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(54) ELECTROCHEMICAL CELLS

(71) We, DURACELL INTERNATIONAL INC., formerly known as P. R. MALLORY & CO., INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 3029 East Washington Street, Indianapolis, Indiana 46206, United States of America, 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:

The present invention relates to electrical devices and to means and methods for enclosing or containing electrical devices. More particularly, the invention relates primarily to enclosures or housings for electrochemical cells. The invention is particularly useful with electrochemical cells of the lithium/sulphur dioxide type, which develop an internal pressure in excess of ambient pressures.

Electrochemical cells in general inlcude two dissimilar electrodes in a reactive medium enclosed within a housing, the housing comprising two or more electrically conductive component parts electrically connected to the electrodes but electrically isolated from each other, and the housing providing external electrical terminations for the cell. A common construction for the housing for an electrochemical cell is a hollow, cylindrical, electrically conductive container having an open end, and a closure assembly adapted to seal the open end of the container. The closure assembly may comprise an electrically conductive, disc shaped closure member and an electrically insulating gasket about the periphery thereof to isolate the member electrically from the container. The closure assembly is in general held in close engagement with the container by an external edge of the container which is bent inwardly to physically restrict outward movement of the closure assembly, thereby to hold the closure assembly securely against the effect of increased internal pressure.

In the operation of an electrochemical cell, the housing should be and remain sufficiently hermetic to minimize leakage of the reactive medium from the cell, because leakage can cause damage to the cell itself or to apparatus to be energized by the cell. In addition, the housing should minimize the entry of harmful contaminants from the ambient atmosphere, which might cause deterioration of the electrical characteristics of the cell.

Cells having housings of the type described above, especially those of the lithium/SO_2 type, have been difficult to fill and, when filled, often do not achieve the desired degree of hermeticity, especially when the cell is subjected to temperature cycling. The integrity of the seal between the container and the closure assembly has not been totally satisfactory and has even led to the use of welding techniques and to the use of expensive glass-to-metal seals in order to obtain hermeticity.

It is therefore an object of the present invention to provide an electrical device having a housing which minimizes the leakage of materials from the interior of the device, and is able to withstand temperature cycling without a significant loss in hermeticity. The housing should be relatively easy to manufacture using available equipment.

According to the present invention we provide an electrochemical device comprising a pressurized container having a cylindrical can body with a cylindrical side wall, a closed bottom end and an open upper end, the upper open end of said can body being curled to the shape of a torus, the innermost portion of which has a diameter not greater than the diameter of said can body; a closure for said container, said closure comprising a metallic element having a curved lip crimped against said torus; means to insulate said can body from said closure; and electrodes and an electrolyte operatively positioned within said container, one of said electrodes being electrically connected to said can body and the other electrode being electrically connected to said closure.

The invention also provides a method of forming a pressurized electrochemical device comprising the steps of: curling the open upper end of a cylindrical metallic can body to form a torus the innermost portion of which has a diameter less than the diameter of said can body; positioning electrodes within said can body, electrically connecting one of said electrodes to said can body and the other to a closure for said can body, evacuating the gas from said can body, cooling a normally gaseous electrolyte to a temperature below its liquefaction point and introducing the thereby liquefied electrolyte into said can body, immediately closing said can body with said closure, and crimping said closure against said torus to close said electrochemical cell.

Generally, the present invention relates to a means and method for providing an electrical device including a housing. The electrical device comprises an electrical body in a housing including an elongated cylindrical container or can body having a height substantially greater than its diameter and an open end defined by a rim, the rim of the container being rolled over, preferably inwardly of the wall of the container, and a closure assembly or cover over and closing the open end of the container. The closure assembly includes a member having its periphery generally complementary to the shape of the rolled over rim of the container. The closure assembly is sealed to the rolled over rim of the container by crimping the closure radially outwardly or inwardly (or both) to seal against said rolled over rim which provides couterpressure support for the crimping operation. In order to provide two terminals of opposite polarity when, in the preferred embodiment, the electrical device is an electrochemical cell, an electrically insulating layer is positioned between the closure and the rolled rim. In a preferred embodiment, the electrical body of the cell includes a lithium-containing electrode and an SO_2 depolarizer, and the container and member consist essentially of aluminium, although other materials such as steel, etc. can of course be used.

In the accompanying drawing:

Figure 1 is a view of the component parts of an electrical device embodying the invention, shown in partial cross-section, prior to closure of the housing; and

Figure 2 is a partial cross-sectional view of the electrical device of Figure 1 after closure.

A preferred embodiment of the invention is shown in Figures 1 and 2. In Figure 1, the electrical device shown shown in an electrochemical cell 10 comprising a metallic container 12, a closure assembly 14, and electrical body 16 within the container. Electrical body 16 comprises convolutely wound anode and cathode electrodes 18 and 20 in an electrolyte (not shown). Positioned between adjacent turns of electrodes 18 and 20 are plastics separator strips 19 which are also convolutely wound. In electrical contact with the anode electrode 18 is an anode current collector 21, the collector shown being of nail-like form with a head 22 and a shank 23. Electrical contact is made from the cathode electrode 20 to the container 12 by a suitable connector (not shown). The entire rim 24 of container 12 is rolled inwardly to the shape of a torus to provide support for attachment and sealing of closure assembly 14. It is to be noted that the rolled-over rim 24 of container 12 does not touch the side wall of the container.

Closure assembly 14 comprises an electrically conductive member 26 and electrically insulating material 28. Member 26 includes a hollow protuberance or cup 30 adapted to receive the end 22 of anode collector 21, and a lip portion 32 in a configuration that conforms generally to the shape of the rolled-over rim 24 of container 12. Electrically insulating material 28 is extended over the underside of edge portion 32 so as to electrically isolate the member 26 from container 12 in the completed device.

Figure 2 illustrates the completed closure of the electrochemical cell 10 of Figure 1. The hollow protuberance or cup 30 has been brought into electrical contact with anode current collector head 22, and the insulating material 28 disposed on edge portion 32 is in engagement with rolled-over rim 24 of the container 12. The member 26 has been crimped, by a suitable tool or tools (not shown), inwardly beneath the lower edge of the head portion 22 of anode collector 21 and radially outwardly beneath the rolled-over rim 24 of container 12, to form an annulus 25 which extends beneath torus formed by the rim 24. Member 26, excluding shaped edge portions 32, now has a diameter greater than the diameter of the inner portion of rolled-over rim (torus) 24. Thus, closure assembly 14, including member 26, is effectively held in close engagement with container 12 and thereby provides a seal for the open end of the container.

Typically, the forming or crimping of member 26 about rolled-over rim 24 is accomplished by crimping or forming the member 26 to container 12 by what is known as an "expanding collet" crimping machine of a type which is well known in the manufacture of aerosol containers. Similarly, member 26 is formed about anode collector head 22 by forming or crimping the protuberance or cup 30 about the anode collector head 22 by a "pedestal" crimping machine having a contracting collet. This machine forms the walls of protuberance or cup 30 under the nailhead portion of anode collector head 22, to help to provide good electrical contact between the member 26 and the anode collector. These steps can be carried out simultaneously or seriatim. To further ensure good electrical contact, it may be desirable to weld the anode collector 22 to the member 26 by any suitable method such as parallel electrode resistance welding.

As can be seen from Figure 2, the crimping of member 26 into the configuration shown causes member 26 to have a larger diameter inside the container 12 than the diameter of the innermost periphery of the torus 24. With such a construction, closure assembly 14 is not likely to become disengaged if internal pressures are generated by the electrical body 16. In addition, because the toroidal rim 24 is not completely rolled over to engage the wall of container 12, excess crimping forces on member 16 can be tolerated by virtue of the slight resiliency of the rolled over rim. Any increase in internal pressure also acts to decrease leakage, because it increases the pressure of annulus 25 against torus 24.

In a preferred embodiment of the present device the container 12 is an aluminium can into which the electrochemical elements are placed, and a small punch press thereafter curls over the can lip to form torus 24. The torus will have a ring shaped cross section of about 3.3 mm (0.13 inch) diameter, which gives the torus itself an inside opening of about 25 mm (1 inch) diameter based upon the diameter of the can body which has an outside diameter of about 32 mm (1.25 inch). The use of this size of can and curl is extremely advantageous because it conforms to the areosol industry standard and closely approximates the standard D cell diameter. This makes it possible to utilize ordinary aerosol industry filling and sealing technology to produce the cells of the invention. Such technology as used in the aerosol industry has been highly developed whereby the cells can be filled with a pressurized, normally gaseous electrolyte which is analogous to the Freons or other volatile propellants which are in common use in the aerosol industry.

A preferred filling method that has been adapted from the aerosol industry involves placing the open ended can, having torus 24 thereon and complete with electro-chemical elements therein, under an evacuation-electrolyte fill head. The gas is evacuated from the can and replaced with a metered amount of electrolyte which in this instance is SO_2 that has been chilled to a temperature sufficient to maintain it as a non-volatile liquid. Normally a temperature in the range of -17 to $-35°C$ will be adequate. While the boiling point of the electrolyte is approximately $-10°C$ the use of a substantially lower temperature as set forth above is highly desirable so that the mass of chilled electrolyte will be adequate, when introduced into the can 12, to immediately chill the can and contents below the boiling point of the electrolyte and to maintain the entire article below that point for at least about 30 seconds during which time cap 26 can be placed on said container 12 and crimped into sealing relation in the manner indicated above. Thereafter, one or more layers 35, 37 (Figure 2) of insulating plastics material can be placed around the cylindrical side wall of can body 12 to extend from the closure to the bottom of said can body. Advantageously such layers will be formed by heat shrinking one or more tubes of shrinkable plastics material around said can body in a manner known in the art.

An alternative method which is useful for filling the electrical devices of this invention involves the evacuation of the can and the pressure filling of electrolyte at room temperature. In this case the closure 14 is loosely placed on the can body 10, having the electrochemical elements previously placed therein and having torus 24 previously formed thereon. The loosely covered can is placed under a filling head, the filling head seals the upper end of the can from the external environment, and a vacuum is drawn whereupon the air is removed from the container. Thereafter, electrolyte under pressure is filled into the can body through the space between the can and the loosely fitting closure. The closure thereafter is forced onto the upper edge of the can body and crimped into sealing relationship with the torus. Thereafter, one or more layers of insulating material may be placed around the side wall of the can body.

Member 26 is analogous to the valve mounting cup commonly used in the aerosol industry but, because no valve means are provided, member 26 is referred to as a blind mounting cup. Thus, it will be understood that the highly developed technology of the aerosol industry has been adapted to the non-alalogous field of batteries whereby it has been made possible to form batteries in an inexpensive manner utilizing existing equipment and know how from the non-analogous aerosol field thereby eliminating the necessity of developing special machinery to achieve results which were apparently unobtainable in the battery field except by the provision of expensive technology and hermetic sealing methods and equipment.

Although the device shown in Figures 1 and 2 is an electrochemical cell, it should be realized that the housing could be adapted to enclose other electrical devices such as electrolytic capacitors.

Preferably container 12 is a unitary structure, although the container could be made from an assembly of more than one component. Suitable electrically conductive materials for the container include steel, aluminium, copper, silver, alloys thereof and the like, aluminum being preferred for some electrochemical cell applications.

In the same fashion, member 26 may be a unitary structure or a composite of different structures. Suitable electrically conductive materials for the member also include steel, aluminum, copper, silver, alloys thereof and the like; steel is preferred for use in Li/SO_2 electrochemical cells. For certain applications, it may be desirable for the member to contain both electrically conductive portions and electrically insulative portions. By selecting appropriate materials for the container 12 and members 22 and 26, the device 10 can be made substantially non-magnetic and thereby useful in systems for detecting magnetic items.

In the embodiment shown in Figures 1 and 2, electrically insulating material 28 is disposed between edge portion 32 of the closure member 26 and the rolled rim 24 of the container 12 to electrically isolate these portions of the device 10. Such insulating material 28 is necessary when the member 26 is entirely electrically conductive. However, if member 26 is a composite of electrically conductive portions and electrically insulating portions, insulating material 28 disposed between the member 26 and the rolled rim 24 may not be necessary.

In those preferred embodiments where electrically insulating material 28 is used, it may take several different forms. A preformed gasket or grommet of a suitable inert polymeric material such as is disclosed in British Patent application No. 41031/77 (Serial No. 1590006), which is a polyhalogenated hydrocarbon resin may be utilized. Alternatively, a prepolymer or polymer resin material may be applied to either the edge portion 32 of member 26 or to the rolled rim 24 of container 12 or to both and then caused to flow and/or cured by methods such as the application of heat after closure of the device 10. Suitable insulating, polymeric, inert materials for a preformed gasket or for applied resin material include polytetrafluoroethylene, neoprene, polyurethane, polypropylene, polyethylene, and the like. Heat shrinkable resin sleeves may also be applied to the rim 24 of container 12 prior to or after rolling of the rim.

Materials that will adhere to the rolled-over rim 24 and the member 26 are preferred for use as element 28. Suitable materials of this type inlcude polymeric, polyhalogenated hydrocarbon materials such as: FEP copolymers which are copolymers of fluorinated ethylene and propylene; PVF_2 which is a homopolymer of vinylidene fluoride; ETFE copolymers which are copolymers of ethylene and tetrafluoroethylene; CTFE polymers which are chlorotrifluoroethylene resins and E-CTFE copolymers which are copolymers of poly (ethylene-chlorotrifluoroethylene); and polymers having a fluorocarbon backbone and perfluoro alkoxy (PFA) side chains wherein the alkoxy radical contains from 1-6 carbon atoms.

While the present invention is particularly useful for electrochemical cells in which the anode 18 is preferably lithium metal, other active metals above hydrogen in the activity scale or electromotive series including sodium, potassium, rubidium, calcium, magnesium, strontium, barium and cesium may be used either singly or in combination. The cathode current collector 20 on which the solvent or co-solvents are electrochemically reduced will advantageously be a screen, having applied thereto a mixture of an inert and electrically conductive material such as carbon black, graphite, or other electrical conductors of high surface area, and, preferably, including absorbing and binding agents. Normally gaseous electrolytes for which the cells of the present invention are particularly useful include such materials as sulphur dioxide (SO_2), nitryl chloride (NO_2Cl), nitrosyl chloride ($NOCl$), and nitrogen dioxide (NO_2).

While the present invention has been described with reference to particular embodiments thereof, it will be understood that the structure and method defined herein will be useful for the formation of other electrical devices such as, for example, electrochemical cells having other fluid electrolytes.

WHAT WE CLAIM IS:

1. An electrochemical device comprising a pressurized container having a cylindrical can body with a cylindrical side wall, a closed bottom end and an open upper end, the upper open end of said can body being curled to the shape of a torus, the innermost portion of which has a diameter not greater than the diameter of said can body; a closure for said container, said closure comprising a metallic element having a curved lip crimped against said torus; means to insulate said can body from said closure; and electrodes and an electrolyte operatively positioned within said container, one of said electrodes being electrically connected to said can body and the other electrode being electrically connected to said closure.

2. The electrochemical device of claim 1 wherein a portion of said closure is positioned beneath said torus and has an external diameter greater than the diameter of the innermost portion of said torus but less than the diameter of said can body.

3. The electrochemical device of claim 1 or 2 wherein said closure is additionally crimped inwardly beneath the head of a nail-shaped electrode current collector disposed in the can body.

4. The electrochemical device of claim 1, 2 or 3 wherein the curled upper end of said can body is radially spaced from the inner surface of said side wall.

5. The electrochemical device of claim 1, 2, 3 or 4 wherein said means to insulate said can body from said closure comprises a polymer dielectrically separating, and adhered to, said can body and said closure.

6. The electrochemical device of any preceding claim wherein said cylindrical side wall has a height greater than its diameter.

7. The electrochemical device of any preceding claim wherein the entire device is formed of nonmagnetic materials.

8. The eletrochemical device of any preceding claim wherein said electrolyte is a pressurized, normally gaseous material.

9. The electrochemical device of claim 8 wherein said electrolyte is sulfur dioxide.

10. The electrochemical device of claim 9 comprising a current-producing cell, wherein one said electrode is a lithium anode.

11. The electrochemical device of any preceding claim wherein the outermost portion of said curled upper end of said can body which forms a torus has a diameter not greater than the diameter of said can body.

12. The electrochemical device of any preceding claim wherein there is additionally provided an insulating jacket extending around the cylindrical portion of said can body from the bottom end thereof to said closure.

13. A method of forming a pressurized electrochemical device comprising the steps of: curling the open upper end of a cylindrical metallic can body to form a torus the innermost portion of which has a diameter less than the diameter of said can body; positioning electrodes within said can body, electrically connecting one of said electrodes to said can body and the other to a closure for said can body, evacuating the gas from said can body, cooling a normally gaseous electrolyte to a temperature below its liquefaction point and introducing the thereby liquefied electrolyte into said can body, immediately closing said can body with said closure, and crimping said closure against said torus to close said electrochemical cell.

14. The method claimed in claim 13 wherein an insulating polymeric material is placed between said can body and said cover to dielectrically separate said closure and said can body.

15. The method claimed in claim 13 or 14 wherein said electrolyte is cooled to a temperature sufficiently below its liquefaction point to enable the mass of electrolyte to cool the can body and its contents below said point.

16. A mehtod as claimed in claim 13 and substantially as herein described.

17. An electrochemical device substantially as herein described with reference to the accompanying drawings.

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1590005 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

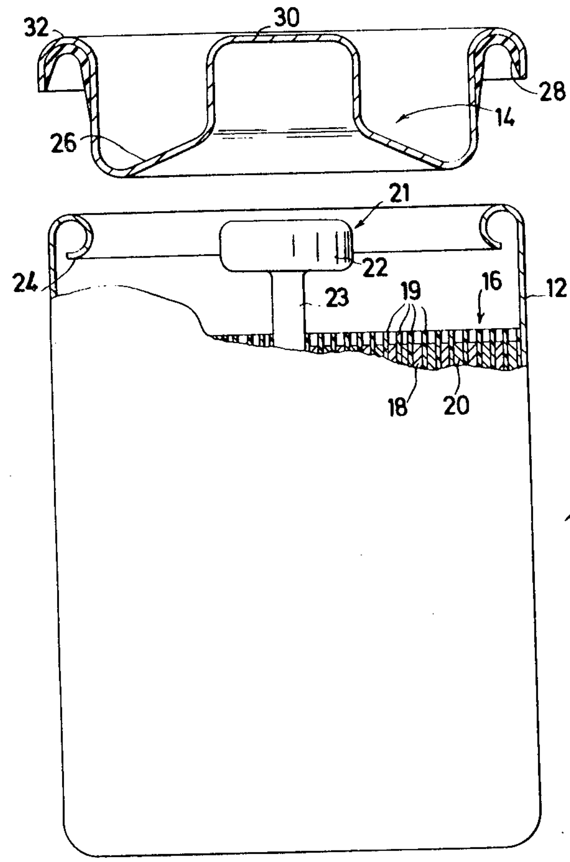

FIG. 1

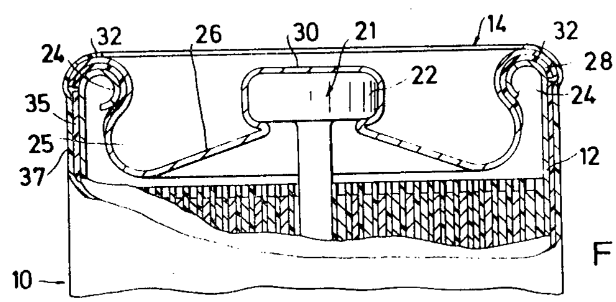

FIG. 2