

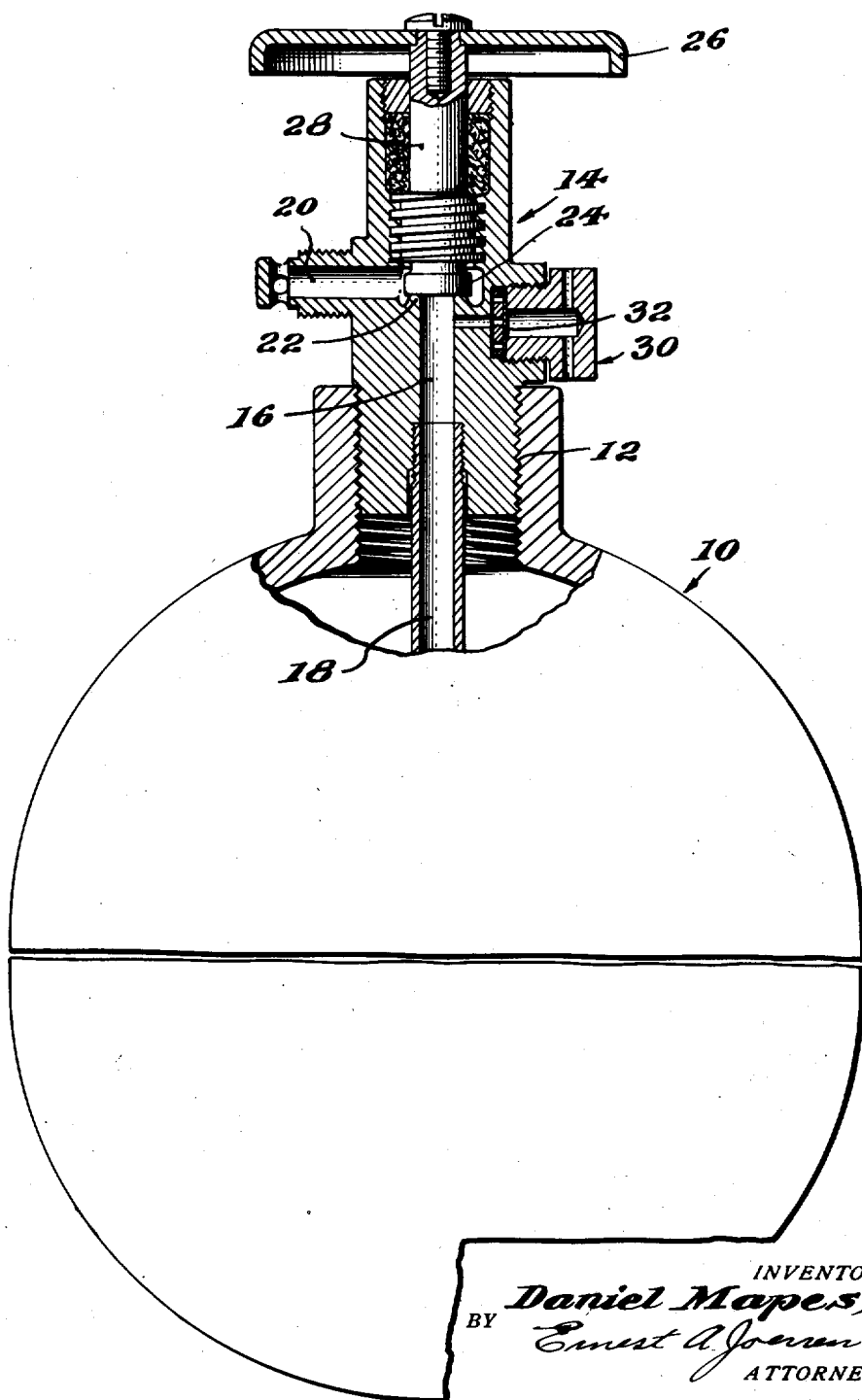
Feb. 9, 1954

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2,668,419

FLUID CARBON DIOXIDE COMPOSITION

Filed Oct. 26, 1951



## UNITED STATES PATENT OFFICE

2,668,419

## FLUID CARBON DIOXIDE COMPOSITION

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Application October 26, 1951, Serial No. 253,243

10 Claims. (Cl. 62-1)

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The present invention relates to charges of liquid carbon dioxide capable of being stored and discharged at extremely low temperatures, and, more particularly, relates to improvements over my prior United States patent, No. 2,521,526, issued September 5, 1950.

The aforementioned patent discloses the provision of charges of carbon dioxide confined under pressure in a fluid-tight storage container having a closure controlled discharge passage and adapted to be discharged from the container at a relatively high rate at temperatures as low as about  $-60^{\circ}\text{F.}$  without a tendency to clog the passage. This is accomplished by establishing a charge in the container comprising principally carbon dioxide and a compressed gas inert to carbon dioxide, such as nitrogen for example, which is capable of exerting a substantial pressure at low temperatures while confined within the container. The weight of the charge in relation to the volumetric capacity of the container is such that the charge is safely confineable in the container without building up excessive pressures at temperatures as high as about  $140^{\circ}\text{F.}$ , and the compressed gas is present in proportion to the carbon dioxide to coat with the carbon dioxide to cause the charge to exert on the container, at low temperatures, a pressure sufficient to effect discharge of the charge.

While the charges provided in the foregoing manner can be discharged effectively and reliably at about  $-60^{\circ}\text{F.}$  and in some instances at about  $-65^{\circ}\text{F.}$ , extensive tests have indicated that such charges cannot be safely recommended for discharge at temperatures approaching  $-70^{\circ}\text{F.}$  and even lower, which temperatures, due to the development of higher altitude flying and the extension of arctic operations, are now more frequently encountered.

Theoretically, liquid carbon dioxide normally would solidify in the container at  $-69.88^{\circ}\text{F.}$ , its triple point temperature, but, with the addition of the compressed gas, it may well be that solidi-

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fication is inhibited to some extent at the triple point temperature. However, carefully conducted tests have indicated that effective discharge of the carbon dioxide cannot be attained at  $-70^{\circ}\text{F.}$  even if the confined charge exerts a pressure of about 400 pounds per square inch on the container, because such a charge, upon expansion through the closure controlled passage, has a tendency to solidify and clog the passage.

It has also been established that where intermittent discharge of this carbon dioxide charge is a requirement in the operation of the apparatus utilizing the charge, that is, the charge is to be released by several on and off operations of the closure controlled passage, solidification of carbon dioxide in the passage becomes even more acute. In fact, it has been determined that charges which can be released in a continuous stream by a single opening of the closure controlled passage at low temperatures, exhibit a tendency to clog the passage when an attempt is made to release the same by on and off operation. Thus, at temperatures of about  $-60^{\circ}\text{F.}$ , charges which can be reliably released in a continuous stream cannot be safely recommended for on and off operation. At temperatures of about  $-65^{\circ}\text{F.}$ , a second discharge is seldom attained.

Accordingly, an object of the present invention is to provide a charge of the character indicated herein which is not subject to the foregoing difficulties.

Another object is to provide such a charge which can be effectively released in a continuous or intermittent stream at or below the triple point temperature of carbon dioxide without solidification in the passage, whereby the charge meets the requirements of the present low temperature operational standards.

Another object is to provide such a charge which will not exert excessive pressures on the container in which it is confined at temperatures of about  $160^{\circ}\text{F.}$

Another object is to provide such a charge

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which is fully operative, reliable and can be safely recommended for use over a wider temperature range than has been found possible heretofore.

A further object is to provide such charges in a simple, convenient, practical and economical manner.

A still further object is to provide such charges which can be confined in and discharged from existing types of carbon dioxide storage and dispensing apparatus utilized for extinguishing fires, inflating rescue devices, operating pneumatically powered mechanisms and many other uses in which carbon dioxide is employed.

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 can be accomplished by providing a charge of fluid medium confined under pressure in a fluid-tight storage container having a closure controlled discharge passage, the charge comprising principally carbon dioxide; a halogenated hydrocarbon having a freezing point temperature much lower than  $-70^{\circ}\text{F}$ . and having a boiling point temperature higher than  $-70^{\circ}\text{F}$ . while under a pressure of about 150 pounds per square inch absolute and having a vapor pressure at  $160^{\circ}\text{F}$ . which is lower than that of carbon dioxide at such temperature, the halogenated hydrocarbon being in admixture with the carbon dioxide in an amount sufficient to maintain the carbon dioxide in fluid state at and below its triple point temperature while confined in the container; and a compressed gas inert to carbon dioxide and the halogenated hydrocarbon, which gas is capable of exerting a pressure of at least 100 pounds per square inch absolute at  $-80^{\circ}\text{F}$ . while confined within the container, 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  $160^{\circ}\text{F}$ . and the inert gas being present in an amount sufficient to coact with the carbon dioxide and the halogenated hydrocarbon to cause the charge to exert on the container a pressure in excess of about 100 pounds per square inch absolute at about  $-80^{\circ}\text{F}$ ., whereby the charge is continuously and intermittently dischargeable from the container at a relatively high rate at temperatures below  $-70^{\circ}\text{F}$ . without a tendency to solidify and clog the passage through which it is discharged.

In the drawing, the single figure is a fragmentary, longitudinal sectional view of apparatus including a container provided with a valve having a closure controlled discharge passage, such apparatus being adapted for confining and discharging the charges in accordance with the present invention.

Referring to the drawing, there is shown a metallic container 10 of the type generally utilized 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 or such other pressures at which the charge therein is to be confined.

In compliance with existing Interstate Commerce Commission regulations, the weight of the

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carbon dioxide in a container of such design shall not exceed 68% of the weight of the water at  $4^{\circ}\text{C}$ . which would completely fill the container, such 68% filling being known in the art as the "normal filling capacity" or the "normal volumetric carbon dioxide capacity" of the container. While the present invention is adapted to be practiced in connection with containers coming within these regulations, it will be understood that the invention can likewise be practiced in connection with containers not subject to Interstate Commerce Commission regulations wherein higher filling percentages are permitted; and that the description of the present invention in connection with containers filled to less than their normal capacity is to be taken as illustrative of the optimum advantages adapted to be attained.

As shown, the upper end of the container is provided with an opening 12 in which is secured a suitable valve or discharge fitting 14. The valve has a discharge passage including an inlet 16 to which is attached a syphon tube 18 extending to the bottom of the container, and including an outlet 20 for connecting a hose or the like adapted to conduct the carbon dioxide to its point of use. Intermediate the inlet and outlet, a valve seat 22 is provided for receiving a valve member 24 adapted to control the flow of the carbon dioxide charge confined in the container through the passage. A manually operable handwheel 26 and a threaded stem 28, adapted to effect unseating and seating of the valve member 24 to open and close the passage at will, are shown by way of example.

A safety discharge assembly 30 may be 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 predetermined safe working pressure. Discharge of the contents of the container in this manner is controlled by a disc 32 adapted to rupture when the predetermined pressure has been exceeded.

The compressed inert gas (other than carbon dioxide) may be a gas or mixture of gases adapted to exist in gaseous state and adapted to exert a substantial pressure at the low temperatures contemplated herein. Such gases may be air, argon, carbon monoxide, carbon tetrafluoride, helium, hydrogen, neon, nitrogen and oxygen. These gases all have a much lower critical temperature than the triple point temperature of carbon dioxide, and, for example, are adapted to exist in compressed gaseous state and exert at least 100 pounds per square inch absolute when confined in the container at a temperature of about  $-80^{\circ}\text{F}$ .

For all-around purposes, nitrogen is preferred because of its inert properties, but compressed air may be used to good advantage because of its general availability and low cost.

By the term "halogenated hydrocarbons" is meant hydrocarbons having one or more hydrogen atoms substituted by an atom of the halogens, to wit, bromine, chlorine, fluorine and/or iodine. This term in its broad sense is intended to include ethers of such compounds and halocarbons wherein all of the hydrogen atoms have been substituted by halogen atoms. Such compounds need not necessarily be in pure form, but may be of the commercial variety and may contain incompletely halogenated fractions in minor quantities. It is also contemplated that such halogenated hydrocarbons may be used singly or in admixture. In the following table,

examples of such halogenated hydrocarbons and the pertinent available physical properties thereof are given.

oxide at this temperature and therefore will not adversely affect the over-all pressure of the charge at such temperature.

| No. | Compound                                      | Molecular Weight | Critical Temperature<br>° F. | Critical Pressure<br>P. s. i. | Freezing Point*<br>° F. | Boiling Point*<br>° F. |
|-----|-----------------------------------------------|------------------|------------------------------|-------------------------------|-------------------------|------------------------|
| 1   | CClF <sub>3</sub>                             | 105              | 84                           | 540                           | -296                    | -112                   |
| 2   | CCl <sub>2</sub> F <sub>2</sub>               | 120              | 233                          | 582                           | -232                    | -22                    |
| 3   | CClF <sub>2</sub>                             | 137              | 388                          | 635                           | -168                    | 75                     |
| 4   | CF <sub>3</sub> Br                            | 210              | 389                          | 600                           | -112                    | 76                     |
| 5   | CF <sub>3</sub> Br                            | 149              | 158                          | 635                           | -356                    | -76                    |
| 6   | CHF <sub>3</sub>                              | 70               | 90                           | 730                           | -256                    | -116                   |
| 7   | CHClF <sub>2</sub>                            | 86.5             | 205                          | 716                           | -256                    | -41                    |
| 8   | CHCl <sub>2</sub> F                           | 103              | 353                          | 750                           | -211                    | 45                     |
| 9   | CH <sub>2</sub> Cl <sub>2</sub>               | 85               | 421                          | 640                           | -143                    | 104                    |
| 10  | CH <sub>3</sub> F                             | 34               | 113                          | 892                           | <-238                   | -108                   |
| 11  | CH <sub>3</sub> Br                            | 95               | 381                          | 760                           | -135                    | 38                     |
| 12  | C <sub>2</sub> F <sub>6</sub>                 | 138              | 76                           | 480                           | -150                    | -109                   |
| 13  | C <sub>2</sub> F <sub>4</sub> O               | 164              | 112                          | 400                           | <-100                   | -74                    |
| 14  | C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> | 171              | 294                          | 474                           | -137                    | 38                     |
| 15  | C <sub>3</sub> F <sub>8</sub>                 | 188              | 165                          | 353                           | -298                    | -36                    |
| 16  | C <sub>4</sub> F <sub>10</sub>                | 238              | 217                          | 300                           | <-112                   | 27                     |
| 17  | C <sub>4</sub> F <sub>8</sub> O               | 216              | 120                          | 385                           | <-80                    | 56                     |
| 18  | CF <sub>3</sub> ClBr                          | 165              | 309                          | 595                           | -257                    | 25                     |
| 19  | CH <sub>2</sub> ClBr                          | 129              |                              |                               | -126                    | 155                    |
| 20  | CH <sub>3</sub> I                             | 142              |                              |                               | -84                     | 108                    |
| 21  | C <sub>2</sub> F <sub>5</sub> ClBr            | 276              | 554                          | 600                           | -98                     | 200                    |
| 22  | C <sub>2</sub> F <sub>5</sub> Br              | 260              | 418                          | 500                           | -171                    | 117                    |
| 23  | CCl <sub>3</sub> Br                           | 198              |                              |                               |                         | 219                    |
| 24  | CHF <sub>2</sub> Br                           | 131              |                              |                               |                         |                        |
| 25  | CHCl <sub>2</sub> Br                          | 164              |                              |                               |                         |                        |
| 26  | CHClBr <sub>2</sub>                           | 208              |                              |                               |                         |                        |
| 27  | CF <sub>3</sub> CH <sub>2</sub> Br            | 163              |                              |                               |                         | 79                     |

\*At atmospheric pressure.

It will be noted that compounds Nos. 1 to 22 all have a freezing point temperature lower than the triple point of carbon dioxide and therefore are adapted to exist in fluid state at about -70° F. Also, these compounds (with the exception of compounds Nos. 1, 5, 6, 10, 12, and 13) have a boiling point temperature higher than the triple point of carbon dioxide. However, compounds Nos. 1, 5, 6, 10, 12, and 13 have a boiling point temperature higher than -70° F. while confined under a pressure of about 150 pounds per square inch, whereby all of these compounds are adapted to exist in liquid state when so confined at a temperature of about -70° F. Thus, when these compounds are admixed with carbon dioxide and the mixture is confined in a fluid-tight container at -70° F. or lower, a mutually solvent liquid system is believed to be established.

It will further be noted that compounds Nos. 2 to 11 and 13 to 17 have a higher critical temperature than that of carbon dioxide (87.8° F.), and have a lower critical pressure than that of carbon dioxide (1070 pounds per square inch absolute). Consequently, these compounds at about 160° F. have a lower vapor pressure than that of carbon dioxide at such temperature, whereby the vapor pressure of such compounds will not materially contribute to the over-all pressure of the charge at such temperature, and in fact a lower over-all pressure will result where a portion of the carbon dioxide of the charges illustrated and described in the aforementioned patent is substituted by an amount of such compounds. In this manner, carbon dioxide and these halogenated hydrocarbons can be utilized together in a charge without building up, at 160° F., pressures exceeding the safe working pressure of the container, provided of course the combined weight of the carbon dioxide and the halogenated hydrocarbon components of the charge in relation to the volumetric capacity of the container is within safe limits.

Compounds Nos. 1 and 12 have a critical temperature slightly lower than that of carbon dioxide, but have a critical pressure much lower than that of carbon dioxide. These compounds at 160° F. have a lower pressure than carbon di-

The critical temperature and the critical pressure data of compounds Nos. 19 and 20 could not be located, but, from general observations these compounds are believed to be adapted for use in connection with practicing the invention. Similarly, pertinent data on compounds Nos. 23 to 27 were not available. However, these compounds are closely related to either compound No. 5 or compound No. 19, and are believed to be suitable.

In practicing the invention, the selection of any particular compound or compounds listed in the table depends primarily on cost and general availability in commercial quantities and also on non-flammability and non-toxicity. Where the charge is utilized in the extinguishment of fires, non-flammability and high stability are desirable, and good extinguishing characteristics are preferred. Where the charge is to be released into the atmosphere in the vicinity of human beings, non-toxicity is an important factor. The molecular weight of the compound may also be a factor, in view of the fact that tests have indicated that in using equal amounts by weight of compounds having different molecular weights, those compounds having the lower molecular weights appear to be most effective in maintaining the carbon dioxide in liquid state at temperatures below -70° F.

The amounts of carbon dioxide, inert compressed gas and halogenated hydrocarbon compound comprising the charge may be varied considerably but in all cases the carbon dioxide is the principal component of the charge. Preferably, the combined amounts of the carbon dioxide and the halogenated hydrocarbon are equivalent to between about 65 and about 140 parts by weight, and the amount of nitrogen or other gas is equivalent to between about 3 and 10 parts by weight. Charges comprising such proportions of components, when confined in containers in amounts to provide between about 50% and about 95% normal filling thereof, exert a pressure of between about at least 100 and about 400 pounds per square inch at -70° F. and exert a pressure at 160° F. which does not exceed the working pressure the container can safely withstand.

The proportion of carbon dioxide to halogenated hydrocarbon may vary considerably, the weight of carbon dioxide being at least equal to the weight of the halogenated hydrocarbon. This proportion may vary between at least one and about thirty parts by weight of carbon dioxide to about one part by weight of halogenated hydrocarbon depending in general on the particular halogenated hydrocarbon compound or compounds selected and the temperature at which the charge is to be released.

In reducing the invention to practice, it has been found that charges comprising 90 to 120 parts by weight of carbon dioxide, 15 to 45 parts by weight of a halogenated hydrocarbon compound, and 4 to 8 parts by weight of compressed nitrogen or other gas could be readily discharged at  $-70^{\circ}\text{F.}$  and lower.

In preparing the charges, any of the methods disclosed in the aforementioned patent may be utilized, that is, the carbon dioxide, the halogenated hydrocarbon and the compressed inert gas may be introduced into the container in any desired order and the carbon dioxide may be introduced in either liquid or solid state.

The following examples illustrate the present invention more specifically.

#### Example I

A charge was prepared in a container having a normal filling capacity of about 5 pounds of carbon dioxide and a volume of about 205 cubic inches by first introducing one pound of compound No. 5 of the table, next introducing about .2 pound of dry nitrogen gas, and finally introducing 3.5 pounds of liquid carbon dioxide. The charge confined in the container was stored in a low temperature refrigerator for a sufficient time to bring the temperature thereof to about  $-70^{\circ}\text{F.}$  The charge was then released by opening the valve completely, and it was found that more than 90% of the charge was discharged through an orifice about .082 inch in diameter in about 28 seconds. Such discharge compares favorably with that of 5 pounds of carbon dioxide from a similar container and through a similar orifice at  $70^{\circ}\text{F.}$

#### Example II

A second charge was prepared in the foregoing manner, and was discharged while at  $-70^{\circ}\text{F.}$  by intermittently opening the valve for about 3 seconds and closing the valve for 10 seconds. Practically the entire charge was released from the container by such intermittent valve opening operations, thereby demonstrating that on and off operation is possible with such charges at about the triple point temperature of carbon dioxide.

#### Example III

A third charge was prepared in the foregoing manner but the temperature thereof was brought down to about  $-80^{\circ}\text{F.}$ , and the charge was released as before at this temperature. Continuous discharge of about 90% of the charge required 32 seconds, thereby demonstrating that such charges can be released at a good rate while at temperatures below the triple point temperature of carbon dioxide.

#### Example IV

A fourth charge was prepared in the foregoing manner comprising 3.5 pounds of carbon dioxide, one pound of compound No. 19 of the table, and .2 pound of nitrogen. About 90% of this charge was discharged at about  $-70^{\circ}\text{F.}$  in about 27 seconds.

#### Example V

A fifth charge was prepared in the foregoing manner comprising 3.5 pounds of carbon dioxide, one pound of compound No. 2 of the table, and .2 pound of nitrogen. This charge had about the same discharge characteristics at  $-70^{\circ}\text{F.}$  as the charge of Example I.

#### Example VI

A sixth charge was prepared in the foregoing manner comprising 3.5 pounds of carbon dioxide, one pound of compound No. 2 of the table and .2 pound of nitrogen. This charge had about the same discharge characteristics at  $-80^{\circ}\text{F.}$  as the charge of Example III.

#### Example VII

A seventh charge was prepared in the foregoing manner comprising 3.5 pounds of carbon dioxide, .5 pound of compound No. 2 of the table, and .2 pound of nitrogen. At  $-70^{\circ}\text{F.}$ , more than 90% discharge was accomplished by on and off operation of the valve.

#### Example VIII

The tests in accordance with Examples I to VII were repeated with the weight of the nitrogen adjusted to .15 pound in one instance and to .25 pound in another instance. In all cases, more than about 90% discharge was effected, but the use of the larger amount of nitrogen resulted in a slightly higher discharge rate.

A charge consisting of 5 pounds of carbon dioxide and another charge consisting of 4 pounds of carbon dioxide and .2 pound of nitrogen were each confined in a container identical to that used in connection with the foregoing examples. At  $-70^{\circ}\text{F.}$ , both of these charges failed to discharge due to solidification of carbon dioxide in the valve controlled passage and/or in the container.

Further tests were made in connection with the charges in accordance with Examples I to VII to test their fire extinguishing effectiveness, and in every instance it was found that these charges at  $-70^{\circ}\text{F.}$  extinguished standard tub fires at least as effectively as charges consisting of carbon dioxide at  $70^{\circ}\text{F.}$  It was also observed that, where these charges were directed through a carbon dioxide snow forming shield or horn of the usual construction, the accumulation of electrostatic charges on the shield or horn was greatly minimized under conditions of low temperature and low humidity thereby indicating that the addition of the halogenated hydrocarbon compounds has a desirable electrostatic charge inhibiting effect.

The pressure/temperature characteristics of charges in accordance with Examples I to VIII were determined by connecting a pressure gage to the outlet of the containers. At about  $-80^{\circ}\text{F.}$ , the pressure exerted by the charges in all cases exceeded 100 pounds per square inch absolute, and, at about  $160^{\circ}\text{F.}$ , the pressure exerted by the charges in all cases did not exceed 3000 pounds per square inch absolute which pressure is well within the safe working pressure of the container considering that the usual carbon dioxide charges at 68% filling exert a pressure of about 3100 pounds per square inch.

From the foregoing description and examples, it will be seen that the present invention provides improved charges comprising principally carbon dioxide which can be discharged continuously and intermittently at a relatively high

rate at extremely low temperatures and which do not exert excessive pressures at high temperatures. These charges can be provided in a simple and economical manner, and can be utilized for many useful purposes without the need of specially designed apparatus.

It will be understood that the details and examples hereinbefore set forth are illustrative only, and the invention, as broadly described and claimed, is in no way limited thereby.

#### I claim:

1. 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; a halogenated hydrocarbon having a freezing point temperature much lower than  $-70^{\circ}\text{F}$ . and having a boiling point temperature higher than  $-70^{\circ}\text{F}$ . while under a pressure of about 150 pounds per square inch absolute and having a vapor pressure at  $160^{\circ}\text{F}$ . which is lower than that of carbon dioxide at such temperature, said halogenated hydrocarbon being in admixture with said carbon dioxide in an amount sufficient to maintain said carbon dioxide in fluid state at and below its triple point temperature while confined in the container; and a compressed gas inert to carbon dioxide and said halogenated hydrocarbon which gas when present in sufficient quantity is capable of exerting a pressure of at least 100 pounds per square inch absolute at  $-80^{\circ}\text{F}$ . while confined within the container, 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  $160^{\circ}\text{F}$ . and said inert gas being present in an amount sufficient to coact with the carbon dioxide and said halogenated hydrocarbon to cause the charge to exert on the container a pressure in excess of about 100 pounds per square inch absolute at about  $-80^{\circ}\text{F}$ ., whereby the charge is dischargeable from the container at a relatively high rate at temperatures below  $-70^{\circ}\text{F}$ . without a tendency of the carbon dioxide to solidify and clog the passage through which it is discharged.

2. A charge according to claim 1 which is equivalent to between about 50% and about 95% of the normal carbon dioxide filling capacity of the container.

3. A charge according to claim 2 which comprises between about 65 and about 140 parts by weight of carbon dioxide and said halogenated hydrocarbon combined, and between about 3 and 10 parts by weight of said inert gas.

4. A charge according to claim 3 which comprises between about two and about eight parts by weight of carbon dioxide to one part by weight of said halogenated hydrocarbon.

5. A charge according to claim 1, wherein said halogenated hydrocarbon is substantially non-toxic and non-flammable

6. A charge according to claim 1, wherein the closure controlled passage includes a valve constructed and arranged for on and off operation and said charge is characterized in that it can be released by intermittent operation of the valve without solidifying and clogging the passage.

7. A charge according to claim 1 which consists essentially of about 35 parts by weight of carbon dioxide, about 10 parts by weight of  $\text{CF}_3\text{Br}$ , and about 2 parts by weight of nitrogen.

8. A charge according to claim 1 which consists essentially of about 35 parts by weight of carbon dioxide, about 5 to 10 parts by weight of  $\text{CCl}_2\text{F}_2$ , and about 2 parts by weight of nitrogen.

9. A charge according to claim 1 which consists essentially of about 35 parts by weight of carbon dioxide, about 5 to 10 parts by weight of  $\text{CH}_2\text{ClBr}$ , and about 2 parts by weight of nitrogen.

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; a halogenated hydrocarbon having a freezing point temperature much lower than  $-70^{\circ}\text{F}$ . and having a boiling point temperature higher than  $-70^{\circ}\text{F}$ . while under a pressure of about 150 pounds per square inch absolute, said halogenated hydrocarbon being in admixture with said carbon dioxide in an amount sufficient to maintain said carbon dioxide in fluid state at and below its triple point temperature while confined in the container; and a compressed gas inert to carbon dioxide and said halogenated hydrocarbon which gas when present in sufficient quantity is capable of exerting a pressure of at least 100 pounds per square inch absolute at  $-80^{\circ}\text{F}$ . while confined within the container, 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  $160^{\circ}\text{F}$ . and said inert gas being present in an amount sufficient to coact with the carbon dioxide and said halogenated hydrocarbon to cause the charge to exert on the container a pressure in excess of about 100 pounds per square inch absolute at about  $-80^{\circ}\text{F}$ ., whereby the charge is dischargeable from the container at a relatively high rate at temperatures below  $-70^{\circ}\text{F}$ . without a tendency of the carbon dioxide to solidify and clog the passage through which it is discharged.

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