful temperature range compared to liquids. Near- supercritical liquids also demonstrate solubility characteristics and other pertinent properties similar to those of supercritical fluids. The solute may be a liquid at the supercritical temperatures, even though it is a solid at lower temperatures.

One unique property of supercritical fluid carbon dioxide is the ability of the material to act as a solvent carrier or medium for a variety of materials. The behavior of supercritical fluids at high pressures creates a solubilizing capacity greater than non-critical materials. A variety of compounds become soluble in supercritical fluids, even at relatively low temperatures when similar materials are not soluble under non-critical conditions.

Densified near critical, critical, and supercritical fluids have attracted increasing attention in recent years. Supercritical carbon dioxide has been in use for many years and are known to be environmentally compatible. The Concise Encyclopedia of Chemical Technology (Kirk-Othmer) Fourth Edition, 1999, pp. 1943-1 944, discloses a basic discussion of densified near critical and supercritical fluids.

Densified fluid carbon dioxide has a viscosity that allows convenient application of the laundry finishing agent.

In a preferred embodiment, the laundry finishing agent is selected so that it is compatible with, soluble in, or dispensable through the fluid, particularly upon release from their container. Preferably, the laundry finishing agent is soluble in

the densified fluid carbon dioxide to at least about 0.01 % by weight of the total composition, more preferably about 1 wt-%, more preferably about 5 wt-%, further preferred up to 25 wt-%, still further preferred up to 40 wt-%.

Densified fluids such as carbon dioxide are suitable because of the non-toxic, environmentally compatible and non-flammable nature of the resulting materials. Mixtures of compressed carbon dioxide and nitrous oxide (N_2O) can be useful because nitrous oxide and carbon dioxide have different polarity and solvent properties.

The densified fluid carbon dioxide comprising the laundry finishing agent can also include other ingredients, such as another fluid (e.g., water) or gas, a carrier, solvent or co-solvent, co-pressurizing gas or gases, a buffering agent, an acidulant, a source of alkalinity, a rheology modifier or a mixture thereof.

Supercritical, subcritical, near supercritical, and other dense fluids and solvents that can be employed with such fluids are disclosed in U. S. Patent No. 5,306,350, issued April 26,1 994 to Hoy et al., which is incorporated herein for such disclosure. Emulsions of water in carbon dioxide and surfactants used in their formation are described in Lee, Jr. et al. Langmuir 15, pp. 6781 -6791 (1999), which is incorporated herein by reference for such disclosure.

For the purposes of the present invention, densified carbon dioxide can be produced and used under a range of conditions, such as at various temperatures and pressures. Temperatures suitable for densified carbon dioxide include temperatures in the range of about -77 °C to about 100 °C, preferably about -10 °C to about 60 °C, and more preferably about 20 °C to about 50 °C.

Temperatures suitable for near critical carbon dioxide include temperatures in the range of about 25 °C to about 100 °C, preferably about 30 °C to about 60 °C, and more preferably about 17 °C to about 50 °C. Temperatures suitable for supercritical carbon dioxide include temperatures in the range of about 31 °C to about 100 °C, preferably about 31 °C to about 60 °C, and most preferably about 31 °C to about 50 °C.

Pressures suitable for densified carbon dioxide include pressures in the range of about 1050 hPa to about 70 MPa, preferably about 4.9 MPa to about 49 MPa, and more preferably about 5.6 MPa to about 21 MPa. Pressures suitable for near

critical carbon dioxide include pressures in the range of about 6.3 MPa to about 70 MPa, preferably about 7 MPa to about 28 MPa, and more preferably about 7.35 MPa to about 21 MPa.

Pressures suitable for supercritical carbon dioxide include pressures in the range of about 7.5 MPa to about 70 MPa, preferably about 7.5 MPa to about 28 MPa, and most preferably about 7.5 MPa to about 14 MPa. A preferred densified carbon dioxide system includes pressure exceeding about 4.9 MPa at about 20 °C.

Carbon dioxide densified fluid compositions can take the form of, for example, single-phase or multi-phase solutions, emulsions, micro-emulsions, or suspensions. Compositions including a solvent that is miscible with the densified carbon dioxide typically take the form of a single-phase solution. Compositions including a solvent that is not miscible with the densified carbon dioxide typically take the form of a multi-phase solution, an emulsion, a micro-emulsion, or a suspension. Even a single solvent containing different solutes can produce either single or multi-phase densified carbon dioxide compositions, depending on the solute.

Supercritical and other dense forms of carbon dioxide, and cosolvents, co-surfactants, and other additives that can be employed with these forms of carbon dioxide are disclosed in U. S. Patent No. 5,866,005, issued February 2, 1999 to DeSimone et al., which is incorporated herein by reference for such disclosure.

Modifiers of Densified Fluid Compositions

Modifiers of densified fluid compositions alter properties of the composition significantly, even in relatively low concentration, advantageously increasing solubility for certain solutes. A preferred modifier increases solubility of a preferred solute, such as a laundry finishing agent by at least about 1.5-fold, preferably at least about 2-fold, preferably at least about 5-fold. Such modifiers include co-solvents, surfactants, and solutes, particularly those that include a CO_2 (carbon dioxide)-philic group linked to a CO_2-phobic group. One or more modifiers can be included in the compositions of the invention.

Surfactant Modifiers

Numerous known surfactants can be suitable as modifiers. See, e.g., McCutcheon's Volume 1: Emulsifiers & Detergents (1995 North American Edition) (MC Publishing Co., 175 Rock Road, Glen Rock, N. J. 07452). Surfactants employed as additives in CO_2 systems are disclosed in patents U. S. 4,592,348, U.S. 5,676,705, U.S. 5,683,473, U.S. 5,783,082, U.S. 5,858,022, U.S. 5,866,005, and PCT Application W0 96/27704, each of which is incorporated herein by reference for such disclosure. Examples of the major surfactant types that can be used as modifiers include: alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, alkylbenzenes, amine acetates, amine oxides, amines, sulfonate amines and amides, betaine derivatives, block polymers, carboxylated alcohol or alkylphenol ethoxylates, carboxylic acids and fatty acids, diphenyl sulfonate derivatives, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and/or amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic- type products, imidazolines and imidazoline derivatives, isethionates, lanolin-based derivatives, lecithin and lecithin derivatives, alkyl glycosides and glucosamines, lignin and lignin derivatives, maleic or succinic anhydrides, methyl esters, monoglycerides and derivatives, olefin sulfonates, phosphate esters, lecithin and its derivatives, phosphorous organic derivatives, polyethylene glycols, polymeric surfactants (e.g., polysaccharides, acrylic acid, and acrylamide), propoxylated and ethoxylated fatty acids alcohols or alkyl phenols, protein-based surfactants, quaternary surfactants, sarcosine derivatives, silicone-based surfactants, soaps, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of benzene, cumene, toluene and xylene, sulfonates of condensed naphthalenes, sulfonates of dodecyl and tridecylbenzenes, sulfonates of naphthalene and alkyl naphthalene, sulfonates of petroleum, sulfosuccinamates, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, tridecyl and dodecyl benzene sulfonic acids, and the like. Sulfonates of oils and fatty acids are preferred, in particular sulfonated oleic acid.

Co-solvent Modifiers

Preferred co-solvents for use as modifiers include 2- (2-aminoethoxy) ethanol, monoethanolamine, diethanolamine, triethanolamine, amyl acetate, amyl alcohol, butanol, 3-butoxyethyl-2-propanol, butyl acetate, n-butyl propionate, cyclohexanone, diacetone alcohol, diethoxyethanol, diethylene glycol methyl ether, diethylene glycol n-butyl ether, diisobutyl carbinol, diisobutyl ketone, dimethyl heptanol, dipropylene glycol n-butyl ether, dipropylene glycol methyl ether, dipropylene glycol propyl ether, dipropylene glycol tert-butyl ether, ethanol, ethyl acetate, 2-ethylhexanol, ethyl propionate, ethylene glycol butyl ether, ethylene glycol methyl ether acetate, hexanol, isobutanol, isobutyl acetate, isobutyl heptyl ketone, isophorone, isopropanol, isopropyl acetate, methanol, methyl amyl alcohol, methyl n-amyl ketone, 2-methyl-1 -butanol, methyl ethyl ketone, methyl isobutyl ketone, 1-pentanol, n-pentyl propionate, 1-propanol, n-propyl acetate, n-propyl propionate, propylene glycol n-butyl ether, propylene glycol ethyl ether, propylene glycol methyl ether, propylene glycol n-propyl ether, tripropylene glycol methyl ether and tripropylene glycol n-butyl ether. Ethylene glycol butyl ether and dipropylene glycol n-butyl ether are more preferred cosolvents. Mixtures of cosolvents can be used if desired.

Commercially available cosolvents (all of which are available from Union Carbide Corp.) include those sold under the trade names: Butoxyethyl PROPASOL™, Butyl CARBITOL™ acetate, Butyl CARBITOL™, Butyl CELLOSOLVETM™ acetate, Butyl CELLOSOLVE™, Butyl DIPROPASOL™, Butyl PROPASOL™, CARBITOL™ PM-600, CARBITOL™ Low Gravity, CELLOSOLVE™ acetate, CELLOSOLVE™, Ester EEPTM™, FILMER 1ST™, Hexyl CARBITOL™, Hexyl CELLOSOLVE™, Methyl CARBITOL™, Methyl CELLOSOLVE™ acetate, Methyl CELLOSOLVE™, Methyl DIPROPASOL™, Methyl PROPASOL™ acetate, Methyl PROPASOL™, Propyl CARBITOL™, Propyl CELLOSOLVE™, Propyl DIPROPASOL™ and Propyl PROPASOL™.

Densified Fluid Emulsions

A densified fluid can also form an emulsion with a solvent such as water in the presence of a surfactant. The compositions of the present invention include and the methods of the invention can employ emulsions of a densified fluid including a

laundry finishing agent. In particular, perfluoroether ammonium carboxylate surfactants can aid formation of emulsions between water and densified carbon dioxide that include up to 70 volume-% water. Without surfactant, carbon dioxide dissolves water only to about 0.1 wt-%. Preferred surfactants for forming emulsions of densified fluids include those containing a fluorine-containing or a siloxane-containing $C0_2$-philic segment. Preferred solvent combinations that form emulsions in the presence of surfactants include hydrocarbons, benzyl alcohol, glycol ethers, flavorants, fragrances.

Solvent for use with densified fluid carbon dioxide

A solvent fraction mixed with the densified fluid as part of the densified fluid laundry finishing agent can include any active organic solvent and/or non-aqueous diluent which is at least partially miscible with the fluid and can form a solution, dispersion, or suspension with the densified fluid and the laundry finishing agent. Certain preferred solvents are at least partially miscible with water and can form a single phase of the solvent, water, and the fluid.

Solvents that can be employed in the present invention include, but are not limited to, C-i-16 aliphatic and aromatic alcohols and esters such as methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol, amyl alcohol, octanol, nonanol, and other aliphatic alcohols, acetamidophenol, acetanilide, acetophenone, [2-acetyl-1 - methylpyrrole, benzyl acetate, benzyl alcohol, phenethanol, benzyl benzoate, amyl acetate, methyl acetate, ethyl acetate and other alkyl carboxylic esters; ethers, hydroxyethers, or glycol ether esters including ethers, such as methyl t-butyl ether, dibutyl ether, methyl phenyl ether and other aliphatic or alkyl aromatic ethers; glycol ethers such as ethoxy ethanol, butoxy ethanol, ethoxy 2-propanol, propoxy ethanol, butoxy 2-propanol, benzyloxyethanol, ethylene glycol phenyl ether, DOWANOL EPH™ (commercially available from Dow Chemical Co.), propylene glycol phenyl ether (commercially available as DOWANOL PPH™ from Dow Chemical Co.), butoxy ethanol, propoxy ethanol, hexoxy ethanol, isopropoxy 2-propanol, butoxy 2- propanol, propoxy 2-propanol, tertiary butoxy 2-propanol, ethoxy ethanol, butoxy ethoxy ethanol, propoxy ethoxy ethanol, hexoxy ethoxy ethanol, methoxy ethanol, methoxy 2-propanol, and ethoxy ethoxy ethanol and other glycol ethers; glycol ether esters such as butoxy ethoxy acetate, ethyl 3-ethoxy propionate; essential oils (e.g., benzaldehyde, pinenes (alphas, betas, and

the like), terpineols, terpinenes, carvone, cinnamealdehyde, borneol and its esters, citrals, ionenes, jasmine oil, limonene, dipentene, linalool and its esters); dibasic esters such as dimethyl adipate, dimethyl succinate, dimethyl glutarate (often available in a mix; including products available under the trade designations DBE, DBE-3, DBE-4, DBE-5, DBE-6, DBE-9, DBE- IB, and DBE-ME from DuPont Nylon Intermediates and Specialties), dimethyl malonate, diethyl adipate, diethyl succinate, diethyl glutarate, dibutyl succinate, and dibutyl glutarate; dialkyl carbonates such as dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, and dibutyl carbonate; C_{1-16} protonated carboxylic acids such as 2-ethyl-1 -hexanoic acid, butyric acid, octanoic acid, heptanoic acid, nonanoic acid, and decanoic acid; C_{1-12} organic anhydrides such as acetic anhydride, succinic anhydride, phthalic anhydride, maleic anhydride, and alkyl or alkenyl succinic anhydrides; organo-nitriles such as benzonitrile; C_{3-} ie in organo-phosphates and phosphonates such as tributyl phosphate, tripropyl phosphate, 2-ethyl-1 -hexyl phosphate; and phthalate esters such as dibutyl phthalate, diethylhexyl phthalate, and diethyl phthalate. Also included are C_{4-16} lactones and lactams such as n-methyl-2-pyrrolidone, and cyclic ureas such as dimethyl ethylene urea. Mixtures of solvents can be used if desired.

Other solvents which may be employed in the methods and compositions of the present invention include ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone and other aliphatic ketones; aromatic hydrocarbons such as toluene, xylene, and other aromatics or mixtures of aromatic solvents; aliphatic hydrocarbons such as VM&P naphtha and mineral spirits, and other aliphatics or mixtures of aliphatics; nitro alkanes such as 2-nitropropane; fluorinated and other halogenated solvents (e. g., chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, and sulfur hexafluoride); amides (e.g. dimethyl acetamide), and the like.

For the purposes of this invention, said laundry finishing agent may be compositions or agents which impart softness or crease-resistance, reduce static, or make laundry easier to iron. These compositions or agents may include conditioning, antistatic, and softening agents, as well as perfumes and fragrances. Examples of softening agents and/or anti-static agents typically found in fabric

softeners are well known in the art and include, but are not limited to, cationic and nonionic softeners, such as quaternary ammonium salts, including ditallow quaternary ammonium salts, imidazolinium salts, esters of quaternary ammonium salts, amidoamines, carboxylic salts of tertiary alkylamines, fatty acid polyglycol esters, fatty acid alkanol amides, organic phosphoric acid esters, tertiary phosphine oxides, tertiary amine oxides, alkylated party ethoxylated polyamines, anionic soaps, sulfates, sulfonates, and the like. Specific examples of softening and/or anti-static agents include methyl bis(tallow amidoethyl)-2-hydroxyethyl ammonium methyl sulfate, ditallow dimethyl quaternary ammonium chloride, methyl bis(tallow amidoethyl)-2-tallow imadazolinium ammonium methyl sulfate, and methyl bis(ethyl tallowate)-2-hydroxyethyl ammonium methyl sulphate, diethylester dimethyl ammonium chloride. Other examples of anti-static agents include polyhydric alcohols, amines, amides, polyoxy ethylene derivatives, amine soaps, amine salts of alkyl sulfates, alkyl phosphates, and the like.

Examples of suitable fabric softening agents, are provided in U.S. Pat. No. 5,234,610, which is herein incorporated by reference.

In various embodiments, the fragrance makes up from 0.0001 weight percent of the densified fluid carbon dioxide mixture. In various embodiments fragrance will be present in an amount from 0.0001 to 10 weight percent of the densified fluid carbon dioxide mixture. The fragrance, or perfume, may be any fragrant substance or mixture of substances, including natural and synthetic substances, that have a favorable aroma. In addition, the fragrance or perfume may contain auxiliary materials such as fixatives, extenders, stabilizers and solvents. Examples of suitable fragrances include, but are not limited to, silicon oils, essential oils, absolutes, resinoids, resins, and synthetic perfume components such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitrites, including saturated and unsaturated compounds, aliphatic, carbocyclic and heterocyclic compounds. Examples of such perfume components are geraniol, geranyl acetate, linalool, linaly acetate, tetrahydrolinalool, citronellol, citronellyl acetate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, 2-phenylethanol, 2-phenylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, benzyl benzoate, styrallyl acetate, amyl salicylate,

dimethylbenzylcarbinol, trichloromethylphenylcarbinyl methylphenylcarbinyl acetate, p-tert-butyl-cyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, alpha-n-amylcinammic aldehyde, alpha-hexyl-cinammic aldehyde, 2-methyl-3-(p-tert-.butylphenyl)-propanal, 2-methyl-3-(p-isopropyl-phenyl)propanal, 3-(p-tert.butylphenyl)propanal, tricyclodecenyl acetate, tricyclodecenyl propionate, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde, 4-acetoxy-3-pentyltetrahydropyran, methyl dihydrojasmonate, 2-n-heptylcyclopentanone, 3-methyl-2-pentyl-cyclopentanone, n-decanal, n-dodecanal, 9-decenol-1 , phenoxyethyl isobutyrate, phenylacetaldehyde dimethyl acetal, phenylacetaldehyde diethyl acetal, geranonitrile, citronellonitrile, cedryl acetal, 3-isocam-phylcyclohexanol, cedryl methyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropine, coumarin, eugenol, vanillin, diphenyl oxide, hydroxycitronellal ionones, methyl ionones, isomethyl ionomes, irones, cis-3-hexenol and esters thereof, indane musk fragrances, tetralin musk fragrances, isochroman musk fragrances, macrocyclic ketones, macrolactone musk fragrances, ethylene brassylate, aromatic nitro-musk fragrances. A specific example of a suitable fragrance is Softy AR 3329, a fragrance manufactured by CPL Aromas UK. Softy AR 3329 contains dipropylene glycol, HHCB (1,3,4,6,7,8-hexahydro-4,6,6, 7,8, 8-hexamethylcyclopenta-(g)-2-benzopyran), and 1,1,6,7-tetramethyl-6-acetyldecalene, in addition to small quantities of various essential oils, alcohols, esters, hydrocarbons, and aldehydes.

Examples of suitable fragrances, or perfumes, are provided in U.S. Pat. No. 5,234,610, which is herein incorporated by reference.

The dose of a fragrance component refers to an amount and type of fragrance that provides a residual fragrance to the textiles dried that can be detected on the fabric at least 24 hours after the drying operation. For example, more than 50% of a panel of at least nine people can detect the presence of a fragrance on towels at least 24 hours after the towels are dried in a dryer in the presence of the fragrance dispenser wherein the fragrance dispenser is dispensing a desired amount or dose of the fragrance component. Preferably, the fragrance dispenser can satisfy a panel test where at least six of nine panelists correctly identify the towel, from a group of three towels, that is different. Either one towel or two towels of the three towels are dried in a dryer in the presence of the fragrance dispenser

at least 24 hours earlier. The other towel or towels are not dried in the presence of a fragrance dispenser. The panelists are asked to identify the towel that is different from the other two towels without being told that the difference relates to fragrance. The panelists that can detect the presence of residual fragrance either select the towel that has no residual fragrance if the other two towels have a residual fragrance or select the towel that has the residual fragrance is the two other towels do not have residual fragrance. This type of panel test can be referred to as a "triangle test." It should be understood that the panelists are individuals not suffering from an impairment of olfactory sense from, for example, illness or activity that may limit one's ability to detect fragrance (e.g., smoking or exposure to certain chemicals).

The densified fluid carbon dioxide comprising a fragrance composition may be best suited for addition during the cool-down cycle in the dryer. In another embodiment, the densified fluid carbon dioxide comprising conditioning composition is adapted to be added to laundry in a dryer in the beginning, or at an early stage, of the drying process while the densified fluid carbon dioxide comprising a fragrance composition is adapted to be added during a later stage, for example, during the cool-down cycle. In yet another embodiment, the densified fluid carbon dioxide comprising a conditioning composition is adapted to be added over a period of time during the drying process.

Suitable conditioning compositions for use with densified fluid carbon dioxide may include conventional conditioning, softening, and antistatic agents well known in the art, in addition to water and other additives, as discussed above. The conditioning composition may itself contain a fragrance or perfume.

Soil release agents are preferably polymeric soil release agents, preferably those comprising block copolymers of polyalkylene terephthalate and polyoxyethylene terephthalate, and block copolymers of polyalkylene terephthalate and polyethylene glycol. Preferably, these polymeric soil release agents contain one, or more, negatively charged functional groups such as the sulfonate functional group, preferably as capping groups at the terminal ends of said polymeric soil release agent. Examples of soil release agents are provided in U.S. Pat. No. 5,234,610, which is herein incorporated by reference.

For the purposes of this invention dryers include any type of conventional laundry dryer. Such dryers are well known in the art. Examples of suitable dryers are described in U.S. Pat. Nos. 2,807,893 and 5,749,163, which are herein incorporated by reference. Dryers that can be used in conjunction with the present invention include conventional automatic clothes dryers. The dryers may be gas, electric, or steam powered and may be of the type used in homes or of the type used in industries, such as those used by the hotel industry. As will become clear in the following discussion, the present invention is particularly useful in industrial dryers which operate at temperature of up to, or greater than, 80 °C, and sometimes at temperatures of up to 95 °C. This is much hotter than the operating temperatures of home dryers which are typically run at temperatures below about 65 °C. These higher temperatures exacerbate the problem of fragrance volatilization and loss during drying because most fragrances have flash points much lower than 95 °C. Industrial dryers often achieve a temperature in the range of about 75 °C to about 115°C. It should be understood that these ranges are not necessarily strictly adhered to. Domestic dryers and industrial dryers can operate at lower temperatures or higher temperatures as desired.

Examples

The examples according to the present invention were carried out as follows: The desired laundry finishing agent to be applied to laundry articles was provided in a cylinder. The densified fluid carbon dioxide was added to the cylinder under a pressure above 5.5×10^6 Pa. The laundry finishing agent suspended, dissolved or was otherwise incorporated in the densified fluid carbon dioxide and evenly distributed therein. The method for dispensing the laundry finishing agent was carried out in a drier. For carrying out the method of the present invention a supply line for feeding densified fluid carbon dioxide was arranged for connecting the cylinder containing said densified fluid carbon dioxide with the inner space (chamber) of the drier. The dryer drum of the drier was filled with the laundry article. Upon opening the valve of the supply line the densified fluid carbon dioxide comprising the laundry finishing agent was fed into the dryer and thereby immediately expanded in its gaseous form. The laundry finishing agent when losing its liquid carbon dioxide carrier was released and may form an aerosol and

was thereby dispensed or deposited on and taken up or absorbed by the laundry articles in the drier. In order to feed densified fluid carbon dioxide from the storage cylinder the storage cylinder was equipped with a dip tube having a sufficient length that the lower opening of the dip tube was immersed in the densified fluid carbon dioxide.

Complete incorporation of the given amount of the given laundry finishing agent into the densified fluid carbon dioxide was checked by different methods:

One method to confirm that the laundry finishing agent was completely incorporated into the densified fluid carbon dioxide was that the vessel in which the densified fluid carbon dioxide was mixed with the laundry finishing agent was completely emptied by dispensing the densified fluid carbon dioxide. If no residual laundry finishing agent remained in the vessel then the complete amount of laundry finishing agent was incorporated in the densified fluid carbon dioxide.

In an alternative method, excess laundry finishing agent was added to densified fluid carbon dioxide. Then the densified fluid carbon dioxide/laundry finishing agent-mixture was transformed into a solid dry ice block. Subsequently, the dry ice block was subjected to complete evaporation. The amount of laundry finishing agent which remained after complete evaporation of the dry ice represented the maximum amount which was incorporated in the given amount of formerly densified fluid carbon dioxide.

Uptake or absorption of the laundry finishing agent by the laundry article was checked by comparing untreated laundry articles with treated laundry articles. Laundry articles treated with densified fluid carbon dioxide comprising a fragrance were subjected to a smell test by a panel of individuals who confirmed that the treated laundry articles did comprise the fragrance while no smell of fragrance was detected in respect to the untreated laundry. As test the triangle test was used which was described above.

Uptake or absorption of silicone (polymethylsilicone) as softener by the laundry article was checked by comparing untreated laundry articles with treated laundry articles. Laundry articles treated with densified fluid carbon dioxide comprising polymethylsilicone were subjected to a touch test by a panel of individuals who confirmed that the treated laundry articles did comprise the polymethylsilicone

while the untreated did not. Polymethylsilicone treated laundry articles gave the feeling of a greasy softness.

A further method to check if the laundry article took up or absorbed the respective laundry finishing agent was by comparing treated and untreated laundry articles by spectroscopic methods, with which the presence of the respective laundry finishing agent was identified.

Tables 1 and 3 summarize the type of laundry finishing agent, the product name and chemical description of the added laundry finishing agent, the amount of the laundry finishing agent in the total composition of densified fluid carbon dioxide, the amount of densified fluid carbon dioxide/laundry finishing agent mixture dispensed to the laundry articles, the type and amount of the laundry article and the conditions under which the method was run in the drier.

Tables 2 and 4 summarize the results of the methods relating to checking if the complete amount of the respective laundry finishing agent was incorporated in the densified fluid carbon dioxide, and if the dispensed laundry finishing agent was taken up or absorbed by the laundry articles.

The examples 1 to 19 show that a diversity of laundry finishing agents alone or as mixtures were introduced into densified fluid carbon dioxide and that the respective densified fluid carbon dioxide/laundry finishing agent mixtures were successfully dispensed and taken up and absorbed, respectively, by the laundry articles.

Table 1:

Example No:	type of laundry finishing agent	product name / chemical description	amount comprised in total compositon of densified fluid CO_2 [weight %]	dispensed amount of densified fluid CO_2 comprising laundry finishing agent	type of laundry article; parameter and conditions of dryer when mixture is added
1	perfume	perfume oil 071105-N (mixture comprising terpenes, aldehydes, ketones)	0.6	2.0 kg	wet terry towel: 39 kg: dryer closed, blower set to 40 ºC
2	perfume	perfume oil 071105-N (mixture comprising terpenes, aldehydes, ketones)	0.6	4.0 kg	wet terry towel: 39 kg: dryer closed, blower shut off, addition during cooling down phase at 40ºC
3	softener	silicone (polymethylsiloxane)	3.9	2.5 kg	wet terry towel: 39 kg; dryer closed; blower set to 30 - 100 ºC
4	softener	coconut fatty acid (a carboxylate)	4.4	6.0 kg	wet terry towel: 40 kg dryer closed, blower set to 50 ºC, addition during cooling down phase
5	soil release agent	SRN 300 (polyethylene terephtalate (PET)) and polyoxyethylen terephtalate (POET)	2.0	5.3 kg	wet terry towel: 40 kg dryer closed, blower set to 30 - 100 ºC
6	surfactant (for pre-wash preparation)	Lutensol® TO3 (non-ionic tensides, alkyl oligoethyl ether alcohols)	9.7	3.3 kg	wet cleaning mops: 40 kg dryer closed, blower set to 30 - 80ºC
7	paraffin	SN80 from Repsol (hydro carbon complex)	21.4	3.0 kg	wet cleaning mops: 40 kg dryer closed, blower set to 30 - 80ºC
8	paraffin / tenside mixture	mixture of SN80 from Repsol and Lutensol® TO3; ratio 2.77:1	13.3 (9.77/3.52)	5.0 kg	wet cleaning mops: 40 kg dryer closed, blower set to 30 - 80ºC

Table 2:

Example No:	complete incorporation of the amount of laundry finishing agent given in table 1 into densified fluid carbon dioxide	uptake/absorption of laundry finishing agent by laundry article
1	Yes	Yes
2	Yes	Yes
3	Yes	Yes
4	Yes	Yes
5	Yes	Yes
6	Yes	Yes
7	Yes	Yes
8	Yes	Yes

Table 3:

Example No:	type of laundry finishing agent	product name / chemical description	amount comprised in total compositon of densified fluid CO_2 [weight %]	dispensed amount of densified fluid CO_2 comprising laundry finishing agent	type of laundry article; parameter and conditions of dryer when mixture is added
9	softener	Stepantex® VL 90 A (alkylester ammonium chloride (50-100%)) dissolved in isopropanole	4.3	3.0 kg	wet terry towel: 40 kg: dryer closed, blower set to 30-110ºC
10	softener	DOW DC-28035	4.3	3.0 kg	wet terry towel: 40 kg: dryer closed, blower set to 30-110ºC
11	softener	Wacker LSM 21210	4.3	3.0 kg	wet terry towel: 40 kg: dryer closed, blower set to 30-110ºC
12	softener	DEEDMAC® (diethylester dimethyl ammonium chloride)	4.3	3.0 kg	wet terry towel: 40 kg: dryer closed, blower set to 30-110ºC
13	mangle waxes	silicone oils	6.0	2.0 kg	wet flat ware: 40 kg: dryer closed, blower set to 30-110ºC
14	hydrophobing agent	Repellan® NFC (fluoropolymer)	10.0	1.5 kg	wet flat ware: 40 kg: dryer closed, blower set to 30-110ºC
15	soil repellent	PVI or PVP	5.0	2.0 kg	wet flat ware: 40 kg: dryer closed, blower set to 30-110ºC
16	disinfection	phenoxyethanol (polyoxyethanol)	1.0	0.5 kg	wet terry towel: 40 kg: dryer closed, blower shut-off, 30-110ºC
17	disinfection	aldehyde	1.0	0.5 kg	wet terry towel: 40 kg: dryer closed, blower shut-off, 30-110ºC
18	perfume and softener	perfume oil 071105-N+ / silicone (polymethylsiloxane) 1:9	25.0	3.0 kg	wet terry towel: 40 kg: dryer closed, blower shut-off, 50ºC
19	antioxidant (scavenger)	butylhydroxyltoluene (BHT, E321)	5.0	2.0 kg	wet cleaning mops: 40 kg dryer closed, blower set to 30-80ºC

Table 4 :

Example No:	complete incorporation of the amount of laundry finishing agent given in table 3 into densified fluid carbon dioxide	uptake/absorption of laundry finishing agent by laundry article
9	Yes	Yes
10	Yes	Yes
11	Yes	Yes
12	Yes	Yes
13	Yes	Yes
14	Yes	Yes
15	Yes	Yes
16	Yes	Yes
17	Yes	Yes
18	Yes	Yes
19	Yes	Yes

Claims

1. A method for applying at least one laundry finishing agent to laundry articles, comprising the step of feeding a densified fluid carbon dioxide comprising said laundry finishing agent into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

2. The method according to claim 1, wherein due to said densified fluid carbon dioxide becoming gaseous said laundry finishing agent comes into contact with the laundry articles.

3. The method according to claim 1 or 2, wherein the laundry articles are transported through said chamber or are agitated when feeding said densified fluid carbon dioxide comprising said laundry finishing agent into said chamber containing said laundry articles.

4. The method according to any one of claims 1 to 3, wherein the gaseous medium contained in said chamber is withdrawn from the chamber.

5. The method according to any one of claims 1 to 4, wherein the gaseous medium contained in said chamber is withdrawn from the chamber, and wherein excess laundry finishing agent comprised in the withdrawn gaseous medium is collected and may be discarded or recycled.

6. The method according to any one of claims 1 to 5, wherein the laundry finishing agent is selected from the group consisting of fragrance, conditioning agent, softening agent, anti-soil-re-deposition agent, soil release agent, ease ironing agent, ease drying agent, antistatic agent, fungistatic, bacteriostatic, hydrophobic agent, oleophobic agent, impregnation material, flame retardant, repellent, scavenger, surfactant, bleaching agent, peracid compound, H_2O_2, bleach activator, bleach catalyst, oxidizing agent, optical brightener, chelating agent, builder, radical scavenger, paraffin, enzyme and compositions comprising one or more of said agents.

7. The method according to any one of claims 1 to 6, wherein said densified fluid carbon dioxide carrying said laundry finishing agent is a mixture comprising densified fluid carbon dioxide and said laundry finishing agent.

8. The method according to any one of claims 1 to 6, wherein said densified fluid carbon dioxide carrying said laundry finishing agent is a mixture comprising densified fluid carbon dioxide, said laundry finishing agent and at least one co-solvent.

9. The method according to any one of claims 1 to 8, which is carried out after the wet treatment of said laundry articles, said wet treatment comprising the steps of washing, rinsing and drainage.

10. The method according to any one of claims 1 to 9, which is carried out before, during or after a drying process of said laundry articles, or during the cool-down cycle of a drying process.

11. The method according to any one of claims 1 to 9, which is carried out during ironing of the laundry articles in an ironer.

12. The method according to any one of claims 1 to 9, which is carried out during processing the laundry articles in a steam tunnel.

13. The method according to any one of claims 1 to 12, wherein during carrying out the method the pressure in said chamber containing said laundry articles is 1500 hPa or less, preferably ambient pressure.

14. The method according to any one of claims 1 to 13, wherein said method is carried out at a temperature of 0°C to 150°C, preferably at a temperature of 10°C to 100 °C, further preferred at a temperature of 15°C to 80 °C.

15. The method according to any one of claims 1 to 14, wherein said densified fluid carbon dioxide comprising said laundry finishing agent is provided in a storage tank prior to the application to the laundry articles.

16. The method according to any one of claims 1 to 14, wherein said densified fluid carbon dioxide is loaded with said laundry finishing agent by feeding densified fluid carbon dioxide through a cartridge containing said laundry finishing agent, whereby the densified fluid carbon dioxide is taking up the laundry finishing agent, and then immediately is applied to the laundry articles.

17. The method according to any one of claims 1 to 14, wherein prior to dispensing to said laundry articles said densified fluid carbon dioxide is loaded with said laundry finishing agent by dosing said laundry finishing agent to a stream of densified fluid carbon dioxide, whereby the densified fluid carbon dioxide is taking up the laundry finishing agent.

18. A method for the wet treatment of laundry articles comprising the steps of washing, rinsing and drainage, wherein after the steps of washing rinsing and drainage a laundry finishing agent is applied to the laundry articles, by bringing laundry articles into contact with a gaseous medium immediately after the gaseous medium has been formed by depressurizing a mixture comprising densified fluid carbon dioxide and said laundry finishing agent.

19. The method for the wet treatment of laundry articles according to claim 18, wherein the application of said laundry finishing agent is carried out as defined in any one of claims 1-17.

20. A drier for drying laundry articles, adapted for carrying out the method of any one of claims 1 to 19.

21. A method for applying at least a chemical compound to laundry articles having the property to deliver a soil modifying property to soils, comprising the step of feeding a densified fluid carbon dioxide comprising said chemical compound into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

22. A method for the wet treatment of laundry articles comprising the steps of washing, rinsing and drainage, wherein a chemical compound having the property to deliver a soil modifying property to soils is applied to the laundry articles, by feeding a densified fluid carbon dioxide comprising said chemical compound into a chamber containing said laundry articles, wherein upon entry into said chamber said densified fluid carbon dioxide becomes gaseous.

23. The method of claim 22, wherein the densified fluid carbon dioxide comprising said chemical compound is fed into said chamber comprising said laundry articles before the washing step, after the washing step, after the rinsing step or after the drainage step.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/056852

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06F35/00 D06F58/20
ADD.

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)
D06F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	EP 2 042 645 Al (BSH BOSCH SIEMENS HAUSGERAETE [DE]) 1 April 2009 (2009-04-01) paragraphs [0001], [0002], [0023] - [0038], [0044] - [0049], [0063] - [0067]; claims 1-5; figures	1-10, 13-17, 19,20,23 22 11,12, 18,21
X Y A	W0 01/06052 Al (RAYTHEON CO [US]) 25 January 2001 (2001-01-25) page 5, line 24 - page 7, line 12; claims; figures	1-8,15, 21 22 9-14, 16-20,23
A	W0 2004/082858 Al (LINDE AG [DE] ; LINDQVIST KENNETH STIG [SE] ; HAMREF0RS JAN [SE]) 30 September 2004 (2004-09-30) page 2, line 9 - page 6, line 4 ; page 7, line 34 - page 11, line 9 ; claims	1-23

-/- .

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

"L" documentwhich may throw doubts on priority claim(s) orwhich is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2012	27/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Clivio, Eugenio

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/056852

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/70141 A1 (MICELL TECHNOLOGIES INC [US] ; DEYOUNG JAMES P [US] ; ROMACK TIMOTHY J [ ) 23 November 2000 (2000-11-23) the whole document ---	1-23

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/056852

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2042645 A1	01-04-2009	DE 102007046549 A1	23-04-2009
		EP 2042645 A1	01-04-2009
WO 0106052 A1	25-01-2001	AU 749611 B2	27-06-2002
		AU 4845300 A	05-02-2001
		CN 1302343 A	04-07-2001
		EP 1114217 A1	11-07-2001
		ID 27373 A	05-04-2001
		JP 3497851 B2	16-02-2004
		JP 2003505609 A	12-02-2003
		MX PA01002648 A	06-05-2002
		TW 554116 B	21-09-2003
		US 6569210 B1	27-05-2003
		WO 0106052 A1	25-01-2001
WO 2004082858 A1	30-09-2004	NONE	
WO 0070141 A1	23-11-2000	AT 290114 T	15-03-2005
		AU 4845400 A	05-12-2000
		CA 2373309 A1	23-11-2000
		CN 1365408 A	21-08-2002
		DE 60018407 D1	07-04-2005
		EP 1179099 A1	13-02-2002
		JP 2002543951 A	24-12-2002
		US 6148645 A	21-11-2000
		US 6269507 B1	07-08-2001
		US 6499322 B1	31-12-2002
		US 2002194681 A1	26-12-2002
		WO 0070141 A1	23-11-2000