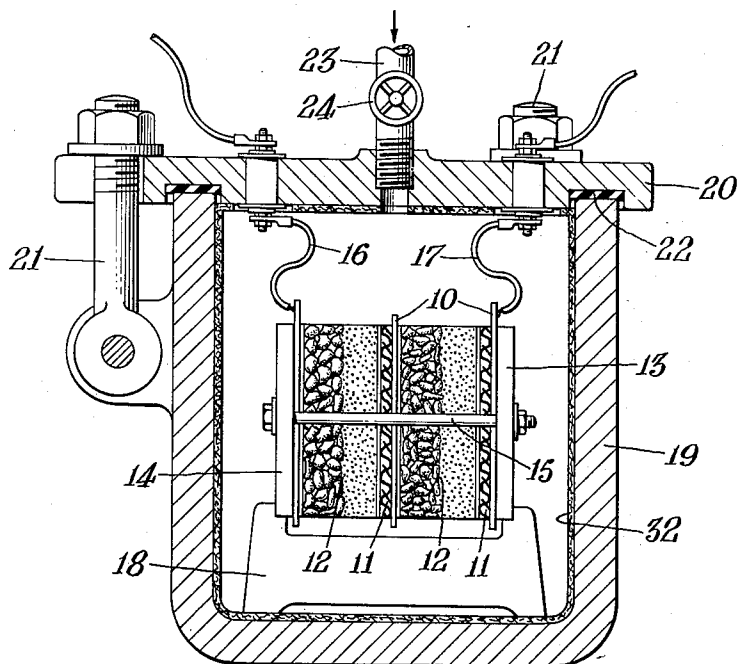


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G. W. HEISE ET AL
DEFERRED ACTION TYPE GAS DEPOLARIZED DRY
CELL HAVING PROLONGED SHELF LIFE
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INVENTORS
GEORGE W. HEISE
RUSSELL P. FOX
BY *D.C. Harrison*
ATTORNEY

UNITED STATES PATENT OFFICE

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DEFERRED ACTION TYPE GAS DEPOLARIZED DRY CELL HAVING PROLONGED SHELF LIFE

George W. Heise, Rocky River, and Russell P. Fox, Cleveland, Ohio, assignors, by mesne assignments, to Union Carbide and Carbon Corporation, a corporation of New York

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This invention relates to a deferred action, gas depolarized dry cell and has for an object to improve the performance characteristics of such a cell after a period of storage.

In a preferred form of such a cell and battery of them, there is a casing hermetically enclosing the battery in a partial vacuum or in an oxygen-free atmosphere of inert gas. Variations in external temperature encountered in normal storage, such as that between day and night, cause sufficient loss of moisture from the cell, after a prolonged storage period, to impair the cell efficiency through increase in internal resistance, deterioration of electrode-immobilized electrolyte contact, and general lowering of overall capacity. The most rapid loss in moisture was found to be from the wet mix portion of the cathode, although some was found to be from the immobilized electrolyte through the diffuser portion of the cathode. A number of temperature drops on succeeding nights caused deposition of moisture at the bottom of the casing. Subsequent rises in temperature during the days did not succeed in getting all the moisture back into the cell.

According to this invention, a way has been discovered for retarding the loss of moisture from the cells and for accelerating the uniform return of condensate to the cells from the deposited moisture in the enclosing casing. Specifically, this has been accomplished by providing a large area surface of bibulous and, also, preferably fibrous, material inside the casing. Such surface is preferably arranged as a liner for the casing sides, top, and bottom. This liner should desirably contain sufficient moisture either as water or as electrolyte to saturate the atmosphere inside the casing prior to such saturation by the liquid of the cells and thus reduce evaporation of liquid from the battery cells. After precipitation on a temperature drop outside the casing, the precipitated moisture is absorbed by the liner and better available to be returned to the cells after equilibrium in vapor pressure is reached or during a subsequent increase in temperature and resaturation of the casing atmosphere at the higher temperature. Where the prior cells, such as those described in the application of Zimmerman and Cahoon, Serial No. 53,174, filed October 7, 1948, now U. S. Patent 2,572,296 granted October 23, 1951 for "Primary Cell and Battery and Method of Making Same," could be deteriorated in periods, depending on the variation of the storage temperature, of from a few weeks to perhaps two months,

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the present invention has enhanced their shelf life, enabling them to be stored for at least six months under the same conditions of variable temperature without significant deterioration.

After precipitation of moisture within the casing and upon a rise in external temperature or the attainment of vapor pressure equilibrium, irrespective of temperature, transfer of moisture to the cells takes place at a rapid rate from a saturated bibulous liner and more rapidly from the highly developed surface of a bibulous fibrous liner than it would from individual droplets or a small pool, and the cells remain in operating condition for indefinitely prolonged periods of time. Of great importance, further, is the fact that, in the absence of the liner, subsequent evaporation of water collecting at the bottom of the container will result in transfer of moisture sooner and in larger quantity to the lower than to the more remote portions of the battery, causing transient inequalities in moisture content which may seriously affect cell operation and shelf quality. The liner may be wet or dry initially through a liner moistened with water or electrolyte is preferred. The weaker the solution of electrolyte in the liner, the more rapid will be the transfer of moisture into the cells.

Referring to the single figure of the drawing, the drawing illustrates a deferred action type dry battery of the sort described in the said prior patent of Zimmerman and Cahoon, 2,572,296, dated October 23, 1951, for "Primary Cell and Battery and Method of Making Same," of which the present invention is an improvement.

A battery of two cells is illustrated but it will be understood that any number of cells may be used according to the voltage desired from the battery. Each cell comprises a zinc anode 10 contiguous with which is an immobilized electrolyte layer 11 separating the anode 10 of a cell from its cathode 12. End clamping plates 13 and 14 preferably of insulating material hold the battery elements under a compressive stress exerted by the clamping bolts 15 extending between the plates 13 and 14. Terminal leads 16 and 17 conduct current from the battery through bushings illustrated in the top of the battery casing. A pedestal support 18 preferably of insulating material carries the battery so that each of the various cell elements is out of contact with such support, thus enabling gas within the casing to be brought into intimate contact with the cathode of each cell.

The enclosing casing 19 is provided with a

cover 20, and bolts 21 pivotally secured to the casing 19 hold the cover in place, clamping a gasket 22 between the cover 20 and casing 19. An inlet pipe 23 controlled by a shut-off valve 24 conducts depolarizing gas to the battery casing when the battery is to be actuated and an outlet passage from the casing as shown in the aforementioned patent of Zimmerman et al. may or may not be provided.

A liner 32 of fibrous bibulous material such as blotting paper or more especially filter paper, such as Eaton & Dikeman #608, covers all interior walls of the casing. The liner might be some appropriately absorptive material such as flock sprayed against the inside of the casing. This lining material 32 is impregnated with a regulated amount of moisture of a solution of controlled vapor pressure, prior to the casing being closed and hermetically sealed. The moisture in the bibulous liner 32 has a far larger portion of its surface exposed than does moisture in the battery cells. Since the moisture in the lining has a higher vapor pressure than that in the battery cells, as well as a larger area, the moisture from this liner 32 will evaporate until the atmosphere within the casing is substantially saturated, leaving the cell relatively unchanged. When that is so there is no tendency for moisture from the cell to be evaporated so that the shelf life of the cell is greatly prolonged. Upon any increase in temperature of the casing, the bibulous sheet 32 is adapted to give up more of its moisture to the casing atmosphere. When the casing increases in temperature moisture evaporates and condenses on the cells, which are cooler. This action tends to heat up the battery cells and to create temperature equilibrium. In event of drop in temperature and condensation of moisture from the gas within the casing, such moisture is condensed on the liner 32. Thus characteristics of the liner are its large capacity for moisture so that moisture does not quickly deposit in droplets and collect in the bottom of the container, its ability to pass moisture from one part to another so that it is substantially uniformly wet as long as any part of it contacts with any water collected in the bottom of the container, and its large exposed surface area so that moisture is rapidly given up by the liner to the casing atmosphere. When the casing atmosphere becomes uniformly separated from the liner the shelf life of the battery is greatly prolonged by reason of the fact that moisture returns to the battery, as stated previously, and there is no further tendency for moisture to be vaporized from the battery element.

Among the advantages of this invention may be mentioned the increase in battery shelf life of substantially 2000% from the present invention which prevents the battery cells from becoming dried out as was found to happen prior to the present invention, through maintenance of a relatively stable moisture condition in the cell or battery. The provision of a liner of highly developed surface facilitates uniform moisture distribution. The liner being a moist porous medium can be wet with regulated amounts of solution of controlled vapor pressure, such as electrolyte solution to maintain relatively stable moisture conditions in a cell. When the external casing is chilled the battery will tend to come to temperature equilibrium since the heat is not transferred from the battery by conduction, convection, or radiation, but is lost by evaporation of water, which condenses on the inside of the

casing and must be returned as soon as possible. The moisture loss that might otherwise occur but for this invention would be largely from the mix and diffuser portions of the cathode and to a lesser extent from the immobilized electrolyte. Moisture deposited on the liner during a drop in temperature is to a large extent returned to the battery on a rise in temperature when the atmosphere within the battery can absorb more moisture from the liner, and even without a rise in temperature there will for a while, or until an equilibrium in vapor pressure is reached, be a transfer of moisture to the cells, due to the larger area of the liner and higher vapor pressure of moisture in the lining. Having the liner wet with a weaker electrolyte solution than is used in the wet mix portion of the cathode creates a tendency for the electrolyte solution in the cells and in the liner to become equalized in strength. The moisture from the liner dilutes the electrolyte in the cells, which is one reason for controlling the amount of moisture initially placed in the liner. The total moisture in the liner may be substantially less than that in the cathodes and the smaller amount of moisture in the liner is sufficient due to its large exposed surface. At a constant temperature, when the atmosphere in the casing has not been saturated, there is more tendency for moisture to be taken from the liner than from the cell due to area and greater vapor pressure. A partial vacuum in the casing is useful in expediting activation of the cell on the admission of chlorine, but such reduced pressure is objectionable by facilitating interchange of moisture due to temperature differences such as may exist between those during the day and those at night. Instead of a partial vacuum, an atmosphere of inert gas such as nitrogen within the casing has been found advantageous in retarding the interchange of moisture due to temperature differences, provided the inert gas is evacuated from the casing before the depolarizing gas is introduced or is adapted to be swept to one side and not retard actuation of the battery. Before being placed in the cell ready for use, the filter paper liner mentioned above or other bibulous lining is preferably dried at 90° to 100° C. for several hours and stored adjacent calcium chloride until ready for use in the cell. The necessary water or other solution may be added to the liner by rolling another damp bibulous sheet, such as blotting paper, with a glass cylinder, or by pressure when the filter paper is placed next to the damp sheet, or in case of a bibulous liner sprayed onto inner surface by steaming or spraying with solution of desired vapor pressure, etc. To reduce the possibility of anode corrosion occurring during storage, the atmosphere in the casing should be free of oxygen, because if such is present it might act as a depolarizer.

What is claimed is:

1. A deferred action dry cell having an enclosed casing outside of and spaced from said cell on more than one side hermetically sealing the cell, at least one element of the cell containing moisture and being exposed to the casing atmosphere between the cell and casing, and a bibulous material outside of the cell and spaced from the moisture containing cell element, having a larger exposed surface than the exposed surface of the cell within the casing whereby moisture from the bibulous material may spread any deposit of moisture over its surface and tend to saturate the atmosphere within the casing and outside the cell.

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2. A dry cell according to claim 1 in which said bibulous material is in sheet form secured on at least the bottom of the cell casing.

3. A deferred action type dry battery having an enclosing casing hermetically sealed and provided with an opening into which depolarizing gas is adapted to be supplied, the battery having moisture containing elements at least partially exposed to any gas outside of the battery and within the casing, a bibulous sheet in addition to said battery and spaced therefrom on more than one side, of larger exposed area than the exposed area of the moisture containing elements and extending over at least a portion of the casing interior, moisture in said bibulous sheet partially but not entirely filling the said sheet whereby said sheet is adapted either to absorb condensed moisture from any gas in the casing or to supply moisture to such gas by vaporization.

4. A battery according to claim 3 in which the bibulous sheet extends on the inside of all walls of the battery casing.

5. A battery according to claim 4 in which said bibulous sheet is absorbent paper containing about 20% to 30% by weight of moisture when inserted and sealed in said casing.

6. A deferred action type gas depolarized dry battery having an enclosing casing hermetically sealed surrounding and spaced from the battery and provided with an opening into which depolarizing gas is adapted to be supplied, the battery having moisture containing elements at least the edges of which are exposed to any gas within the casing and outside the battery, and a bibulous sheet material in said casing outside of said battery, partially filled with moisture and capable of saturating any gas within the casing.

7. A deferred action type gas depolarized dry battery having an enclosing casing hermetically sealed and spaced at least in two directions from said battery and provided with an opening into which depolarizing gas is adapted to be supplied, the battery having moisture containing elements

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having opposite edges at least partially exposed to any gas within the casing and outside the battery, and a bibulous sheet of material in said casing containing moisture outside of said battery and spaced from said exposed opposite edges of said elements.

8. In a deferred type gas depolarized dry cell containing moisture in an electrolyte solution in at least one element thereof, a casing in addition to said cell hermetically sealed and spaced from edges of said moisture containing element by a gas space for enclosing said cell, the combination therewith of the improvement for prolonging the shelf life of said cell, said improvement comprising a bibulous material within said casing but outside of said cell, spaced from it, and impregnated with a weaker solution of electrolyte than that electrolyte solution in said moisture containing element whereby said bibulous material is adapted to receive moisture deposited from any gas within the enclosing casing on a drop in temperature external to the casing and whereby said bibulous material is adapted to contribute more moisture to any gas within the casing on a rise in temperature than is the cell.

GEORGE W. HEISE.
RUSSELL P. FOX.

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