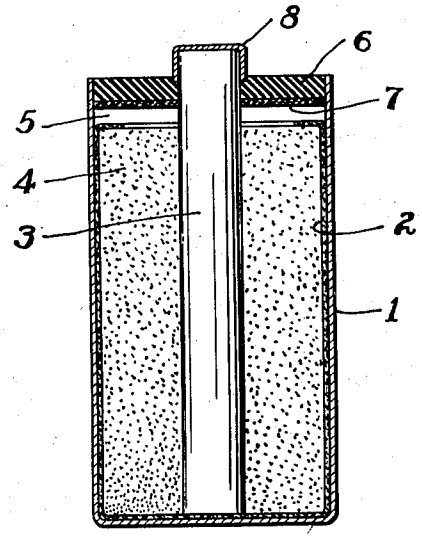
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PRIMARY CELL

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PRIMARY CELL

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This invention relates to an improved primary cell of the "dry" type having an aluminous metal anode and it has special reference to composition of the paste mixture employed in the cell. The term, "aluminous metal," as used herein refers to both aluminum and those alloys which contain more than 50% of that element.

One of the general objects of the invention is to provide a primary cell of the dry type having a high capacity and voltage along with an extended shelf life. Another object is to provide a paste electrolyte for a primary cell having an aluminous metal anode which offers low internal resistance and yet does not attack the anode to any substantial extent in open circuit condition, such as during a period of storage. Still another object is to provide a primary cell of the dry type having an aluminous metal anode which responds immediately when the circuit is closed. A further object is to provide a primary cell of the dry type having an improved aluminous metal anode in combination with an improved paste electrolyte. These and other objects will become apparent from the following description of the invention taken in conjunction with the accompanying drawing showing a cell partially in section.

The dry cells in common use for many years have consisted of a zinc anode can, a carbon rod cathode and a paste containing an electrolyte and a depolarizer. Aluminum has been proposed as a substitute for zinc in both "wet" and "dry" cells but as far as I am aware, none of the cells having aluminous anodes have achieved any commercial importance. This lack of success is accounted for in part by the well known property of aluminum to quickly acquire an oxide film in contact with air, water and many other substances while on the other hand it is sufficiently reactive with many chemicals, especially such halides as ammonium chloride, that it is rapidly consumed. The film forming property has interfered with developing a cell which will yield a high current on demand and will supply a relatively constant current over a period of time. However, in contact with the electrolytes commonly used in the zinc anode type cell, the aluminum reacts so quickly that the cell has a relatively short shelf life. As far as I know no effective means of overcoming the adverse effect of the oxide film or in controlling the rapidity of the reaction with halides has been proposed.

I have discovered that the foregoing difficulties and others can be overcome by employing aluminum chloride hexahydrate and at least one compound selected from the group consisting of ammonium, sodium and potassium chromates in a paste which also contains the conventional finely divided carbon and manganese dioxide depolarizer. The aluminum chloride appears to act as the exciter or active agent in the paste, while the chromates serve both to depolarize the cathode and restrict the attack of the chloride upon the aluminous metal anode. The combination of aluminum chloride and chromate produces a unique result in providing not only

a relatively high open circuit voltage but in giving a high output of current, and at the same time permits a long shelf life. These characteristics have not been obtained heretofore in dry cells having aluminous metal anodes as far as I am aware. In cells made in accordance with my invention I have obtained an open circuit voltage of 1.58 volts and flash currents of as much as 4 amperes and this coupled with the shelf life of 18 months.

To achieve the foregoing results, the electrolyte paste should contain from 2 to 25% by weight of aluminum chloride hexahydrate and from 4 to 25% by weight of at least one chromate of the group consisting of ammonium, sodium and potassium chromates, the weights being in terms of the dry mixture, that is, before water is added to form the paste. The total amount of the chromates should not in any case exceed 25% of the dry mixture. The benefits of my invention are only partially realized if the chloride and chromate are used in the lower portion of the foregoing ranges, that is, below about 10%. For the best results, however, the two components should be employed in substantially equal quantities and within the range of 12 to 20% by weight of each component.

The other essential ingredients of the paste, as mentioned above, are finely divided carbon, usually referred to as carbon black, manganese dioxide and water. The finely divided carbon is of the usual type employed in the dry cell art but preferably is of the type derived from the incomplete combustion of acetylene. Generally, the carbon component should comprise from about 5 to 30% by weight of the dry mixture, 10 to 20% being preferred. The manganese dioxide can be of the grade conventionally used in making dry cells. Ordinarily, this component should be used in amounts of 35 to 80% by weight of the dry mixture, but I prefer to use from 40 to 60%.

The amount of water added should be sufficient to produce a moist paste which can be readily handled and provide sufficient water for continued operation of the cell. Although the amount added may vary over a considerable range, I have found that approximately 10 to 20 parts of water to 80 to 90 parts of the dry mixture produces a satisfactory paste.

The paste electrolyte should exhibit acidic characteristics, that is, it should have a pH of less than 7, a range of 3.5 to 4 being preferred.

The foregoing paste mixture is adapted for use with aluminous metal anodes and carbon cathodes. The aluminous metal, as mentioned above, consists of aluminum and aluminum base alloys. It is preferred that the metal have an electrode potential no lower than that of commercially pure aluminum. For the sake of ease in fabricating the cell container and reducing the cost of manufacturing it is desirable to employ alloys which do not require a solution heat treatment to increase their strength. As a matter of fact, high strength is not required in a cell container. Satisfactory aluminum base alloys are those which consist of aluminum and 0.5 to 1.5% manganese, or 1 to 3% magnesium or 0.001 to 5% zinc. Minor amounts of other elements, such as boron, titanium, chromium and even copper in amounts of less than 0.5%, may be present to refine the grain size or to enhance other characteristics associated with casting and fabrication. Of the foregoing alloys the aluminum-zinc type is preferred where the aluminum employed is of a purity not lower than 99.8%.

Although the aluminous metal anode container may consist of a single alloy, it has been found that improved results are obtained if the anode is of composite construction, that is, a special anode alloy, such as the aluminum-zinc composition mentioned above, is bonded to a less anodic aluminous base. Composite anodes of this character are more fully described and claimed in my

co-pending application Serial No. 486,758, filed on even date herewith.

As an example of a dry cell of the type described above, reference is made to the accompanying drawing where the cell container 1 is provided with an absorbent paper liner 2 and a centrally disposed carbon rod 3. The space between the liner and rod is filled with the electrolyte paste 4 which contains the aluminum chloride and chromate components. Above the paste mixture a space 5 is left to permit expansion of the mixture during the period of use. The cell is sealed by a suitable plastic or resinous substance 6 poured against a pulp board separator 7. A conventional metal cap 8 is provided on the upper end of the carbon rod to establish good electrical connection with any other metallic conductor. Although not shown in the drawing, it is conventional to provide a paper covering for the cell to insulate it from any structure in which it may be mounted.

The dry cell may be manufactured in accordance with conventional procedure. The container or shell can be drawn from sheet or made by impact extrusion of slugs, or produced in any other known practice. Prior to filling the container with paste a suitable paper liner can be inserted. After the container has been filled to the desired depth, the carbon rod is thrust into the paste so as to occupy a central position, a separator pushed into the top of the cell and a suitable plastic or resin poured onto the separator. The container or shell should preferably have a wall thickness of about 0.010 to 0.020 inch depending on the size of the cell and the service expected of it.

Some paste formulations, based on dry weight, which illustrate my invention are as follows:

(I)

	Percent
$AlCl_3.6H_2O$	16
K_2CrO_4	16
MnO_2	59.6
Carbon black	8.4

(II)

	Percent
$AlCl_3.6H_2O$	16
Na_2CrO_4	16
MnO_2	59.6
Carbon black	8.4

(III)

	Percent
$AlCl_3.6H_2O$	16
$(NH_4)_2CrO_4$	16
MnO_2	60.5
Carbon black	7.5

The above formulations can be mixed with water in the proportion of eight parts of the mix to two parts of water.

A flashlight cell having a shell made of 99.8% purity aluminum and filled with paste made from Formulation I was found to have an open circuit voltage of 1.62 volts and produced a flash current of 3.5 amperes. Another flashlight cell made with the same shell metal and filled with Formulation III paste gave an open circuit voltage of 1.58 volts and a flash current of 3 amperes. In a standard continuous discharge test through a 15 ohm resistance, the potential of the first cell decreased to one volt in 38 hours, to 0.9 volt in 46 hours and 0.8 volt in 52 hours. In comparison, with a standard zinc type cell of the same size the voltage dropped to one volt in 16 hours, to 0.90 volt in 24 hours and to 0.8 volt in 45 hours.

The above aluminum cells were found to have a shelf life of 35 weeks. In comparison an aluminum cell filled with a paste containing 12% ammonium chloride was perforated in one week.

Having thus described my invention and certain embodiments thereof, I claim:

1. A dry cell comprising an aluminous metal anode, a carbon cathode and a paste mixture filling the entire space between said anode and cathode, said paste consisting of from 2 to 25% by weight of the dry mixture of aluminum chloride hexahydrate, 4 to 25% by weight of the dry mixture of at least one compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 25%, from 5 to 30% by weight of the dry mixture of finely divided carbon, from 35 to 80% by weight of the dry mixture of manganese dioxide and sufficient water to provide the desired consistency to the paste, said paste having a pH of less than 7.

2. A dry cell comprising an aluminum alloy anode consisting of aluminum of a purity not less than 99.8% and from 0.001 to 5% zinc, a carbon cathode and a paste mixture filling the entire space between said anode and cathode, said paste consisting of from 2 to 25% by weight of the dry mixture of aluminum chloride hexahydrate, 4 to 25% by weight of the dry mixture of at least one compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 25%, from 5 to 30% by weight of the dry mixture of finely divided carbon, from 35 to 85% by weight of the dry mixture of manganese dioxide and sufficient water to provide the desired consistency to the paste, said paste having a pH of less than 7.

3. A dry cell comprising an aluminous metal anode, a carbon cathode and a paste mixture filling the entire space between said anode and cathode, said paste consisting of from 2 to 25% by weight of the dry mixture of aluminum chloride hexahydrate, 4 to 25% by weight of the dry mixture of at least one compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 25%, from 10 to 20% by weight of the dry mixture of finely divided carbon, from 40 to 60% by weight of the dry mixture of manganese dioxide and sufficient water to provide the desired consistency to the paste, said paste having a pH of less than 7.

4. A dry cell comprising an aluminous metal anode, a carbon cathode and a paste mixture filling the entire space between said anode and cathode, said paste consisting of from 12 to 20% by weight of the dry mixture of aluminum chloride hexahydrate, 12 to 20% by weight of the dry mixture of at least one compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 20%, said chloride and chromate components being present in substantially equal amounts, from 10 to 20% by weight of the dry mixture of finely divided carbon, from 40 to 60% by weight of the dry mixture of manganese dioxide and sufficient water to provide the desired consistency to the paste, said paste having a pH within the range of 3.5 to 4.

5. An electrolyte paste for a dry cell having an aluminous metal anode consisting of from 2 to 25% by weight of the dry mixture of aluminum chloride hexahydrate, 4 to 25% by weight of the dry mixture of at least one compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 25%, from 5 to 30% by weight of the dry mixture of finely divided carbon, from 35 to 80% by weight of the dry mixture of manganese dioxide and sufficient water to provide the desired consistency to the paste, said paste having a pH of less than 7.

6. An electrolyte paste for a dry cell containing an aluminous metal anode consisting of from 12 to 20% by weight of the dry mixture of aluminum chloride hexahydrate, from 12 to 20% by weight of the dry mixture

of a compound selected from the group consisting of ammonium, sodium and potassium chromates, the total weight of said chromate component not exceeding 20%, said chloride and chromate components also being present in substantially equal amounts, from 10 to 20% by weight of the dry mixture of finely divided carbon, and from 40 to 60% by weight of the dry mixture of manganese dioxide, said dry mixture being admixed with water in the proportion of from 10 to 20 parts of water to 90 to 80 parts of the dry components, said paste having a pH of less than 7.

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