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DRAWINGS ATTACHED

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(54) PRIMARY DRY CELL

(71) We, UNION CARBIDE CORPORATION of 270, Park Avenue, New York, State of New York 10017, United States of America, a Corporation organized under the laws of the State of New York, United States of America, (Assignee of THOMAS ARTHUR REILLY and WILLIAM BEMER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to primary dry cells.

Primary dry cells are one of the most familiar articles of commerce and are widely used in flashlights, portable radios, photoflash and other devices. One common problem that has been encountered in the use of dry cells is that of leakage of liquid exudate during and after use of the cell. This problem is a particular vexing one since the liquid exudate is corrosive and can damage the device in which the dry cells are used.

Dry cell manufacturers have adopted a more or less common approach to the solution of this problem, that is, to encase the dry cell within a closed container comprising a non-corrodible jacket made from a fibrous cellulosic material usually in the form of a multiple-ply, spirally wound tube which surrounds the cupped electrode of the cell and which is locked in engagement at its peripheral edges with a metallic top and bottom closure. An advantage derived from the use of this non-corrodible jacket or tube is that it is highly absorbent to liquid and can be employed as a liquid reservoir to retain the exudate within the cell. One drawback, however, is that the jacket or tube may become so thoroughly soaked with liquid that it will lose its strength and ability to retain the liquid and thus permit leakage from the cell.

In United States Pat. No. 3,278,339, there is disclosed a primary dry cell comprising the combination of an improved jacket construction composed of a multiple-ply, lamin-

ated tube of a fibrous cellulosic material, but having an innermost layer or ply of a high strength, liquid impermeable material, and a displaceable inner seal position within the upper edges of the cupped electrode just below the metallic top closure of the cell. This dry cell construction represents a somewhat modified approach to the problem of cell leakage in that the innermost layer or ply of the jacket or tube constitutes a liquid impermeable barrier which liquid cannot penetrate as opposed to being used as a liquid reservoir for retaining exudate within the cell.

With this dry cell construction, provision is made for containing the liquid exudate and preventing its escape in the form of leakage from the cell by means of a displaceable inner seal which defines a free space within the upper end of the cupped electrode for the collection of liquid during discharge of the cell. Broadly, the displaceable inner seal consists of a top collar fitted around the central carbon electrode and a relatively thick, soft seal of asphalt or microcrystalline wax, for example, disposed on top of the top collar. The top collar is made from a liquid impermeable material and serves as a liquid barrier to prohibit the exudate from coming into contact and corroding the top closure. If liquid exudate formed on discharge should collect and fill the free space below the displaceable inner seal, the seal is then displaced upwardly allowing additional space for the exudate and also causing the soft seal to tightly seal off the uppermost end of the cupped electrode, thus aiding in prohibiting leakage from the cell.

Another advantage derived from the use of this displaceable inner seal is that containment of liquid exudate is effectively accomplished but without at the same time interfering with the proper venting of gases formed within the cell.

While the concept of a displaceable inner seal has worked well and proven successful in dry cells thus far produced, it nevertheless possesses the disadvantage in that the

seal occupies a relatively large space within the cell proper which might otherwise accommodate a larger volume of liquid or even active ingredients to increase or substantially improve upon the capacity of the cell to deliver electrical current.

The present invention contemplates the provision in a primary dry cell of the type utilizing a noncorrodible jacket which is impermeable to liquid of a novel and improved seal arrangement for containing liquid exudate formed on discharge of the cell, and has for its object to provide such a novel and improved seal arrangement which occupies a minimum amount of space within the cell.

Accordingly, the present invention provides a primary dry cell which comprises a cupped electrode of a consumable metal having an upper open end, the peripheral edges of which are turned slightly inwardly, a depolarizer mix and an electrolyte disposed within the cupped electrode, a central porous carbon electrode embedded within the cupped electrode and extending at its upper end beyond the upper edges of said cupped electrode, a noncorrodible liquid impermeable jacket surrounding the cupped electrode, a metallic cup closure fitted over the top of the carbon electrode, said top closure having its outer edges locked in liquid-tight engagement with the jacket and having gas venting means therein, an inner seal positioned within the open end of the cupped electrode and between the top closure and the depolarizer mix and extending from around the carbon electrode to the inner side walls of said cupped electrode, defining a lower free space between said seal and said depolarizer mix for the collection of liquid from the cell and an upper free space between said seal and said top closure, a liquid and gas impermeable seal washer fitted around the carbon electrode and over the upper peripheral edges of the cupped electrode within the upper free space, the outer edges of said seal washer abutting against the interior wall of the jacket, an outer peripheral head seal disposed below the seal washer in the space left by the inwardly turned upper edges of the cupped electrode and between said cupped electrode and the interior wall of the jacket, an inner peripheral bead seal disposed below the seal washer on the opposite side of the upper peripheral edges of the cupped electrode and an electrode bead seal underlying the inner most edges of said seal washer around the carbon electrode, and an absorbent layer of bibulous material disposed on top of the seal washer just below the top closure of the cell.

In the preferred form of the invention, the non-corrodible jacket for the cell comprises a multiple-ply, laminated tube composed of a first laminate of a high strength,

liquid impermeable plastic and a thermoplastic material, and a second laminate of a thermoplastic material and one or more layers or plies of a fibrous cellulosic material, such as "Kraft" paper ("Kraft" is a registered Trade Mark). The first and second laminates are bound together by joining the thermoplastic material of each laminate by autogenous action under heat. The high strength, liquid impermeable plastic for use in the tube preferably is poly(ethylene terephthalate) other suitable liquid impermeable plastics including the thermoplastic polyhydroxyethers such as poly(oxyphenyl - 2,2 - propylenephenoxy - 2 - hydroxy - 1,3 - propylene) which is the condensation product of equimolar amounts of epichlorohydrin and bisphenol A. The high strength liquid impermeable plastics material should preferably have a higher softening temperature than the thermoplastic material. The thermoplastic material used in the laminated tube is preferably a flexible plastic having a softening point lower than that of the liquid impermeable plastic and preferably is polyethylene. Other suitable thermoplastic materials include polyvinylidene chloride, polyvinyl chloride, polypropylene, polystyrene and mixtures thereof. The fibrous cellulosic material, e.g. kraft paper, may be bonded to the thermoplastic material by a polyvinyl acetate water emulsion which is commonly used in adhering paper, but other suitable adhesives and glues may be used. The multiple-ply tube may be made by spiral winding the first and second laminate together in accordance with conventional methods and then heating to bond the thermoplastic layers of each laminate to form the composite tube.

The primary dry cell of the invention will now be further described by way of example with reference to the accompanying drawing, in which:

Fig. 1 is an elevational view in section of a primary dry cell embodying the invention;

Fig. 2 is an enlarged, fragmentary view of a portion of the jacket used in the dry cell of Fig. 1; and

Fig. 3 is a detail of Fig. 1 on an enlarged scale.

Referring now to Figs. 1 and 3 of the drawing, a primary dry cell embodying the invention may comprise a cupped electrode 10 of a consumable metal, such as zinc, having therein a depolarizer mix 12, an immobilized electrolyte 14 and a porous carbon electrode 16 embedded within the depolarizer mixer 12. Both the depolarizer mix 12 and the carbon electrode 16 may be suitably provided in the form of a conventional bobbin. Separating the bobbin from the bottom of the cupped electrode 10 is a conventional bottom insulating washer 18, suitably of cardboard or paper. On top of the washer 18 is a fibrous

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or paper cup 20 which fits around the bottom edges of the depolarizer mix 12.

Positioned within the upper open end of the cupped electrode 10 and so placed as to define a lower free space 22 above the depolarizer mix 12 and an upper free space 24 is an inner seal composed of a liquid impermeable top collar 26. The top collar 26 is fitted tightly within the upper end of the cupped electrode 10 and around the carbon electrode 16. The top collar 26 is permeable to gas but impermeable to liquid and serves as a liquid barrier, and may be made of paper or other fibrous material which is coated with a liquid-repellent material, for example, a plastic such as polyethylene. Spaced above the top collar 26 and within the upper free space 24 is a liquid and gas impermeable seal washer 28. The seal washer 28 fits tightly around the carbon electrode 16 and rests on the upper peripheral edges of the cupped electrode 10, which peripheral edges are turned slightly inwardly as indicated at 30. The seal washer 28 is impermeable to both liquid and gas and is electrically nonconductive and may be composed of a suitable plastic material such as polystyrene. Mounted on top of the seal washer 28 is a layer 32 of a highly absorbent or bibulous material such as conventional blotting paper, for example. The seal washer 28 and absorbent layer 32 may be formed from a laminated sheet of polystyrene having adhered to one side a layer of blotting paper or other suitable bibulous material.

The top closure of the cell may comprise a one-piece metal plate 34. As clearly shown in Figure 1, this top closure plate 34 is shaped to fit over the top edges of the carbon electrode 16 and has its outer peripheral edges locked in liquid-tight engagement with a non-corrodible cell jacket 36. Similarly, the bottom closure may comprise a metal plate 38 positioned beneath the cupped electrode 10 and having its outer peripheral edges locked in liquid-tight engagement with the jacket 36. The bottom closure plate 38 may also be provided with a central indentation as at 40 which makes electrical contact with the bottom of the cupped electrode 10. In the construction of the dry cell shown in Figure 1, the top closure plate 34 is locked in liquid but not gas-tight engagement with the jacket 36.

As shown in Figure 1, the juncture between the top closure plate 34 and the jacket 36 is positioned over the top of the seal washer 28 and absorbent layer 32 and just above the peripheral edges of the cupped electrode 10. By this construction, the top closure plate 34 is electrically insulated from the cupped electrode 10 and the seal washer 28 is firmly held in place. It will be noted that the seal washer 28 is slightly larger in diameter than the upper end of the cupped electrode 10

and that its outer edges abut tightly against the interior side walls of the jacket 36. Underlying the seal washer 28 in the space left by the inwardly turned edges of the cupped electrode 10 is a peripheral bead seal 42 of wax, for example. This bead seal 42 extends around the periphery of the cupped electrode 10 and adheres to both the cupped electrode 10 and the jacket 36. It will be seen that any electrolyte or exudate which may escape from within the cupped electrode 10, due to perforation of its side walls during discharge, and which passes between the cupped electrode 10 and jacket 36 is barred by the bead seal 42 from contact with the top closure plate 34.

Underlying the seal washer 28 on the interior side of the cupped electrode 10 is a bead seal 44 which extends around the inner peripheral edges of the cupped electrode 10. Similarly, an electrode bead seal 46 underlies the innermost edges of the seal washer 28 surrounding the carbon electrode 10. The combination of these bead seals 44, 46 underlying the seal washer 28 assures that the seal washer 28 effectively seals off the upper open end of the cupped electrode 10, preventing liquid from coming into contact with the top closure plate 34 of the cell.

Figure 2 shows in enlarged detail the multiple-ply laminated tube structure of the jacket used in the dry cell of the invention. As shown, the jacket 36 comprises a first or innermost ply 48 of a high strength, liquid impermeable plastic material, e.g., poly(ethylene terephthalate), which is positioned adjacent to the outer side walls of the cupped electrode 10 and which serves as liquid impermeable barrier, and a second ply 50 of a thermoplastic material, e.g., polyethylene. Both the first and second plies 48, 50 of liquid impermeable and thermoplastic material constitute the first laminate in the multiple - ply laminated tube. The second laminate of the tube comprises a ply 52 of thermoplastic material and three plies 54, 56 and 58 of a fibrous cellulosic material, such as kraft paper.

Having described the features of a primary dry cell embodying the invention, its mode of operation may now be explained. During discharge of the cell, both liquid and gas are formed as a by-product of the cell reaction. The gas normally follows a path from within the depolarizer mix 12 directly into the porous carbon electrode 16 or into the lower free space 22 above the depolarizer mix 12. The gas that passes into the free space 22 enters the carbon electrode 16 or portions of the gas may pass through or around the top collar 26 into the upper free space 24 below the seal washer 28 from whence it also enters the carbon electrode 16. Eventually all of the gas is vented from the cell through the carbon electrode 16 by way of the locked junc-

tion between the top closure plate 34 and jacket 36.

As indicated above, this locked juncture is made liquid but not gas-tight and is capable of venting gas from the cell. The venting path so provided is maintained continuously open and free from liquid blocking the passage of gas by the novel seal arrangement of the invention. The liquid exudate passes into the lower free space 22 where it collects together with gas that is generated in the cell. Under normal conditions, the liquid exudate will be substantially confined within the free space 22 by virtue of the liquid barrier formed by the liquid impermeable top collar 26, but should the cell be subjected to severe conditions of use more liquid exudate may be formed than can be held within the free space 22. The additional liquid exudate which is formed may cause the top collar 26 to become displaced upwardly so as to allow some of the liquid to pass into the upper free space 24. This liquid which passes into the upper free space 24 is barred from contact with the top closure plate 34 (or more importantly with the locked juncture between the top closure plate 34 and jacket 36 through which gas is vented) by the novel seal arrangement composed of the combined seal washer 28 and peripheral bead seals 44, 46 formed respectively around the upper peripheral edges of the cupped electrode 10 and the carbon electrode 16. The seal washer 28 being both liquid and gas impermeable and being held firmly in place by the top closure plate 34 as described above constitutes a permanent or nondisplaceable liquid barrier which liquid cannot penetrate, while at the same time the bead seals 44, 46 effectively prohibit liquid from passing around the edges of the seal washer 28 even under the influence of gas pressure developed within the cell. It should also be mentioned that in order to prevent the liquid exudate which collects within the free space 22 from passing into the porous carbon electrode 16, thus blocking the passage of gas, the carbon electrode 16 is preferably made of a fine grain carbon and is suitably water-proofed in order to prevent liquid penetration. A suitable water-proof treatment may be achieved by impregnation with a solution containing a microcrystalline wax dissolved in a suitable solvent, such as ethylene dichloride. It will thus be seen that the novel seal arrangement of the invention effectively retains liquid exudate which might otherwise result in leakage from the cell but without at the same time taking up a large amount of space within the cell. The novel seal arrangement also provides a continuous venting path for venting gases so that no substantial gas pressure is allowed to build up within the cell.

If perforation of the cupped electrode 10 should occur due to normal consumption of

the zinc during discharge, the liquid exudate that escapes from within the cell is prevented from penetrating and becoming soaked into the jacket 36 by the innermost layer or ply 48 of liquid impermeable material, e.g., poly(ethylene terephthalate), which constitutes a liquid impermeable barrier. This liquid exudate will normally collect between the jacket 36 and the side walls of the cupped electrode 10. For the purpose of retaining this liquid but without causing the jacket 36 to bulge it is generally good practice to fit the jacket 36 loosely around the cupped electrode 10 in order to provide a free space or exudate chamber for the liquid as generally indicated at 60 in Figure 2. If the liquid exudate should collect within this space or chamber in any significant amount, the liquid may force its way towards the top closure, thus endangering the free passage of gas through the locked juncture between the top closure plate 34 and the jacket 36. It will be noted however that in the present dry cell construction the peripheral bead seal 42, which is positioned between the jacket 36 and upper edges of the cupped electrode 10, bars the liquid from reaching the top closure plate 34 or more importantly its locked juncture with the jacket 36.

An important advantage of the dry cell jacket is that leakage of liquid exudate through the locked juncture between the top closure 34 and the jacket 36 due to so called "wicked effect" is eliminated. In prior dry cell constructions where the jacket has been made of a fibrous cellulosic material, or even in those cells where a liquid impermeable barrier layer has been incorporated but as an intermediate ply in the jacket, the liquid exudate would normally become soaked into the first or innermost fibrous ply of the jacket and would eventually creep into or wick through the locked juncture, resulting in blockage of the venting path and even leakage from the cell. In the construction of the present dry cell, the jacket 36 incorporates a liquid impermeable barrier in the first or innermost ply 48 which the liquid cannot penetrate and additionally this first or innermost ply 48 actually forms a seal between the jacket and the top closure plate 34 as shown in Figure 1.

Although the construction of the dry cell of the invention is quite different from conventional construction, an advantage is that its manufacture is simple. The active elements of the cell, the cupped electrode, carbon electrode, depolarizer mix and electrolyte, are all assembled in the conventional manner. It may be mentioned that while the electrolyte may be provided in the form of a "paste", an electrolyte-wet bibulous paper separator may also be used.

While the invention has been described herein with particular reference to the pre-

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ferred form for the jacket of a multiple-ply laminated tube as illustrated in Figure 2, it will be understood that the invention is not so limited but is applicable to the use of almost any dry cell jacket which is impermeable to liquid. Thus the invention is intended to cover the use of many different types of multiple-ply tubes having an innermost layer or ply of a liquid impermeable material as well as a jacket or tube which is composed entirely of a liquid impermeable plastics material.

Dry cells embodying the invention have been subjected to tests ranging from normal usage to severe abuse. These tests demonstrated the effectiveness of the invention, for cells of a conventional construction and not having a jacket which is impermeable to liquid and the novel seal arrangement described herein, showed evidence of leakage while the cells of the invention showed little or no leakage and where the cells did leak under abusive use, the percentage of failure was comparatively far smaller in the case of the dry cells of the invention.

WHAT WE CLAIM IS:—

1. A primary dry cell which comprises a cupped electrode of a consumable metal having an upper open end, the peripheral edges of which are turned slightly inwardly, a depolarizer mix and an electrolyte disposed within the cupped electrode, a central porous carbon electrode embedded within the cupped electrode and extending at its upper end beyond the upper edges of said cupped electrode, a noncorrodible liquid impermeable jacket surrounding the cupped electrode, a metallic top closure fitted over the top of the carbon electrode, said top closure having its outer edges locked in liquid-tight engagement with the jacket and having gas venting means therein, an inner seal positioned within the open end of the cupped electrode and between the top closure and the depolarizer mix and extending from around the carbon electrode to the inner side walls of said cupped electrode, defining a lower free space between said seal and said depolarizer mix for the

collection of liquid from the cell and an upper free space between said seal and said top closure, a liquid and gas impermeable seal washer fitted around the carbon electrode and over the upper peripheral edges of the cupped electrode with the upper free space, the outer edges of said seal washer abutting against the interior wall of the jacket, an outer peripheral bead seal disposed below the seal washer in the space left by the inwardly turned upper edges of the cupped electrode and between said cupped electrode and the interior wall of the jacket, an inner peripheral bead seal disposed below the seal washer on the opposite side of the upper peripheral edges of the cupped electrode and an electrode bead seal underlying the innermost edges of said seal washer around the carbon electrode, and an absorbent layer of bibulous material disposed on top of the seal washer just below the top closure of the cell.

2. A cell as claimed in claim 1 in which the noncorrodible jacket is composed of a multiple-ply laminated tube comprising a first laminate of a high strength, liquid impermeable plastics material and a thermoplastic material and a second laminate of a thermoplastic material and a fibrous cellulosic material, the thermoplastic material of said first and second laminates being bonded together by autogenous action under heat.

3. A cell as claimed in claim 1 or 2 in which the inner seal is composed of a top collar fitted tightly within the open end of the cupped electrode and around the carbon electrode, the top collar being composed of a liquid impermeable material.

4. A cell as claimed in any one of claims 1 to 3, in which the absorbent layer is composed of a bibulous blotting paper.

5. A primary dry cell substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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ferred form for the jacket of a multiple-ply laminated tube as illustrated in Figure 2, it will be understood that the invention is not so limited but is applicable to the use of almost any dry cell jacket which is impermeable to liquid. Thus the invention is intended to cover the use of many different types of multiple-ply tubes having an innermost layer or ply of a liquid impermeable material as well as a jacket or tube which is composed entirely of a liquid impermeable plastics material.

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collection of liquid from the cell and an upper free space between said seal and said top closure, a liquid and gas impermeable seal washer fitted around the carbon electrode and over the upper peripheral edges of the cupped electrode with the upper free space, the outer edges of said seal washer abutting against the interior wall of the jacket, an outer peripheral bead seal disposed below the seal washer in the space left by the inwardly turned upper edges of the cupped electrode and between said cupped electrode and the interior wall of the jacket, an inner peripheral bead seal disposed below the seal washer on the opposite side of the upper peripheral edges of the cupped electrode and an electrode bead seal underlying the innermost edges of said seal washer around the carbon electrode, and an absorbent layer of bibulous material disposed on top of the seal washer just below the top closure of the cell.

2. A cell as claimed in claim 1 in which the noncorrodible jacket is composed of a multiple-ply laminated tube comprising a first laminate of a high strength, liquid impermeable plastics material and a thermoplastic material and a second laminate of a thermoplastic material and a fibrous cellulosic material, the thermoplastic material of said first and second laminates being bonded together by autogenous action under heat.

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