PATENT SPECIFICATION

754,194

Date of Application and filing Complete Specification: Nov. 16, 1954. No. 33089/54.

Application made in United States of America on Nov. 17, 1953.

Complete Specification Published: Aug. 1, 1956.

Index at acceptance:—Class 53, BP1(C: X).

COMPLETE SPECIFICATION

Improvements in Anodes for Primary Galvanic Cells

We, UNION CARBIDE AND CARBON 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 Henry Richard Rade,) 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 consumable metal anodes for primary galvanic cells, and to an improved method of making such anodes.

From the early LeClanche type cells, metal anodes for primary galvanic cells have been cast or fabricated from sheet metal. In relatively large cells such as those used for railway signal service, telephone service, or for flashlights and similar devices, anodes of this type are perfectly satisfactory. However, due to the development of electronic devices of smaller size, such as personal hearing aids and portable radio transmitters, there has been a demand for the production of primary batteries of small size. The continuing trend is to reduce the size of such batteries even further.

As the size of a primary cell is decreased, difficulties are encountered with the anode materials used. One of the difficulties is the lack of surface of anode metal which can be attacked by the electrolyte. The small anode of sheet metal tends to become coated with current-stopping reaction products in so short a time as to render the cell commercially undesirable.

To counter-balance the decrease in anode size necessitated by the continued decrease in cell size, many attempts have been made to increase the effective surface area to ensure more complete utilization of the anodic material. For example, a sheet metal anode has been embossed or perforated not only to provide more surface area, but also to prevent adherence of non-conductive reaction products. While such expedients have been effective to a degree, they have not solved the problem.

It has also been proposed to secure an extension in anode surface area by forming the anode of powdered metal; for example by compressing powdered anodic material into the form of a cylinder. Anodes so formed have a greater effective surface area than a cylinder of the same size cast from molten metal. However, anodes compressed solely of metal powders suffer disadvantages. If an anode is compressed with too little pressure, a structurally weak element results, while on the other hand, if too much pressure is used, the metal particles are pressed so tightly as to resemble a sheet or plate and an appreciable part of the resultant anode will be unattacked by electrolyte, and, therefore, will contribute nothing to the cell reaction. Powdered metal anodes made in this way are porous, and permit internal electrolytic action during cell discharge with the consequent formation of reaction products within the pores of the anode. Since these reaction products occupy considerably more space than the anode metal, internal pressure develops in the anode, which often results in swelling and finally breakage. In our co-pending application No. 33090/54 (Serial No. 754195) there is disclosed an anode comprising finely divided metal bound with a thermoplastic resin.

According to the present invention, an anode for a primary galvanic cell comprises finely-divided metal and a binder, the binder being a thermoplastic resin and constituting a substantially continuous matrix throughout the anode. The invention also includes a method of making the anode.

The most widely-used anode metal in primary galvanic cells is zinc, and for the purpose of conciseness, the invention will be described particularly with reference to zinc anodes. However, the invention is equally applicable to the production of anodes formed of any consumable metal, for example magnesium or aluminium.

Anodes made in accordance with the in-

vention are composed of finely-divided metal and a binder and pressed into shape under heat and pressure. The binder forms a continuous plastic matrix throughout the anode, and the anode metal itself forms a continuous phase. Suitable binding materials include polyethylene, polyvinyl chloride, methyl cellulose, vinyl resins and chlorinated diphenyl resins. Of this group, polyethylene is preferred because of its excellent heat tolerance.

The proportion of binder to anode metal is as small as possible, in order to secure as high electrical conductivity as possible without substantial loss in mechanical strength. Ordinarily, the binder should constitute at least about 1% by weight of the anode, and larger quantities may be used, but some reduction in electrical conductivity of the formed anode results as the proportion of binder is increased. For most purposes, the proportion of binder need not exceed 5% by weight of the anode.

The density of the anode, of course, is dependent upon the ratio of metal to resin in the mixture. Thus, in determining the quantity of thermoplastic binder to be used in making the anodes of the invention, ease of moulding is an important consideration, but even more important is the necessity for providing in the anode the maximum possible quantity of active anode metal. Powdered resin in an amount as little as 1% by weight of the powdered metal may be used to fill the interstices between the metal particles, and mixtures containing only this small proportion of binder may be moulded with relative ease. Whenever greater ease of moulding is desired, larger quantities of the resin may be used, but it must be borne in mind that the finished article must have satisfactory electrical conductivity for its intended purpose and the maximum quantity of binder that can be used is that which causes no undue decrease in the electrical conductivity of the finished anode. Numerically, this upper limit is approximately 12% by weight of the metal powder.

In manufacturing the anodes of this invention, powdered anode metal is dry-mixed with powdered binder resin. Although particle size of the metal is not critical, it is convenient to employ powders of such particle size that they will pass a 40 mesh (0.417 mm.) screen, while being retained on a 170 mesh (0.088 mm.) screen. The size of the resin particles should generally be of the same order. The mixture is compressed in conventional manner under suitable conditions of elevated temperature and pressure to form any desired shape of anode. Generally, dependent upon the resin selected, the temperature should be at least about 200°F., and the pressure applied, which is in part dependent upon the quantity of resin in the mixture, should be at least about 1000 pounds per square inch. Typical examples of suitable mixtures and moulding conditions follow.

Cylindrical anodes $\frac{5}{8}$" in outside diameter by $\frac{5}{16}$" height were prepared from a mixture containing 99% zinc having a particle size such as to pass a 40 mesh (0.417 mm.) screen, and 1% polyethylene and successfully moulded at 300°F. and a pressure of 2000 pounds per square inch.

From a mixture composed of 97.5% zinc and 2.5% polyethylene, the zinc having a particle size sufficiently small to pass a 40 mesh (0.417 mm.) screen, cup-shaped anodes having an outside diameter of $\frac{5}{8}$", a length of $1\frac{5}{8}$" and a side wall thickness of 0.12" were moulded at 350°F. and 3000 pounds per square inch pressure.

Anodes in the form of rods of varying lengths having a diameter of $\frac{5}{16}$" were moulded at 400°F. and 3500 pounds per square inch pressure, from a blend consisting of 200 grams of powdered zinc and 10 grams of powdered polyethylene, the zinc powder was of a particle size sufficiently small to pass through a 40 mesh (0.417 mm.) screen.

Anodes typical of those just described when subjected to the action of electrolyte, are uniformly corroded in such a way that complete utilization of the anode metal is achieved. Actually, corrosion, upon which of course battery action depends, proceeds so uniformly and so completely that when the anodes are immersed in electrolyte, complete consumption of the anode metal can be attained, leaving behind a coherent matrix of thermoplastic binder, which still retains the shape of the original anode. Furthermore, reaction proceeds from the outside surfaces of the anode progressively as the anode is consumed without any tendency to breakage of the anode by spalling, indicating that electrolytic action within the interior portions of the anode is inhibited.

This inhibition of internal electrolytic action conceivably may be due to a lack of porosity of the anode or to the fact that the binder resin has an electrolyte-repellent property or to both of these phenomena. Whatever the explanation, however, the fact remains that the anodes of the invention are uniformly corroded at the active surfaces thereof, rather than in the interior portion. This characteristic assures uniform service life of batteries employing the anodes, and prevents early failure of such batteries prior to the complete utilization of the anode metal.

As has been indicated above, a relatively large number of thermoplastic resins may be utilized as the binder in forming the anodes of this invention. Of the group above referred to, polyethylene is preferred because its excellent heat tolerance enables anodes made in accordance with this invention, utilizing polyethylene as a binder, to be soldered by standard methods without undergoing structural deformation.

A particular advantage of the invention lies in the fact that anodes of any desired shape may be produced with ease, thereby freeing the battery maker from the necessity of employing the shapes traditionally used. Further advan-

tages accrue from the fact that pure metal may be employed, and that uniformity of composition may thereby be achieved. Such uniformity eliminates the possibility of the development of local couples in cells or batteries employing the anodes which tend to shorten battery life. Additionally, by reason of the continuity of both matrix and anode metal, substantially complete utilization of the anodic metal may be achieved.

What we claim is:—

1. An anode for a primary galvanic cell comprising finely-divided metal and a binder, the binder being a thermoplastic resin and constituting a substantially continuous matrix throughout the anode.

2. An anode as claimed in claim 1, in which the thermoplastic resin is polyethylene, polyvinyl chloride, methyl cellulose, a vinyl resin, or a chlorinated diphenyl resin.

3. An anode as claimed in claim 1 or 2, in which the thermoplastic resin is present in an amount between 1% and 12% by weight of the finely-divided metal.

4. An anode as claimed in any one of claims 1 to 3 in which the finely-divided metal is zinc, magnesium or aluminium having a particle size to pass through a screen having openings of 0.417 mm. but to be retained on a screen having openings of 0.088 mm.

5. An anode as claimed in any one of the preceding claims in the form of a pressure-moulded cup having an outside diameter of $\frac{3}{8}$ inch, a length of 1-$\frac{5}{8}$inch and a side wall thickness of 0.012 inch.

6. A method of making an anode for a primary galvanic cell as claimed in any one of the preceding claims which comprises intimately mixing finely-divided metal and a thermoplastic resin which is present in an amount between 1% and 12% by weight of the finely-divided metal, and subjecting such mixture to pressure at the moulding temperature of the resin.

7. A method as claimed in claim 6, in which the mixture is moulded at a temperature between 200°F. and 400°F. at a pressure of at least 1000 lbs. per sq. in.

8. A method of making an anode for a primary galvanic cell as claimed in claim 1 and substantially as hereinbefore described.

9. An anode for a primary galvanic cell whenever prepared by a process according to any one of claims 6 to 8.

10. A primary galvanic cell containing the anode as claimed in any one of claims 1 to 6 or 9.

11. Anodes for primary galvanic cells as claimed in claim 1 and as herein particularly described.

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Printed for Her Majesty's Stationery Office by J. Looker Ltd., Poole, Dorset. 1956.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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4. An anode as claimed in any one of claims 1 to 3 in which the finely-divided metal is zinc, magnesium or aluminium having a particle size to pass through a screen having openings of 0.417 mm. but to be retained on a screen having openings of 0.088 mm.

5. An anode as claimed in any one of the preceding claims in the form of a pressure-moulded cup having an outside diameter of $\frac{3}{8}$ inch, a length of 1-$\frac{5}{8}$inch and a side wall thickness of 0.012 inch.

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7. A method as claimed in claim 6, in which the mixture is moulded at a temperature between 200°F. and 400°F. at a pressure of at least 1000 lbs. per sq. in.

8. A method of making an anode for a primary galvanic cell as claimed in claim 1 and substantially as hereinbefore described.

9. An anode for a primary galvanic cell whenever prepared by a process according to any one of claims 6 to 8.

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