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LIQUID CARBON DIOXIDE SUITABLE FOR DISCHARGE AT LOW TEMPERATURES AND METHOD OF FILLING STORAGE CONTAINERS FOR CONFINING THE SAME

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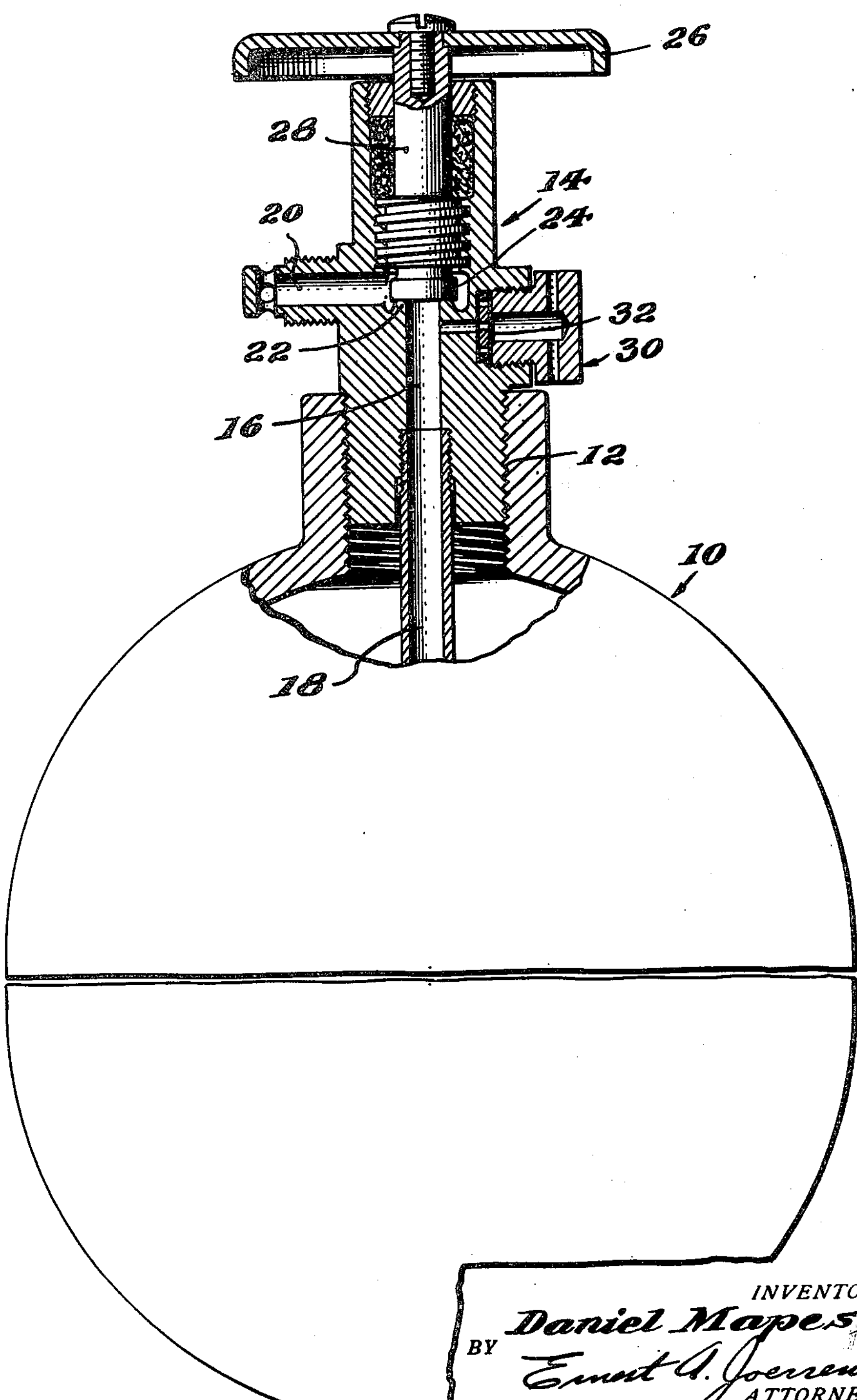

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LIQUID CARBON DIOXIDE SUITABLE FOR DISCHARGE AT LOW TEMPERATURES AND METHOD OF FILLING STORAGE CONTAINERS FOR CONFINING THE SAME

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The present invention relates to apparatus for storing fluid pressure media and a method of filling and discharging such apparatus, and, more particularly, relates to containers to liquid carbon dioxide and a method of filling and discharging the same.

Liquid carbon dioxide is used extensively on land vehicles, vessels and aircraft as a fire extinguishing medium and as a medium for operating pressure operable devices in the event of an emergency. For example, carbon dioxide may be used in connection with portable fire extinguishers; built in fire extinguishing systems for aircraft, vehicles and vessels; gasoline tank purging or vapor dilution systems for aircraft, speed boats and the like; gun chargers; and emergency bomb bay door or landing gear operating systems.

The liquid carbon dioxide generally is stored in cylindrical metallic containers, known as cylinders, which are provided with suitable discharge valves for releasing the stored carbon dioxide. While these containers can safely withstand relatively high working pressure, safety discharge means usually are provided in the valves or elsewhere for releasing the stored carbon dioxide to the atmosphere in the event the pressure within the containers becomes excessive.

While these containers of liquid carbon dioxide have been used advantageously at normal atmospheric temperatures generally ranging from about 0° to 140° F., considerable difficulties have been encountered where the containers were exposed to sub-normal atmospheric temperatures. Such sub-normal temperatures are encountered at high altitudes or in arctic regions where the temperature may be as low as —65° F. or even lower.

At such low temperatures, the pressure in the containers is correspondingly low. For example, at —40° F., the pressure is about 160 pounds per square inch (gauge), at —60° F., the pressure is about 80 pounds per square inch (gauge), and at —65° F., the pressure is about 70 pounds per square inch (gauge). These correspondingly low pressures fail to effect rapid discharge of the carbon dioxide from the containers.

Also, at low temperatures and low pressures, the snow forming tendency of liquid carbon dioxide is greatly increased, resulting in large quantities of snow which may block the valves, tubing or other passages of a fire extinguisher or fire extinguishing system to thereby prevent the carbon dioxide from being discharged.

Also, upon releasing low temperature liquid carbon dioxide from a container, the expansion

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of a portion of the carbon dioxide will refrigerate the carbon dioxide resulting in the formation of solid carbon dioxide in the container which cannot be discharged.

In connection with fire extinguishing, the carbon dioxide is discharged from a nozzle, and, upon expansion, is partially converted into a spray of snow-like particles. Due to the low pressure in the container, the spray may be propelled an insufficient distance to reach the location of the fire.

Accordingly, an object of the present invention is to overcome the foregoing difficulties and disadvantages by confining liquid carbon dioxide under pressure in a manner whereby the carbon dioxide may be effectively discharged at subnormal atmospheric temperature.

Another object is to provide liquid carbon dioxide confined under pressure which is adapted to be safely stored at normal and relatively high atmospheric temperatures.

Another object is to provide liquid carbon dioxide confined in a container and exerting a sufficiently high pressure at sub-normal atmospheric temperatures to effect discharge thereof, but exerting a pressure at relatively high atmospheric temperatures which is less than, or does not substantially exceed, the pressure within a normally filled container of liquid carbon dioxide at about the same temperature.

Another object is to provide a method of filling containers with carbon dioxide to accomplish the foregoing objects and advantages.

A further object is to provide liquid carbon dioxide confined in a container adapted to be discharged rapidly at low temperature, whereby the carbon dioxide will not be refrigerated to form a mass of solid carbon dioxide which cannot be expelled.

Other and further objects of the invention will be obvious upon an understanding of the illustrative embodiment about to be described, or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

In accordance with the invention, it has been found that the foregoing objects and advantages may be accomplished by providing a container charged with liquid carbon dioxide and containing an added gas, other than carbon dioxide, under pressure. The container may be of the type generally used for storing carbon dioxide and may be provided with any suitable valve or discharge fitting. Such a container of liquid carbon dioxide may be provided by charging the container with a quantity of gas having a desired pressure at a given temperature, and charging the container with a desired quantity of carbon dioxide.

A preferred embodiment of the invention has been chosen for purposes of illustration and description and is shown in the accompanying drawing, forming a part of the specification, wherein:

The figure is a fragmentary, longitudinal, sectional view of a container, provided with a valve, illustrating an embodiment of the invention.

Referring to the drawing, there is shown a metallic container **10** which has a generally cylindrical shape and is adapted for storing liquid carbon dioxide. The container is constructed in the usual manner, and, for example, may be of the type adapted to safely withstand internal pressures of about 3600 pounds per square inch. One end of the container is provided with an opening **12** in which is secured a suitable valve or discharge fitting 14.

The valve **14** has an inlet **16**, to which may be attached a syphon tube **18** extending into the container, and has an outlet **20** for connecting a hose or the like adapted to conduct the carbon dioxide to a snow forming horn or the like, of the type illustrated in United States Patent No. 1,760,274. The outlet **20** also may be utilized for coupling a pressure gauge thereto as described hereinafter. Intermediate the inlet and outlet, a valve seat **22** is formed for receiving a valve member **24** adapted to control the discharge of the carbon dioxide from the container. By way of example, a manually operated handwheel **26** and a threaded stem **28** are shown, adapted to effect unseating of the valve member **24**.

A safety discharge assembly **30** is provided intermediate the inlet **16** of the valve and the valve seat **22** for discharging the contents of the container to the atmosphere in the event the pressure within the container exceeds a safe working pressure. The safety discharge of the contents of the container preferably is controlled by a disc **32** or the like adapted to be ruptured when the pressure within the container exceeds a predetermined pressure.

In practicing the invention, the container, preferably, is charged with a gas (other than carbon dioxide) or mixture of gases adapted to exist in a gaseous state at the sub-normal atmospheric temperatures contemplated herein. These gases may be air, argon, carbon monoxide, helium, hydrogen, krypton, neon, nitrogen and oxygen. These gases all have a much lower critical temperature than the critical temperature of carbon dioxide, which is 87.8° F. The critical temperatures of these gases are approximately as follows:

	Degrees F.
Air	−220
Argon	−179
Carbon monoxide	−218
Helium	−450
Hydrogen	−400
Krypton	−80.5
Neon	−338
Nitrogen	−231
Oxygen	−180

Thus, at temperatures as low as −60° F., these gases are adapted to exist in compressed gaseous state, and in such state are capable of exerting a pressure of at least about 200 pounds per square inch absolute.

For all-around purposes, nitrogen is preferred because of its comparative low cost, its general availability, and its inert properties. The critical temperature of nitrogen, that is, the temperature at which nitrogen will exist as a gas regardless of the pressure to which it is subjected, is about −231° F. as will be noted from the foregoing. This temperature is well below the temperatures to which the container and its contents may be subjected, thus assuring that the nitrogen will remain in its gaseous state.

Compressed air may be used advantageously because it can be readily produced by means of any suitable compressor usually available at maintenance and supply depots.

Where the carbon dioxide in the container is intended to be used for fire preventing or fire extinguishing purposes, the gases utilized, preferably, should be substantially inert, non-oxidizing, non-combustible, and non-combustion supporting. These gases may be argon, helium, krypton, neon and nitrogen. However, air (which is composed of about 80% nitrogen and about 20% oxygen, by volume) also has been found suitable for this purpose. The oxygen content of the air appears to be sufficiently small to have a negligible effect.

A preferred method of filling the container comprises first charging the container with a desired quantity of gas and then introducing into the container a desired quantity of liquid carbon dioxide. Alternatively, a desired quantity of solid carbon dioxide may be placed into the container, and thereafter the container may be charged with a desired quantity of gas, either while the carbon dioxide is in its solid state or after it has been permitted to liquefy by exposing the container to normal atmospheric temperatures or by heating the container.

The desired quantity of gas may be determined by charging the empty container with gas having a known pressure at a given temperature. For example, the container may be charged with gas having a pressure of about between 200 and 500 pounds per square inch at about 70° F. Alternatively, the desired quantity of gas may be determined by noting the increase in weight of the container and its contents when the gas has been introduced.

The desired quantity of carbon dioxide in the container may vary in accordance with the strength of the container and its safe working pressure. However, in compliance with existing Interstate Commerce Commission regulations, the weight of the carbon dioxide in a container of a given design shall not exceed 68% of the weight of the water at 4° C. which would completely fill the container. Such 68% filling is known as "normal filling capacity." In practicing the invention with such a container, any suitable quantity of carbon dioxide may be placed in the container which does not exceed 68% filling.

The quantity of carbon dioxide or percent filling, preferably is varied inversely with the quantity or the pressure of the gas (other than carbon dioxide) in the container.

In order to illustrate the invention, sixteen containers were charged with nitrogen to establish various pressures in the containers at 70° F., and the containers were then partially filled with various weights of carbon dioxide. One container was charged with carbon dioxide in the usual manner (without first being charged with nitrogen) to serve as comparison standard.

The containers utilized were steel cylinders complying with Interstate Commerce Commission regulations, and rated as 15 pound cylinders. These cylinders have a volumetric capacity adapted to contain about 15 pounds of carbon dioxide when "68% filled", that is, "normally filled."

Each of the cylinders was fitted with a discharge valve, as shown, and a pressure gauge (not shown) coupled to the outlet **20** of the valve for determining the pressures within the cylinders at various temperatures.

In Table I, about to follow, Example Nos. 1 to 16 are test cylinders charged with nitrogen at between about 200 and about 500 pounds per square inch and containing from about 8 to 14 pounds of carbon dioxide (from about 50% to about 95% normal filling capacity). More specifically, the approximate relationship between the weight of the carbon dioxide and the extent the containers are filled is as follows:

Weight CO_2	Per Cent of Normal Filling
8 lbs.	53
10 lbs.	67
11 lbs.	73
12 lbs.	80
13 lbs.	87
14 lbs.	93

From observation, it was determined that a 15 pound cylinder charged at 70° F. with nitrogen contained approximately the following weights of nitrogen at the given charging pressure:

200 pounds per square inch, .41 lb. of nitrogen
300 pounds per square inch, .61 lb. of nitrogen
400 pounds per square inch, .82 lb. of nitrogen
500 pounds per square inch, 1.03 lbs. of nitrogen

As will be observed from Table I, these weights of nitrogen provided carbon dioxide-nitrogen ratios, by weight, of between about 8/1 and about 34/1 at desired fillings of carbon dioxide from 8 to 14 pounds.

Example No. 17 is the cylinder serving as a standard of comparison and containing 15 pounds of carbon dioxide.

These cylinders were then subjected to temperatures ranging from —80° to 140° F. for a sufficient duration to insure a temperature equilibrium throughout the cylinder and its contents, and pressure readings were taken at the various temperatures.

From the foregoing table it will be observed that at —60° F. the pressures within the containers filled in accordance with the invention (Examples 1 to 16) were equal or much greater than the pressure within the comparison container at 0° F. (Example 17). At 0° F., the pressures within the containers filled in accordance with the invention were from almost twice as great to about two and one half times as great as the pressure within the comparison container at this temperature. As will be illustrated in Table II about to follow, these relatively high pressures at subnormal temperatures provide rapid and effective discharge of the carbon dioxide contents of the containers.

It will also be observed that at 140° F., the containers filled in accordance with the invention have an internal pressure ranging between about 1980 and about 3120 pounds per square inch. These pressures are within the range of the bursting pressures of standard safety discs adapted to rupture at given pressures between 2650 and 3400 pounds per square inch. Specially constructed cylinders and safety discs, thus, are not required to practice the present invention.

In Table II, about to follow, the discharge rates were compared between a cylinder in accordance with Example 8 (12 pounds carbon dioxide, nitrogen at 300 p. s. i.), and a standard cylinder in accordance with Example 17 (15 pounds carbon dioxide), at temperatures of —65°, —40°, 0° and 70° F., for 75% discharge of the contents of the respective cylinders. The cylinders were fitted with a valve **10** having a suitable discharge horn (not shown) coupled to the outlet **20** by means of a hose. The carbon dioxide was discharged into the atmosphere at about sea level.

Table II

Example No.	Temperature	Time	Discharge Rate
	° F.	*Seconds*	*Lbs./sec.*
8	—65	26.5	.357
8	—40	24.0	.392
8	0	19.5	.485
8	70	20.5	.460
17	—65	(1)	(1)
17	—40	49.5	.228
17	0	37.5	.300
17	70	27.5	.410

[1] Discharge stopped after about 15% of the carbon dioxide was discharged due to solidifying of the carbon dioxide in the valve, and/or cylinder.

From the foregoing table, it will be observed that a normally filled contained (Example 17) cannot be effectively discharged at —65° F., while at —40° F. and 0° F., the time required to discharge 75% of its contents is about twice the time required to discharge 75% of the contents

Example No.	CO_2 Lbs.	N_2, p. s. i.	Ratio CO_2N_2 by Wt.	Gauge Pressure in Lbs./sq. in. at Temperature in F.											
				—80	—60	—40	—20	0	20	40	60	80	100	120	140
1	8	300	13/1	------	320	400	480	600	720	860	1,040	1,320	1,600	1,800	1,980
2	8	400	10/1	------	400	480	560	680	780	940	1,140	1,360	1,640	1,900	2,120
3	8	500	8/1	------	480	560	640	760	880	1,040	1,240	1,480	1,740	2,000	2,240
4	10	300	17/1	360	380	440	520	620	740	900	1,080	1,300	1,560	1,850	2,150
5	10	400	12/1	340	400	460	540	640	780	940	1,150	1,400	1,680	1,980	2,260
6	11	300	18/1	360	380	440	520	620	760	920	1,100	1,340	1,630	1,950	2,260
7	11	400	14/1	370	430	490	570	670	800	980	1,200	1,480	1,760	2,080	2,380
8	12	300	20/1	360	380	440	520	620	760	920	1,100	1,400	1,740	2,080	2,440
9	12	400	15/1	400	440	520	600	700	830	1,000	1,220	1,520	1,840	2,180	2,520
10	12	500	12/1	------	520	620	720	840	980	1,160	1,400	1,700	2,040	2,400	2,780
11	13	200	32/1	280	320	360	450	560	680	840	1,000	1,320	1,740	2,160	2,600
12	13	300	21/1	360	380	440	520	640	760	920	1,120	1,420	1,840	2,260	2,650
13	13	400	16/1	400	450	520	600	700	830	1,010	1,240	1,560	1,960	2,360	2,760
14	14	200	34/1	280	320	360	450	560	680	840	1,030	1,350	1,760	2,240	2,700
15	14	300	23/1	380	400	440	520	640	760	920	1,120	1,480	1,950	2,460	2,950
16	14	400	17/1	490	520	570	640	730	860	1,040	1,290	1,640	2,120	2,620	3,120
17	15	------	------	------	80	131	200	290	407	553	734	953	1,445	1,985	2,525

from a container filled in accordance with the present invention (Example 8).

It will also be observed that the discharge rate of a container in accordance with the invention, at −65° F., is greater than the discharge rate of a normally filled container, at 0° F., and compares favorably with the discharge rate of a normally filled container at 70° F.

The high discharge rate is particularly advantageous in cases where the carbon dioxide is introduced into a closed space to extinguish a fire. In such cases, a high carbon dioxide concentration is rapidly established to effect rapid extinguishment of the fire.

From the foregoing tests, it is also apparent that containers filled in accordance with the present invention can be effectively discharged at temperatures approaching −70° F., thus indicating that the presence of nitrogen or other gas has a definite effect on preventing the liquid carbon dioxide from solidifying in the container and the valve at such low temperatures. This effect is believed to be due to the fact that a portion of the nitrogen or other gas is absorbed by the liquid carbon dioxide to lower its freezing point. It has been found that the carbon dioxide in normally filled containers solidifies at temperatures approaching −70° F., and cannot be discharged.

From the foregoing description and examples, it will be seen that the present invention provides improved containers of liquid carbon dioxide and an improved method of preparing and discharging the same. The invention can be practiced with containers and discharge valves and horns used heretofore and without the use of specially designed equipment. The containers, filled in accordance with the invention, can be speedily discharged at relatively low temperatures. The pressure within the containers at these low temperatures effects discharge of the contents without tendency to solidify and clog up the valves and the like. The containers do not have excessive internal pressures at relatively high atmospheric temperatures. The filled containers can be advantageously utilized for numerous purposes as indicated herein.

While the present invention has been described by way of example in connection with a 15 pound cylinder of the portable type, it will be understood that the invention can be practiced with cylinders of any desired capacity or with banks of a number of such cylinders as heretofore employed in systems for storing and discharging carbon dioxide for numerous desired purposes.

As various changes may be made in the form, construction and arrangement of the parts herein, without departing from the spirit and scope of the invention and without sacrificing any of its advantages, it is to be understood that all matter herein is to be interpreted as illustrative and not in any limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

I claim:

1. A method of providing for the continuous discharge, from a closure controlled restricted orifice, of carbon dioxide in a continuous stream even when the temperature at the orifice falls to −60° F., said method comprising forming, at a temperature within the normal range of atmospheric temperatures, in a storage container provided with said orifice a charge capable of exerting on said container at −60° F. a pressure in excess of about two hundred pounds per square inch and consisting principally of carbon dioxide and having as a second component a gas inert to carbon dioxide and having a critical temperature below −80.5° F., the weight of the charge being less than that of a normal charge of carbon dioxide.

2. A method of forming a charge in storage containers which comprises the steps of introducing into the containers at normal temperature a predetermined quantity of carbon dioxide and a predetermined quantity of compressed gas which is capable of exerting a sufficient pressure at −60° F. so that the charge of said gas and carbon dioxide will be confined under a pressure of at least about 200 pounds per square inch absolute at a temperature of about −60° F., the weight of the charge being less than that of a normal charge of carbon dioxide.

3. A method of forming a charge in storage containers which comprises the steps of first partially filling the containers at normal temperatures with carbon dioxide and then introlucing a gas into the containers which gas is capable of exerting a sufficient pressure at −60° F. so that the charge of said gas and carbon dioxide will be confined under a pressure of at least about 200 pounds per square inch absolute at a temperature of about −60° F., the weight of the charge being less than that of a normal charge of carbon dioxide.

4. A method of forming a charge in storage containers which comprises first charging the containers at normal temperature with a compressed gas, and then introducing a predetermined quantity of liquid carbon dioxide, said gas being capable of exerting a sufficient pressure at −60° F. so that the charge will be confined under a pressure of at least about 200 pounds per square inch absolute at a temperature of about −60° F., the weight of the charge being less than that of a normal charge of carbon dioxide.

5. A method of forming a charge in storage containers which comprises the steps of first placing into the containers at normal temperature a predetermined quantity of solid carbon dioxide and then charging the containers with a predetermined quantity of compressed gas which is capable of exerting a sufficient pressure at −60° F. so that the charge of said gas and the carbon dioxide upon liquefying will be confined under a pressure of at least about 200 pounds per square inch absolute at a temperature of about −60° F., the weight of the charge being less than that of a normal charge of carbon dioxide.

6. A method of forming a charge in storage containers which comprises first charging the containers at normal temperature with a compressed gas, and then introducing into the containers a predetermined quantity of liquid carbon dioxide to fill the same to between about 50% and about 95% of their normal filling capacity, said gas being capable of exerting a sufficient pressure at −60° F. so that the charge will be confined under a pressure of at least about 200 pounds per square inch absolute at a temperature of about −60° F.

7. A method of providing for the continuous discharge, from a closure controlled outlet opening, of carbon dioxide in a continuous stream

even when the temperature at the opening falls to −60° F., said method comprising introducing into a storage container a charge of gas having a pressure of between about 200 and about 500 pounds per square inch when confined in the container at a temperature of about 70° F., and then introducing liquid carbon dioxide into the container to fill the same to between about 50% and about 95% of its normal filling capacity, said gas being inert to carbon dioxide, having a freezing point below that of carbon dioxide and being capable of coacting with the carbon dioxide to exert on the container a pressure in excess of about 200 pounds per square inch at −60° F.

8. A charge of fluid medium confined under pressure in a fluid-tight storage container having a closure controlled discharge passage, said charge comprising principally carbon dioxide and a compressed gas inert to carbon dioxide having a critical temperature below −80.5° F., the weight of the charge in relation to the volumetric capacity of the container being such that the charge is safely confineable in the container without building up excessive pressures at temperatures as high as about 140° F. and said other gas being present in proportion to the carbon dioxide to coact with the carbon dioxide to cause the charge to exert on the container a pressure in excess of about two hundred pounds per square inch at about −60° F., whereby said charge is dischargeable from the container at a relatively high rate at temperatures as low as −60° F. without a tendency to solidify and clog the passage through which it is discharged.

9. A charge of fluid medium confined under pressure in a fluid-tight storage container having a closure controlled discharge passage, said charge comprising principally carbon dioxide and a compressed gas inert to carbon dioxide having a critical temperature below −80.5° F., the weight of the carbon dioxide being equivalent to between about 50% and about 95% of the normal carbon dioxide filling capacity of the container and the ratio of carbon dioxide to said other gas by weight being between about 8 and about 34 to one

and the combined weight of carbon dioxide and said other gas not exceeding the weight of a normal charge of carbon dioxide whereby the charge is safely confineable in the container without building up excessive pressures at temperatures as high as about 140° F., and said other gas being present in proportion to the carbon dioxide to coact with the carbon dioxide to cause the charge to exert on the container a pressure in excess of about two hundred pounds per square inch at about −60° F., whereby said charge is dischargeable from the container at a relatively high rate at temperatures as low as −60° F. without a tendency to solidify and clog the passage through which it is discharged.

10. A charge of fluid medium confined under pressure in a fluid-tight storage container having a closure controlled discharge passage, said charge comprising principally carbon dioxide and a compressed gas inert to carbon dioxide having a critical temperature below −80.5° F., the weight of the charge in relation to the volumetric capacity of the container being such that the charge at 140° F. will exert less pressure on the container than a normal charge of carbon dioxide at 140° F. and said other gas being present in proportion to the carbon dioxide to coact with the carbon dioxide to cause the charge to exert on the container a pressure in excess of about two hundred pounds per square inch at about −60° F., whereby said charge is dischargeable from the container at a relatively high rate at temperatures as low as −60° F. without a tendency to solidify and clog the passage through which it is discharged.

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