

May 14, 1968

R. E. RICE

3,382,919

HEAT-STORAGE BREATHHER SYSTEM

Filed June 8, 1966

2 Sheets-Sheet 1

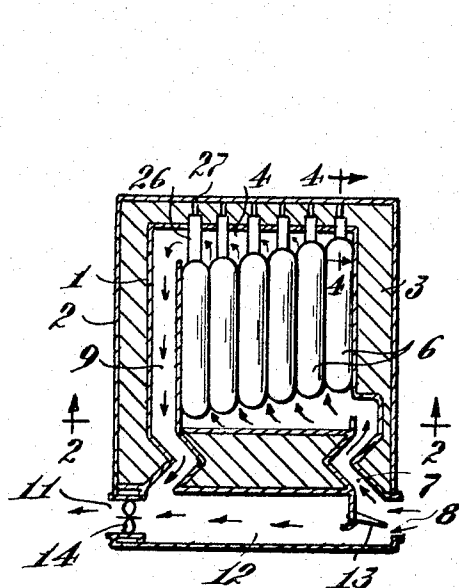


Fig. 1

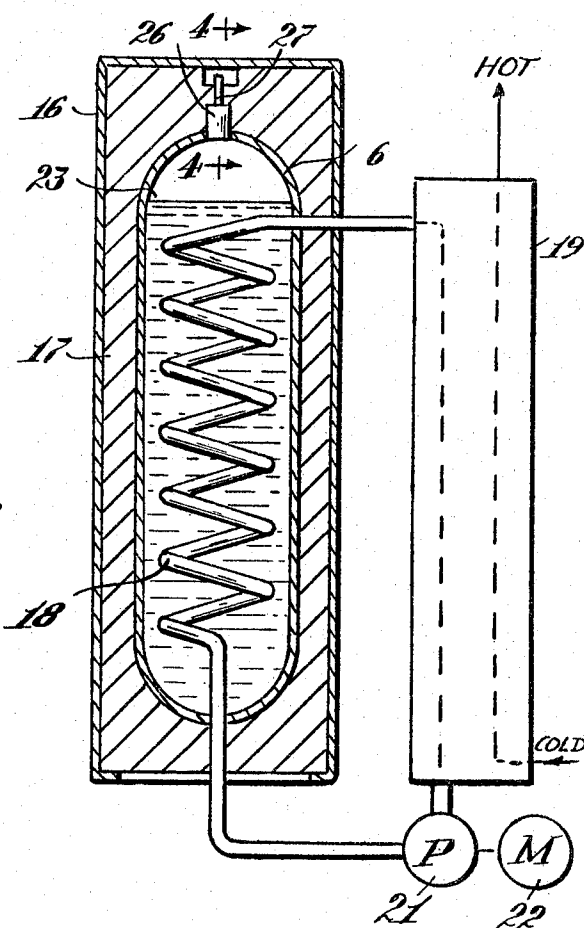


Fig. 3

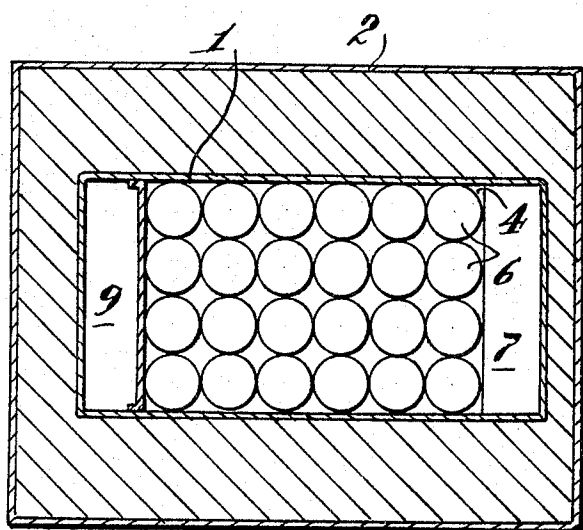


Fig. 2

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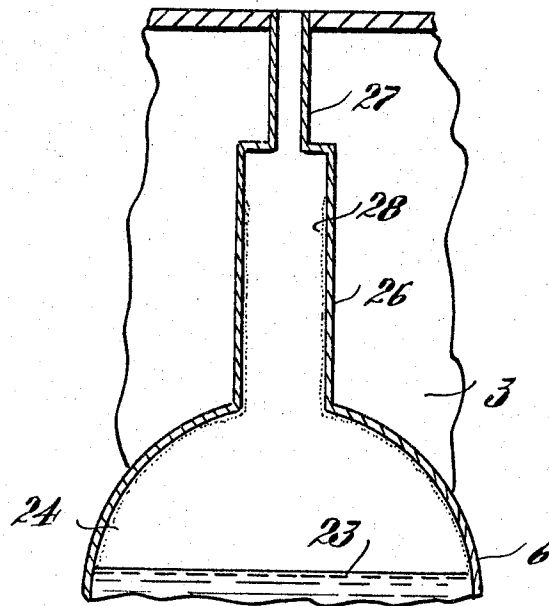


Fig. 4

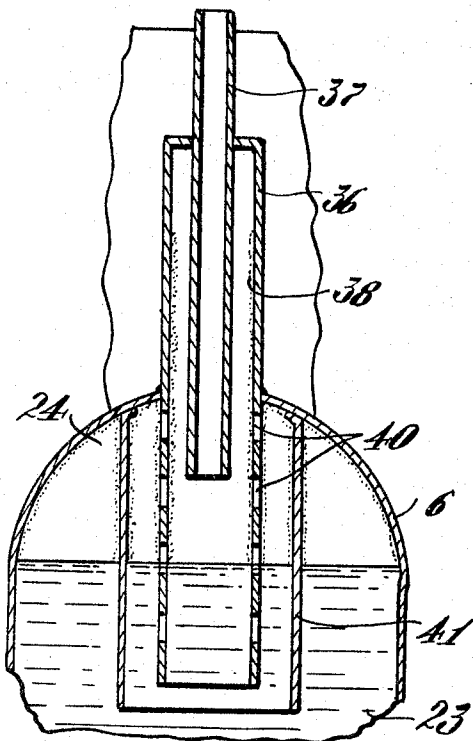


Fig. 5

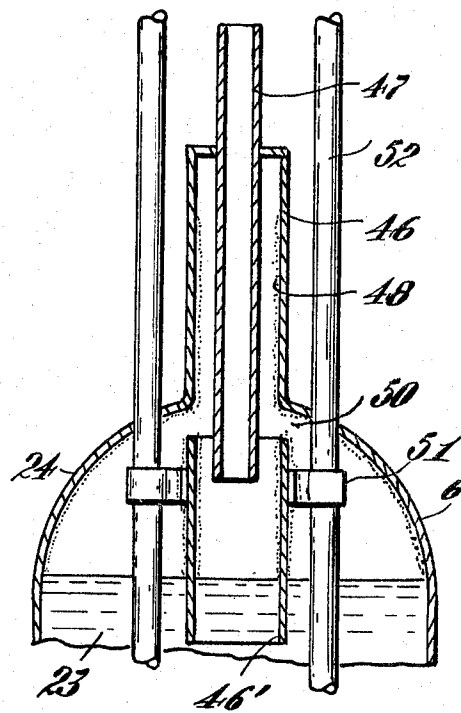


Fig. 6

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HEAT-STORAGE BREATHING SYSTEM

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10 Claims. (Cl. 165—105)

This invention relates to heat-storage apparatus of the type comprising one or more closed containers of heat-storage material such as sodium hydroxide mixed with a small percentage of rust inhibitor, as for example room-heating apparatus such as disclosed in the application of Richard E. Rice and William E. Whitney, Ser. No. 391,676, filed Aug. 24, 1964, now Patent No. 3,299,945, or fluid-heating apparatus such as disclosed in my application Ser. No. 446,955, filed Apr. 9, 1965. The aforesaid material may be cycled over a wide range, for example from a maximum of 900° F. when fully charged with heat to a minimum of 250° F. when almost discharged. Inasmuch as the heat-storage material when heated expands more rapidly than the containers, an air space must be left above the material at the top of each container, and the space must be vented to avoid excessive pressure during heating or sub-atmospheric pressure while heat is being withdrawn from the material. The air space also insures that the heat storage medium is maintained in an oxidizing condition through contact with air, this being necessary to prevent excessive corrosion of the steel container by the heat-storing medium. While the material is being heated air is exhaled and while the material is being cooled it is inhaled.

Among the most effective materials for the storage of heat are the alkali metal hydroxides; sodium, lithium and potassium hydroxides being preferred substances. Heat-storing media may be mixtures which include a substantial proportion of one or more of the alkali metal hydroxides plus corrosion inhibiting ingredients to protect the metallic containers in which they are held. The additives may include nitrates, chromates and manganates, as well as others. The mixtures may contain substantial amounts of water or may be anhydrous.

The containers are commonly made from low carbon steel sheets. A heat-storing system may contain one or more containers; in some instances as many as twenty or thirty containers may be used in a single system.

The thermal expansion coefficients of the alkali metal hydroxides are larger than the coefficients of the metals from which their containers are made. Consequently the clearance, or air space, at the top of the container above the heat-storing medium becomes larger as the medium cools.

A characteristic of the molten alkali metal hydroxides is their propensity for spreading over the surface of metals; this phenomenon is commonly called creeping. The heat-storing medium will creep over all the metal surfaces to which it has access and which are at a temperature above the melting point of the medium. The opening from the clearance space will ordinarily be connected to a breathing tube of relatively small diameter which extends through the thermal insulation around the container and opens to the ambient air. When the medium and container are hot, a temperature gradient will exist along the length of the tube. When the medium is molten, a temperature corresponding to the melting point of the medium will exist at some point between the hot and cool ends of the tube. The molten medium will creep over the inside surfaces of the tube to this point, at which it freezes and cannot creep further.

All of the alkali metal hydroxides have an affinity for CO₂, the reaction between the hydroxide and the CO₂

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forming the corresponding alkali metal carbonate. Air normally contains about .03% CO₂, and may sometimes contain considerably more as a result of the combustion of carbonaceous materials or respiration. When air is drawn inward as the medium cools, the CO₂ is converted to carbonate where it first encounters the alkali metal hydroxide in the breathing tube. The carbonates have higher melting points than the corresponding hydroxides and therefore the carbonates form solid deposits, which are porous enough to soak up molten hydroxide which in turn absorbs more CO₂. The carbonate deposit thus continues to grow until it can finally block the tube and prevent further breathing. If the medium is deprived of oxygen it may become excessively corrosive, and if the tube is closed dangerous pressures may develop in the container.

Another pertinent characteristic of the alkali metal hydroxides is their affinity for water, which is exceedingly high when they are at or near room temperature but very low when they are molten. Some heat storage systems, e.g., those used in connection with space heating of houses and other buildings may remain for several months at a time at room temperature. During such periods a small amount of breathing occurs as a result of barometric pressure and temperature changes in the ambient air. Moisture present in the inhaled air is absorbed upon the exposed surfaces of the heat storing medium within the container and may cause a corrosive condition on the inner surfaces of the container.

The conditions described above which result from the presence of CO₂ and moisture in the inhaled air may be prevented by the means described in my application Ser. No. 391,564, filed Aug. 24, 1964, now Patent No. 3,320,724, according to which these substances are prevented from entering the container through the use of absorbers for the CO₂ and moisture. These means are incorporated in a system of external tubulations through which air enters and leaves the containers. While this method has proved completely effective, it leads to undesirable complications, particularly in those systems which include a number of individual containers.

A practical piece of heat-storage equipment for use in homes or in commercial or industrial buildings must be designed to operate without frequent maintenance for long periods of time. If the well-known methods of absorbing carbon dioxide and moisture from air were applied the quantities of the absorbents required would be very large, adding substantially to the cost and to the bulk of the equipment.

Objects of the present invention are to provide a breather system for heat-storage apparatus which is simple and economical in construction, which requires no sorbent material, which is effective during periods when the apparatus is inactive, which requires minimum maintenance, which eliminates external tubulation and multiple connections, and which is durable and reliable in use. Other objects are the provision of surfaces where carbonate deposits may form harmlessly, and the periodic removal of such deposits automatically as a result of the natural thermal cycling of the heat-storing medium.

According to the present invention the system comprises a container, heat-storage material in the container with a space above the material in the upper part of the container, the material comprising alkali metal hydroxide or other material having affinity for carbon dioxide and water when cool, conduit means through which fluid may be circulated past the container to draw heat from the material, a wall of insulation around the container, and tubular breather means extending from the aforesaid space through the wall, the tubular means including a tube of small diameter and a tube of relatively large diameter, the outer end of the large tube being closed except for an opening which is sealed around the small

tube and the container being closed except for an opening sealed around the large tube, said material tending to creep outwardly along the surface of said large tube when molten, the large tube extending into said wall beyond the location where its temperature reaches the melting point of said material, whereby in creeping along said large tube the material cannot enter the small tube. The inner end of the small tube may terminate at the outer end of the large tube or it may extend into said large tube. Preferably the inner ends of both tubes also extend into said space.

The system may have one or more surfaces in said space on which said carbonates may deposit and means to heat the surfaces to a temperature higher than that of surrounding surfaces. In one embodiment of the invention the inner end of the large tube extends into said material and has an opening into said space above the level of said material, the container has a heater in heat-transfer relationship to the inner end of the large tube, and the aforesaid opening extends substantially around the large tube with heat-conducting means supporting the inner end of the large tube on the heater.

For the purpose of illustration typical embodiments of the invention are shown in the accompanying drawings in which:

FIG. 1 is a diagrammatic view of room-heating apparatus similar to that shown in the aforesaid application Ser. No. 391,676;

FIG. 2 is a section on line 2—2 of FIG. 1;

FIG. 3 is a diagrammatic view of fluid-heating apparatus such as disclosed in the aforesaid application Ser. No. 446,955;

FIG. 4 is an enlarged section of one form of breather tube taken on the line 4—4 of FIG. 1 or FIG. 3;

FIG. 5 is a similar view of a modified breather tube; and

FIG. 6 is a similar view of another modification.

FIGS. 1 and 2 show the invention applied to heat-storage apparatus such as disclosed in the aforesaid application Ser. No. 391,676. This apparatus comprises inner and outer walls 1 and 2 with a space therebetween filled with insulation 3. Inside the housing is a chamber 4 containing cylindrical heat-storage units 6. An air duct 7 leads from an inlet 8 to the bottom of the chamber 4 and a duct 9 leads from the top of the chamber to an outlet 11 which, as disclosed in the aforesaid application Ser. No. 391,676, may lead to a space to be heated. Leading from the inlet 8 to the outlet 11 is a by-pass duct 12. At the inlet is a valve 13, corresponding to the valve 33 of the aforesaid application, to control the proportion of heated and unheated air delivered to the outlet 11. A blower 14 in the outlet produces circulation of air through the apparatus.

FIG. 3 shows the invention applied to fluid-heating apparatus like that disclosed in the aforesaid application Ser. No. 446,955. This apparatus comprises a housing 16 and a heat-storage unit 6 like that in FIGS. 1 and 2. The space between the housing and unit is filled with installation 17. Disposed in the unit 6 is a coiled conduit 18 leading to a heater 19. Fluid is pumped through the conduit by means of a pump 21 driven by motor 22.

As shown in FIG. 4 the heat-storage unit is partially filled with heat-storage material 23 with a space 24 above the material in the upper part of the container. Leading upwardly from this space is a tube 26 the outer end of which is closed except for an opening which is sealed around a smaller tube 27 leading to the outside atmosphere. The large tube extends into the insulation 3 beyond the location 28 where its temperature drops to the melting point of the material 23. Thus the material creeping up along the surface of the container 6 and thence along the surface of the tube 26 cannot enter the small tube 27. At this location the CO_2 in the air entering the breather tubes is absorbed by the film of heat-storage material forming an accumulation of sodium carbonate. If this accumulation occurred in the small tube it would soon plug the tube, but with a large tube there is no

danger of plugging for a long period of time. The accumulation of sodium carbonate may be removed by allowing the container to stand for some time after it cools. During this time ambient air moves in and out of the breather as the result of normal temperature variations and changes in atmospheric pressure. The moisture in the entering air is absorbed on the surface of medium 23 and by the accumulation of carbonate and, when the heat-storing material is reheated, the absorbed moisture is vaporized and condensed on the upper interior surfaces of the breather tubes above the carbonate accumulation so that, when the condensate flows down over the accumulation of sodium carbonate, the accumulation is dissolved and washed down into the container. In this way the accumulation is removed and transferred to the bulk of the heat-storing material in the container where it is dissolved and becomes harmless. In the case of heat-storage systems for space heating, as shown in FIGS. 1 and 2, this sequence of operations occurs periodically inasmuch as the heat-storage units are thermally cycled during the winter heating season and remain idle at room temperature during the summer.

The modification shown in FIG. 5 is like that shown in FIG. 4 in that it comprises a large tube 36 and a small tube 37 corresponding to 26 and 27 of FIG. 4. However the large tube extends into the container 6 below the level of the heat-storage material 23 and its lower end is provided with perforations 40. Surrounding the lower end of the tube 36 is a larger tube 41 which also extends into the heat-storage material 23 and the upper end of which is sealed to the container 6. As in FIG. 4 the heat-storage material creeps up the tube 36 to the location 38, corresponding to 28 in FIG. 4. It also creeps up the outer surface of the tube 36 and also the surfaces of tube 41. As air enters the container through the breather, CO_2 is absorbed and forms an accumulation of carbonate not only on the inside of the lower end of the tube 36 but also on the outside of this tube and the inside of tube 41. As the liquid level rises and falls during thermal cycling a slight capillary flow of the material over the surfaces of the tubes 36 and 41 dissolves the carbonate deposits and transfers them into the body of the heat-storing material where they cause no harm.

The modification shown in FIG. 6 is like that shown in FIG. 5 in that it comprises large and small tubes 46 and 47, corresponding to 36 and 37 of FIG. 5, but instead of having perforations in the lower end of the large tube an opening 50 extends all the way around the large tube. The lower end 46' of the large tube is supported by clamps 51 on the heating units 52 which are provided for reheating the material 23 when its temperature drops to the lower end of its useful range. While the material 23 may creep up the tube 46 to the location 48, corresponding to 38 in FIG. 5, most of the carbonate accumulates on the tube 46' just above the level of the liquid 23 so that, as the level of the liquid rises and falls during the heating and cooling periods, carbonate is dissolved and returned to the body of the heat-storage material. The CO_2 absorbing surface 46' need not be cylindrical; it may have any desired shape.

Heating 46' prevents the formation of corrosion products which tend to accumulate on the cooler surfaces. When the material 23 contains NaOH and the container is made of steel, this corrosion product consists of crystals having the formula $\text{Na}_2\text{Fe}_2\text{O}_4$. Any suitable means may be employed for heating 46'.

From the foregoing it will be understood that the breather tubes 27, 37 and 47 never receive a deposit of carbonate and therefore do not tend to plug.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

I claim:

1. In a heat-storage system comprising a container,

heat-storage material in said container with a space above the material in the upper part of the container, said material being absorptive of carbon dioxide to form carbonates having melting points higher than that of the material, conduit means through which fluid may be circulated past the container to draw heat from the material, a wall of insulation around the container, and tubular breather means extending from said space through said wall, said tubular means including a tube of small diameter and a tube of relatively large diameter, the outer end of the large tube being closed except for an opening which is sealed around the small tube and the container being closed except for an opening sealed around the large tube, said material tending to creep outwardly along the surface of said large tube when molten, the large tube extending into said wall beyond the location where its temperature reaches the melting point of said material, whereby in creeping along said large tube the material cannot enter the small tube.

2. A system according to claim 1 wherein said heat-storage material comprises alkali metal hydroxide.

3. A system according to claim 1 wherein the inner end of said small tube terminates at the outer end of said large tube.

4. A system according to claim 1 wherein the inner end of said small tube extends into said large tube.

5. A system according to claim 4 wherein the inner end of the small tube also extends into said space.

6. A system according to claim 1 wherein the inner end of said large tube extends into said space.

7. A system according to claim 6 wherein the inner end of the large tube extends into said material and has an opening into said space above the level of said material.

8. A system according to claim 7 further characterized by a heater in the container in heat-transfer relationship to the inner end of the large tube.

9. A system according to claim 8 further characterized in that said opening extends substantially around the large tube with heat-conducting means supporting the inner end of the large tube on said heater.

10. A system according to claim 1 further characterized by a surface in said space for the collection of carbonates and means to heat the surface to a temperature higher than that of surrounding surfaces.

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