Oct. 25, 1932. D. H. KILLEFFER 1,883,940

METHOD OF AND APPARATUS FOR CONTROLLING CARBON DIOXIDE GASEOUS MIXTURES

Filed Dec. 31, 1930 2 Sheets-Sheet 1

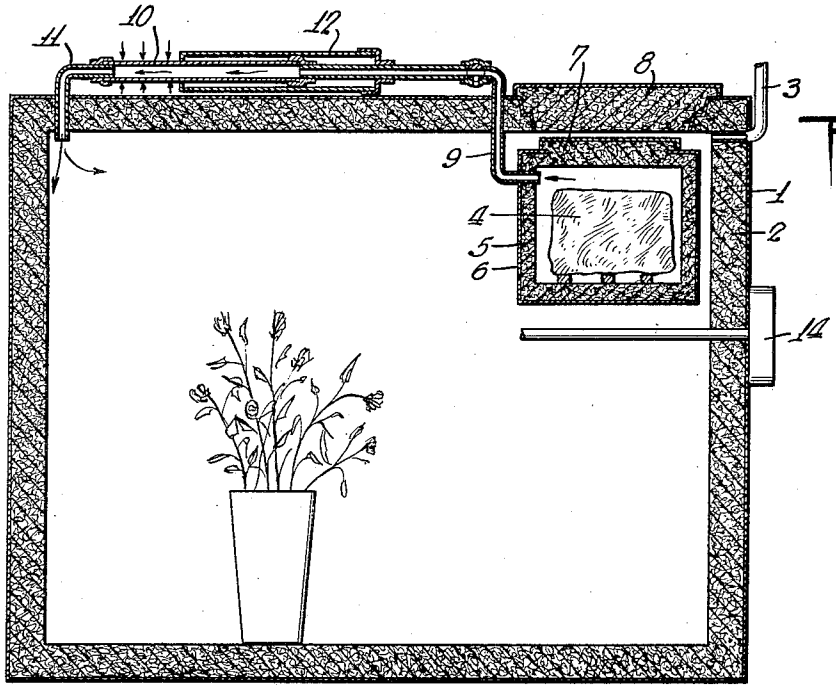



FIG. 1.

FIG. 3.

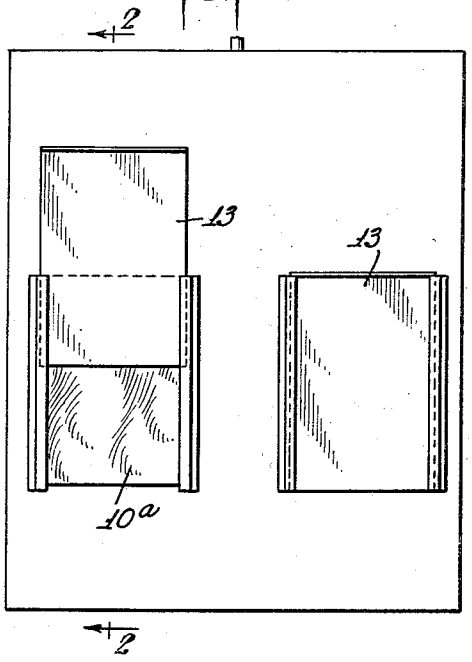
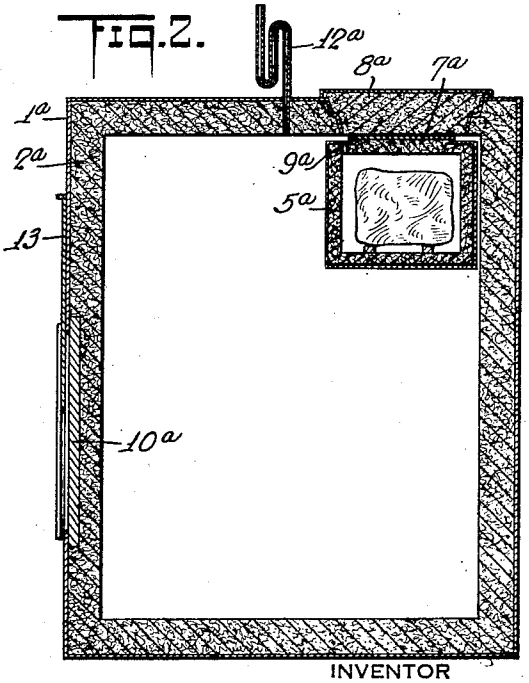



FIG. 2.




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FIG. 4.

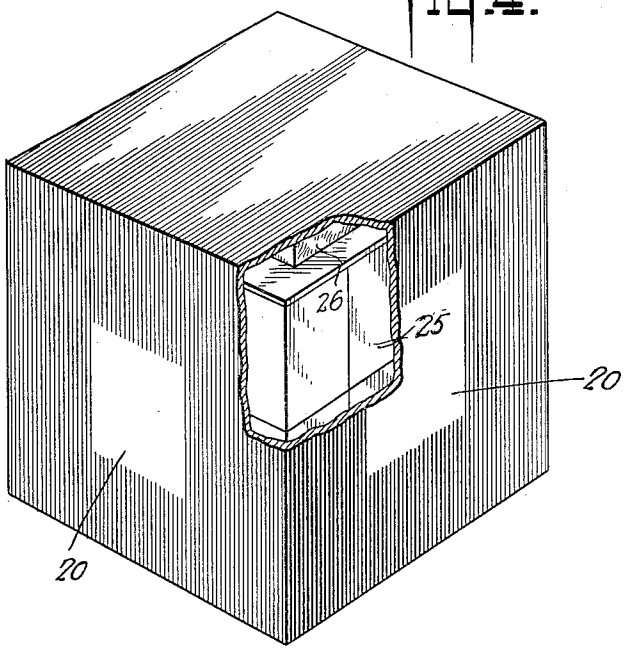
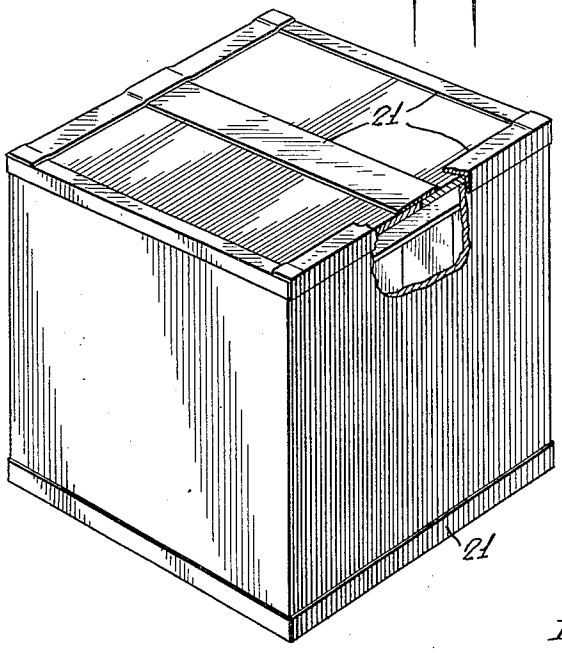



FIG. 5.




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# UNITED STATES PATENT OFFICE

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## METHOD OF AND APPARATUS FOR CONTROLLING CARBON DIOXIDE GASEOUS MIXTURES

Application filed December 31, 1930. Serial No. 505,707.

My present invention is shown as embodied in apparatus for refrigerating by means of solid carbon dioxide, particularly apparatus of the type in which the heavy gas evaporating from the solid is discharged into the atmosphere of the refrigerated space. While certain of the products to be refrigerated are not affected by the gas and others can be easily protected from it, there are still others not easily protected and which may be seriously damaged thereby. As concerns the latter class, it has been proposed to eliminate the difficulty entirely by discharging all the gas outside of the refrigerated space; also it has been proposed to allow the gas to leak out rapidly enough to avoid production of dangerous concentrations. However, experience shows that many products likely to be injured by an atmosphere containing too great percentage of carbon dioxide gas, may be greatly benefited by an atmosphere of air containing only certain limited percentages of the gas; for example, certain vegetables, cut flowers, fruits and the like; and one object of my invention is to regulably control the production of air-gas mixtures in proportions suitable for the atmosphere of the particular product to be preserved thereby.

Obviously, there are many ways in which air and gas may be mingled for such purposes, either by hand or automatic adjustment of inlet or outlet valves; or by leaks as above suggested, but unless very delicate apparatus is employed, the operation is complicated and rendered uncertain by variation of internal or external pressure, specific gravity of the gaseous mixture, etc. Even slight pressure variations of this kind, tend to produce relatively large volume flow through all ordinary leaks or vents, all gases flowing together in the same direction, either in or out, according to the direction of the pressure. Moreover, differences in weight between air and carbon dioxide gases tend to produce gravity outflow of the heavy carbon dioxide gas through low level leaks, thereby causing inflow of air through higher level leaks.

As contrasted with this non-selective, unidirectional flow, my invention contemplates employment of air inlet and gas outlet means, operating by diffusion of the gases so that different gases flow simultaneously in opposite directions, through the same passages, at rates determined by their densities, so that the flow is practically independent of the above described variations of internal or external pressures. The means which I employ for this purpose is a porous septum having one surface exposed to the air, preferably ordinary external atmosphere, and the other surface exposed to carbon dioxide gas, either pure or mixed with varying percentages of air. In such case, the air will diffuse through the pores into the carbon dioxide gas and the carbon dioxide gas will diffuse outward into the air; but other things being equal the air being lighter, will diffuse inward more rapidly than the heavy carbon dioxide gas will diffuse outward. In the case of mixtures, the rate will depend upon the average densities of the bodies of gas on opposite sides of the septum. That is to say, other things being equal, the rate of passage of air on one side of the septum into a fifty-fifty solution of gas and air on the other side of the septum, will be one-half the rate said pores would pass if the gas were pure.

The volume of transfusion of the gas will of course depend on the area, thickness and porosity of the septum.

It will be understood that the difference in functioning between a pore and an ordinary leak is the difference in their minimum diameters, that of the pore being very small as compared with that of the leak. Consequently, a septum may be porous and yet have some passages large enough to operate as leaks, but this is undesirable. A pin hole or other passage large enough to be plainly visible will

function as a leak rather than a pore. Pores small enough for the purpose are such as exist in ordinary paper. Newspaper is especially porous because it has a minimum amount of binder. Pasteboard contains a greater percentage of binder, but is still very porous, and ordinary corrugated paperboard containing only the ordinary percentage of binder is amply porous for most purposes. Dry animal membranes, some kinds of parchment, leather, etc., may also be employed. Where a rigid septum is desired either for structural reasons or to withstand gas pressures, thin, unglazed porcelain, clay or plaster of Paris slabs may be employed.

The above and other features of my invention may be more fully understood from the following description in connection with the accompanying drawings, in which

Fig. 1 is a vertical sectional elevation showing more or less diagrammatically a chamber and means for properly diluting carbon dioxide gas before it is discharged into the chamber;

Fig. 2 is a similar view of an arrangement for adjustably diluting the atmosphere of an air-gas mixture within the chamber;

Fig. 3 is an elevation corresponding to Fig. 2, viewed from the left;

Fig. 4 is a perspective view of a carton, partly broken away, showing one form of my invention applied thereto; and

Fig. 5 is a similar view showing a modified arrangement.

In Fig. 1, the chamber enclosing the atmosphere, the composition of which it is desired to control, may comprise an outer shell 1, preferably of metal with gas-tight joints. For most purposes, an inner wall or layer 2, may be provided for structural strength, usually of heat insulating material, because the diluted carbon dioxide gas mixtures are as a rule more beneficial to cut flowers and the like when the chamber is moderately refrigerated, temperatures of 40° to 50° F. being desirable in many cases. Where the container is air-tight, some form of pressure relief outlet as vent 3, may be arranged to prevent undue pressures of accumulated gas within the chamber.

In the present case, the source of the carbon dioxide gas is shown as solid carbon dioxide 4, enclosed in a container which may be in the form of a box 5, of balsa wood or other insulating material, enclosed in a gas-tight metal casing 6. This box may be charged with a solid through openings which are normally closed by inner cover 7 and outer cover 8. The structure may be designated in any of the ways well known in the art for insuring heat absorption and gas evolution by the solid carbon dioxide at rates required to maintain desired temperatures within the refrigerator, and the gas may be caused to flow through ducts which may be inner and outer walls interposed as insulation to protect the chamber from inleak of heat, the important point being that the gas shall not be discharged into the chamber until it has been properly diluted with air. For purposes of my present invention, I have shown a simple gas conduit 9 through which the gas is conducted to and through an exterior porous conduit section 10 and from which it flows through pipe 11 into the atmosphere of the refrigerator.

The porous section 10 may be merely a cylindrical tube or it may be widened to any extent required for proper dilution of the gas, and this will of course depend on the amount of gas to be diluted and its rate of flow through the porous section of the conduit. In general, the parts will be designed so that the porous area will be adequate for maximum desired dilution for the maximum amount of gas that is likely to flow through the conduit in a given time.

For lesser dilutions or lower rates of flow of the gas, I provide means for adjusting the active area of the porous section. This may be done by any form of shield that will cut off either the internal gas or the exterior air from direct contact with the surface of the porous wall. A very simple way is to provide an exterior slidable sleeve 12 which will shield the exterior surface of the conduit from the exterior air as shown. Sliding the sleeve to the left will decrease the amount of porous surface 10 that is exposed to the air, while sliding it in the opposite direction will increase said surface. As before stated, the circumferential dimension of the surface exposed may be made anything desired, either by varying sizes for a cylindrical tube or varying widths for a flattened tube.

In special cases where the apparatus requires evaporation of relatively large amounts of solid carbon dioxide in order to make the desired temperature within the refrigerated space and at the same time a very dilute mixture of the carbon dioxide gas is desired in the atmosphere of the refrigerated space, part of the gas may be discharged directly into the open air instead of passing through the porous conduit 10 and pipe 11 into the refrigerated space.

So far as concerns the above method of making a desired gas-air mixture for the atmosphere of the container 1, it will be evident that any other source of carbon dioxide gas could be substituted for that shown in Fig. 1. That is to say, a box like 5 could be located outside of the refrigerated space and could be provided with as much insulation as may be necessary to make it yield gas at a desired rate entirely independently of what may be required where it has a refrigerating function inside of the container 1 as shown in the drawings; or a tank of liquid carbon dioxide gas could be used as the source; or any other source of carbon dioxide

gas, or mixture requiring dilution, may be employed.

In the apparatus shown in Fig. 2, the parts may be like those described in Fig. 1, including a gas-tight metallic casing 1*a*, insulation 2*a*, insulated refrigerant container 5*a* and removable covers 7*a*, 8*a*. In this case, however, the gas is discharged directly into the refrigerated space through a vent 9*a* so that the atmosphere tends to be over-rich in carbon dioxide gas. In this case, the porous septum is between the outer air and said atmosphere, as indicated at 10*a*, it being understood that the insulation 2*a* is fibrous like kapok or at least is too porous to prevent outflow of carbon dioxide from the atmosphere within the refrigerator and inflow of air from the exterior atmosphere. The porous septum 10*a* may be a sheet of ordinary permeable pasteboard or corrugated board or unglazed porcelain or, in fact, any of the porous materials hereinbefore mentioned. While the area, thickness and diffusion capacity of such a septum may be designed with reference to the rest of the apparatus, to maintain a normally adequate diffusion rate suitable for maintaining a desired $CO_2$ content of the inner atmosphere, I prefer to employ a slide 13, whereby more or less of the outer surface may be cut off from access of the external air. In this case also a vent as 12*a* may be employed to prevent excessive internal pressures and this may be formed with a reverse bend as shown, operating as a valve on the principle of a plumber's trap. The fluid affording the seal may be a liquid or may be simply the heavy gas or air-gas mixture flowing from the interior. If the interior has a normal tendency toward too high gas concentration, the intake of this vent may be extended toward the bottom of the space where the mixture is richest in carbon dioxide gas.

As shown in Fig. 3, there are two slides 13, controlling two porous septums 10*a*, and obviously there may be as many of them and their areas may be as great as necessary for the purpose in view.

In this connection it will be understood that while there are great differences in the percentages of the carbon dioxide gas that various perishable products such as fruits and flowers will stand without injury, and also in the percentages that are most beneficial, there are special cases where the maximum beneficial percentage is quite low. Thus, while 80% carbon dioxide may not injure rhubarb, 50% may be all that is desirable for oranges, 20% for peaches, 15% for strawberries, etc. The point is that any desired percentage of gas-air mixture may be attained by the above or any other equivalent adjustment of the effective area of the porous septum and, in extreme cases, discharge of part of the carbon dioxide gas supply outside the refrigerator. Furthermore, the ranges between helpful percentages and those that begin to be substantially injurious are so wide that in any particular apparatus it would be quite possible to get improved results by adjustment for known average conditions in any apparatus of predetermined, tested design. For testing and standardizing, a carbon dioxide gas analysis indicator 14 may be employed as in Fig. 1; or it may be a permanent part of the equipment.

Known or predetermined designs are shown in Figs. 4 and 5. In Fig. 4 the container is a corrugated paper carton of ordinary construction, comprising the usual walls and top and bottom double flaps. The walls are of porous permeable material, but the exterior is coated with material substantially impervious both to air and carbon dioxide gas as, for instance, bakelite varnish, except certain areas as 20, 20, which are left uncoated. The amount of such area is determined by the evaporation rate of the solid carbon dioxide and the requirements of the products to be preserved therein. It is of course possible to cut down the porous areas by additional varnish, to suit special cases.

Fig. 5 shows a special case of a carton where all the walls and flaps are made up with a substantially gas-tight layer, which may be a layer of asphalt or bakelite varnish and such layer may be interposed between the corrugated element and the outer flat layers which constitute the "corrugated board". In this case, the porous diffusion element is afforded by the porous sealing tape 21. In this connection it will be understood that ordinary paper binder tape with only the usual thin coating of ordinary glue or paste, will be sufficiently porous to afford paths for very substantial diffusion of exterior air into the package and interior gas out of the package.

In Figs. 4 and 5, the cartons may be provided with vents of relatively small flow capacity, sufficient to prevent substantial pressure of gas within the carton, but preferably not enough to permit inflow of air.

In both Figs. 5 and 6 the carton is broken away to show products 25 and solid carbon dioxide 26, packed therein.

It is understood that the containers shown in Figs. 1, 2 and 3 have the usual openings, with gas-tight closures, for insertion and removal of perishable products.

I claim:—

1. A method of preserving products of a class injured by over-concentrations of carbon dioxide gas, which includes enclosing said products in a refrigerating container having walls substantially impermeable to carbon dioxide gas, cooling said container and producing gas by evaporating solid carbon dioxide by heat absorbed from within said container, diluting said gas by exposing it in contact with a surface of a porous dif-

fusion medium having external atmosphere in contact with another surface thereof; adjusting the effective area of the diffusion medium to control the amount of the dilution; and discharging the diluted product of said diffusion, into the atmosphere of the refrigerated space.

2. A method of preserving products of a class injured by over-concentrations of carbon dioxide gas, which includes enclosing said products in a refrigerating container, cooling said container and producing gas by evaporating solid carbon dioxide within said container, diluting said gas by exposing it in contact with a surface of a porous diffusion medium having external atmosphere in contact with another surface thereof; adjusting the effective area of the diffusion medium to control the amount of the dilution; and discharging the diluted product of said diffusion, into the atmosphere of the refrigerated space.

3. A method of preserving products of a class injured by over-concentrations of carbon dioxide gas, which includes enclosing said products in a refrigerating container, cooling said container and producing gas by evaporating solid carbon dioxide by heat absorbed from within said container, diluting said gas by exposing it in contact with a surface of a porous diffusion medium having external atmosphere in contact with another surface thereof; and discharging the diluted product of said diffusion, into the atmosphere of the refrigerated space.

4. A method of preserving products of a class injured by over-concentrations of carbon dioxide gas, which includes enclosing said products in a container; supplying carbon dioxide gas to produce an air-gas atmosphere in said container; controlling dilution of said atmosphere by diffusion through a surface of a porous diffusion medium having external atmosphere in contact with another surface thereof.

5. A method of preserving products of a class injured by over-concentrations of carbon dioxide gas, which includes enclosing said products in a container; supplying carbon dioxide gas to produce an air-gas atmosphere in said container; controlling dilution of said atmosphere by diffusion through a surface of a porous diffusion medium having external atmosphere in contact with another surface thereof and by varying the effective diffusion capacity of said diffusion medium.

6. Apparatus for preserving products of a class injured by over-concentrations of carbon dioxide gas, including a source of over-concentrated gas and means for diluting it, said means including a porous diffusion septum, means for exposing the gas to be diluted in contact with a surface of said septum having external atmosphere in contact with another surface thereof.

7. Apparatus for preserving products of a class injured by over-concentrations of carbon dioxide gas, including a source of over-concentrated gas and means for diluting it, said means including a porous diffusion septum, means for exposing the gas to be diluted in contact with a surface of said septum having external atmosphere in contact with another surface thereof, in combination with means for adjusting the effective exposed surface of said septum.

8. A refrigerator of the type cooled by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator and in combination therewith; means for diluting the gas before it is discharged into said atmosphere, said means including a porous diffusion septum having a surface exposed to atmosphere and conduit means for passing the evaporated gas in diffusion relation to the opposite surface of said septum.

9. A refrigerator of the type cooled by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator and in combination therewith; means for diluting said atmosphere including a porous diffusion septum in a wall of the refrigerator having an inner surface exposed in diffusion relation to the refrigerated atmosphere and an outer surface exposed to the external air.

10. A refrigerator of the type cooled by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator and in combination therewith; means for diluting said atmosphere including a porous diffusion septum in a wall of the refrigerator having an inner surface exposed in diffusion relation to the refrigerated atmosphere and an outer surface exposed to the external air, a surface of said septum having a fibrous heat insulating covering that is permeable to gas and air.

11. A refrigerator having means for cooling it by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator, and in combination therewith, adjustable means for diluting the gas in said atmosphere.

12. A refrigerator having means for cooling it by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator, and in combination therewith, adjustable means for diluting the gas in said atmosphere, and a gas analysis indicator for determining the carbon dioxide content of the resulting mixture.

13. A refrigerator having means for cooling it by evaporation of carbon dioxide and discharge of the resulting gas into the atmosphere of the refrigerator, and in combination therewith, adjustable means for di-

luting the gas in said atmosphere, said means including a porous diffusion septum having a surface exposed to atmosphere, conduit means for passing the evaporated gas in diffusion relation to the opposite surface of said septum, means for cutting off more or less of the exposed area of the septum, and a gas analysis indicator for determining the carbon dioxide content of the resulting mixture.

Signed at New York in the county of New York, and State of New York this 30th day of December, A. D. 1930.

DAVID H. KILLEFFER.