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COMPLETE SPECIFICATION

Improvements relating to Alkaline Electric Dry Cells

We, RAY-O-VAC COMPANY, a Corporation organised under the laws of the State of Wisconsin, United States of America, of 212, East Washington Avenue, Madison, in the State of Wisconsin, 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:—

This invention relates to primary electric dry cells and with more particularity, to primary dry cells wherein an alkaline electrolyte is employed.

The well known form of dry cell, usually known as the "Leclanche" cell has been used for many years with quite satisfactory results in numerous fields of which one of the most common is in electric torches but it has certain disadvantages. Leclanche cells are normally made in cylindrical form. They have relatively short life when heavy currents are drawn from them. There has, for many years, existed a field of use and a potential demand for a dry cell battery which is not limited to the cylindrical shape of the Leclanche ~~cell~~ and which has the properties of longer life or greater capacity even at relatively higher discharge rates than can be satisfied by the Leclanche dry cell. Somewhat more recently, there has been a potential demand for a dry cell which can be assembled into a battery formed of multiple cells and which, when assembled, does not suffer from the unwieldy size, the space-wasting cylindrical shape and the limited life or low capacity of the Leclanche dry cell. This more recent demand relates to cells used in portable hearing aids, portable radio receivers, and like miniature equipment.

It has been considered theoretically that some of the disadvantages of the Leclanche dry cell could be overcome by utilizing an alkaline electrolyte in place of the electrolyte usually employed in the Leclanche cell. The earliest efforts along this line were directed toward alkaline wet cells, but such cells have at most very restricted uses. They are not readily portable and can only be operated in a fixed position, a factor which makes them incapable of being used in portable electrical equipment.

Further in the period from about 1890 to about 1920, many workers in the field, particularly workers outside the United States of America and more particularly German or Swiss inventors, proposed various forms of alkaline dry cells as improvements on the Lalande cell. So far as is known, these relatively ancient, suggestions were never followed by the commercial production within or importation into the United States of America of satisfactory alkaline dry cells. Somewhat more recently, alkaline dry cells have been proposed in the United States of America which, on first inspection, appear to have marked advantages over either the Leclanche or Lalande dry cell but which when subjected to use are found to have some very appreciable disadvantages.

Thus, the depolarisers employed including Ag_2O, HgO, and CuO, are expensive and cause a marked increase in the cost of production. The construction employed is complicated and does not lend itself readily to mass production, likewise greatly increasing the costs of production. Recognising the corrosive nature of the electrolyte, efforts have been made to reduce the possibility of electrolyte damage by placing the cell contents in a steel cup, or can, and sealing into the upper surface of the can an insulated metallic cover. Since the can, or cup, functions as one of the terminals of the cell, while the metallic cover functions as the second cell terminal, both cell terminals are in effect disposed at the same end or side of the cell. This form of

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construction makes it difficult to superimpose one cell upon another so as to set up a multiple cell battery, because extra connectors and insulating members are required between the cells of each pair. The chemical materials selected as depolariser materials and the other chemically active ingredients in the cell, are prone to generate gas after discharge. Such uncontrolled generation of gas gives rise to the possibility of explosion or leakage of the caustic electrolyte and, sometimes, of liquid mercury. The overcoming of this disadvantage incurs further cost in the construction of the cell or in the use of additional expensive depolariser. The creation of an effective insulating seal between the steel cup and the metallic top plate requires an expensive grommet and even when this expense is incurred, the danger of leakage of electrolyte is not eliminated. The cells generally have had an abrupt voltage drop near the end point of discharge; thus a user has virtually no warning that the battery is approaching the end of its useful life. Notwithstanding their expense, the depolarisers suggested according to the more recent suggestions are at least slightly soluble in alkaline electrolyte and are capable of causing serious degrading effects in the cell. There is also the danger of deposition of foreign materials such as metallic copper on the zinc or negative electrode, thus stimulating excessive corrosion of the zinc. Efforts have been made to avoid such deleterious results by incorporating in the cells barrier members to augment the cellulosic spacers. Even when such barriers are used, the internal malfunctioning of the cell is not entirely eliminated. Where, as is recommended, an absorbent or spacer material is employed, there is a distinct danger of oxidation and resultant degradation of the ~~cellulose~~ cellulosic spacer materials.

The present invention aims at producing an alkaline dry cell which not only is not subject to the disadvantages mentioned above, but which, for the first time, will make available for mass production and reliable use a primary alkaline dry cell which will have the following properties and features:—

High capacity per unit volume, its terminals located at opposite ends (or sides) of the cell, thus making quite simple the construction of multiple cell batteries, such a size and shape as to permit the construction of multiple cell batteries which will not be cylindrical in overall shape, or if constructed as cylindrical batteries, will have dimensions which will be a mere fraction of the overall dimensions of a Leclanche battery of equivalent capacity, virtually no leakage of electrolyte or other materials after discharge, or during discharge, gas generation is so minimised, both during and after discharge that no provision need be made for venting the cell, and the increased danger of electrolyte leakage which accompanies such vents thereby avoided, such gas as is generated is in such small amounts that the generated gas may be confined within the interior of the cell and when so generated, at most has a tendency to expand, very slightly, the end terminals of the cell thus increasing desired cell-to-cell contact in multiple cell batteries. The invention further aims at providing a dry cell having a gradual voltage drop near the end point so that the need of replacement is indicated to the user, a depolariser which is not only cheap but is formed of ingredients which are almost completely insoluble in alkaline electrolytes, thus, eliminating the harmful effects on any absorbent material, and on the zinc electrode, which have occurred in previous alkaline cells; an alkaline dry cell which does not require the use of an expensive grommet and which does not require the use of a barrier between the depolariser and any absorbent used and which is capable of withstanding relatively high rates of discharge and which under abnormal rates of discharge, possesses longer life and greater capacity than previous dry cells of either the Leclanche type or the Lalande type.

In order to obtain the above mentioned objects, according to the present invention, the body of the cell container consists of a tubular insulating spool having imperforate side walls and a flange at either end and a pair of ~~conducive~~ metal caps have their side walls crimped respectively around the said flanges and have flat end surfaces so that they form positive and negative terminals at opposite ends of the cell and insulated from each other thus providing a symmetrical form of cell. The zinc electrode is placed adjacent one of these terminals which may consist of steel having a coating containing tin, at least on its inner surface next to the zinc electrode as claimed in our Patent Application No. 20809 A.D. 1952 (Serial No. 705,554). The latter is thus disposed within the bore of the tubular spool and may take the form of a zinc disc. Furthermore, a compressed mass of depolarising material may be placed in the bore of the tubular spool in ~~conducive~~ contact with the inner surface of the positive terminal cap. Finally, an electrolyte-immobilising wafer may be disposed,

construction makes it difficult to superimpose one cell upon another so as to set up a multiple cell battery, because extra connectors and insulating members are required between the cells of each pair. The chemical materials selected as depolariser materials and the other chemically active ingredients in the cell, are prone to generate gas after discharge. Such uncontrolled generation of gas gives rise to the possibility of explosion or leakage of the caustic electrolyte and, sometimes, of liquid mercury. The overcoming of this disadvantage incurs further cost in the construction of the cell or in the use of additional expensive depolariser. The creation of an effective insulating seal between the steel cup and the metallic top plate requires an expensive grommet and even when this expense is incurred, the danger of leakage of electrolyte is not eliminated. The cells generally have had an abrupt voltage drop near the end point of discharge; thus a user has virtually no warning that the battery is approaching the end of its useful life. Notwithstanding their expense, the depolarisers suggested according to the more recent suggestions are at least slightly soluble in alkaline electrolyte and are capable of causing serious degrading effects in the cell. There is also the danger of deposition of foreign materials such as metallic copper on the zinc or negative electrode, thus stimulating excessive corrosion of the zinc. Efforts have been made to avoid such deleterious results by incorporating in the cells barrier members to augment the cellulosic spacers. Even when such barriers are used, the internal malfunctioning of the cell is not entirely eliminated. Where, as is recommended, an absorbent or spacer material is employed, there is a distinct danger of oxidation and resultant degradation of the ~~cellulose~~ cellulosic spacer materials.

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under pressure, within the bore of the tubular spool and between the zinc electrode and the depolarising mass.

An example of the improved alkaline dry cell in accordance with the invention will now be more fully described with reference to the accompanying drawings, in which:—

Figure 1 is a composite sectional elevation of the various elements of the cell in the separated position;

Figure 2 is a similar sectional elevation showing the positive sub-assembly partially assembled and the negative sub-assembly partially assembled, the two sub-assemblies being arranged in the manner in which they may be brought together for final assembly;

Figure 3 is a similar view to a somewhat larger scale of the assembled cell;

Figure 4 is a perspective view of the assembled cell as seen from a point to one side and slightly above the cell;

Figure 5 is a detailed perspective view of one of the caps; suitable for use on either end of the cell, as viewed from a position to one side and slightly above;

Figure 6 is a plan of the cap shown in Figure 5;

Figure 7 is a detailed perspective view of one of the pellet cups as seen from a position to the side and slightly above;

Figure 8 is a plan of the pellet cup shown in Figure 7;

Figure 9 is a detailed perspective view of the insulating spool as seen from a position to the side and slightly above;

Figure 10 is a plan of the insulating spool shown in Figure 9; and

Figure 11 is a plan of the cap, similar to Figure 6, but having the pellet cup fixed in it.

Referring first to Figures 1 and 2, the components shown comprise the positive metal cap 1 the negative metal cap 2 the insulating spool 3 the metal pellet cup 4, the mass of depolarising material 5 in pellet form, sealing rings or gaskets 6, 7 and the zinc disc electrode 8 with the electrolyte carrier which is a porous wafer or gel 9.

The positive cap 1 should be inactive, or at least passive, in contact with an alkaline electrolyte. Plain steel or stainless steel containing more or less chromium, or nickel-plated steel are suitable materials since such materials have the required strength and rigidity when of the required gauge. However ordinary plain steel is preferred because of its cheapness. It is desirable that the material used in the positive cap be resistant to any chemical action with the depolariser 5 alone, or with the depolariser 5 when in contact with an alkaline electrolyte in the porous carrier 9.

The negative cap 2 may for some purposes be formed of plain steel like the positive cap 1. Preferably, however, the negative cap 2 should be formed of a metal which is compatible with the zinc electrode 8 so that undesirable corrosion of the latter is not caused by contact with the negative cap 2. As stated in our Patent Application No. 20809 A.D. 1952 (Serial No. 705,554) tin plated steel has been found to be very suitable material for the negative cap. The tin may be applied to the steel either by a hot dip process or by electro-plating. In some cases, further improvement can be effected by amalgamating the tin coating of the negative cap 2 either before assembly or after the cell has been completely assembled. Negative caps 2 made entirely of zinc, or of cadmium-coated steel, however, have also been successfully used. Where ordinary steel has been used, it has been found desirable to take some precautions against unwanted corrosion of the zinc electrode. One precaution which may be taken is to employ an auxiliary thin disc of zinc, inside of the negative cap 2, to separate the zinc electrode 8 from the surface of the steel cap 2. It has, however, been found preferable to avoid the use of such an auxiliary zinc disc wherever possible since such a disc is likely to become amalgamated by any mercury which migrates from the zinc electrode 8. The embrittlement resulting from such amalgamation is liable to cause the zinc disc to crack and to cause the possibility of leakage of electrolyte. This same relative disadvantage exists when zinc is used for the negative cap 2.

It is desirable to have both of the caps 1, 2 formed of a metal which has both the requisite inherent strength and sufficient thickness so as to be strong enough to resist expansion caused by any internal pressure generated within the cell while still having some flexibility so as to deform slightly. At the same time, the caps 1, 2 should be strong enough to retain a firm grip on the flanges 17, 18 of the insulating spool 3.

The insulating spool 3 must be of such a composition that it will be resistant to attack from a strong alkaline electrolyte and from the products of any chemical reaction occurring within the cell. It must also be sufficiently rigid so that it retains its shape and dimensions at all ordinary temperatures. It must be a non-conductor. While glass or other ceramic materials may be employed for the insulating spool, it is preferable to use a spool formed of a synthetic plastic composition. A material, such as polystyrene,

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which has the advantages of relative cheapness and which may be easily formed by injection molding or by machining or grinding from tubular stock has definite advantages in reducing the difficulties and costs of forming the spool 3. The insulating spool 3 is a tube or cylinder having a cylindrical inner bore bounded by the inner surface 16. A considerable portion of the wall 19 of the insulating spool 3 is relatively thin. The upper and lower ends of the spool 3 are thickened and extend as flanges 17, 18 beyond the surface of the thinner part 19 of the wall of the spool. These flanges, 17, 18 may be formed with sharp corners as shown or the corners may be somewhat rounded. The top and bottom end sufaces 20 and 21 of the spool are smooth and flattened for a purpose which will be explained below.

It will be observed that the positive cap 1 has a marginal wall 10 which extends outwardly at an angle from the main horizontal plane of the top 31 of the cap. The top is circular and has a flat outer surface 12 and a flat inner surface 11. The marginal periphery of the wall 10 is crimped or fluted as shown at 33. While the negative cap 2 may differ in actual form from the positive cap 1, it is desirable from the viewpoint of manufacturing economy, to make it identical with the positive cap 1. Thus, the negative cap 2 has a side wall 13, and a flat circular portion 32 with a flat outer surface 14 and a flat inner surface 15. The marginal edges of the wall 13 are crimped or fluted as shown at 34. The inner diameters of the inner surface 11 of the positive cap 1 and the corresponding inner surface 15 of the negative cap 2 are the same as, or depart but slightly from, the greatest diameter of the insulating spool 3, at its top surface 20 and bottom surface 21.

The pellet cup 4 is made of the same material as the positive cap 1. The pellet 5 should make efficient electrical contact with the positive cap 1 in order to keep the internal resistance of the cell at a low value. This object can be accomplished by providing small projections on the top surface 24 of the pellet cup 4, or by embossing small projections on the inner surface 11 of the positive cap 1. It is preferred, however, to weld the top surface 24 of the pellet cup 4, to the inner surface 11 of the positive cap 1 as indicated at 27. Spot welding has proved to be a very quick and satisfactory method for joining the pellet cup 4 and the positive cap 1 in the desired relative positions and with efficient electrical contact. It is even possible to provide the joint by soldering, but welding is preferred since a surer contact is established and no foreign metal is introduced as it would be in soldering. The cup 4 has a flattened top which presents a circular outer surface 24 and a circular inner surface 22; its annular marginal wall 23 is substantially at right angles to the plane of the bottom of the cup 4. The external diameter of the pellet cup 4 is necessarily somewhat less than the diameter of the positive cap 1 and is practically the same as the diameter of the bore of the insulating spool 3. The marginal wall 23 of the pellet cup 4 will be somewhat higher, or longer, than the marginal wall 10 of the positive cap 1 and, in turn, will be somewhat shorter than the axial length of the bore of the insulating spool 3.

The depolariser pellet 5 is formed of an intimate mixture of finely divided manganese dioxide and graphite. It has been found desirable to preform the mixture by compressing under high pressure the mixed components into the form of a pellet and then inserting the pellet 5 into the pellet cup 4. It is preferred to adjust the thickness of the depolariser pellet so that it rests slightly below the outer rim of wall 23 of the pellet cup 4 as seen in Figure 2. It is difficult to insert the depolariser pellet 5 into the pellet cup 4, while having the exposed surface of the depolariser pellet 5 flush with the outer marginal rim of the wall 23, without some chipping along the edges of the depolariser pellet 5 occurring. The loosening or detaching of fragments of the depolariser caused by such chipping may give rise to some internal short-circuits, a result which is avoided by adjusting the thickness of the pellet so the pellet 5 is recessed within, and does not occupy the entire capacity, of the pellet cup 4.

A suitable seal, which may be formed by a washer ring or gasket 6 is inserted in the recess of the negative cap 2 so as to lie parallel to and adjacent the inner surface 15. The bore of the ring 6 has a diameter closely approximating to the inner diameter of the insulating spool 3 and the effective body of the seal or gasket 6 is wide enough to extend substantially coextensively with the bottom flat end surface 21 of the insulating spool 3. A similar sealing ring 7 is provided adjacent the inner surface 11 of the positive cap 1. This sealing ring has a bore the diameter of which is substantially the same as the outer diameter of the pellet cup 4. The effective body of the sealing ring 7, should be wide enough to extend substantially coextensively with the top flat end surface 20 of the insulating

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spool 3.

The zinc electrode 8 may be used in several forms but in any form used is preferably amalgamated to a considerable degree. It is possible to use a circular zinc plate of appreciable thickness as shown, or a number of parallel thin zinc discs. Where the electrode is made of coherent zinc of the forms just discussed, a somewhat lower degree of amalgamation is preferable since less mercury is necessary to depress the rate of solution of the zinc in the electrolyte. The zinc electrode 8 is, however, preferably made in the form of a zinc wafer, pellet or disc by amalgamating zinc powder and then pressing the amalgamated zinc powder into the form of a pellet under moderate pressure. This produces a pellet having appreciable porosity and increases the ability of the pellet to absorb some electrolyte. The zinc powder should be of relatively high purity and particular care should be taken to see that it is free from metals such as nickel, cobalt, or iron which are passive in an alkaline electrolyte. The amount of mercury required in the amalgamation varies somewhat depending upon the method used in the amalgamation and the ultimate area of the zinc anode which is to be exposed to the electrolyte. By "ultimate area," it will be understood that reference is made not only to the actual external surface area, but to the internal surface area of voids occurring within the pellet. In general, the amount of mercury used depends somewhat on the exact electrolyte used, but in most cases, a suitable zinc pellet is formed from about 5 per cent. to about 15 per cent. of mercury, by weight, with about 95 per cent. to about 85 per cent. of zinc, by weight. Whether a coherent zinc plate or a compressed powdered zinc pellet is used, the electrode 8 is preferably formed in the shape of a thin flat circular disc which has an exterior diameter very slightly less than the diameter of the insulating spool 3.

The electrolyte carrier 9 may be a gelled electrolyte but is preferably a porous wafer which should be formed of a highly porous material capable of absorbing and holding the electrolyte. It must also be capable of acting as a resilient spacing element so as to insure the physical separation of the zinc electrode 8 from the depolariser pellet 5. The wafer 9 should be capable of retaining a high degree of moisture while being expanded or contracted by forces operating within the cell; thus it should not readily lose its absorbed electrolyte when compressed. The porous wafer 9 should be highly resistant to chemical decomposition such as might be caused by an alkaline electrolyte. Ordinary paper and some other forms of cellulosic materials have been tested but have been found to possess a tendency to shrink upon continued exposure to alkaline electrolyte. This shrinkage is probably caused by chemical change rather than purely physical change in the structure of the cellulosic fibres. This tendency may be overcome by employing such materials as finely porous cellulose sponge or pads made of loose absorbent paper composed of cotton fibres. As stated above, the electrolyte can also be in the form of a gel electrolyte. A pre-cast or pre-cut wafer of gel may be used. It is possible to use a film which swells to a gel when the electrolyte is added. It is also possible to combine a gel and a base such as a cellulosic wafer, by using alternate layers of these or by impregnating the wafer with the gel, so as to obtain the advantages of both a gelled electrolyte and porus wafer. There are several suitable gelling agents but sodium carboxymethylcellulose which has already been proposed for this purpose in Patent Specification No. 646,799, has been found to give good results since it is quite stable in the presence of concentrated alkaline electrolyte and an adequate gel can be formed with but small amounts of the compound.

The electrolyte is essentially an aqueous solution of an alkaline hydroxide, such as sodium or potassium hydroxide and preferably the latter. It is satisfactory to employ as the electrolyte, a solution of potassium hydroxide or sodium hydroxide or of a mixture of the two. Certain variations are possible. Thus, solutions of lithium hydroxide or even alkaline earth hydroxides may be employed as the electrolyte but these are not preferred. While the use of the more common potassium or sodium hydroxides alone produce satisfactory results, even better results are obtained by careful control of the concentration of the electrolyte solution of potassium or sodium hydroxide and by modifying it by adding zinc oxide, dissolved in the electrolyte as zincate as has long since been proposed. When the zinc is added to the electrolyte in the form of zinc oxide there is produced a solution of the zincate of the alkali metal, present in the electrolyte as hydroxide. For example, where the electrolyte comprises a solution of potassium hydroxide and zinc oxide is added to the solution, zinc oxide reacts with some of the potassium hydroxide to form potassium zincate in the solution. When

so added, the chemical reaction by which the zincate is formed is reversible. It has been found, contrary, to the prior proposals referred to, that the amount of dissolved zinc oxide required for beneficial results ~~varied~~ inversely with the concentration of the electrolyte. The more concentrated electrolytes require less dissolved zinc oxide and produce an electrolyte which gives rise to a practical minimum rate of gas generation; they are, however, relatively more viscous and less conductive. The less concentrated electrolytes have greater conductivity, are somewhat easier to distribute within the cell and require larger quantities of dissolved zincate. In general, the zinc oxide added to form the zincate in solution is a small fraction of the amount of zinc oxide required to form truly saturated solutions of zincate in the electrolyte. As an example, a suitable electrolyte may be prepared by using 100 parts, by weight, of potassium hydroxide, 100 parts, by weight, of water, and 5 parts, by weight, of zinc oxide. The electrolyte solution is formed by using chemically pure potassium hydroxide, containing 85 per cent or more potassium hydroxide, computed on a dry basis, which is dissolved in sufficient water to form a solution, the desired amount of pure zinc oxide dissolved in this solution, using heat if necessary to insure complete solution of the zinc oxide, and then make-up water added to give the desired relative amounts of water, dissolved potassium hydroxide and dissolved potassium zincate.

The alkaline dry cell, described above, may be assembled in the following way. The cell consists of four components which are the positive sub-assembly 1, 4, 5, 7, the insulating spool 3, the electrolyte carrier 9, and the negative sub-assembly 2, 6, 8.

Starting with the positive sub-assembly, the pellet cup 4 may be spot-welded at 27 (Figure 2) to the positive cap 1 in such a manner that the pellet cup is properly centered on the internal surface of the positive cap 1. Next, the depolariser mix is pressed or formed into a pellet 5 which is preferably of substantially the same dimensions as the interior of the pellet cup 4. The depolariser pellet 5 is moistened during formation, or immediately after it has been pressed within the pellet cup 4 and is then subjected to compression so as to tamp the pellet 5 firmly and solidly in place within the pellet cup 4. As a result of these operations, the outer surface of the depolariser pellet 5 will lie very slightly below the outer edges of the pellet cup 4.

Then, in regard to the negative sub-assembly, the negative cap 2 has placed on its inner face the sealing ring 6, or the inner face of the cap 2 may be coated near its periphery with a sealing compound, so as to provide a seating for one end 21 of the insulating spool 3. When a sealing compound is used, it is desirable to coat the appropriate end surface 21 of the spool 3, in preference to the inner face of the negative cap 2. The insulating spool 3 is then placed on the sealing ring 6 or on the internal surface of the negative cap 2 and the edges of the negative cap 2 are then crimped over the outer flange 18 of the insulating spool 3. The crimping operation should be conducted under pressure so that the annular ends surface 21 of the insulating spool 3 is firmly urged against the internal surface 15 of the negative cap 2 and held tightly in this position during and after the edges of the cap 2 are crimped. Thereafter, the zinc pellet or disc 8 is dropped into the hollow bore of the insulating spool in such a manner that the juxtaposed surfaces of the zinc pellet 8 and the negative cap 2 are in contact. The zinc pellet is lightly tamped on or pressed into place in a manner somewhat similar to the tamping of the depolariser pellet 5 in the depolariser pellet cup 4. Thereafter, the absorbent wafer 9 is dropped into place immediately over the zinc pellet 8 and within the bore of the insulating spool 3. The top, or open end surface 20 of the insulating spool 3 may then be coated with a sealing compound and additionally, or alternatively, a sealing ring is placed within the positive cap 1 in the annular space between the side wall 23 of the depolariser cup 4 and the side wall 10 of the positive cap 1.

With the positive sub-assembly having been prepared as indicated above, and the negative sub-assembly having been prepared with one end of the insulating spool crimped in position within the negative cap 2, the two sub-assemblies appear as shown in Figure 2. The required amount of electrolyte is then measured and poured into the top open end of the bore of the insulating spool 3 in the negative sub-assembly. The measured amount of electrolyte is absorbed by the absorbent wafer 9 and the subjacent zinc pellet 8 in the negative sub-assembly. The positive sub-assembly is then turned over into the position seen in Figure 2 so that its inner face is opposed to the inner face of the negative sub-assembly, the depolariser pellet cup 4 is slid into the bore of the insulating spool 3 and sufficient pressure is exerted so that the open end of the insulating

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spool 3, as yet unsealed, presses firmly against the sealing ring or gasket 7 in the annular space between the pellet cup 4 and the positive cap 1. While being held together under this pressure, the edges of the positive cap 1 are crimped firmly around the upper flange 17 of the insulating spool.

The positive and negative sub-assemblies of the cell are now insulated from each other by the insulating spool 3 yet are each held firmly in position by having the positive cap 1 and negative cap 2 both crimped around the flanges 17, 18 of the insulating spool 3. The marginal end surfaces 20, 21 of the insulating spool 3 are sealed within the caps 1, 2 and to the internal faces of the negative cap and the positive cap respectively. Within the cell, the depolariser pellet 5, held in position within the depolariser pellet cup 4, is in physical contact with the absorbent wafer 9 and the absorbent wafer 9 is in physical contact with the zinc pellet 8. The zinc pellet 8 is in conductive contact with the negative cap 2 and the electrolyte-wet absorbent wafer 9. The depolariser pellet 5 is in electrical contact with the electrolyte-wet absorbent wafer 9 and, through the depolariser pellet cup 4, is in electrical contact with the positive cap 1.

This method of assembly may be modified in certain respects. Thus, in preparing the positive sub-assembly, it has been found that instead of prefabricating a depolariser pellet 5 from the mixture of depolariser compounds and then moistening the preformed pellet, either before or after insertion into the depolariser pellet cup 4, it is possible and in some cases desirable, to measure a desired amount of loose depolariser mix and pour it directly into the pellet cup 4 and then by placing the mix under pressure, consolidate the mix into a pellet 5 formed *in situ* in the depolariser pellet cup 4. When the depolariser pellet is preformed, it is preferable to pre-wet the mix with electrolyte before inserting the pellet 5 into the depolariser pellet cup 4. It has also been found desirable, in some instances, to insert the depolariser pellet 5 into the cup 4 or form the pellet 5 *in situ* within the cup 4, as explained above, before the depolariser pellet cup 4 is welded to the positive cap 1. Thus, the depolariser cup 4 may first be welded to the positive cap 1 and then filled with the depolariser or the depolariser cup 4 may be filled with depolariser and the filled cup then welded to the positive cap 1.

In the negative sub-assembly, certain modifications may be employed. In some instances, the use of a sealing ring or gasket 6 as a seal or sealing for the lower end surface 21 of the insulation spool 3 has been resorted to without any further treatment. In general, however, it is preferred either to augment the sealing ring 6 with a sealing compound or to replace the ring 6 with one or more types of sealing compound. Where a sealing ring is employed, it may be made of natural or synthetic rubber. Certain synthetic compounds having the properties of rubber, such as neoprene (chloroprene) or Buna N or nitrile rubber have been found to give excellent results under severe tests. When the sealing ring 6 is replaced, or supplemented by sealing compound, it has been found that a thin film of material which possesses both resiliency and adhesion may be applied to the end surface 21 of the insulating spool 3. Suitable compounds for this seal may contain water dispersion or latex of either natural or synthetic rubbers. However, other suitable compounds exist and may be applied, either as solutions in suitable organic solvents, or as liquids which have been heated to give the desired ~~velocity~~ viscosity and film-forming properties when hot and which, when cool, will possess the desired sealing properties of resiliency and adhesion. Hot-melt compositions containing plastics, certain of the micro-crystalline waxes and silicones having the properties mentioned above have been found to stand up as sealing compounds successfully under many test conditions.

It is, however, recognised that dry cells may be subjected to use under very rigorous conditions far beyond the normal contemplated conditions. To safeguard against failure under such extreme conditions, it may be desirable to augment a given sealing compound by the application of a second coating of a different nature. This may be applied on both the positive and the negative caps 1, 2 of the cell or may be employed only at the negative end of the cell. As such secondary sealing compound, hydrocarbon, or petroleum hydrocarbon, derivatives, such as petroleum jelly or a lubricating oil may be employed. It is also possible to use, either mixed with, or in place of, such petroleum compounds, a rust-inhibiting compound, such as a barium salt of a sulphonated alicyclic acid. In view of the recognised solvent properties of hydrocarbon oils on natural rubber, where an essentially oily compound is used as a secondary sealing compound, it is advisable either to use for the sealing ring 6, 7 one of the synthetic rubbers, such as chloroprene or nitrile rubber or

Buna N, which have more resistance to oils and greases, or to replace the sealing ring with a hot melt or silicone primary seal.

In the form of construction shown in the drawings, the top and bottom end surfaces 20 and 21 of the insulating spool 3 are flat over their entire areas. Under some circumstances, it is desirable to groove or cut away the peripheral edge of the bottom surface 21, and in some cases the top surface 20 as well. The grooving of the edge, or edges, of the insulating spool 3 provides an annular seating which will accommodate a gasket, or a seating ring, of slightly greater internal diameter than the ring shown at 6 in Figure 1. The advantage of this modification is that the gasket or sealing ring has a vertical seating as well as a horizontal seating against the insulating spool 3.

In preparing the depolariser pellet 5, finely divided manganese dioxide and finely divided graphite are the preferred materials. Where the symbol MnO_2 is used in this specification, they will be understood to mean a product which largely consists of the dioxide of manganese as such but which neither consists exclusively of the chemically pure dioxide (100% MnO_2) nor contains any significant amounts of oxides of manganese in chemical combination with the oxides of other metals in the form of permanganates. The relative proportions of graphite to MnO_2 may vary within certain ranges, depending upon the use for which the cell is designed and depending also upon the source, purity and physical properties of the several depolariser materials. Thus an amount of from about 2 parts to about 50 parts, by weight, of MnO_2 may be employed for each part, by weight, of graphite. However, a narrower range of between about 6 parts to about 30 parts of MnO_2 for each part of graphite, on the same weight basis, is preferred.

In general, the selection of MnO_2 from a particular source will be largely governed by the use for which a given cell is designed and by its ability to mix with graphite and other depolariser materials such as other forms of carbon and certain inactive metals in forming a mass which is sufficiently strong to withstand the handling required in assembling the cell. After considerable trials it has been found that MnO_2 from some natural ores as well as some forms of artificially prepared MnO_2 may be used. The kind and quantity of graphite employed may also be varied if the considerations governing the selection of NnO_2 are likewise observed. The graphite may, for some purposes, be replaced wholly or in part by certain types of conductive carbon blacks and may also be partially replaced by finely divided or powdered inactive metals, such as iron and nickel.

For some purposes it has been found desirable to add mercuric oxide, HgO, to the depolariser mix, to replace a portion of the MnO_2. For certain extreme uses, as much as 75 per cent of the MnO_2 may be replaced by HgO but smaller amounts are preferred. It has been found that where HgO is used in the mix it should replace not less than about 25 per cent, and not more than about 65 per cent of the MnO_2.

The preferred ratio of materials in the depolariser-cathode mix may be expressed as follows (all figures being parts by weight):

A. From 1 part of graphite mixed with about 6 parts of MnO_2 to 1 part of graphite with about 30 parts of MnO_2; or B from 1 part of graphite mixed with about 6 parts of a mixture of between 1 to 3 parts of MnO_2 and 3 to 1 parts of HgO to 1 part of graphite with about 30 parts of a mixture of between 1 to 3 parts of MnO_2 and 3 to 1 parts of HgO. It should be understood that the graphite in the tables may be replaced by conductive carbon black and may partially be replaced by inactive metals. However, the presence of copper or its oxides should be avoided.

In all of the depolariser mixes referred to above, the materials to be mixed should be of small particle size. For the graphite, an average particle size of between about 5μ and about 10μ has been found most satisfactory. For the MnO_2, an average particle size of between 5μ and about 10μ has given satisfactory results with indications that somewhat better results are obtained with average particle sizes of 10μ and slightly higher, even up to 25μ. This may be illustrated somewhat differently by saying that finely divided MnO_2, 98 per cent of which passes through a 200 mesh screen and 85 per cent of which passes through a 300 mesh screen is of a satisfactory average particle size.

In preparing the depolariser pellets from the above materials, the selected materials should first be mixed very intimately to form a homogeneous mass. One method of effecting this is to feed the selected proportions of dry powdered MnO_2 and powdered graphite into a double cone type of mixer and therein forming a homogeneous powder. The mixing should be thoroughly performed

since materials of substantially different densities are being treated. When thoroughly mixed, the homogeneous powder is then preferably condensed. This may be accomplished either by moistening the powder slightly or by omitting any moistening, and pressing the powder into large pellets or slugs. Fairly high pressures, such as may be obtained in a tabletting machine or by a hydraulic press should be employed in forming the slugs. The slugs are then ground up to form small granules, which nevertheless are are more free-flowing and dense than the initial powders. The steps of forming slugs and re-grinding the slugs to form dense powders may be repeated as often as may seem desirable to produce a homogeneous, compacted mix.

The homogeneous, compacted mix may either be charged as such into a pellet cup and tabletted in it *in situ*, or may be compressed into preformed depolarizer pellets. Preformed pellets may be made on a tabletting machine employing pressures of between about 20,000 to about 30,000 pounds per square inch. When so formed, the completed pellet should be dense enough to withstand considerable handling so that it may be inserted into a pellet cup without breaking or marginal chipping. In fact, it is desirable, after the preformed pellet has been inserted into the pellet cup, to subject the inserted pellet to further compression under pressures of slightly above about 20,000 to about 30,000 pounds per square inch. This further compression may be under steady pressure or by impact. This step not only serves to compact the pellet within the cup, but also serves to smooth and flatten the exposed face of the pellet and depress the exposed face below the marginal lips of the wall of the pellet cup. Where the powdered compacted mix is charged into the pellet cup, the pellet may be formed *in situ* by compacting under steady or impact pressures of slightly higher magnitude than the pressures used in the preforming pellets.

Mention has been made above of moistening the depolarizer mix. This treatment, which may be termed "pre-wetting," may be effected in certain different manners. It is preferable to use, as the pre-wetting liquid, a solution which is similar to the cell electrolyte in nature and concentration. An excellent pre-wetting liquid is the selected electrolyte. For some purposes, a solution of approximately the same concentration of the same alkali metal hydroxide as used in the electrolyte, but without any zinc oxide, as zincate, dissolved in it is preferred. However, the concentration of the pre-wetting liquid need not be the same as the concentration of the electrolyte. For instance, where the electrolyte solution, containing zincate, has a concentration of 43 per cent KOH on the dry weight basis, a pre-wetting solution of KOH, without zincate, of 30 per cent to 25 per cent on the dry weight basis, or even lower, is very satisfactory.

It will be understood that the amount and concentration of the pre-wetting liquid added to the depolariser mix should be very carefully controlled so that the aggregate amount and average concentration of the combined pre-wetting solution and subsequently added electrolyte will be properly adjusted.

The zinc wafer or disc may, as explained above, be formed of one or more thin circular sheets of coherent zinc or be formed of pelleted zinc powder. In either case, the zinc should be amalgamated. Where zinc powder is pelleted, the powder should be amalgamated before pelletting for best results. The amalgamation of zinc powder has been known for many years and may be carried out in a variety of manners all well known. As an illustration, in one such method, the pure zinc powder is dropped into an aqueous solution containing mercuric nitrate, slightly acidified with nitric acid and permitted to remain until most of the mercury has been combined with the zinc powder. The amalgamated zinc powder is then washed thoroughly in water until entirely free from nitrate; the wash water is then filtered off and the washed amalgamated zinc powder is then dried, by vacuum drying, to remove the last traces of water and minimize danger of oxidation. The amalgamated zinc powder, so prepared, is then pressed into porous pellets in a tabletting machine or the like. It is preferred to use tabletting pressures of the order of 5,000 pounds per square inch, which pressure is sufficient to compact the amalgamated zinc particles to the desired limited degree. This results in the establishment and maintenance of appreciable interior voids within the pellet and the avoidance of undue compacting.

The preformed zinc pellet is formed as a relatively thin circular wafer or disc proportioned to fit within the interior bore of the insulating spool 3. It has been found that the pellets may more readily be inserted within the insulating spool 3, if during the pellet-forming operation, the peripheral edges of the pellet are compacted under somewhat greater pressure than the major surfaces of the pellet. This edge-compacting provides a

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denser, stronger rim. The zinc electrode may also be formed *in situ* by pouring the desired measured amount of amalgamated zinc powder into the bore of the insulating spool 3 and compressing the powder into a pellet in it. It will be understood that such an operation is performed after the negative cap 2 has been crimped around the negative end of the insulating spool 3.

After the zinc pellet has been placed in position, or formed *in situ* in the negative sub-assembly, it is desirable to pour a measured few drops of electrolyte on to the zinc pellet to pre-wet the pellet.

The characteristics and size of the porous wafer 9 are of considerable importance. The wafer should preferably be shaped in the form of a disc having a diameter just slightly larger than the interior bore of the insulating spool 3. Its height or thickness should be slightly greater than the distance between the otherwise opposed interior surfaces of the depolariser pellet 5 and the zinc pellet 8 when the cell is in the completely assembled condition (Figure 3). When so dimensioned, the wafer 9 will be slightly compressed in the final assembly of the cell and will completely fill the space formed between the inner exposed surfaces of depolariser pellet 5, zinc pellet 8, insulating spool side wall 16, and marginal rim of the pellet cup 4. It should be understood that the foregoing dimensional requirements for the porous wafer should be satised both when the wafer is dry and when wetted with electrolyte.

The wafer 9 should moreover be formed of material which has certain definite related properties. It should be capable of absorbing, and holding absorbed, considerable quantities of liquid. However, it should not expand unduly when wet with liquid and, conversely, it should not contract unduly when deprived of absorbed liquid. It is important for it to be capable of exhibiting these properties in the prolonged presence of the alkaline electrolyte solution; therefore, it must not be attacked by alkali metal hydroxide solutions of varying concentrations nor by the reactants, or products of any chemical reaction which may occur within the cell. Certain essentially cellulosic materials possess the required properties as shown by many tests. One such material is that commonly known as cellulose sponge producer by E. I. du Pont de Nemours and Company. One difficulty with this material is the lack of ease with which it may be cut into discs of the required small size. Another satisfactory product is an alkali resistant matted paper produced under the trade-name "Webril."

As indicated above, the electrolyte may be gelled and discs or wafers of the gel used either in place of, or in conjunction with, a cellulosic porous wafer. The two cellulosic materials which have been given as illustrations just above, have been found satisfactory without the use of a gelled electrolyte.

The amount and concentration of the electrolyte are also factors of considerable importance. From a broad viewpoint, the electrolyte is primarily a solution of an alkali metal hydroxide in water. The more common sodium hydroxide and potassium hydroxide may be used with practically equal facility, but of the two, potassium hydroxide is preferred in spite of its relatively higher cost because of its relatively greater conductivity. The aspect of cost tends to discourage the use of the other less common alkali metal hydroxide, such as those of lithium or caesium, but such hydroxides are satisfactory in performance and may be used. The concentration of the hydroxide, as determined on a dry weight basis, in a given solution, may vary within a considerable range. Concentrations of between about 20 per cent KOH to about 75 per cent KOH may be employed. In general, somewhat better conductivity is experienced at lower concentrations. A preferred concentration is about 45 per cent KOH, or within a narrower range of 30 per cent to 50 per cent KOH.

It has been found that the performance of the cell under a wide variety of conditions is greatly improved by adding to the alkaline hydroxide solution small amounts of zinc oxide to form, in solution, a mixture of the alkali metal hydroxide and the corresponding alkali metal zincate. The literature on this subject is not altogether clear in regard to the amounts of zinc oxide required to saturate given solutions of alkali metal hydroxide. As the result of numerous tests, it is now believed that a solution consisting of 100 parts of water and 100 parts of potassium hydroxide (dry weight basis) can dissolve considerably more than 20 parts, by weight, of zinc oxide without forming a super-saturated solution or one which will precipitate the zinc salts. In other words, in such a solution, 20 parts by weight of added zinc oxide do not completely saturate what is initially a 50 per cent potassium hydroxide solution. According to the present invention, zinc oxide is added to the potassium hydroxide (or other alkali metal hydroxide) solution, in amounts which are far less than those required to

saturate the solution with potassium zincate. In general, it is preferred to use, as the electrolyte solution, an alkali metal hydroxide solution which contains in solution between about 2 parts by weight and about 10 parts by weight of dissolved zinc oxide for each 100 parts of alkali metal hydroxide originally present. Such solutions, with potassium hydroxide as an example, may be prepared by dissolving in a small amount of water sufficient chemically pure potassium hydroxide pellets (which may contain 88 per cent KOH on a dry weight basis, and about 12 per cent water and minor impurities), dissolving zinc oxide therein and then adding enough water to adjust the concentration of potassium hydroxide solution to the desired figure.

By way of example, a small amount of water, say 50 grams, is added to 114 grams of 88 per cent chemically pure KOH pellets. This mixture will consist of 100 grams of KOH (dry weight) and 50 plus 14, or 64 grams of water. The mixture is heated to 150° C., at which temperature, all of the KOH will have quickly gone into solution. To this solution, at this temperature, are added 5.57 grams of ZnO, which dissolves rapidly. This solution is then cooled to about 90° C. and 36 grams of water are added to make the desired final electrolyte solution. This final solution will contain 101.22 grams of water having dissolved therein, as such, 92.33 grams of KOH and 12 grams of K_2ZnO_2, each on a dry weight basis. The final solution will contain 48 per cent of KOH and 10.6 per cent of K_2ZnO_2, based on the water and each salt separately computed. The weight ratio of KOH to K_2ZnO_2 in the solution is 92.33 to 12 or approximately 8 to 1. The foregoing is clear from the equation:

$$2\,KOH + ZnO \rightarrow K_2ZnO_2 + H_2O$$

$$112 + 81.4 \rightarrow 175.4 + 18$$

In compliance with this equation, the added 5.57 grams of ZnO consumes 7.67 grams of KOH and produces 1.22 grams of water while forming 12 grams of K_2ZnO_2. The original 100 grams of KOH in the solution is reduced by 7.67 grams leaving 92.33 grams of free, uncombined, dissolved KOH. The original 100 grams of H_2O in the solution is increased by 1.22 grams, leaving 101.22 grams of H_2O in the solution.

If a solution of 100 grams of KOH in 100 grams of H_2O is similarly prepared, but with the addition of 2 grams of ZnO, the final solution will contain 100.44 grams of H_2O, 97.25 grams of KOH as such, and 4.31 grams of K_2ZnO_2 as such, in solution. The concentration of uncombined, dissolved KOH is 49.3% and the concentration of K_2ZnO_2 is 4.12%. The weight ratio of KOH to K_2ZnO_2 in this solution is 22.5 to 1. In general, KOH to K_2ZnO_2 weight ratios of from about 3.5 to 1 to about 10 to 1 are preferred, although ratios of from about 3.1 to 1 to about 25 to 1 may be employed.

As stated above, the amount of zincate which is required to saturate any given potassium hydroxide solution is not fully established in the literature. It is possible that the reason for this lies in the failure of earlier workers to mention the temperatures at which the given solutions were formed or subsequently maintained. Additionally, the earlier workers seem to have ignored the chemical fact that the formation of potassium zincate by the addition of zinc oxides uses up some of the potassium hydroxide in the solution and liberates water thereby modifying the actual potassium hydroxide concentration in the final solution. To avoid any ambiguity, the recommended electrolyte solution in this specification is to be understood as consisting of the three components—water, potassium hydroxide and potassium zincate, each computed as such and existing as such in the ultimate solution. The presence of potassium zincate in the potassium hydroxide electrolyte is intended to reduce attack on the zinc anode and to keep gassing within the cell to a practical minimum. The foregoing considerations are partially achieved by increasing the concentration of potassium hydroxide in the electrolyte solution but are augmented by the presence of dissolved zincate. In general, the amount of dissolved zinc oxide present as zincate and required for optimum results varies inversely with the concentration of the electrolyte. Thus, the more concentrated electrolytes require less dissolved zinc, present as zincate, while the less concentrated electrolytes require appreciably more dissolved zincate. In any event, the amount of zincate provided for in the electrolyte used in accordance with the present invention is very much less than 50 per cent of the amount of zincate required to saturate the given electrolyte solution.

In an example of the cell as shown in the drawings, the positive and negative caps 1 and 2 have, when crimped, a width of ½ inch. Referring to Figure 3 of the drawings, the assembled cell, from the top of the positive cap 1 to the bottom of the negative cap 2, has a thickness of

approximately $\frac{1}{4}$ inch. The bore of the insulating spool 3 has a diameter of approximately $\frac{3}{8}$ of an inch. The pellet cup 4 has a depth of slightly less than $\frac{1}{8}$ of an inch. From these dimensions, it will be seen that the complete cell is quite small and that the zinc pellet 8 and porous wafer 9 are quite thin. Within a cell of the dimensions given above, a total of .22 grams of electrolyte solution may be utilised. In pre-wetting the depolarizer pellet 5, it is preferred to use .06 grams of electrolyte solution. Thus in assembling the cell, .06 grams of electrolyte are added as pre-wetting liquid in the depolarizer pellet 5, also a drop or two, barely measurable in amount, may be added in pre-wetting the zinc pellet 8. The remainder consisting of approximately .16 grams of electrolyte, is poured onto the porous spacer 9 immediately before the final assembly of the cell. It has been found that when the electrolyte is added in such increments to the depolariser pellet 5 and to the zinc pellet 8, the porous wafer 9 tends to retain the optimum amount of absorbed electrolyte. In other words, the essentially porous zinc pellet 8 and the considerably less porous depolariser pellet 5 do not absorb electrolyte thereby leaving the porous wafer 9 impoverished with respect to absorbed electrolyte. Reference has been made above to the desired property of the porous wafer of retaining absorbed electrolyte without shrinking even during prolonged exposure to a relatively concentrated potassium hydroxide solution. It may be stated more specifically, that the porous wafer 9 should retain, for best results, a minimum of 0.14 grams of electrolyte for a cell of the dimensions given above.

In describing the improved cell, certain variables and equivalents have been mentioned from time to time for several of the elements of the cell. For the sake of illustration, a preferred completed cell may consist of a plain steel positive cap 1, a tin-plated steel negative cap 2, an insulating spool 3 of a methyl methacrylate plastic, such as Lucite, a plain steel pellet cup 4, and a pelleted, amalgamated zinc powder electrode 8. The depolariser pellet 5 may consist of 1 part graphite to 20 parts of MnO_2 and 10 parts of HgO each by weight, pelleted as described above and pre-wetted with a small amount of electrolyte. The porous wafer 9 is of "Webril" resistant paper and the electrolyte has a final concentration of 48 per cent of KOH and a final concentration of 10.6 per cent of K_2ZnO_2; the latter two dissolved components being present in a weight ratio of 8 to 1. The primary seal 6, 7 at each end of the cell is a neoprene washer and the secondary seal 6, 7 is a thin coating of petroleum jelly applied to each end of the insulating spool 3 just prior to applying the end caps 1, 2.

In this typical cell, a modified method of forming the electrolyte solution is desirably employed. The pure zinc oxide powder is moistened with sufficient (measured amount) water to form a pasty suspension. The measured amount of pure solid KOH (pellets of known purity and water content) is added to the zinc oxide paste. The mixture is then heated to about 150° C. at which temperature both solids readily dissolved in the water present, attended, of course, by the desired chemical reaction between the zinc oxide and part of the KOH. The clear solution is cooled to about 90° C. and sufficient make-up water is added to give the desired concentration. The solution is then filtered to remove any solid impurities such as dust particles and cooled to room temperature.

The cell system used in the cells described above may be written as $Zn/KOH/MnO_2$. The voltage of cells with this system is about 1.52 when new, and decreases in a few weeks at room temperature to a stable value of about 1.48 volts. The voltage varies slightly with the type of manganese dioxide used and also with the ratio used in the depolarising mix. Higher proportions of manganese dioxide give cells of slightly higher voltages.

At the zinc electrode, the zinc is converted during discharge into a soft paste of ZnO or zinc hydrates. Although the electrolyte is far from saturated with zincate, the rate of solution of the ZnO is so slow at room temperature that very little dissolves to form the zincate. The colour and form of the ZnO varies considerably with the rate of discharge. At relatively high discharge rates, the ZnO is medium to dark blue and is quite firm. At relatively low discharge rates, the ZnO is in the form of a soft light blue paste.

The depolariser is used mainly according to the equation:—

$$2MnO_2 \rightarrow Mn_2O_3 + 2F$$

Where F represents one Faraday and thus 2F represents the liberation of one atom of divalent nascent oxygen. During use, the depolariser changes from a black to a brown colour, the degree of brownness roughly indicating the extent to which the cell has been discharged. The above conversion takes place at a rela-

tively high efficiency of about 90 to 100 per cent at moderate rates of discharge and to the lower end points such as .90 and .80 volts per cell. At very low rates of discharge and to low end points, the depolariser becomes a yellow-red colour, probably due to the formation of some manganese oxides lower than Mn_2O_3. During discharge, the depolariser gradually absorbs electrolyte from the absorbent layer and expands considerably in height, the amount of expansion being a very good indication of the extent to which the cell has been used. At the same time, a very hard crust is formed on the surface of the depolariser.

Both the total amount of electrolyte and the ratio of electrolyte to absorbent are very important in these cells in order to obtain the highest capacity and greatest efficiency. It is usually desirable to use an absorbent which will give a high ratio of absorbed electrolyte to absorbent, since the cells are usually made with the total amount of electrolyte near the lower critical limit to avoid excessive migration of electrolyte within the cell. Because of this factor, it is desirable to have some electrolyte initially in the depolariser pellet 5 thereby increasing the total amount of electrolyte and also improving the capacity of the cell when subjected to relatively heavy discharge currents. During discharge, the electrolyte from the carrier 9 is absorbed by both the zinc 8 and depolariser 5, mostly by the latter. During use, the absorbent carrier 9 continually becomes drier and is compressed more by the expansion of both of the depolariser 5 and the conversion of Zn to ZnO at the zinc electrode. At the end of the useful life of the cell, the absorbent carrier 9 is almost completely dry. The latter is a very important effect since no leakage can occur after discharge, and such cells then really become capable of leaking. This is the direct opposite effect to that sometimes occurring in Leclanche dry cells which tend to leak after discharge has been completed.

Cells made as described above have very high capacity per unit volume. In fact, this factor is about 2 or 3 times that of Leclanche dry cells of the same size, the ratio depending slightly upon the magnitude of the discharge current. The discharge curve is about the same as for the Leclanche dry cell, but is slightly flatter in the middle portion. Because of the high efficiency in the conversion of the MnO_2 into Mn_2O_3, the capacity of cells can be readily calculated from the ampere-hour rating which depends directly on the amount of depolariser and zinc. The efficiency usually decreases slightly as the discharge current is increased within the normal range suitable for a cell of a particular size. A cell of about $\frac{1}{2}$ inch in diameter and slightly less than $\frac{1}{4}$ inch high has a capacity of about 150 milliampere-hours at discharge rates of 2 milliamperes or less. Because the terminals are at opposite ends, such cells are admirably suited for making high tension batteries for electron discharge tubes by simply stacking one on the other. This method of cell assembly is easy and provides a cheap battery construction.

During discharge, there is a slight increase in the external height of the cell. However, most of the considerably greater expansion of the depolariser 5 and of the conversion of zinc to ZnO at the electrode 8 is taken up by compression of the absorbent carrier 9. This effect has a definite advantage since the internal pressure within the cell increases during discharge, thus insuring good contacts, and the reduced thickness of the absorbent carrier 9 keeps the internal resistance low, even when the electrolyte is being absorbed from the carrier 9 by the anode and cathode. A slight external expansion is also advantageous since it helps to maintain good contacts between the cells in batteries consisting of stacks of the cells.

The most desirable depolariser ratio depends considerably on the discharge current for which the cells are to be used. The capacity of the cells also depends considerably on the packing factors of the various ratios of depolarising mix. In order to insure complete use of the depolariser, an excess of zinc in the electrode 8 is used, this excess usually being about 20 to 30 per cent. The exposed area of the zinc electrode 8 also has an important effect on the permissible discharge current from the cells. For most applications, a highly porous zinc pellet is preferred for the electrode 8 since it has a relatively large surface area and also holds some electrolyte. For very light discharge currents, a flat zinc plate or a series of such plates is quite satisfactory.

Small cells made as described above are very suitable for use in high tension batteries for the electron discharge tubes in hearing aids, pocket and small portable radio receivers. Larger cells may be used as low tension batteries for hearing aids and pocket radio receivers and also in high tension batteries for larger portable radio receivers. There are also many military uses for this type of cell since such cells have a high efficiency at relatively high rates of discharge and are

small in volume and of light weight. In many other applications, these cells will give about twice the capacity of the ordinary Leclanche dry cells for the same volume, or batteries of about the same capacity can be made which are about one-half the size of the usual dry cell batteries.

What we claim is:—

1. An electric alkaline dry cell comprising a pair of conductive metal caps, the side walls of each of which are secured around opposite ends of a tubular insulating spool having imperforate side walls, the said metal caps having flat exterior end surfaces and forming, respectively, symmetrical positive and negative terminals for the cell insulated from each other and disposed at opposite ends of the cell.

2. An electric alkaline dry cell according to claim 1, in which the metal caps are secured in position by crimping them around flanges at opposite ends of the insulating spool.

3. An alkaline dry cell according to claim 1, in which an amalgamated zinc electrode is disposed within the hollow bore of the insulating spool, and in physical contact with the inner face of the negative metal terminal cap.

4. An alkaline dry cell according to claim 1, in which a compressed, depolariser mass is disposed within the hollow bore of the insulating spool, adjacent to and in conductive contact with the inner face of the positive metal terminal cap.

5. An alkaline dry cell according to claims 3 and 4, in which an electrolyte-immobilising wafer is disposed, under compression, within the hollow bore of the insulating spool between the zinc electrode and the depolariser mass.

6. An alkaline dry cell according to claim 1, in which a compressed depolariser mass is located within a metal cup, the base of which is fixed substantially centrally to the inner surface of the positive metal cap in physical and conductive contact with it, and the side walls of which are located within the hollow bore of the insulating spool.

7. A flat, essentially symmetrical electric alkaline dry cell comprising a dish-shaped positive metal cap, an opposed dish-shaped negative metal cap, said caps being placed at the opposite ends of a tubular insulating spool having peripheral flanges at both ends and having imperforate side walls, the caps being crimped over and under the respective flanges of the spool, a metal cup having its base fixed substantially centrally to the inner face of the positive cap and its side walls extending into and fitting the hollow bore of the spool, a compressed depolariser pellet located within the metal cup, a compressed amalgamated zinc electrode, an electrolyte-immobilising wafer disposed under compression between the zinc electrode and the exposed face of the depolariser pellet, the zinc electrode, wafer and pellet all being located within the hollow bore of the spool.

8. An alkaline dry cell according to claim 7, in which the ends of the insulat- spool are sealed against the inner surfaces of the positive and negative caps respectively.

9. An alkaline dry cell according to claim 7, in which the zinc electrode is a compressed disc of amalgamated zinc particles.

10. An alkaline dry cell according to claim 7, in which the depolariser pellet comprises a compressed homogeneous mixture containing a minor amount of graphite and a major amount of manganese dioxide or a mixture of manganese dioxide and mercuric oxide.

11. An alkaline dry cell according to claim 7, in which the electrolyte-immobilising wafer is a disc of essentially cellulosic fibres, having properties of high retentiveness of moisture, resistance to shrinkage when exposed to strong alkaline solutions and limited expansion where wetted.

12. An alkaline dry cell according to claim 1, in which a compressed, homogeneous mass of fine particles of a depolariser mix is supported within an open-end metal cup, the base of which is fixed to the interior surface of the positive cell terminal and in which the exposed face of the compressed mass is disposed within the marginal rim of the side walls of the cup.

13. An alkaline dry cell according to claim 12, in which the homogeneous mass of fine particles of depolariser mix is moistened with an alkaline aqueous solution and then compressed within the cup.

14. An alkaline dry cell according to any one of the preceding claims, in which a homogeneous, compressed depolariser mass is provided which comprises a mixture of graphite having an average particle size not greatly exceeding 10μ and a metallic oxide compound consisting of manganese dioxide or a mixture of manganese dioxide and mercuric oxide and having an average particle size not greatly exceeding 25μ, the graphite being present in an amount of one part by weight to between about 2 parts and 50 parts by weight of the metallic oxide present.

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15. An alkaline dry cell according to claim 14, in which a mixture of manganese dioxide and mercuric oxide is provided and contains mercuric oxide and manganese dioxide in the proportions, by weight, between about one part of mercuric oxide to about three parts of manganese dioxide and about three parts of mercuric oxide to about one part of manganese dioxide.

16. An alkaline dry cell according to any one of the preceding claims, in which an amalgamated zinc electrode is provided and a depolariser containing graphite and manganese dioxide, and an electrolyte comprising a solution of alkali metal hydroxide in water, said hydroxide being initially present in an amount between about 20 per cent, by weight, and about 75 per cent, by weight, of the water present, and said solution containing dissolved alkali metal zincate and dissolved unreacted alkali metal hydroxide in proportions by weight which fall between the ratios of from about 3.1 parts to about 25 parts of alkali metal hydroxide for each part of alkali metal zincate.

17. An alkaline dry cell according to claim 16, in which the alkali metal hydroxide is potassium hydroxide.

18. An alkaline dry cell according to claim 1, in which a rubber-like sealing element, resistant to electrolyte, is compressed between at least one of the metal caps and the corresponding end surface of the insulating spool.

19. An alkaline dry cell according to claim 18, in which the sealing element is formed of a synthetic rubber.

20. An alkaline dry cell according to claim 18, in which the sealing element is formed of chloroprene.

21. An alkaline dry cell according to claim 18, in which the sealing element is formed by applying natural or synthetic rubber in a liquid form to an end surface of the insulating spool and allowed to dry before being compressed by the metal cap.

22. An alkaline dry cell according to claim 18, in which the sealing element is initially caused to adhere to one of the sealed surfaces before being compressed by the other sealed surface.

23. An electric alkaline dry cell according to claim 7, having its components formed and assembled, substantially as described with reference to the accompanying drawings.

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