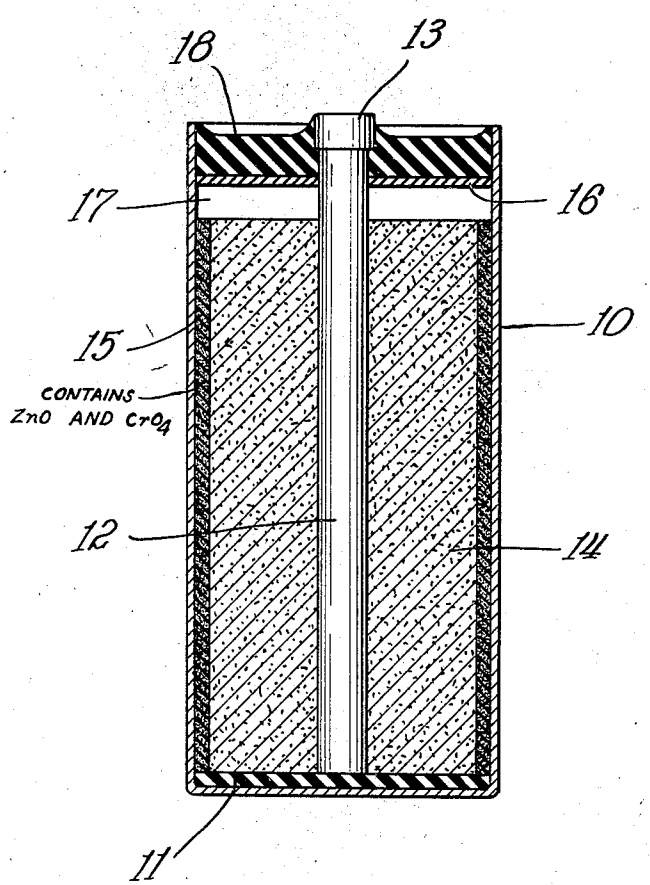
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DRY CELL

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DRY CELL

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This invention relates to dry cells, and particularly to improvements in the construction of such cells which result in better shelf life, that is, which result in a reduction in the deterioration of such cells during periods of storage and inactivity.

It is the object of the invention to provide a dry cell which has improved shelf life, and other improved properties as will be described hereinafter.

Briefly, the improvements are attained by providing zinc oxide in solution in the electrolyte to which the zinc anode is exposed. In accordance with the invention, it has been discovered that the presence of zinc oxide at the surface of the zinc anode which is exposed to the electrolyte has the effect of inhibiting the corrosion of the zinc anode which so commonly occurs during periods of inactivity.

The invention will be described in connection with a cylindrical dry cell which is in common use. It is not limited to this form of cell, however, but is applicable to any dry cell of the LeClanche type. A sectional elevation of the dry cell is illustrated in the accompanying drawing, and it comprises an open-top cylindrical zinc can 10 which constitutes the anode of the cell. Upon the bottom of the can 10 is arranged a layer of electrical insulating material 11, which may be composed of a heat-fusible pitch or wax, a resin, or a fibrous material such as paperboard or pulpboard, treated so as to be resistant to the electrolyte of the cell. A carbon rod 12 is arranged substantially centrally of the can 10 and forms the cathode of the cell. The rod 12 has a metal cap 13 upon its upper end, and is electrically insulated and mechanically separated at its lower end from the bottom of the can 10 by the insulating layer 11. The cathode 12 is surrounded by a mass of depolarizing material 14, which may be composed of a mixture of powdered manganese dioxide and carbon or graphite, ammonium chloride, zinc chloride, and other well known ingredients, and may be moistened with the aqueous electrolyte of the cell. Between the depolarizing body 14 and the zinc can 10 is arranged a layer of bibulous separating material 15 which may be composed of cellulose fibers, paper or paper pulp, gelatinized starch or gelatinized cereal flour. The bibulous layer 15 carries the aqueous electrolyte of the cell, and the depolarizing body 14 is moistened with the electrolyte. The electrolyte is a water solution containing ammonium chloride, zinc chloride and a small amount of chromic acid, dichromic acid or a water soluble salt of chromic acid or dichromic acid, such as an alkali metal chromate or dichromate.

A top washer 16 is arranged in spaced relation above the depolarizing body 14 to form an expansion space 17, and a heat-fusible seal 18, of wax or pitch, rests upon washer 16 and forms a seal closure for the open top of the can 10.

In accordance with the present invention, zinc oxide is incorporated in the electrolyte of the cell and it there exhibits the property of inhibiting corrosion of the zinc anode during periods of inactivity. Zinc oxide is substantially insoluble in water, but in the presence of dissolved ammonium salts or mineral acids, it goes into solution in water to an appreciable extent. An example of a suitable electrolyte, made in accordance with the present invention, is one composed of 26 parts by weight of ammonium chloride, 33 parts of zinc chloride, 2.5 parts of zinc oxide, 0.30 part of chromium trioxide and 41 parts of water. The chromium trioxide forms chromic acid and probably some dichromic acid upon going into solution in the water. The 2.5 parts of zinc oxide is substantially all that will go into solution in an electrolyte of this composition. Such a solution has a hydrogen ion concentration equal to a pH value of 4.5. A similar solution from which the zinc oxide is absent, has a hydrogen ion concentration equal to a pH value of 3.5. The above amount of zinc oxide is equivalent to approximately .004 gram of zinc oxide per square centimeter of zinc surface exposed to the electrolyte in a dry cell of the type described. The zinc oxide may react, in whole or in part, with some of the other ingredients to form in the solution a zinc compound other than the oxide. With respect to the zinc oxide, the solution may, therefore, be what is called a chemical solution or it may be in part a chemical solution and in part a physical solution. When the recitation is made herein, in the specification or the claims, that the zinc oxide is dissolved in the electrolyte, or is in solution in the electrolyte, it includes within its scope a condition in which the zinc oxide may have reacted to form a different zinc compound, that is, it embraces a chemical solution, as well as a physical solution, of zinc oxide.

The foregoing electrolyte composition is illustrative of that which is suitable, but variations may be made in such composition within the scope of the invention. The zinc oxide contributes the zinc corrosion-inhibiting effect when it is present in very small amounts, and an appreciable effect is obtained when it is present in an amount equal to 0.1% of the weight of the electrolyte solution.

This is equivalent to approximately .00016 gram of zinc oxide per square centimeter of zinc exposed to the electrolyte. On the other hand, an amount of zinc oxide up to 20% of the weight of the electrolyte solution has been employed with satisfactory results. This is more zinc oxide than will go into solution in the electrolyte, and the excess may be added in solid particle form to either or both of the bibulous layer 15 and the depolarizing mixture 14. The above larger amount of zinc oxide is equivalent to approximately .033 gram of zinc oxide per square centimeter of zinc exposed to the electrolyte.

The amount of chromic acid, dichromic acid or salt of such acid may also vary. An amount containing as little as 0.01% of CrO_3 based on the weight of the electrolyte solution may be used. An excessive amount should be avoided such as will interfere with the operation of the cell or produce a more highly acidic condition than is desired. It is preferred that the electrolyte solution have a pH value not lower than approximately 1.0. The content of ammonium chloride and zinc chloride may be varied in accordance with known practice.

The action by which the zinc oxide accomplishes the corrosion inhibiting function is not fully understood. In addition to the corrosion inhibiting effect, the presence of the zinc oxide provides other advantages. It may be employed with great advantage with the highly active depolarizers, such as the artificial manganese dioxides which are available. Such artificial manganese dioxides are more highly active than the natural manganese dioxide ores which are used as depolarizers, and it has been found that their use frequently results in a serious increase in zinc corrosion during storage of the cells. This corrosion promoting property of such more highly active depolarizers is greatly inhibited when zinc oxide is incorporated in the electrolyte in accordance with the present invention. The zinc oxide is also beneficial when the natural manganese dioxide ore is used as a depolarizer.

In addition, the presence of zinc oxide in the electrolyte causes a reduction in the evolution of gases within the cell and the swelling which results therefrom. It also greatly reduces the formation of crystalline structures in the electrolyte, which is a common phenomenon in dry cells and is recognized as being objectionable.

I claim:

1. A dry cell of the Le Clanche type having a zinc anode, a carbon cathode, a depolarizing mixture and an aqueous electrolyte between the anode and the cathode, said electrolyte comprising ammonium chloride as a principal ingredient and containing in solution therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid.

2. A dry cell in accordance with claim 1, in which the zinc oxide is present in an amount up to approximately 2.5% of the weight of the aqueous electrolyte.

3. A dry cell of the Le Clanche type having a zinc anode, a carbon cathode, a depolarizing mixture and an aqueous electrolyte between the anode and the cathode, said depolarizing mixture having particles of zinc oxide intimately mixed therein, and said electrolyte comprising ammonium chloride as a principal ingredient and having dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid.

4. A dry cell in accordance with claim 3, in which the zinc oxide is present in an amount up to approximately 20% of the weight of the aqueous electrolyte.

5. A dry cell of the Le Clanche type having a zinc anode, a carbon cathode, a depolarizing mixture and an aqueous electrolyte between the anode and the cathode, said electrolyte comprising ammonium chloride as a principal ingredient and containing in solution therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid and having a pH not lower than 1.

6. In a dry cell of the Le Clanche type having a zinc anode and an aqueous electrolyte adjacent said anode, said electrolyte comprising ammonium chloride as a principal ingredient and containing dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid.

7. In a dry cell of the Le Clanche type having a zinc anode and a bibulous layer of a material from the group consisting of cellulose fibers, gelatinized starch and gelatinized cereal flour adjacent said anode, said bibulous layer carrying an aqueous electrolyte comprising ammonium chloride as a principal ingredient and containing dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid.

8. In a dry cell of the Le Clanche type having a zinc anode and an aqueous electrolyte adjacent said anode, said electrolyte comprising ammonium chloride as a principal ingredient and containing dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid, said zinc oxide being present in an amount up to approximately .004 gram per square centimeter of zinc exposed to the electrolyte.

9. In a dry cell of the Le Clanche type having a zinc anode and an aqeous electrolyte adjacent said anode, said electrolyte comprising ammonium chloride as a principal ingredient and containing dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid, said zinc oxide being present in an amount up to approximately 2.5% by weight of said electrolyte.

10. In a dry cell of the Le Clanche type having a zinc anode and an aqueous electrolyte adjacent said anode, said electrolyte comprising ammonium chloride as a principal ingredient and containing dissolved therein zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid and having a pH not lower than 1.

11. The method of increasing the shelf life of a dry cell of the Le Clanche type having a zinc anode and an aqueous ammonium chloride electrolyte adjacent said anode, which comprises incorporating in said electrolyte zinc oxide and a compound from the group consisting of chromic acid, dichromic acid and the water soluble salts of chromic acid and dichromic acid.

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