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(54) DRY ICE PRODUCTS AND METHOD OF MAKING SAME

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**AIR LIQUIDE INTELLECTUAL PROPERTY DEPT.**
**2700 POST OAK BLVD.**
**SUITE 1800**
**HOUSTON, TX 77056 (US)**

(21) Appl. No.: **11/537,993**

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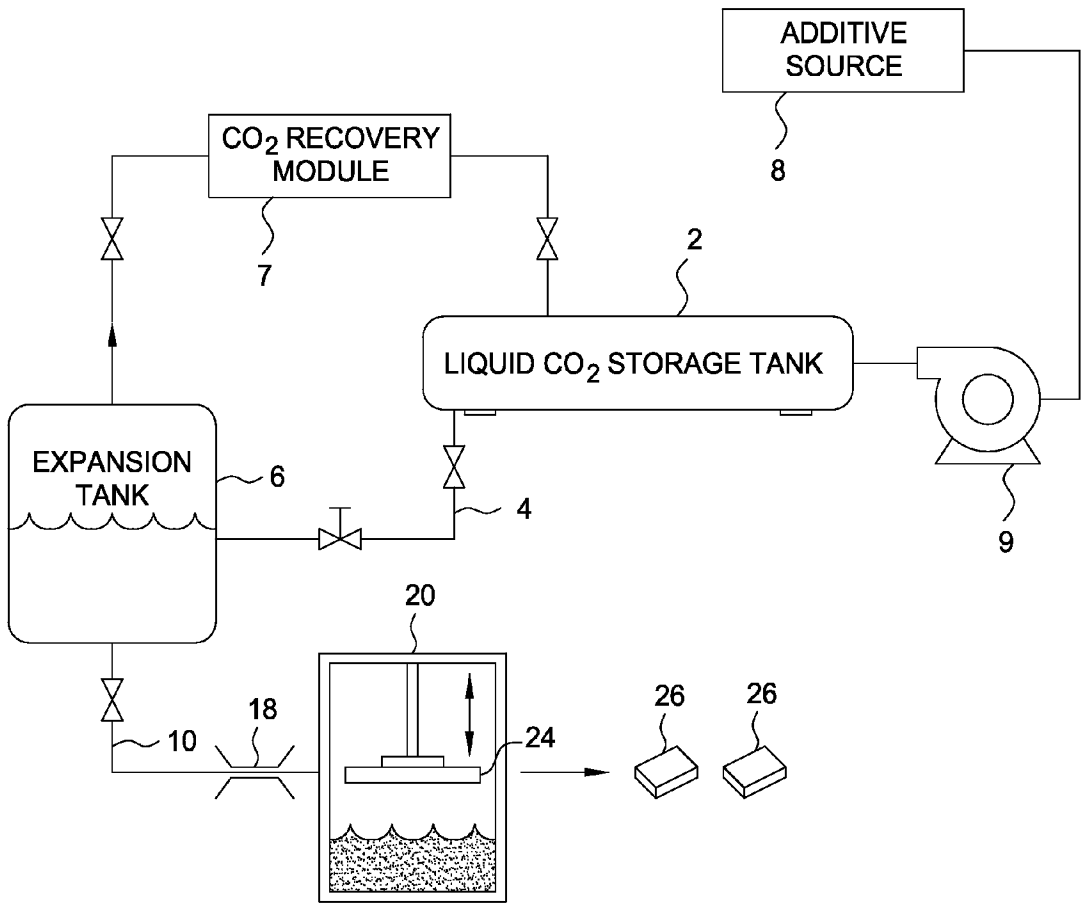
*F25J 1/02* (2006.01)

(52) **U.S. Cl.** ................................ **62/604**; 62/384; 62/605

(57) **ABSTRACT**

Solid carbon dioxide with enhanced sensory properties, such as color and scent. Additives are incorporated into solid carbon dioxide by any variety of processes. The additives are selected on the basis of desired visual or olfactory effects.



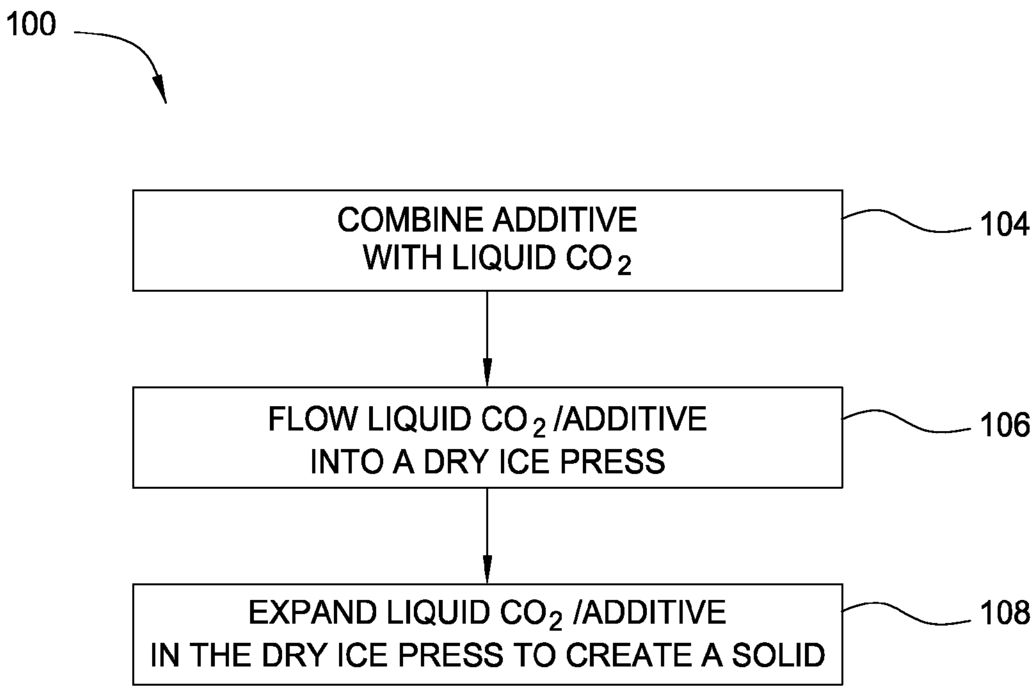

100
COMBINE ADDITIVE
WITH LIQUID $CO_2$
104
FLOW LIQUID $CO_2$ /ADDITIVE
INTO A DRY ICE PRESS
106
EXPAND LIQUID $CO_2$ /ADDITIVE
IN THE DRY ICE PRESS TO CREATE A SOLID
108

FIG. 1

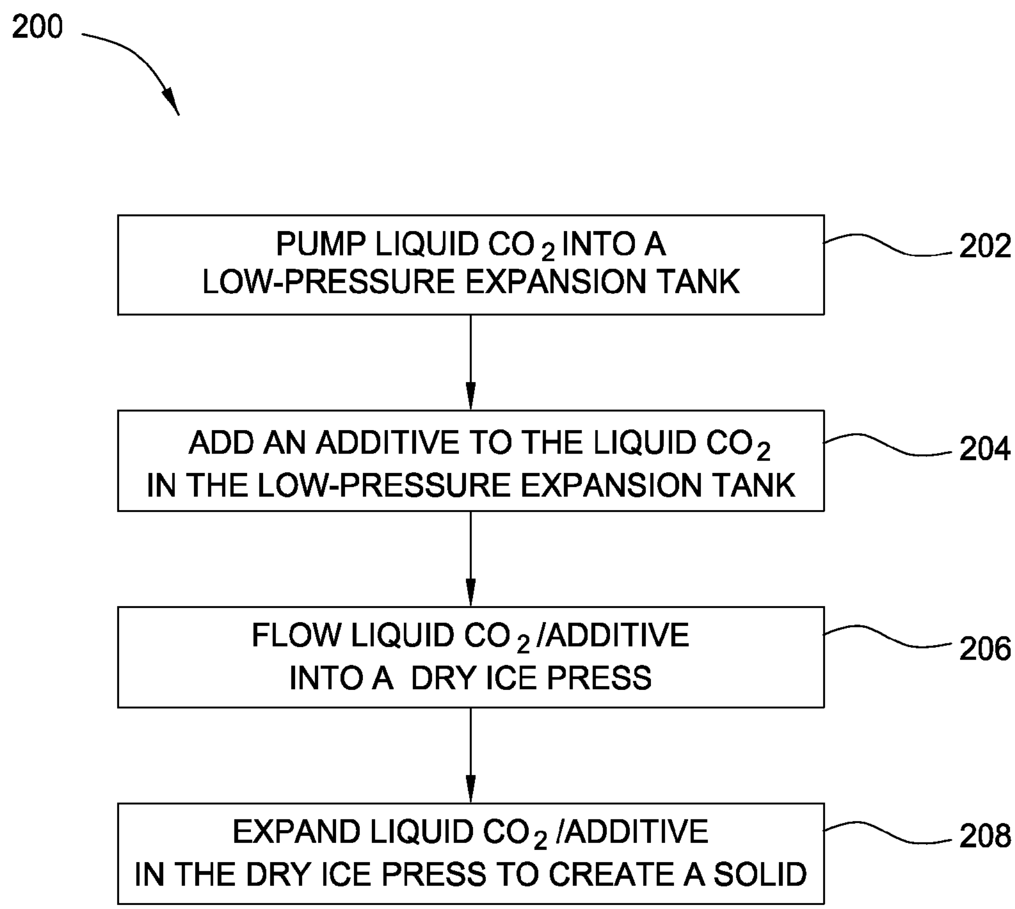
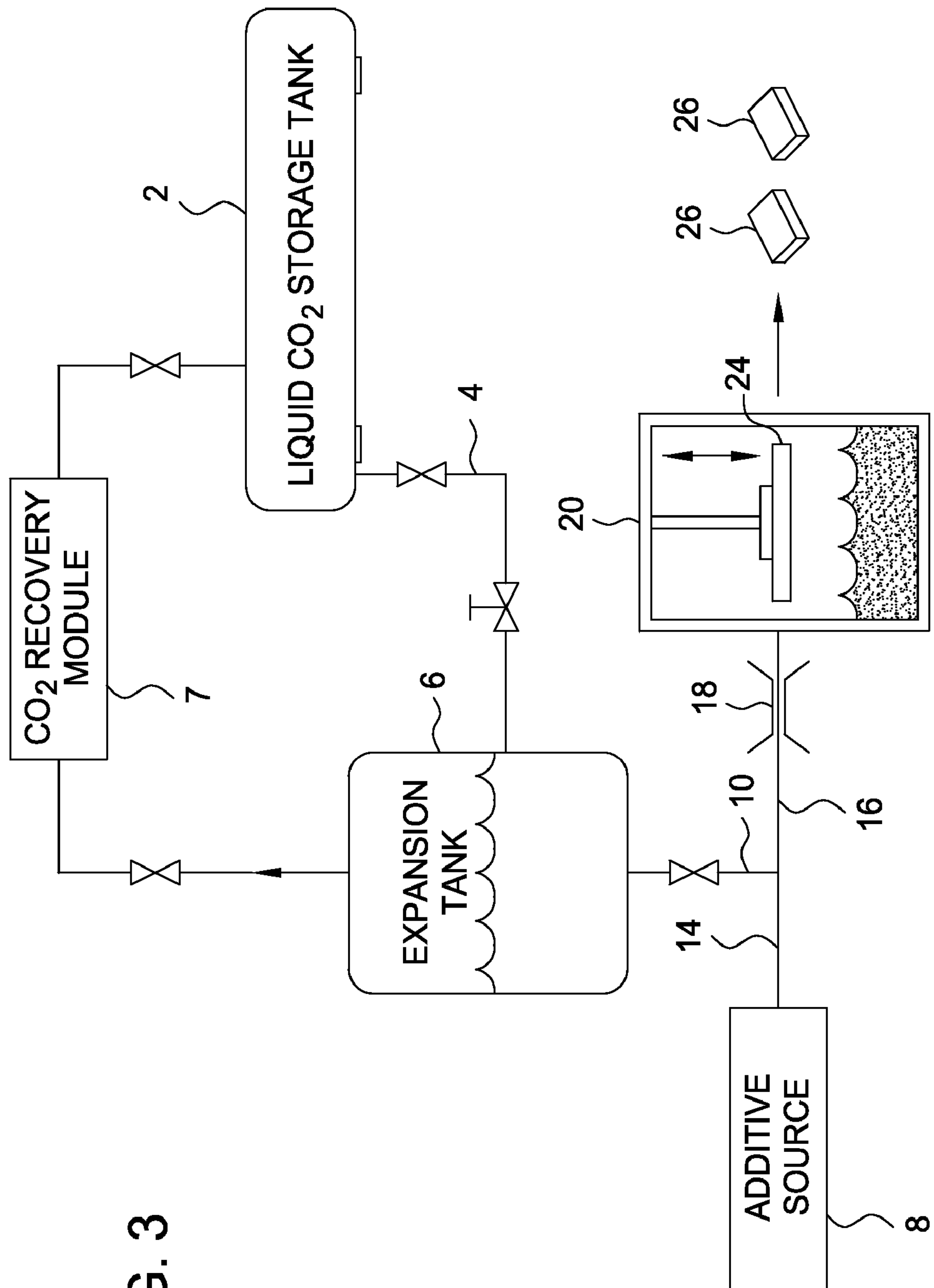

200
PUMP LIQUID $CO_2$ INTO A LOW-PRESSURE EXPANSION TANK
202
ADD AN ADDITIVE TO THE LIQUID $CO_2$ IN THE LOW-PRESSURE EXPANSION TANK
204
FLOW LIQUID $CO_2$/ADDITIVE INTO A DRY ICE PRESS
206
EXPAND LIQUID $CO_2$/ADDITIVE IN THE DRY ICE PRESS TO CREATE A SOLID
208

FIG. 2



LIQUID $CO_2$ STORAGE TANK
2
4
$CO_2$ RECOVERY MODULE
7
6
EXPANSION TANK
10
14
16
18
20
24
26
26
ADDITIVE SOURCE
8


FIG. 3

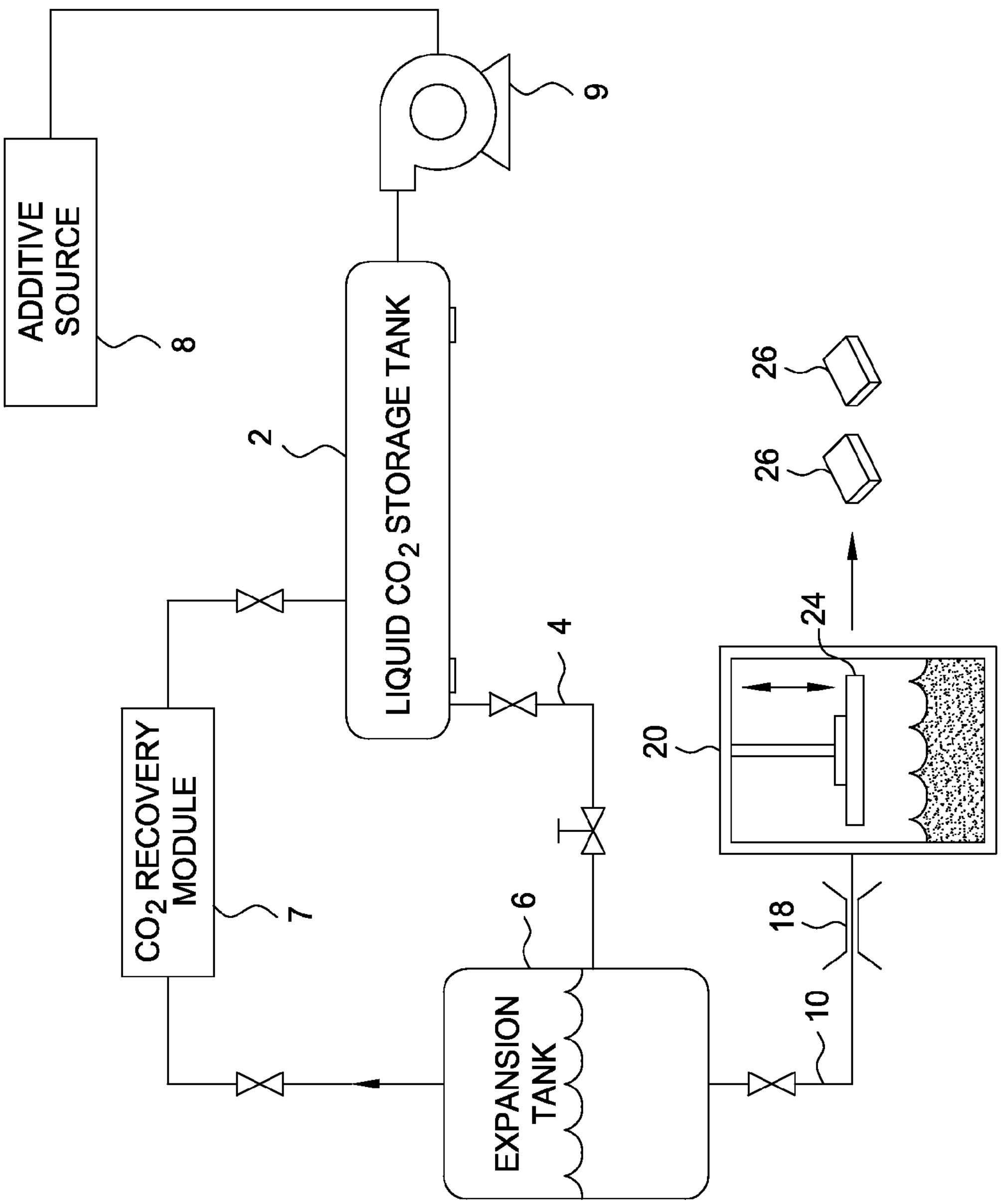

ADDITIVE SOURCE
8
9
LIQUID $CO_2$ STORAGE TANK
2
26
26
4
24
$CO_2$ RECOVERY MODULE
7
20
6
18
10
EXPANSION TANK

FIG. 4

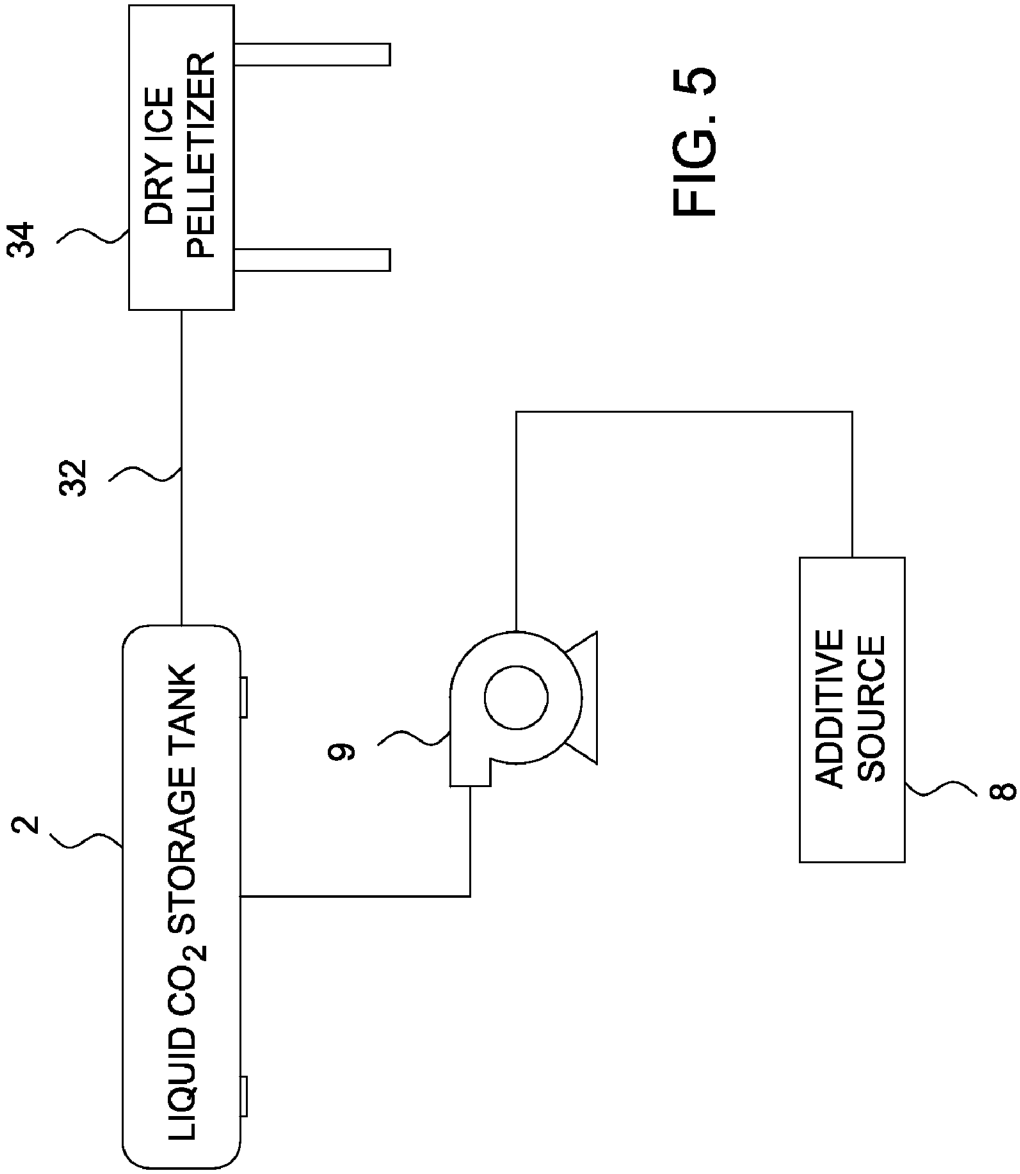

DRY ICE PELLETIZER
34
32
LIQUID $CO_2$ STORAGE TANK
2
9
ADDITIVE SOURCE
8

FIG. 5

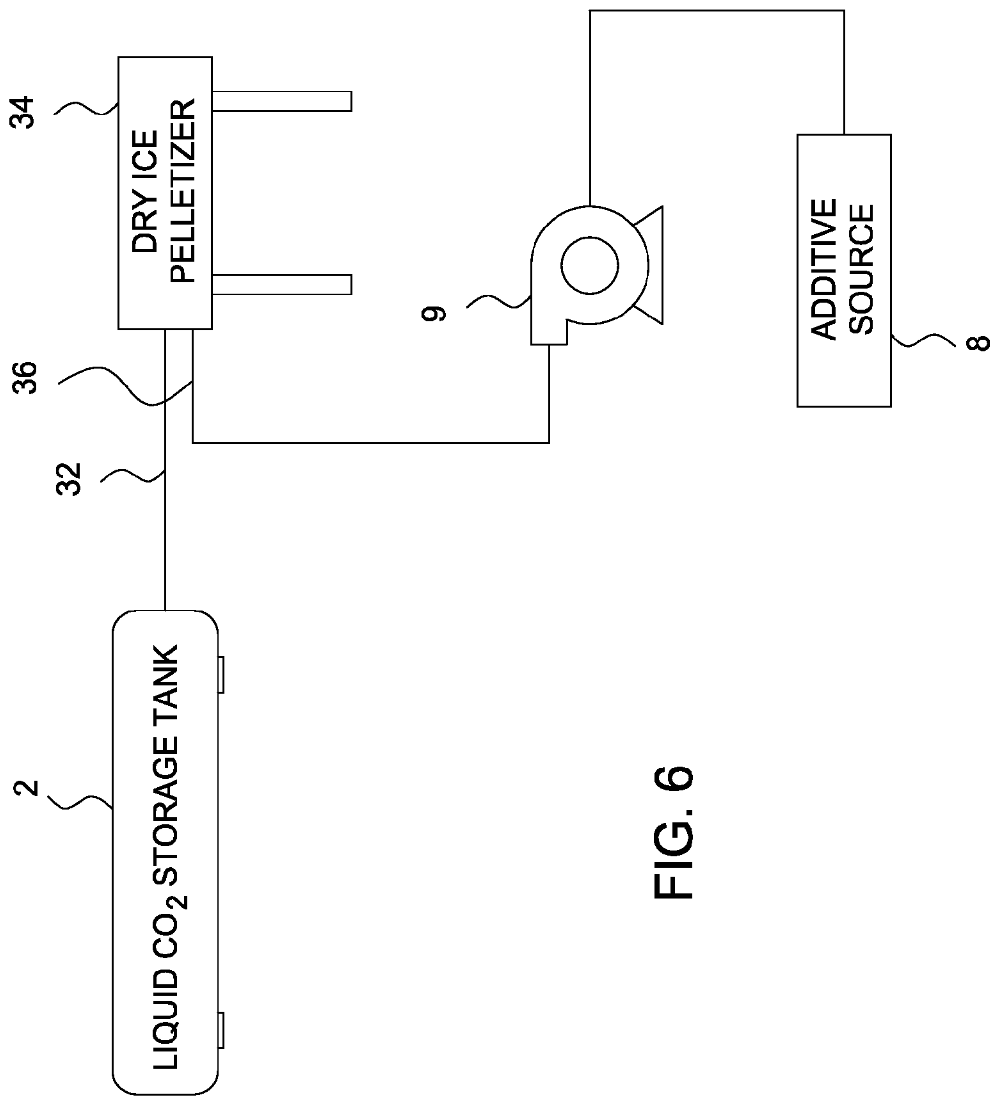

34
DRY ICE PELLETIZER
36
32
9
ADDITIVE SOURCE
8
2
LIQUID $CO_2$ STORAGE TANK

FIG. 6

# DRY ICE PRODUCTS AND METHOD OF MAKING SAME

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit under 35 U.S.C. § 119(e) to provisional application No. 60/765,040, filed Feb. 3, 2006, the entire contents of which are incorporated herein by reference.

## BACKGROUND

[0002] 1. Field of the Invention

[0003] Embodiments of the invention relates to chemicals and the making and using of the same; more specifically the invention relates to dry ice products.

[0004] 2. Description of the Related Art

[0005] Solid carbon dioxide (dry ice) is generally used in chilling and cooling applications in the food industry, but it also has applications in the entertainment area. It is well known in the art to cool products, such as foods, during processing with some type of refrigerant to slow down the growth of unwanted microbes and enzymatic reactions in foods. For instance, the shelf life and quality of food products are improved by processing, transporting, and storing under refrigerated conditions.

[0006] Dry ice sublimes by going directly from a solid to a gas without passing through the liquid stage. The cold temperature of dry ice and the fact that it leaves no residue makes it an excellent cooling agent in some applications. Food products that must remain frozen can be packed with dry ice during transportation. The contents will be frozen when they reach their destination and there will be no messy liquid residue as found with traditional water ice.

[0007] In the entertainment area dry ice may be used to produce smoke like fog in fog machines and food grade dry ice may be used to cool drinks and produce entertaining effects in punchbowls, such as in "witches brew" popular on Halloween.

[0008] Conventional dry ice is an odorless and colorless solid. Therefore, there remains a need to provide dry ice having improved sensory appeal such as dry ice in different colors and with different scents.

## SUMMARY

[0009] Embodiments of the invention generally provide for solid carbon dioxide with enhanced sensory properties, such as color and scent. One embodiment of the invention provides a cooling agent including solid carbon dioxide and one or more additives. The one or more additives provide color and/or odor to the solid carbon dioxide.

[0010] Another embodiment of the invention provides a method for preparing a cooling agent by providing a liquid carbon dioxide source, combining one or more additives with liquid carbon dioxide from the liquid carbon dioxide source, and expanding the liquid carbon dioxide with the one or more additives to form solid carbon dioxide. The one or more additives provide color or odor to the solid carbon dioxide.

[0011] Another embodiment of the invention provides a method for preparing a cooling agent by providing a liquid carbon dioxide source, expanding liquid carbon dioxide from the liquid carbon dioxide source to form solid carbon dioxide, and combining one or more additives with the solid carbon dioxide. The one or more additives provide color or odor to the solid carbon dioxide.

[0012] Another embodiment of the invention provides a system for preparing a cooling agent including a liquid carbon dioxide expanding unit, a liquid carbon dioxide source in fluid communication with the liquid carbon dioxide expanding unit, and at lease one additive source in fluid communication with one of the liquid carbon dioxide source and the liquid carbon dioxide expanding unit. The at least one additive source contains at least one of an odorant and a colorant.

[0013] Another embodiment of the invention provides witches brew, including a beverage and one or more pieces of cooling agent in a container (e.g., a bowl or cauldron). The one or more pieces of cooling agent includes dry ice and one or more additives. The one or more additives provide color or odor to the solid carbon dioxide and may be embedded in or adsorbed to the solid carbon dioxide. In one embodiment, the witches brew includes one or more carbonated fruit juices or a mixture of one or more fruit juices combined with one or more carbonated beverages.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

[0015] FIG. **1** is a flow chart of a process for forming a dry ice product containing an additive chemical, according to one embodiment of the invention;

[0016] FIG. **2** is a flow chart of a process for forming a dry ice product containing an additive chemical, according to another embodiment of the invention;

[0017] FIG. **3** is a schematic illustration of one embodiment of the invention for incorporating an additive into dry ice and forming pressed blocks of dry ice;

[0018] FIG. **4** is a schematic illustration of another embodiment of the invention for incorporating an additive into dry ice and forming pressed blocks of dry ice;

[0019] FIG. **5** is a schematic illustration of one embodiment for forming extruded pellets of dry ice containing an additive chemical; and

[0020] FIG. **6** is a schematic illustration of another embodiment for forming extruded pellets of dry ice containing an additive chemical.

## DESCRIPTION OF PREFERRED EMBODIMENTS

[0021] The words and phrases used herein should be given their ordinary and customary meaning in the art by one skilled in the art unless otherwise further defined.

[0022] In the following, reference is made to embodiments of the invention. However, it should be understood that the invention is not limited to specific described embodiments. Instead, any combination of the following features and elements, whether related to different embodiments or not, is contemplated to implement and practice the invention. Furthermore, in various embodiments the invention provides numerous advantages over the prior art. However, although embodiments of the invention may achieve advantages over other possible solutions and/or over the prior art, whether or not a particular advantage is achieved by a given embodiment is not limiting of the invention. Thus, the following aspects, features, embodiments and advantages are merely illustrative and are not considered elements or limitations of the appended claims except where explicitly recited in a claim(s). Likewise, reference to "the invention" shall not be construed as a generalization of any inventive subject matter disclosed herein and shall not be considered to be an element or limitation of the appended claims except where explicitly recited in a claim(s).

[0023] Dry ice may be produced by a controlled expansion of liquid $CO_2$ into dry ice snow. Additives may be added to the liquid $CO_2$ before the expansion of the liquid $CO_2$ into dry ice snow, or the additives may be sprayed onto the surfaces of dry ice snow. Liquid $CO_2$ is usually maintained at a temperature of about −60° C. at a pressure of 5.11 atm, although embodiments of the invention are not limited to particular temperature or pressure values for maintaining liquid $CO_2$. In embodiments of the invention, the additives used may have freezing points higher, lower, or similar to that of liquid $CO_2$. Embodiments of the invention can involve mixing one or more additives with a carrier chemical to a final concentration without affecting the freezing point of the carrier chemical. In a particular embodiment, a combined solution prepared using a carrier chemical and one or more additives should not have a freezing point higher than that of liquid $CO_2$. In one embodiment of the invention, liquid $CO_2$ combined with a carrier chemical and an additive is fed to an ice press to form dry ice. Yet another embodiment of the invention involves feeding liquid $CO_2$ and a carrier chemical and an additive to an ice press as separate streams, which then combine in the press to generate dry ice "snow" containing the additives. In embodiments of the invention, the additives are listed by the U.S. Food and Drug Administration as being GRAS (Generally Recognized as Safe).

[0024] In various embodiments, the additive formulation can include an alcohol, a terpene, or polyethylene glycol as a carrier chemical. An alcohol is any organic compound in which a hydroxyl group (—OH) is bound to a carbon atom of an alkyl or substituted alkyl group. The general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$. Food grade alcohol, ethanol, is a carrier chemical that has a very low freezing point, and can be used in one embodiment of the invention. Terpenes are another large group of chemical compounds found in nature that act as effective carrier chemicals with low freezing points. One such example is d-limonene, present in orange peel and extracted from the orange skin and provides a lemon-orange scent. The freezing point of d-Limonene is suitable for liquid $CO_2$ storage conditions, and is also considered to be an effective carrier chemical used in formulation preparations. Polyethylene glycol is a non-toxic liquid with low molecular weight, and is a common ingredient of pharmaceuticals.

[0025] Various food additives listed as GRAS can be dissolved directly into the carrier chemical and then mixed with liquid $CO_2$ or $CO_2$ in "snow" form before being extruded as pellets or blocks. Another embodiment of the invention can involve mixing one or more food additives with water, and then adding the resulting solution to the carrier chemical to a final concentration without affecting the freezing point of the carrier chemical.

[0026] GRAS chemical additives may include flavoring agents, flavor enhancers, intensifiers, emulsifiers, binders, fillers, gelling agents, plasticizers, stabilizers, suspending agents, whipping agents, sweetening agents, flavoring agents, colors, enzymes, antioxidants, sequestrants, wetting agents, surfactants, curing and pickling agents, firming agents, fumigants, humectants, leavening agents, processing aids, surface active agents, surface finishing agents, synergists, and texturizers.

[0027] The dry ice product can be manufactured in the form of blocks, pellets, flakes, powders, and other possible forms containing carbon dioxide and terpene. The dry ice product is essentially void of water. What is meant by "essentially void of" is that the dry ice product, if it contains water, will comprise less than 5% by weight (wt. %) water, according to one embodiment. Typically, the water content will be less than 1 wt. % in a particular embodiment. Moisture levels of up to 5,000 ppm may be helpful in maintaining the desired shape of the product. The carrier and additives concentrations in the dry ice may vary widely and may depend upon the end use of the product.

[0028] The exact form of dry ice may vary and, accordingly, a wide variety of forms can be manufactured and used depending upon the target purpose of the dry ice. For example, blocks of dry ice ranging from 5 to 50 lbs. may be used. Additionally, smaller manufactured shapes may be provided, such as dry ice pellets. Pellets of dry ice in the range of 1/16 inch to 1 inch may be formed. In addition, powders such as snow, flakes, or chips may be formed by methods known in the art.

[0029] In one embodiment of the invention, the additive is incorporated into the carbon dioxide during the dry ice manufacturing process. The traditional first step in making dry ice is to manufacture carbon dioxide liquid. This is done by compressing $CO_2$ gas and removing any excess heat. The $CO_2$ is typically liquefied at pressures ranging from 200-300 pounds per square inch and at a temperature of −20° F. to 0° F., respectively. It is typically stored in a pressure vessel at lower than ambient temperature. The liquid pressure is then reduced below the triple point pressure of 69.9 psi by sending it through an expansion valve. This can be done in a single step or, in many cases, by reducing the liquid pressure to 100 psi at a temperature of −50° F. as a first step to allow easy recovery of the flash gases. The liquid $CO_2$ is expanded inside a dry ice manufacturing press to form a mixture of dry ice snow and cold gas. The cold gas is vented or recycled and the remaining dry ice snow is then compacted to form blocks. Dry ice is typically compacted to a density of approximately 90 lb/ft$^3$.

[0030] FIG. **1** is a flow diagram of a process **100** used to create a dry ice product, according to one embodiment of the present invention. In general, to manufacture the dry ice product, an additive and a carrier chemical are combined with liquid carbon dioxide (step **104**) at a pressure above the triple point of $CO_2$ (70 psi), allowing the additive and carrier to fully dissolve in the liquid $CO_2$. The mixture of liquid $CO_2$, additive, and carrier chemical is then allowed to flow into a dry ice press in processing step **106**. Finally, the liquid carbon dioxide/additive mixture is then expanded in the dry ice press to generate dry ice or "snow" in processing step **108**.

**[0031]** FIG. **2** is a flow diagram of a process **200** used to create a dry ice product, according to another embodiment of the present invention. The process **200** includes a processing step **202** involving pumping liquid $CO_2$ into a low-pressure expansion tank and allowing the liquid $CO_2$ to expand to pressures above the triple point of carbon, typically to pressures from about 70 psi to 100 psi. Processing step **204** involves adding an additive to the liquid $CO_2$ after the slight expansion of liquid $CO_2$ in the low-pressure expansion tank. The additive may be co-introduced with a carrier chemical into the liquid $CO_2$. The mixture of liquid $CO_2$ and liquid additive is then allowed to flow into a dry ice press in processing step **206**. Finally, the liquid carbon dioxide/additive mixture is then expanded in the dry ice press to generate dry ice or "snow" in processing step **208**. Alternatively, the additive composition can be introduced to $CO_2$ in "snow" form and further extruded into any desired shape and form. This modified dry ice can then be collected or shaped such as by pressing or extrusion. In yet another embodiment, some amount of a liquid additive can be flashed together with gaseous $CO_2$ during pellet and block formation. The flashed gas, when recompressed to liquid $CO_2$, will contain the additive in addition to any fresh liquid additive added during pellet and block formation. This process can be successfully adapted to existing dry ice plants. While not bound by any theory of operation, if the additive is added during expansion, it is believed to be trapped in the structural lattices of dry ice.

**[0032]** FIGS. **3**-**6** depict representative apparatus and corresponding methods of forming a desired dry ice product according to the processing steps described in processes **100** and **200**. Each figure represents a typical dry ice manufacturing apparatus and process in which FIGS. **3** and **4** are processing environments used to form blocks of dry ice, while FIGS. **5** and **6** depicts a processing environment used to form dry ice pellets. These processing environments can be modified to incorporate additives into the dry ice product.

**[0033]** In FIG. **3**, liquid carbon dioxide is stored in tank **2**, typically at pressures of 200 to 300 psi. The liquid carbon dioxide from storage tank **2** is then passed via line **4** to a low-pressure expansion tank **6** wherein the liquid $CO_2$ is expanded to a pressure above the triple point of carbon dioxide (69.9 psi). Typically, the liquid $CO_2$ is expanded to pressures of from about 70 to 100 psi in expansion tank **6**. What results is a mixture of gas and a dense, viscous carbon dioxide liquid. $CO_2$ gas from expansion tank **6** may be recovered by $CO_2$ recovery module **7** where the $CO_2$ is liquefied and recycled into liquid $CO_2$ storage tank **2**. It is important that the liquid $CO_2$ is not formed into solid dry ice at this point because solids in the piping would disadvantageously reduce transport of the liquid. An additive from a vessel **8** is then injected into the liquid carbon dioxide. Injection of the additive can be done in the low-pressure expansion tank. The additive may be co-introduced with a carrier chemical into the liquid $CO_2$. As shown in FIG. **2**, the additive from vessel **8** is fed via line **14** to mix with the liquid $CO_2$ from line **10**. The mixture additive and liquid $CO_2$ is passed via line **16** through an expansion orifice **18** into the dry ice press **20**. Alternatively, although not shown, the mixture of additive and liquid $CO_2$ can be passed to a separate refrigeration unit, wherein the liquid $CO_2$ is frozen into a solid containing the entrapped additive chemical.

**[0034]** As further shown in FIG. **3**, the mixture of liquid $CO_2$ and additive is then allowed to expand inside the dry ice press **20**. During expansion, the liquid $CO_2$ is converted to a solid form and the additive is trapped in the structural lattices of the dry ice during dry ice formation. Once the dry ice solid is formed, the solid particles can be compressed via platen **24** in press **20** into dry ice blocks **26**.

**[0035]** FIG. **4** depicts a variation of the method of FIG. **3**. In FIG. **4**, the additive in a vessel **8** is pumped through high pressure dosage pump **9** into the liquid $CO_2$ storage tank **2**. The additive may be co-introduced with a carrier chemical into the liquid $CO_2$. In one embodiment, the tank **2** contains any variety of mixing means such as agitators, stirrers, etc. to mix the liquid $CO_2$ with the additive and/or carrier chemical. If the additive and/or carrier are in gas form, then a sparger may be disposed in the tank **2** through which the additive (and carrier, if present) are introduced. The liquid carbon dioxide and additive mixture from storage tank **2** is then passed via line **4** to a low-pressure expansion tank **6** wherein the liquid $CO_2$ is expanded as described above in relation to FIG. **3**. The additive and liquid $CO_2$ mixture is then passed via line **10** through the expansion orifice **18** into the dry ice press **20**. Alternatively, although not shown, the mixture of additive and liquid $CO_2$ can be passed to a separate refrigeration unit, wherein the liquid $CO_2$ is frozen into a solid containing the entrapped additive chemical.

**[0036]** In another embodiment of the invention, the additive/liquid $CO_2$ mixture in liquid storage tank **2** of FIG. **4** may be flowed to a snow horn, where $CO_2$ expansion occurs and dry ice snow is formed. Snow horns are well known in the art, and it is believed that any snow horn is capable of use with this embodiment. The dry ice snow may then be compressed into dry ice blocks as described above.

**[0037]** FIG. **5** depicts a processing environment used to form dry ice pellets using a similar apparatus to that in FIGS. **3** and **4**. Liquid $CO_2$ is stored in tank **2**, typically at pressures of 200 to 300 psi. The additive in the vessel **8** is pumped through high pressure dosage pump **9** to mix with the $CO_2$ in the liquid $CO_2$ storage tank **2**. The liquid carbon dioxide and additive from storage tank **2** are then passed via line **32** directly to a dry ice pelletizer **34**. Dry ice pelletizers are well known in the art, and it is believed that any dry ice pelletizer is capable of use with this embodiment. In the pelletizer, the liquid $CO_2$ is expanded to a pressure below 70 psi, resulting in a mixture of gas and carbon dioxide solid particles. The solid $CO_2$ particles are extruded into pellets, typically ranging from 1/16 inch to 1 inch in diameter.

**[0038]** FIG. **6** depicts a variation of the method of FIG. **5**. In FIG. **6**, the additive from a vessel **8** is pumped through high pressure dosage pump **9** and introduced into dry ice pelletizer **34** via a nozzle **36**. The additive may be co-introduced with a carrier chemical via a nozzle **36** into dry ice pelletizer **34**. High pressure dosage pump **9** may be connected to the pelletizer **34** in a manner such that when the piston of the pelletizer **34** is retracted a measured quantity of additive is distributed on dry ice snow formed in the pelletizer **34**. Additive is thus adsorbed to the dry ice snow, and as the piston is extended, the dry ice snow with additive adsorbed is pressed into pellets of dry ice and additive. In one embodiment, the pellitizer **34** may produce 100 kg/hour pellets. In this embodiment, the high pressure dosage pump may be set to deliver an additive flow rate of between about 1 mL/min and between about 10 ml/min.

**[0039]** Although FIG. **6** depicts only one additive source **8**, high pressure dosage pump **9**, and nozzle **36**, it is contemplated that any number of additive sources, high pressure dosage pumps, and nozzles may be used to separately introduce a plurality of additives to the pelletizer. In one embodiment, any number of between two and ten additive sources, high pressure dosage pumps, and nozzles are provided.

**[0040]** In another embodiment of the invention the additive may be sprayed onto the surface of ready made dry ice snow, pellets or blocks. The additive may be sprayed together with a carrier chemical.

EXAMPLES

**[0041]** Conventionally produced dry ice is an odorless and colorless solid, thus, the physical and/or chemical properties of dry ice may be changed to effect a desired sensory experience with the dry ice, for example, by incorporating color and scents into the dry ice. Colorful dry ice may be used in place of conventional dry ice in color schemes appealing to consumers. Additionally, colored dry ice may be used in color coding schemes, wherein each color may be designated a specific property. For example, different colored dry ice may symbolize different tissue or blood types of organs during organ transport. Further, a given dry ice product may contain any number of discrete colors or even graphical images. For example, individual pellets of varying colors may be arranged together to form a desired image. Alternatively or additionally, the image may be sprayed onto the dry ice product. Further, the additives added to the dry ice product may be florescent to achieve a desired visual effect. Scented dry ice may be used to create a pleasurable scent or to release aromas to mask unpleasant odors.

**[0042]** In one embodiment of the invention, the additive may be an odorant. Upon sublimation of the dry ice, the odorant is released to provide scent or to neutralize unpleasant odors. Examples of suitable odorants are 1-methoxy-4-(1-propenyl)benzene (licorice), methoxybenzene (anis seed), 2-methoxy-4-(2-propenyl)phenol (clove oil), (R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol (grapefruit), 2,3-benzopyrrole (jasmine), methyl 2-hydroxybenzoate (oil of wintergreen), 2-ethoxynaphthalene (orange flowers), and 3-hydroxy-4,5-dimethylfuran-2(5H)-one (maple syrup, curry, fenugreek).

**[0043]** Several alcohols may also be suitable as odorants, such as cis-3-Hexen-1-ol (fresh cut grass), 2-ethyl-3-hydroxy-pyran-4-one (sugary, cooked fruit), 4-hydroxy-2,5-dimethyl-furan-3-one (strawberry), 5-methyl-2-propan-2-yl-cyclohexan-1-ol (peppermint), and 1-hexanol (herbaceous, woody).

**[0044]** Several aldehydes may also be suitable as odorants, such as benzaldehyde (marzipan, almond), hexanal (green, grassy), cinnamaldehyde (cinnamon), cis-3-hexenal (green tomatoes), (2E)-3,7-dimethylocta-2,6-dienal (lemongrass, lemon oil), furan-2-carbaldehyde (burnt oats), (2Z)-3,7-dimethylocta-2,6-dienal (citrus, lemongrass), and 4-hydroxy-3-methoxy-benzaldehyde (vanilla).

**[0045]** Several esters may also be suitable as odorants, such as ethyl acetate (fruity, solvent), ethyl butanoate (fruity), methyl butanoate (apple, fruity) pentyl butanoate (pear, apricot), pentyl pentanoate (apple, pineapple), isoamyl acetate (banana), hexyl acetate (apple, floral, fruity), ethyl hexanoate (sweet, pineapple, fruity), ethyl octanoate (wine, fruity), ethyl decanoate (brandy, fruity), and ethyl 3-methyl-3-phenyl-oxirane-2-carboxylate (strawberry).

**[0046]** Several terpenes may also be suitable as odorants, such as 1,7,7-trimethylnorbornan-2-one (camphor), 3,7-dimethyloct-6-en-1-ol (rose), 3,7-dimethylocta-1,6-dien-3-ol (floral, citrus, coriander), (2E)-3,7-dimethylocta-2,6-dien-1-ol (rose), 3,7,11-trimethyl 1,6,10-dodecatrien-3-ol (fresh bark), 2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol (citrus woody), (1S,4R,5R)-4-methyl-1-propan-2-yl-bicyclo[3.1.0]hexan-3-one (juniper, common sage, wormwood), and 5-methyl-2-propan-2-yl-phenol (thyme-like).

**[0047]** In one embodiment the odorant may be d-limonene. D-limonene is a terpene which may be extracted from the rind of citrus fruit and is used in food manufacturing as a flavoring, and added to cleaning products such as hand cleansers to give a lemon-orange fragrance. Because d-limonene has a melting point of −95° C. and dissolves in the liquid $CO_2$, it is suitable for dry ice production. Thus, d-limonene may also be used as a carrier chemical. While not bound by any theory of operation, if the d-limonene is added before or during $CO_2$ expansion, the d-limonene is believed to be trapped in the structural lattices of the dry ice. As the dry ice sublimes d-limonene is released from the structural lattices of the dry ice, and a pleasant citrus scent emanates from the dry ice.

**[0048]** In one embodiment of the invention the odorous chemical may be vanillin. Both methyl-vanillin and ethyl-vanillin may be used. In one embodiment, the vanillin may be co-introduced to the $CO_2$ with a carrier chemical such as ethanol or polyethylene glycol. Natural vanilla extract may also be used. As the dry ice sublimes vanillin is released from the structural lattices of the dry ice, and a pleasant vanilla scent emanates from the dry ice.

**[0049]** In one embodiment of the invention the odorous chemical may be mint extracts or artificial mint flavoring. In one embodiment, the mint flavoring may be co-introduced into the liquid $CO_2$ with a carrier chemical such as ethanol or polyethylene glycol. As the dry ice sublimes mint flavor is released from the structural lattices of the dry ice, and a pleasant vanilla scent emanates from the dry ice.

**[0050]** In other embodiments, the additive may consist of natural or artificial compounds having cherry odors, strawberry odors, coconut odors, chocolate odors, or any other natural of artificial odors possible. Depending on the solubility of the selected additive in liquid $CO_2$, carrier chemicals may or may not need to be co-introduced with the additive to the $CO_2$, according to different embodiments.

**[0051]** In one embodiment of the invention, the scented solid $CO_2$ may be used in fog machines to create a scented fog.

**[0052]** In one embodiment of the invention, the additive may be a colorant such as a pigment or a dye. Many colorants are water-soluble, and may be dissolved in a small amount of water and combined with a carrier such as ethanol before the colorants are introduced to the $CO_2$. The solubilized colorants may be introduced to liquid $CO_2$ before the $CO_2$ is expanded to a solid, or the solubilized colorants may be introduced to the pelletizer **34** described above in relation to FIG. **6**. Alternatively, the colorants may be sprayed on to the surfaces of ready made pellets.

[**0053**] In one embodiment of the invention, food grade colorants are used. Often the food grade colorants are available in water and propylene glycol which may be mixed with carrier ethanol and co-introduced to the $CO_2$. Food grade colored solid $CO_2$ may have many uses. Various color combinations may provide aesthetically pleasing color schemes for dry ice snow, pellets, or blocks used as a cooling agent of food products. Colored dry ice may also be used in color coding schemes, wherein each color may be designated a specific property. For example, in the transportation of organs for organ transplantation, different tissue types, blood types, etc, may be assigned different colors for a quick reference to these properties of the organs.

[**0054**] Examples of currently FDA approved colorants for food are FD&C Blue No. 1 (ethyl-[4-[[4-[ethyl-[(3-sulfophenyl)methyl]amino]phenyl]-(2-sulfophenyl)methylidene]-1-cyclohexa-2,5-dienylidene]-[(3-sulfophenyl)methyl]azanium, blue shade), FD&C Blue No. 2 ((2Z)-3-oxo-2-(3-oxo-5-sulfo-1H-indol-2-ylidene)-1H-indole-5-sulfonic acid, dark blue shade), FD&C Green No. 3 (sodium 4-[(4-dimethylaminophenyl)-(4-dimethylazaniumylidene-1-cyclohexa-2,5-dienylidene)methyl]-3-hydroxy-naphthalene-2,7-disulfonate, bluish green shade), FD&C Red No. 40 (disodium (5Z)-5-[(2-methoxy-5-methyl-4-sulfonato-phenyl)hydrazinylidene]-6-oxo-naphthalene-2-sulfonate, red shade), FD&C Red No. 3 (disodium 2-(2,4,5,7-tetraiodo-3-oxido-6-oxo-xanthen-9-yl)benzoate, pink shade), FD&C Yellow No. 5 (trisodium (4Z)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazinylidene]pyrazole-3-carboxylate, yellow shade), and FD&C Yellow No. 6 (disodium (5Z)-6-oxo-5-[(4-sulfonatophenyl)hydrazinylidene]naphthalene-2-sulfonate, orange shade).

[**0055**] In one embodiment of the invention, the solid carbon dioxide may be in the form of multicolored pellets. To obtain such multicolored pellets, multiple colorants may be separately introduced to pellitizer **34** through different nozzles **36** and sprayed into the dry ice snow, and multicolored pellets may then be extruded.

[**0056**] Food grade colored solid $CO_2$ may also be used to cool drinks and produce entertaining effects in punchbowls, such as in "witches brew" popular on Halloween. In one embodiment, dry ice blocks with appropriate color schemes may be added to the punchbowls to increase the diabolical effects of the bubbling and foggy brew. Diabolic colors may include red, black, orange, and purple colors. In one embodiment, a combination of one or more fruit juices may be combined with one or more carbonated beverages in a bowl or cauldron with colored dry ice added. In one embodiment, ethanol containing liquids may also be added to the beverage. In an alternative embodiment, the dry ice may, in addition to one or more color additives, also include one or more odor additives, thus providing the beverage with added flavor as the dry ice sublimes.

[**0057**] Preferred processes and apparatus for practicing the present invention have been described. It will be understood and readily apparent to the skilled artisan that many changes and modifications may be made to the above-described embodiments without departing from the spirit and the scope of the present invention. The foregoing is illustrative only and that other embodiments of the integrated processes and apparatus may be employed without departing from the true scope of the invention defined in the following claims.

What is claimed is:

**1**. A cooling agent, comprising:

a) solid carbon dioxide; and

b) one or more additives, wherein the one or more additives provide at least one of color and odor to the solid carbon dioxide, whereby the one or more additives produce a perceptible sensory effect.

**2**. The cooling agent of claim 1, wherein the one or more additives is a colorant.

**3**. The cooling agent of claim 2, wherein the colorant is selected from the group consisting of FD&C Blue No. 1, FD&C Blue No. 2, FD&C Green No. 3, FD&C Red No. 40, FD&C Red No. 3, FD&C Yellow No. 5, FD&C Yellow No. 6, and combinations thereof.

**4**. The cooling agent of claim 1, wherein the one or more additives is an odorant.

**5**. The cooling agent of claim 4, wherein the odorant is selected from the group consisting of 1-methoxy-4-(1-propenyl)benzene methoxybenzene, 2-methoxy-4-(2-propenyl)phenol, (R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol, 2,3-benzopyrrole, methyl 2-hydroxybenzoate, 2-ethoxynaphthalene, and 3-Hydroxy-4,5-dimethylfuran-2(5H)-one, cis-3-Hexen-1-ol, 2-ethyl-3-hydroxy-pyran-4-one, 4-hydroxy-2,5-dimethyl-furan-3-one, 5-methyl-2-propan-2-yl-cyclohexan-1-ol (peppermint), 1-hexanol, benzaldehyde, hexanal, cinnamaldehyde, cis-3-hexenal, (2E)-3,7-dimethylocta-2,6-dienal, furan-2-carbaldehyde, (2Z)-3,7-dimethylocta-2,6-dienal, 4-hydroxy-3-methoxybenzaldehyde, ethyl acetate, ethyl butanoate, methyl butanoate, pentyl butanoate, pentyl pentanoate, isoamyl acetate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl 3-methyl-3-phenyl-oxirane-2-carboxylate, 1,7,7-trimethylnorbornan-2-one, 3,7-dimethyloct-6-en-1-ol), 3,7-dimethylocta-1,6-dien-3-ol, (2E)-3,7-dimethylocta-2,6-dien-1-ol, 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol, 2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol, (1S,4R,5R)-4-methyl-1-propan-2-yl-bicyclo[3.1.0]hexan-3-one, 5-methyl-2-propan-2-yl-phenol, and combinations thereof.

**6**. The cooling agent of claim 1, wherein the one or more additives comprise one or more colorants and one or more odorants.

**7**. The cooling agent of claim 1, further comprising a carrier chemical for suspending the one or more additives in the solid carbon dioxide.

**8**. The cooling agent of claim 7, wherein the carrier chemical is selected from the group consisting of ethanol, propylene glycol, and d-limonene, and combinations thereof.

**9**. The cooling agent of claim 1, wherein the solid carbon dioxide is in at least one of pellet form and block form.

**10**. The cooling agent of claim 1, wherein the solid carbon dioxide is in snow form.

11. A method for preparing a cooling agent, comprising:

a) providing a liquid carbon dioxide source;

b) combining one or more additives with liquid carbon dioxide from the liquid carbon dioxide source to produce a mixture; and

c) expanding the mixture to form solid carbon dioxide, wherein the one or more additives provide at least one of color and odor to the solid carbon dioxide.

12. The method of claim 11, wherein the one or more additives is a colorant.

13. The method of claim 12, wherein the colorant is selected from the group consisting of FD&C Blue No. 1, FD&C Blue No. 2, FD&C Green No. 3, FD&C Red No. 40, FD&C Red No. 3, FD&C Yellow No. 5, FD&C Yellow No. 6, and combinations thereof.

14. The method of claim 11, wherein the one or more additives is an odorant.

15. The method of claim 14, wherein the odorant is selected from the group consisting of 1-methoxy-4-(1-propenyl)benzene methoxybenzene, 2-methoxy-4-(2-propenyl)phenol, (R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol, 2,3-benzopyrrole, methyl 2-hydroxybenzoate, 2-ethoxynaphthalene, and 3-Hydroxy-4,5-dimethylfuran-2(5H)-one, cis-3-Hexen-1-ol, 2-ethyl-3-hydroxy-pyran-4-one, 4-hydroxy-2,5-dimethyl-furan-3-one, 5-methyl-2-propan-2-yl-cyclohexan-1-ol (peppermint), 1-hexanol, benzaldehyde, hexanal, cinnamaldehyde, cis-3-hexenal, (2E)-3,7-dimethylocta-2,6-dienal, furan-2-carbaldehyde, (2Z)-3,7-dimethylocta-2,6-dienal, 4-hydroxy-3-methoxybenzaldehyde, ethyl acetate, ethyl butanoate, methyl butanoate, pentyl butanoate, pentyl pentanoate, isoamyl acetate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl 3-methyl-3-phenyl-oxirane-2-carboxylate, 1,7,7-trimethylnorbornan-2-one, 3,7-dimethyloct-6-en-1-ol), 3,7-dimethylocta-1,6-dien-3-ol, (2E)-3,7-dimethylocta-2,6-dien-1-ol, 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol, 2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol, (1S,4R,5R)-4-methyl-1-propan-2-yl-bicyclo[3.1.0]hexan-3-one, 5-methyl-2-propan-2-yl-phenol, and combinations thereof.

16. The method of claim 11, wherein the one or more additives comprise one or more colorants and one or more odorants.

17. The method of claim 11, further comprising compressing the solid carbon dioxide into pellets.

18. The method of claim 11, further comprising compressing the solid carbon dioxide into blocks.

19. The method of claim 11, wherein the additive is combined with a carrier chemical before being combined with the liquid carbon dioxide.

20. The method of claim 19, wherein the carrier chemical is selected from the group consisting of ethanol, propylene glycol, and d-limonene, and combinations thereof.

21. A method for preparing a cooling agent, comprising:

a) providing a liquid carbon dioxide source;

b) expanding liquid carbon dioxide from the liquid carbon dioxide source to form solid carbon dioxide; and

c) combining one or more additives with the solid carbon dioxide, wherein the one or more additives provide at least one of color and odor to the solid carbon dioxide.

22. The method of claim 21, wherein the additive is combined with a carrier chemical before being combined with the solid carbon dioxide.

23. The method of claim 21, wherein the one or more additives is a colorant.

24. The method of claim 23, wherein the colorant is selected from the group consisting of FD&C Blue No. 1, FD&C Blue No. 2, FD&C Green No. 3, FD&C Red No. 40, FD&C Red No. 3, FD&C Yellow No. 5, FD&C Yellow No. 6, and combinations thereof.

25. The method of claim 21, wherein the one or more additives is an odorant.

26. The method of claim 25, wherein the odorant is selected from the group consisting of 1-methoxy-4-(1-propenyl)benzene methoxybenzene, 2-methoxy-4-(2-propenyl)phenol, (R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol, 2,3-benzopyrrole, methyl 2-hydroxybenzoate, 2-ethoxynaphthalene, and 3-Hydroxy-4,5-dimethylfuran-2(5H)-one, cis-3-Hexen-1-ol, 2-ethyl-3-hydroxy-pyran-4-one, 4-hydroxy-2,5-dimethyl-furan-3-one, 5-methyl-2-propan-2-yl-cyclohexan-1-ol (peppermint), 1-hexanol, benzaldehyde, hexanal, cinnamaldehyde, cis-3-hexenal, (2E)-3,7-dimethylocta-2,6-dienal, furan-2-carbaldehyde, (2Z)-3,7-dimethylocta-2,6-dienal, 4-hydroxy-3-methoxybenzaldehyde, ethyl acetate, ethyl butanoate, methyl butanoate, pentyl butanoate, pentyl pentanoate, isoamyl acetate, hexyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl 3-methyl-3-phenyl-oxirane-2-carboxylate, 1,7,7-trimethylnorbornan-2-one, 3,7-dimethyloct-6-en-1-ol), 3,7-dimethylocta-1,6-dien-3-ol, (2E)-3,7-dimethylocta-2,6-dien-1-ol, 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol, 2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol, (1S,4R,5R)-4-methyl-1-propan-2-yl-bicyclo[3.1.0]hexan-3-one, 5-methyl-2-propan-2-yl-phenol, and combinations thereof.

27. The method of claim 21, wherein the one or more additives comprise one or more colorants and one or more odorants.

28. The method of claim 22, wherein the carrier chemical is selected from the group consisting of ethanol, propylene glycol, and d-limonene, and combinations thereof.

29. The method of claim 21, further comprising compressing the solid carbon dioxide into pellets.

30. The method of claim 21, further comprising compressing the solid carbon dioxide into blocks.

31. A system for preparing a cooling agent, comprising:

a) a liquid carbon dioxide expanding unit;

b) a liquid carbon dioxide source in fluid communication with the liquid carbon dioxide expanding unit; and

c) at least one additive source in fluid communication with one of the liquid carbon dioxide source and the liquid carbon dioxide expanding unit, wherein the at least one additive source contains at least one of an odorant and a colorant.

32. The system of claim 31, further comprising a carrier chemical source in fluid communication with the at least one additive source.

33. The system of claim 31, wherein the at least one additive source is in fluid communication with the liquid carbon dioxide source.

**34**. The system of claim 31, wherein the at least one additive source is in fluid communication with the liquid carbon dioxide expanding unit.

**35**. The system of claim 31, wherein the at least one additive source is an odorant source.

**36**. The system of claim 31, wherein the at least one additive source is a colorant source.

**37**. The system of claim 31, wherein the liquid carbon dioxide expanding unit is a dry ice press.

**38**. The system of claim 31, wherein the liquid carbon dioxide expanding unit is a pelletizer.

**39**. A solution, comprising:

one or more fruit juices combined with one or more carbonated beverages and one or more pieces of a solid cooling agent in a container, wherein the one or more pieces of solid cooling agent comprises dry ice and one or more additives, wherein the one or more additives provide at least one of color and odor to the solid carbon dioxide and are incorporated into the solid carbon dioxide.

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