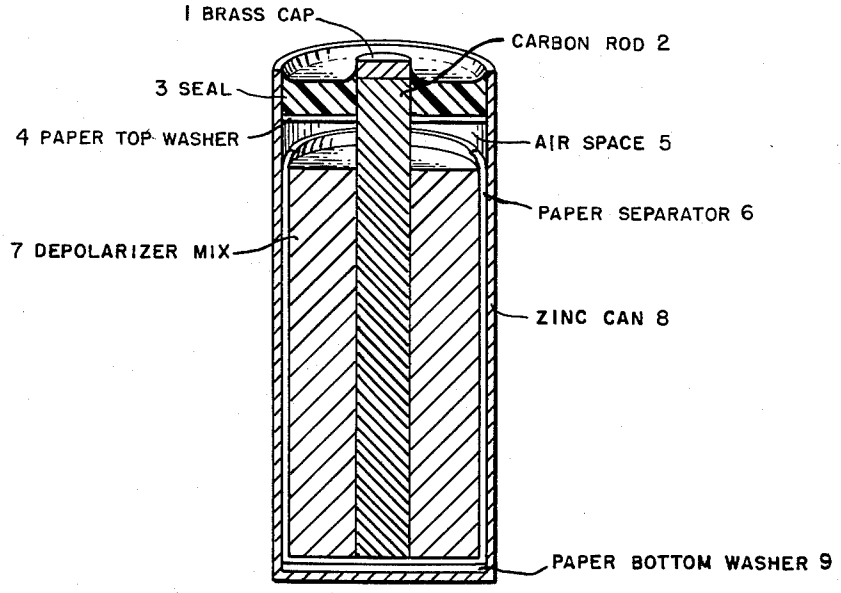
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LECLANCHÉ TYPE DRY CELLS OF HIGH STORAGEABILITY

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LECLANCHÉ TYPE DRY CELLS OF HIGH STORAGEABILITY

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The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

This invention relates to Leclanché type dry cells having greatly improved storageability at elevated temperatures.

The reaction occurring at the zinc anode in Leclanché dry cells are of two types. The first is the discharge reaction which furnishes the desired electrical energy without liberation of hydrogen; it may be summarized in the equation

$$Zn+2MnO_2 \rightarrow ZnO.Mn_2O_3$$

This reaction does not occur on open circuit and is therefore not the cause of deterioration during storage.

The second reaction is the result of adjacent anodic and cathodic areas on the zinc leading to local corroding action and liberation of hydrogen gas. At the anodic areas the reaction is

$$Zn \rightarrow Zn^{++}+2e$$

and at the cathodic areas

$$Zn^{++}+2NH_4Cl+2e \rightarrow Zn(NH_3)_2Cl_2+H_2$$

Thus the reactions which occur on open circuit during storage lead to the development of hydrogen gas, represent waste energy and result in deterioration and leakage of the cell.

It has been known for more than 100 years that the corroding reactions at the zinc may be reduced by amalgamating the surface of the zinc electrode, e.g. with the help of mercuric chloride (Hg_2Cl_2). However, the beneficial effect of amalgamation is materially decreased when the cells are exposed to higher temperatures. Above 130° F. the effect of amalgamation is almost negligible since at that temperature the pace of the corroding reactions is greatly increased. Since at higher temperatures the hydrogen gas is forming at a higher rate the pressure within the cell builds up and increases the leakage tendency.

It has also been known that chromates, for instance, ammonium chromate are useful in Leclanché type dry cells as corrosion inhibitor and that at higher temperatures the results with chromates are better than those achieved with the conventional mercuric chloride. Wether these chromates form a film on the surface of the zinc is questionable but actual tests have shown that a substantial increase in storageability is achieved if ammonium chromate is added to the cell in amounts of ½ to 1½% by weight of the electrolyte, but by using these amounts the leakage tendency at higher temperatures is not at all decreased. If, however, higher amounts of ammonium chromate such as from 2 to 4% are used the cell shows even at higher temperatures no leakage but the zinc appears to be passivated; the capacity of the cell is reduced to less than one half of its initial capacity.

I now have found that leakproof Leclanché type dry cells having greatly improved storageability and full capacity even at elevated temperatures may be obtained by using chromate inhibitors in amounts of 1½ to 2½% by weight of the electrolyte, if at the same time excessive amounts of ammonium chloride are used in the dry mix. The conventional dry mix contains up to about

12% of ammonium chloride. I have found however that in order to be effective in combination with chromate inhibitors the amount of ammonium chloride in the dry mix has to be increased to between 20 to 30% by weight of the dry mix.

It has been assumed in the art that the decreased capacity of the Leclanché type cells containg 2 to 4% of ammonium chromate is caused by a chromate film that is forming on the zinc and becomes so thick that the zinc is passivated. I have found, however, that the cell appears to dry out at the separator and that this drying out causes the initial delay in voltage during discharge. However, on continued discharge the voltage comes up which means that moisture is being produced which probably occurs according to the reaction

$$2NH_4^+ \rightarrow 2NH_3+H_2$$

whereupon the hydrogen gas thus developed is being oxidized by the manganese dioxide to form water. This reaction may be the explanation of the fact that the use of excessive amounts of ammonium chloride in the dry mix leads to a substantial increase in storageability without decreasing the capacity of the dry cell, because additional water is being formed on discharge.

The invention will be described in more detail with the help of a specific embodiment shown in the accompanying drawing which shows in elevational cross-section a Leclanché type dry cell made according to the present invention.

The battery shown in the drawing consists of a zinc can **8** having a paper bottom washer **9** and a paper separator **6** consisting of untreated kraft paper. The depolarizer is made by mixing together in a dry state in a ball mill at a speed of 72 r.p.m. for 15 to 30 minutes, a mixture of manganese oxide, carbon black and ammonium chloride. Conventionally, the amount of ammonium chloride does not exceed 12% by weight of the depolarizer mix which amount is sufficient to bind the manganese oxide and the carbon black. According to the invention, however, the mix contains between 20 and 30% of ammonium chloride by weight of the depolarizer mix.

The resulting mix is then wetted by adding the liquid electrolyte. According to the invention the electrolyte is made by dissolving about 26% ammonium chloride, 22% zinc chloride and 1½ to 2½% of ammonium chromate in 49½ to 50½% of water. This solution is stirred at room temperature until all the salts are dissolved and then filtered to take out a slight amount of insoluble substances. The filtered solution is used to wet the depolarizer mix. Wetness may vary from 35 ml. per 100 gms. of mix to 55 ml. per 100 grams of mix depending upon the type of manganese dioxide and its granular size. The wet depolarizer mix is then extruded thru a properly sized die and sheared by a shearing device to the proper length forming a cylindrical slug.

The mix slug **7** is then inserted into the paperlined zinc can **8** and consolidated under pressure to assure tightness to the can wall and complete wetting of the paper separator **6**. The carbon rod **2** is inserted into the mix slug **7** while the latter is under the consolidation pressure. The paper top washer **4** is then set in place leaving an adequate air space **5**, the carbon rod **2** is capped with a brass cap **1** and the top washer **4** is then covered with the sealing compound **3**.

Instead of ammonium chromate, equimolecular amounts of other chromates such as the chromates of potassium, lithium, sodium, calcium and magnesium, or mixtures of these compounds may also be used.

Batteries made according to this invention show unexpectedly high capacity retention (more than 50%) after two weeks of storage at 160° F., after three months at 130° F. and after 12 months at 113° F.

It will be obvious to those skilled in the art that various changes and variations may be resorted to in the making of the cells according to the invention without departing from its scope as defined in the following claims.

What is claimed is:

1. In a Leclanché type dry cell comprising a zinc can, a depolarizer mix consisting essentially of manganese dioxide, carbon black and ammonium chloride, and an electrolyte consisting essentially of an aqueous solution of ammonium chloride and zinc chloride, characterized in that said depolarizer mix contains about 20 to 30% by weight of ammonium chloride while the electrolyte contains about 25% by weight of ammonium chloride and about 1½ to 2½% of a compound selected from the group consisting of ammonium chromate, potassium chromate, lithium chromate, sodium chromate, calcium chromate and magnesium chromate.

2. In a Leclanché type dry cell according to claim 1 in which the chromate consists of ammonium chromate.

3. In a Leclanché type dry cell according to claim 1 in which said chromate consists of potassium chromate.

4. In a Leclanché type dry cell according to claim 1 in which said chromate consists of sodium chromate.

5. In a Leclanché type dry cell according to claim 1 in which dry depolarizer mix contains about 22% by weight of ammonium chloride.

6. In a Leclanché type dry cell according to claim 1 in which the electrolyte contains about 2% by weight of ammonium chromate and the dry depolarizer mix contains about 22% by weight of ammonium chloride.

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