

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in and relating to Cathodes for Electric Batteries

We, UNION CARBIDE CORPORATION, of 30, East 42nd Street, New York, State of New York, United States of America, a Corporation organised under the Laws of the State of New York, United States of America, (assignee of KARL KORDESCH), 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 bonded cathodes for use in dry cells. More specifically, it relates to improved cathodes for use in dry cells employing a metallic container.

Cathode elements used in primary dry cells conventionally consist of mixtures of oxidic depolarizers, non-reactive conductive powders and, in some cases, a suitable electrolyte. The mixtures are molded or compressed into a bobbin or plate, and then inserted in the metallic container.

In most dry cell systems, graphite and acetylene black generally are the conductive powders. In other systems the conductive component in the cathode element may include metal powders such as nickel powder. The oxidic depolarizer may be manganese dioxide, nickel hydroxide or vanadium pentoxide. However, such known systems are not entirely satisfactory because during use the particles separate or swell, thus increasing internal resistance.

The cathodes of the present invention have improved resistance to swelling and the particles are maintained in intimate contact, thereby improving cell efficiency.

According to the present invention, a shaped dry cell cathode comprises finely divided carbonaceous particles and finely divided oxidic depolarizing particles, such particles being integrally united by Sorel and Portland cement, the cement constituting a

substantially continuous common matrix for both carbonaceous and depolarizing particles.

In the accompanying drawings:—

Fig. 1 is a fragmentary view of cell having a cathode embodying the principles of the invention;

Fig. 2 is a vertical sectional view of a bonded plate cathode in a flat cell; and

Fig. 3 is a graph comparing the performance of "D" size LeClanche cells using the cathodes of the invention with cells of the same size using conventional unbonded cathodes.

Among the oxidic depolarizing materials suitable for use in making the electrodes of the invention are manganese dioxide, mercuric oxide, silver oxide, copper oxide, vanadium pentoxide or nickel hydroxide.

Suitable carbonaceous particles for use in the cathode of the invention include carbon black, acetylene black, graphite and mixtures thereof.

The cement binder for forming a substantially continuous common matrix is employed in an amount from 5 to 20 per cent by weight of the cathode and is either Portland cement or "Sorel" cement (a mixture of magnesium oxide and magnesium chloride).

The cement binder integrally unites the depolarizer and cathodic particles, and constitutes a substantially continuous common matrix for both types of particles.

Referring now to Fig. 1, there is shown a fragment of a cell consisting of a shaped cement bonded cathode 10, fitting in a steel can 12, and separated from anode 14 by separator 16. This anode may be composed of aggregates of consumable metal held in a semi-rigid state by a binding agent compatible with the electrolyte. However, the herein-described cathode can be used also in conjunction with conventional cell constructions using sheet anodes.

[Price 3s. 6d.]

EXAMPLE I

A cathode was made from the following mix:—

Electrolytic manganese dioxide	200 grams
Graphite	40 grams
Portland cement	20 grams
Steel wool	10 grams

The above mix was moistened with from 10 to 12 milliliters of 9 normal potassium hydroxide per 100 grams of mix. The mix was then pressed into shape, and allowed to dry for one day.

EXAMPLE II

Cathodes were made from the following mix:—

Electrolytic manganese dioxide	100 grams (particle size over 10 microns)
Graphite	20 grams (particle size below 5 microns)
Portland cement	15 grams
Water	13 milliliters

Thirty-five grams of the above mix were formed into a cylinder having an inner diameter of $1\frac{1}{4}$ inches (34 mm.), a wall thickness of $\frac{1}{8}$ inch (3.3 mm.) and a length of $2\frac{1}{4}$ inches (56.5 mm.). The article was formed under pressure of $1\frac{1}{2}$ tons (1.36 metric ton) but well below 10 tons (9 metric tons) per square inch. These cathodes were used in "D" size cells with zinc anodes, and saturated ammonium chloride as the electrolyte.

Their performance was as follows:—

Open circuit voltage—1.53 volts
Closed circuit voltage—1.43 volts (continuous discharge over 3 ampere bulb)
After one-half hour—1.34 volts
After one hour—1.32 volts
After two hours—1.27 volts
After four hours—1.20 volts
After six hours—1.15 volts
After eight hours—1.07 volts
After 10 hours—1.03 volts
After 12 hours—0.96 volts
After 14 hours—0.88 volts
After 16 hours—0.80 volts
After 18 hours—0.75 volts
After 20 hours—0.68 volts
After 22 hours—0.48 volts
Initial resistance—0.16 ohms
Resistance at end—0.4 ohms
Ampere hours to 0.9 volts—4 ampere hours
to 0.6 volts—6 ampere hours

By contrast, the "D" size LeClanche cell discharged under the same conditions produced 1.25 ampere hours to 0.9 volts and 2.5 ampere hours to 0.6 volts.

The curves of Fig. 3 indicate a comparison between cells using the cathode of the invention and commercial photoflash cells, both being under an 0.5 ampere continuous load. Curve "a" shows the performance of a "D" size cell containing the cathode of the inven-

Copper oxide	100 grams
Graphite	20 grams
Portland cement	20 grams
Potassium hydroxide	4.2 grams

Tubular cathodes such as that shown on Fig. 1 were made from 60 grams of the above mix by extrusion into a zinc cell container formed to have a $\frac{1}{8}$ inch (3.3 mm.) wall thickness. They were used to fabricate exceptionally efficient "D" size copper oxide zinc cells having a capacity of more than 15 ampere hours.

EXAMPLE III

Cathodes were made from a mix of the following composition:—

tion in conjunction with an alkaline electrolyte, while curve "b" shows the same for an identical cell using an unbonded cathode.

It should be noted from these curves that even after only one ampere hour the cell using the herein-disclosed cathode exceeds the voltage of a conventional cell by 0.2 volts. After three ampere hours, the latter gives a voltage reading less than that shown by the former after ten hours.

As also shown by Fig. 3, the internal resistance of the cell using a bonded cathode goes from 0.07 initially to 0.25 ohms after 8 ampere hours; the internal resistance of the cell using an unbonded cathode rises to about 0.8 ohms after only 3 ampere hours.

It should be understood that cathodes of any desired shape dictated by the geometry of the cells wherein they are intended to be used, may be fabricated in accordance with the invention. Thus, there is shown in Fig. 2 a bonded plate cathode for use in flat stacked cells. Suitably, such a construction comprises a zinc anode 20, having a conductive carbon coating 22, and a film liner 24, a paper blanket 26, and a cement bonded cathode mix cake 28, the entire unit being enveloped by a vinyl envelope 30.

Similarly, the cathodes of the invention can be used in various cell systems, including storage cells employing, for example, an alkaline electrolyte in conjunction with manganese dioxide and zinc. In this application, cells often show a considerable deficiency of electrolyte after discharge. This undesirable condition may be remedied by employing a modified mode of fabrication to produce cathodes which are more porous and elastic than those hereinabove described. The following example describes such mode of fabrication:—

EXAMPLE IV

A mix containing 100 g. MnO_2 , 20 g.



and

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100

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graphite, 10 g. Portland cement and 12 ml. of 9 normal KOH is pressurized into a cake. After one day setting, to obtain particles having diameters between 0.7 mm. and 0.15 mm., this mass is pulverised and sieved. Such particles are moistened with additional KOH solution and molded into the electrode shape. A small graphite and cement addition (about 1 g. of each) during the rebonding gives a better conductivity and higher strength, but is not absolutely necessary since the original cement mix binds again if put under pressure as the hydration continues for a period of several weeks.

15 WHAT WE CLAIM IS:—

1. A shaped dry cell cathode, which comprises finely divided carbonaceous particles and finely divided oxidic depolarizing particles, such particles being integrally united by Sorel or Portland cement, the cement constituting a substantially continuous common matrix for both carbonaceous and depolarizing particles.

25 2. A cathode as claimed in Claim 1, in which the inorganic cement is present throughout the cathode in an amount between 5% and 20% by weight of the cathode.

30 3. A cathode as claimed in Claim 1 or 2 in which the oxidic depolarizing particles are particles of manganese dioxide, mercuric oxide, silver oxide, copper oxide, vanadium pentoxide or nickel hydroxide.

35 4. A cathode as claimed in any of the preceding claims in which the carbonaceous particles are carbon black, acetylene black, graphite or mixtures thereof.

5. A method for producing shaped cathodes for dry cells, which comprises intimately mixing finely divided carbonaceous particles and oxidic depolarizing particles with Sorel or Portland cement, wetting the resulting mixtures with a dry cell electrolyte and forming the wet mixture under pressure to a desired shape. 40

6. A method as claimed in Claim 5, in which forming is effected by extruding the wet mixture into a cell container. 45

7. A method as claimed in Claim 5, in which the pressed shape is dried and pulverized, the resulting particles sieved, moistened with an alkaline electrolyte and moulded into a cathode. 50

8. A method as claimed in Claim 7 in which additional cement and the carbonaceous particles in the form of graphite are added to the sieved moistened particles prior to moulding the same into a cathode shape, such additional amount being up to 10% by weight of the initial cement and up to 5% by weight of the initial carbonaceous particles, respectively. 55 60

9. A shaped dry cell cathode substantially as hereinbefore described and shown in the accompanying drawings.

10. A method for producing shaped cathodes for dry cell substantially as hereinbefore described in any of the examples. 65

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3. A cathode as claimed in Claim 1 or 2 in which the oxidic depolarizing particles are particles of manganese dioxide, mercuric oxide, silver oxide, copper oxide, vanadium pentoxide or nickel hydroxide.
4. A cathode as claimed in any of the preceding claims in which the carbonaceous particles are carbon black, acetylene black, graphite or mixtures thereof.
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