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# Index at acceptance—14B[LVIII(1)].

## PROVISIONAL SPECIFICATION.

# IMPROVEMENTS IN OR RELATING TO LECLANCHE TYPE DRY CELLS.

COUNCIL OF SCIENTIFIC & INDUSTRIAL REGISTRATION RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE RECISTRATION OF SECRETIES ACT (AACT XXI of 1860).

THIS IS AN INVENTION BY MAHADEV GOVIND POTDAR, SCIENTIST, HANDADY UDUPA, SCIENTIST, AND KADARUNDALIGE SITARAMA DOSS GURURAJA VENKATAKRISHNA DOSS, DIRECTOR, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, MADRAS STATE, INDIA, ALL

The following specification describes the nature of this invention.

This invention relates to improvements in or relating to Leclanche' type dry cells.

Hitherto it has been proposed to make Leclanche' type dry cells in the routine manner as indicated in a general form in any good text book on this subject. The individual operations are very important and need careful control. The normal practice is to use a starch and flour composition for the paste to be used in combination with the cell electrolyte.

This is open to the objection in that the quantity needed for a fair thickness of the paste is quite large This step increases the cell resistance and reduces the quantity of electrolyte that can be added. This reduction in the quantity of electrolyte affects the performance of cells fabricated. For good performance, it is essential to have the paste as thin as possible, keeping the electrolyte content of the paste as high as possible. The paste should not diffuse into the bobbin and the constituents of the paste should not be attached by the contents of black mix or the corrosion products of zinc.

The object of this invention is to obviate these disadvantages by using as little starch as possible because starch is attacked by active manganese dioxide and its use in larger quantities needed for good paste formation increases the internal resistance of the cell resulting in poor performance.

The quantity of electrolyte added should be creased as much as possible as this will reduce the internal resistance and will increase the utilization of manganese dioxide by keeping the products of zinc corrosion in solution.

To these ends, the invention broadly consists in making a paste composition out of starch and carboxy methyl cellulose (CMC). This has improved the performance of the dry cell remarkably.

The following examples are given to illustrate the invention :

Time taken (hrs.) to reach 1.0V when discharged continuously through 4.5 ohms

C.E.C.R.I cells using

Commercial cells

2.5 to 3

Starch	CMC	Starch
only	only	+CMC
2.5 to 3	2.5 to 3	3 to 4

The following are among the main advantages of the invention:

- 1. Dry cells can be made using indigenously available manganese dioxide ores.
- 2. Indian straches (tapioca) can be used for making paste electrolyte.
- 3. A mixture of starch and carboxy methyl cellulose (CMC) gives longer bright life and greater utilization of manganese dioxide.

R. BHASKAR PAI,

PATENTS OFFICER.

Council of Scientific and Industrial Research.

Dated this 14th day of December, 1965.

### COMPLETE SPECIFICATION.

### IMPROVEMENTS IN OR RELATING TO LECLANCHE TYPE DRY CELLS.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

THIS IS AN INVENTION BY MAHADEV GOVIND POTDAR, SCIENTIST, HANDADY UDUPA, SCIENTIST, AND KADARUNDALIGE SITARAMA DOSS GURURAJA VENKATAKRISHNA DOSS. DIRECTOR, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, MADRAS STATE, INDIA, ALL

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to Leclanché type dry cells. The general methods of making Leclanché type dry cells are given in good text books on this subject. The individual operations are very important need careful control.

The normal practice is to mix the components of blackmix (manganese dioxide, carbon, ammonium chloride, zinc chloride, water) thoroughly and to press this mix round a central carbon rod for cylindrical cells or to make in a form of duplex electrode for layer or flat type cells. The black mix is then given a wrapping of cloth or a suitable chemical composition in the case of cylindrical type cells. This bobbin is then placed in position in a washered zinc can and

the space between the can and the bobbin is filled with gelatinised paste electrolyte. In the case of layer type, the paste is coated on to the separator between the black mix electrode and zinc electrode. For this purpose of gelatinization, starches and/or wheat flour compositions are used in combination with the cell electrolyte (ammonium chloride, zinc chloride, water). The top is then washered and sealed with pitch compositions in the case of cylindrical cells and the stacks are given a final dip in wax in the case of layer type cells.

Drawbacks connected with hitherto known process/devices

The quantity of starch needed for a fair thickness

Price: TWO RUPEES.

of the gelatinized paste is quite large and varies with the variety of the starch or flour used and also the composition of the electrolyte.

This step reduces the quantity of electrolyte that can be added and thus increases the internal resistance of the cell.

For good performance of a cell, it is essential (1) to have the paste as thin as possible, (2) to have the electrolyte content of the paste as high as possible, (3) the paste should not diffuse into the bulk of the bobbin, (4) the constituent of the paste should not be attacked by the contents of the black mix and (5) the constituents of the paste should not be attacked by the corrosion products of zinc.

The main object of the invention :

The above mentioned disadvantages can be surmounted or avoided by using (1) as little starch and/or flour as possible, (2) and by adding as much electrolyte as possible.

The main finding (the new principle) underlying the invention:

The performance characteristics can be improved by making a paste composition out of starch and carboxy methyl cellulose (CMC) which significantly improves the discharge characteristics of the cell.

According to the present invention, the dry cell of Leclanche' type comprises a zine can, electrolyte paste, manganese dioxide and carbon made by well known techniques wherein a paste composition consisting of a mixture of starch and carboxy methyl cellulose, ammonium chloride, zinc chloride and water is employed, and indigenous manganese dioxide orca are used as depolarizer.

The dry cell utilizes indigenously available manganese dioxide ore having 75 per cent, or above manganese dioxide content, either alone and/or in admixture with (a) synthetic manganese Coxide or (b) any other manganese dioxide ores.

The cell uses starch to the extent of 20 to 40 per cent, and carboxy methyl cellulose to the extent of 2 to 10 per cent, preferably using 24 to 25 per cent, tapioca starch and 7 to 8 per cent, carboxy methyl cellulose.

For forming a fairly good paste out of starch alone, it is necessary to add from 30 to 40 g. of same for 100 cc. of electrolyte. The cells made using this paste electrolyte on an average give only 2.5 to 3 hours time of discharge period for a cut off voltage of 1.0V on 4.5 ohms. load.

The quantity of CMC needed to get a good paste is of the order of 20 to 30 g. for 100 cc. electrolyte. The cell characteristics remain as indicated above and the assembly method has to be suitably altered for its

However, it is possible to improve upon the performance characteristics by mixing starch with CMC in suitable proportions i.e., starch 20 to 30 per cent. and CMC 4 to 10 per cent., the preferred composition being 24-25 per cent. starch and 7-8 per cent. CMC.

The new result flowing from the new finding :

The cells made by using the paste composition as mentioned above and using indigenously availably starches and CMC in combination with bobbins made out of Indian manganese dioxide ores containing manganese dioxide above 75 per cent. show a better performance to a cut off voltage of 1.0V as indicated in the table below:

#### TABLE

Time (hrs) taken to reach 1.0V when discharged continuously through 4.5 ohms

C.E.C.R.I cells

For making dry cells of the Leclanche' type, the ingredients of the blackmix indicated earlier are mixed and pressed round a central carbon rod for cylindrical cells. A duplex electrode is made for layer type cells. The bobbin is warpped in a cleth or coated with a chemical composition. The bobbin is put in a zinc can washered arlier, filling the space between the can and the bobbin by a paste electrolyte, washering the top and capping and sealing the cell. The invention replaces the starch paste electrolyte by a suitable composition of starch and carboxy methyl cellulose (CMC) giving better performance of the cell, making it possible to use particularly indigenously available nature manganese dioxide ores either alone or in admixture with synthetic manganese dioxide as well as other manganese dioxide ores.

The novelty of the invention is that it makes use of natural untreated ores and cheap starches like tapioca starch.

This improvement does not involve any additional expenditure for its application by any running industry in the field.

Main advantages of the invention:

- (i) Dry cells can be made using indigenously available manganese dioxide ores.
- (ii) Indian starches (tapioca) can be used for making paste electrolyte.
- (iii) A mixture of starch and carboxy methyl cellulose (CMC) gives longer bright life and greater utilization of manganese dioxide.

Summary :

This invention has made it possible for the utilization of the naturally occurring manganese dioxide ores of India which are normally believed by the battery industry as unsuitable for use.

The percentage impurities like iron allowed are very low whereas in this invention it is seen that iron is not a serious impurity upto 10 per cent.

The indigenously available starch (tapioca) in combination with CMC gives optimum paste composition and extends the bright life of the cell.

This gives an improved utilization of manganese dioxide.

#### We claim :

- 1. A dry cell of Leclanche' type comprising a zinc can, electrolyte paste, manganese dioxide and carbon made by well known techniques wherein a paste composition consisting of a mixture of starch and carboxy methyl cellulose, ammonium chloride, zinc chloride and water is employed, and indigenous manganese dioxide ores are used as depolarizer.
- 2. A dry cell prepared as in Claim 1 which utilizes indigenously available manganese dioxide ore having 75 per cent. or above manganese dioxide content, either alone and/or in admixture with (a) synthetic manganese dioxide or (b) any other manganese dioxide ores.
- 2 cell as claimed in Claim 1 or 2 which uses starct to the extent of 20 to 40 per cent, and carboxy methyl cellulose to the extent of 2 to 10 per cent, preferably using 24 to 25 per cent, tapioca starch and 7 to 8 per cent, carboxy methyl cellulose.
- 4. A dry cell substantially as hereinbefore described.

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Dated this 23rd day of September, 1966.