

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Seals for Electric Batteries

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organized under the laws of the State of New York, United States of America, (Assignee of ROBERT CARMICHAEL jointly with WILLIAM ANTHONY VULPIO), 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 and secondary galvanic cells or batteries having a seal gasket having therein a combined safety blow-out and gas permeable membrane.

The chemical nature of many electrochemical systems employed for the production of electricity is such that gas, usually hydrogen, is generated during storage and sometimes during or following service use. When sealed cell containers are employed, as is the case in certain primary and secondary cells, the build up of gas-pressure within the sealed container has proven dangerous.

In the past, a dangerous build up of pressure generally has been prevented by some sort of continuous venting means or by periodic release through valve systems. These means have included venting slits or apertures in gasket membranes or sealing gums which pass gas bubbles and then reform after release.

Alleviation of built-up gas pressure from alkaline cells has been found to be particularly difficult. Alkaline electrolytes are not easy to contain within a sealed container and they will creep along almost any sealing surface and contaminate the outside of the cell package. Accordingly, it has been the practice in order to prevent creepage and loss of electrolyte to seal the cell container very tightly. Unfortunately, higher and more dangerous pressure build-ups are a direct result of tightly sealed cells.

Most venting systems which have been devised, will satisfactorily relieve high gas pressures, but unfortunately, they will in addition

permit electrolyte leakage. For example, release valves which are intended to reseal after activation under pressure, are too easily fouled by caustic electrolyte salts. These salts are formed when caustic electrolyte, which has crept along the sealing surface of the valve, combines with the carbon dioxide in the air to form a carbonate. The carbonate salt cakes the valve surface and prevents proper resealing of the valve and more electrolyte will then leak through the partially opened valve. The other means which have been devised to permit pressure release, all evidence comparable difficulties.

According to the present invention there is provided an electric battery having a gasket with a safety blow-out area distinct from the main body of the gasket and extending across the gasket, at least a portion of the safety blow-out area being gas permeable.

More specifically, the combined safety blow-out and gas vent of the seal gasket of the battery of the present invention comprises a diffusion membrane which is an integral part of a synthetic plastic gasket used to seal an alkaline cell container. The membrane is designed to vent gases formed within the cell during normal shelf storage by diffusion of gas therethrough, and to rupture rapidly upon excessive build-up of gases under abusive conditions, such as excessive over-charge, at pressures below the point at which the cell container is likely to explode. This integral membrane, which may be provided in the gasket by either proper molding procedures or machining, positively prevents any electrolyte leakage at this point.

In the design of any particular combined safety blow-out and gas permeable membrane, there are a number of variables which must be taken into account.

The blow-out or rupture function of the membrane is dependent upon the physical properties of the membrane material, such as tensile strength and elongation, and also the dimensions of the membrane, i.e., the area

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of the membrane surface under stress and the thickness of the membrane at its periphery, which is the point of localized stress when pressure is exerted upon the membrane. For any given material, the rupture pressure increases with increased thickness in the periphery of the membrane and, conversely, decreases with increased membrane area. The operating or deflecting area for membrane rupture is the total area that will be deflected under stress, and deflection will occur at the thinnest section of the membrane.

Table I below, indicates the relationship between blow-out pressure and membrane

thickness for the circular membrane illustrated in Figs. 1 and 2. The data in Table I were obtained from tests in which seal gaskets employing the blow-out membrane were fixed to a specially adapted hydrogen blow-out apparatus. Except for the presence of an alkaline electrolyte, a factor which has no effect on the function of the membrane, all the elements of the alkaline cells were present in the cells tested. The membrane in each test had a diameter of 0.260 inches and the thickness of the membranes were varied as shown. The membranes were made of nylon.

TABLE I

Membrane Blow-out Pressure (pounds per square inch)		Membrane Thickness inches $\times 10^{-3}$	
Average	Range	Average	Range
225	200—250	3.5	3.0—4.0
285	275—300	4.5	4.0—5.0
335	300—375	5.5	5.0—6.0

As can be observed from the table, the membrane blow-out pressure varies in a linear fashion with increased membrane thickness.

The venting rate of the membrane is dependent upon the membrane material employed, the gas permeability of the material, the membrane area and its thickness, and the pressure differential across the membrane. It has been generally observed that the rate of gas transmission through the membrane of a given material under constant conditions varies in inverse proportion with increasing thickness of such membrane.

Table II below, indicates the hydrogen gas permeability characteristics of various synthetic plastic materials from which the combined safety blow-out and gas permeable membrane of the invention may suitably be made. In addition, the table shows the calculated hydrogen gas venting rate for each material when employed for the circular membrane

shown in Figs. 1 and 2, in a "D" size alkaline cell; size "D" being as defined in Circular 466 of the National Bureau of Standards of the United States Department of Commerce. The dimensions of a "D" size cell are as follows: Diameter: 3.2 cm. — Height: 5.7 cm. — Nominal volume: 45 cm.³ — Approximate weight: 96 grams. Cell calculations were based upon a constant membrane area and thickness and upon a pressure differential across the membrane of 6 atmospheres. The numbers in the table below found in the column headed Permeability Constant in each instance is the number of centimeters of hydrogen at standard temperature and pressure that would be transferred through a cube of the specified material of cross section of one square centimeter and one centimeter thick per second at a pressure of one centimeter of mercury times 10^9 .



55 Height

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TABLE II

Calculated Hydrogen Gas Venting for "D"
Size Alkaline Cells Through Membranes Under
Six Atmospheres Pressure Differential

Material	Membrane Area Square Inches	Membrane Thickness Inches	Permeability Constant	Calculated Hydrogen Gas Venting CC/Week
Ordinary Nylon	0.031	0.003	0.10	.7
Vinyl chloride- vinyl acetate copolymer	0.031	0.003	0.99	7.33
Polyethylene	0.031	0.003	0.8	5.92

It is apparent from Table II, that some materials will diffuse gases, hydrogen in this instance, at a much faster rate than others. Vinyl chloride- vinyl acetate copolymers and polyethylene plastics, for example, will diffuse hydrogen gas approximately ten times faster than nylon. Accordingly, if nylon is used in the practice of the invention, it may be necessary, depending upon the requirements of the cell, to alter the design of the membrane so that the desired venting rate is obtained. Similarly, the characteristics and properties of the particular galvanic cell in which the membrane is to be employed, must be considered.

The present invention will be further illustrated by way of the accompanying drawings/ in which:—

Fig. 1 is a front elevation, partially in section of an alkaline manganese dioxide zinc cell according to the present invention;

Fig. 2 is an enlarged fragmentary view of the gasket shown in Fig. 1; and

Fig. 3 is an enlarged fragmentary view of an alternative gasket.

Referring to the drawings, Fig. 1 illustrates an alkaline-manganese dioxide zinc cell comprising a cupped container 10, provided with an insulating jacket 11, having an anode 12 and cathode 14, separated by a separator 16 and electrolyte 18, disposed therein. The open-cupped polarized container 10 is sealed at its open end by an annular "U" shaped seal gasket 20 having an unpolarized metallic cover 22, which is provided with a venting aperture 23, recessed therein and a polarized centrally located terminal 24 which is in contact with the anode current collector 25. The seal gasket 20 is radially compressed between the terminal 24 and the cover 22 and between the cover 22 and the container 10 thereby resulting in an extremely leak resistant gas tight cell.

The combined gas permeable and safety blow-out membrane is an integral part of the

seal gasket 20 and comprises, as is more readily seen in Fig. 2, a machined or molded membrane 26 located in the seal gasket 20 and extending there across. The membrane 26 has a membrane thickness T and a membrane area of diameter A. The seal gasket 20 may of course be provided with one or more membranes 26 according to requirements, as shall later be described. In the embodiment shown in Fig. 2, the membrane venting area of diameter A is equal to the membrane blow-out area of diameter A, that is to say, diffusion of gases will take place across the entire cross-section of the membrane 26. In this embodiment, all other things being equal, the blow-out or rupture pressure of the membrane 26 is dependent solely upon membrane thickness T.

Fig. 3 illustrates a membrane 26 which is particularly suitable for use where a low venting rate for a given membrane area is desired. In this embodiment, the membrane has a blow-out area of diameter A, but a membrane venting area of diameter A—B or C, that is, diffusion of gases will take place through the area of diameter C. The membrane thickness T being also the membrane peripheral thickness, where deflection stresses are localized, regulates and determines the rupture pressure of the membrane. It will be noted that the low venting rate membrane of Fig. 3, assuming it to have the same area and thickness as the membrane of Fig. 2, will rupture at the same pressure, while the venting rate is much lower. An additional feature of the low venting rate membrane of Fig. 3 is that for a given membrane area of diameter A and thickness T, the diffusion or venting rate may easily be controlled for a desired application merely by varying the membrane area C without altering the designed rupture pressure.

A seal gasket embodying the integral blow-out and venting membrane of the invention

5 suitable for use where a high venting rate and a high rupture pressure is desired, would comprise a seal gasket provided with a plurality of membranes of the type illustrated in Fig. 2. Each membrane is made to rupture at the desired rupture pressure, while at the same time the multiple members would increase the membrane venting area whereby greater diffusion of gas is obtained without lowering the rupture pressure.

10 It should be obvious to one skilled in the art, that in each of the embodiments shown, the membrane need not be circular in shape and in fact may assume many configurations, such as a kidney shaped membrane which is suitable for a high venting rate, low rupture pressure membrane, keeping in mind that large areas provide lower rupture pressures for any given membrane thickness. In small size

20 cells the membrane may be in the shape of an annular ring surrounding the negative terminal aperture.

25 In cells employing the membrane of the invention, it is desirable to provide an external insulator 28 and metallic cover 30, which is in contact with the polarized terminal 24, to contain the membrane 26 in the event it should rupture or blow-out.

30 Table III below, contains the results obtained from tests in which a quantity of "D" size cells were deliberately overcharged to provide high gas build-ups. All the cells tested were of the type illustrated in Fig. 1. A portion of the cells tested were provided with the combined safety blow-out and venting membrane of Fig. 2 in the seal gasket, another portion with membrane of Fig. 3, and another portion had no membrane in the seal gasket.

TABLE III

Membrane	Number of Cells Charged	% of Safe Membrane Blow-out	% of Violent Cell Rupture
Fig. 2	50	100	0
Fig. 3	50	100	0
No Membrane	50	0	100

40 As can be seen from the table, the safety blow-out and gas permeable membrane of the invention absolutely prevents violent cell rupture upon overcharge or excessive gassing of a galvanic alkaline cell.

45 It should be appreciated by one attempting to practice the invention, that although the design of a suitable gas diffusion membrane which will vent gas at the desired rate is calculable from the physical properties of the synthetic plastic membrane material and from the dimensions of the membrane chosen, the relationship between rupture pressure and membrane thickness or area is empirical. Since most plastics are fairly elastic, there is no defined stress-strain relation from which the bursting strength of a particular membrane may be calculated with complete certainty. Thus, the design of a membrane which will burst at a given pressure and which will vent gases at the desired rate, involves a trial and error technique to some extent.

WHAT WE CLAIM IS:—

1. An electric battery having a gasket with a safety blow-out area distinct from the main body of the gasket and extending across such

gasket at least a portion of said safety blow-out area being gas-permeable.

2. A battery as claimed in Claim 1 in which the safety blow-out area is made of ordinary nylon or a copolymer of vinyl chloride and vinyl acetate, or polyethylene.

3. A battery as claimed in Claim 1 or 2, in which all of the blow-out area is gas-permeable.

4. A battery as claimed in Claim 1 or 2, in which the gas-permeable portion is less than the blow-out area and is connected to the main body of the gasket.

5. A battery as claimed in any of Claims 1 to 3, in which the gasket has a plurality of safety blow-out areas distinct from the main body of the gasket and extending across such gasket, at least a portion of each safety blow-out area being gas-permeable.

6. An electric battery substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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