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# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Improvements in and relating to Battery Electrodes

We UNION CARBIDE CORPORATION, of 270, Park Avenue, 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 ROBERT LAWRENCE DAVEE and DEMETRIOS VASILIOS LOUZOS), 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:—

The present invention relates to improved electrodes for use primarily in secondary batteries of the alkaline type, and to a process for producing the same.

In the manufacture of alkaline secondary batteries, it has recently become the practice to employ electrodes in cylindrical form wherein elongated strips of porous electrode material are wound into cylindrical bodies. Such electrode structures are characterized by the provision of high capacities per unit volume of active material.

Presently, electrodes of the aforementioned type are made from porous sintered metal plaques impregnated with a solution of an active material. The main disadvantage of these electrodes is that they are difficult and expensive to manufacture. For instance, it is generally necessary in manufacturing the electrodes to impregnate the plaques several or more times, followed by washing and drying the plaques, in order to achieve a desired electrode capacity. Such procedures are time-consuming, costly and require expensive equipment. Another disadvantage resides in the brittleness and consequent inability of the sintered plaques to be shaped into cylindrical form without cracking, spalling and the resultant loss of active material.

It is therefore the principal object of the present invention to provide an improved electrode for use primarily in secondary bat-

teries of the alkaline type, which is inexpensive and easy to manufacture, is highly flexible and especially adapted to use in cylindrical form without cracking, spalling and the attendant loss of active material.

Another object is to provide a process for producing an improved electrode, which eliminates the use of sintered metal plaques and the necessity for impregnating the plaques with an active material, and is simple and adapted to a single, continuous operation.

Accordingly, the present invention provides a flexible electrode comprising dry powders of active material embedded within, and pressure bonded to, a conductive carrier grid, wherein the grid is a continuous web of expanded metal composed of a plurality of metal strands interconnected at bond joints and defining a network of open pockets within which the dry powders of active material are embedded, the grid traversing the cross section of the electrode from one surface to the other such that edge portions of the bond joints are exposed at the electrode surfaces, the carrier grid and the powder being compressed along the plane of the electrode surface so as to physically bond the dry powders of active material within the open pockets of the grid. The term 'dry powder' as used herein and in the appended claims is meant to include powders containing up to 10 per cent of moisture or liquid, although it is preferred to employ essentially dry powders of an active material in the practice of the present invention.

The present invention also provides a process for producing a flexible electrode, which comprises continuously feeding a conductive carrier grid together with a dry powder of an active material to a pair of horizontal rollers, spaced from each other at a distance less than the thickness of the grid to define a pressure gap therebetween and provided with roll covers extending in

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close proximity to said pressure gap and defining a compression zone thereabove, passing the grid between the roll covers and through the dry powder to fill the openings in the grid with said powder, passing the filled grid through the compression zone to compact the dry powder in the grid openings, pulling the filled grid through the pressure gap and compressing the said grid to between 5 per cent and 60 per cent of its original thickness.

In the accompanying drawings:

Fig. 1 is a perspective view of an apparatus for carrying out the process of the present invention;

Fig. 2 is an enlarged side elevational view of the apparatus shown in Fig. 1;

Fig. 3 is an enlarged fragmentary view of a portion of the apparatus shown in Fig. 2;

Fig. 4 is a plan view of adjustable shim means for controlling the powder gradient or density across the width of the electrode;

Fig. 5 is a similar view of a modification of the adjustable shim means shown in Fig. 4;

Fig. 6 is a plan view of a preferred conductive grid for use in the invention;

Fig. 7 is a sectional view taken along the line 7-7 in Fig. 6;

Fig. 8 is a fragmentary plan view of an electrode of the present invention; and

Fig. 9 is a sectional view taken along the line 9-9 in Fig. 8.

Referring to the accompanying drawings and particularly to Figs. 1 and 2, a hopper 10 is provided for continuously feeding a dry powder 12 of an active material to a pair of horizontal rollers 14, 16, suitably composed of steel. The pair of horizontal rollers 14, 16 are oppositely driven by a suitable gear mechanism, not shown, and are spaced apart so as to provide a pressure gap 18 therebetween i.e. the gap between the rollers where pressure is applied to the dry powder and the grid, as shown in Fig. 2.

The dry powder 12 is fed between roll covers 20, 22 mounted over the pair of horizontal rollers 14, 16. These roll covers 20, 22 terminate a short distance above the pressure gap 18 as shown in Figs. 2 and 3, and define a zone of compression in close proximity thereto. The compression zone is the unshielded area (not protected by the roll cover) of the pressure rollers where the dry powders are compacted or forced under high pressures into the expanded metal grid. To vary the depth of the compression zone, the roll covers 20, 22 are mounted to adjustable supports as at 24, 26, respectively. The roll covers 20, 22 are preferably composed of a corrosion-resistant material, as for

example steel coated with a layer of fused ceramic or glass.

A continuous strip of a conductive carrier grid 28 is fed to the pair of horizontal rollers 14, 16 together with the dry powder 12 of active material. As best seen in Figs. 2 and 3, the grid 28 is preferably fed along the surface of one of the roll covers, for example roll cover 22 and at a tangent to the corresponding roller 16. In this manner, the dry powder 12 is drawn into the grid openings as the grid 28 is fed between the pair of rollers 14, 16. When the grid 28 enters the compression zone, the dry powder 12 substantially entirely fills, and is compacted in, the openings of the grid 28. To aid in filling the grid 28 as it passes to the compression zone, vibrator rods may be provided as shown at 30.

The conductive carrier grid 28 enters the pressure gap 18 and is compressed between the pair of horizontal rollers 14, 16. It will be noted that the spacing of the pressure gap 18 is less than the grid thickness so that the grid 28 is compressed a predetermined amount in order to lock the dry powder 12 therein as shall be described hereinafter in greater detail.

With the provision of the roll covers 20, 22, the distribution of the dry powder 12 is substantially uniform along the length of the grid 28. It has been found, however, that the powder gradient or density varies somewhat across the width of the grid 28 since the dry powder 12 tends to spread and accumulate intermediate the center and longitudinal edges of the grid 28 as both enter the compression zone between the pair of horizontal rollers 14, 16. Furthermore, the powder gradient or density may vary across the width of the grid 28 depending on other factors, i.e., the grid feed rate, powder size, the uniformity and nature of the grid structure, the diameter of the horizontal rollers 14, 16 and the thickness of the grid 28.

For the purpose of uniformly distributing the dry powder 12 across the width of the grid 28, adjustable shim means may be provided underneath the roll covers 20, 22. The adjustable shim means is composed of a metal sheet 32, the leading edge of which is contoured to control the flow of dry powder 12 into different portions of the grid 28. Preferably, the metal sheet 32 is positioned beneath only the roll cover 20 on the corresponding roller 14 and opposite the roll cover 22 against which the grid 28 is fed tangentially as shown in Figs. 2 and 3. It will also be seen that the leading edge of the metal sheet 32 extends slightly beyond the roll cover 20 and determines the bite point between the dry powder 12 and the roller 14. The metal sheet 32 may be adjusted by any suitable means, as for

example by a simple locking slide mechanism (not shown) into which the metal sheet 32 is clamped.

Fig. 4 shows an adjustable shim means composed of a single sheet 32a, the leading edge of which is contoured to direct a maximum amount of dry powder 12 into the center and longitudinal edges of the grid 28.

Another adjustable shim means is shown in Fig. 5 wherein two metal sheets 32b, 32c are provided, each of which is separately movable into the compression zone for varying the effective contour, and hence the powder flow into the grid 28. The use of the two contoured sheets 32b, 32c may be preferred where the flow characteristics of a specific powder composition require it.

Continuous strips of paper 34, 36 are preferably fed into the compression zone and pressure gap 18 from underneath the metal sheet 32 and the roll cover 22 in order to aid the compression of the dry powder 12, i.e., the paper strips 34, 36 provide a rough surface which increases the coefficient of friction of the pair of horizontal rollers 14, 16. The presence of the paper strips 34, 36 also prevents the surfaces of the resulting electrode from becoming polished or glazed by the pair of rollers 14, 16. In addition, the comparatively soft paper strips 34, 36 serve to recess the dry powder 12 into the grid openings and to ensure that substantially all of the dry powders are contained within the grid. Furthermore, the paper strips 34, 36 shield the surfaces of the rollers 14, 16 so as to keep them clean, and also are sufficiently porous to permit egress of some air as the dry powder 12 is compressed. A soft porous paper having a thickness of approximately 0.003 inch has been found suitable in the process of the present invention.

The finished electrode strip 38 emerges from the pressure gap 18 between the pair of horizontal rollers 14, 16 together with the continuous strips of paper 34, 36 which are then withdrawn therefrom. Suitably, the electrode strip 38 is cut into individual lengths or is fed to a take-up roll, not shown, for storage or subsequent treatment.

Preferably the continuous strips of paper 34, 36 are maintained under slight tension in order to prevent buckling as they are fed into the pair of rollers 14, 16. Although not shown, the paper strips 34, 36 are suitably fed from a supply roll and similarly wound on take-up rolls for disposal or possible reuse. In a similar manner, the continuous strip of conductive carrier grid 28 is fed from the supply roll and is maintained under substantially constant tension by any suitable means desired.

Generally, the dry powder 12 of active material should be kept at a relatively constant level above the compression zone as the grid 28 is fed therethrough. Further, a fixed force may be applied to the dry powder 12 to assure a more uniform powder distribution. The speed (rpm) of the pair of horizontal rollers 14, 16 essentially determines the grid feed rate since the grid 28 is actually drawn through by the rollers 14, 16 as it is continuously fed into the dry powder 12. A grid feed rate of approximately 8 to 30 feet per minute has been used successfully for different powder compositions. Although the dry powder 12 is preferably fed vertically from a hopper 10 as shown in Fig. 1, it may be convenient to use another arrangement, as for example a horizontal feed screw of a conventional design.

Referring now to Figs. 6 and 7, a preferred conductive carrier grid for use in the invention is shown. The preferred grid comprises a continuous web of expanded metal having a plurality of strands 40 integrally joined as at 42. In the direction of the arrows indicated, i.e., the direction of feed of the grid, the strands 40 are joined atop one another at the junctures 42 in a somewhat co-linear fashion as best shown in Fig. 7.

In comparison to conventional expanded metal wherein the grid openings are elongated or "diamond" shaped, the preferred grid structure of the present invention is composed of a plurality of substantially square openings or "pockets" 44, these openings providing larger regions bound by the grid to contain the dry powder 12 with a minimum of grid material per unit volume. To achieve this structure, it is necessary to stretch the grid to a greater amount than in the manufacture of the conventional expanded metal, i.e., an amount generally sufficient to form co-linear junctures 42. It should also be noted in Fig. 7 that the junctures 42 are disposed at an angle to the direction of feed (approx. 45 to 90 degrees) so that as the grid passes into the compression zone, the grid openings 44 are "up and open" to receive the dry powders 12 and to actually draw them into the grid as before described.

It will of course be understood that almost any conductive carrier grid may be used in the practice of the present invention so long as it can be compressed a sufficient amount to lock the dry powder 12 in grid openings. In addition to the preferred grid structure, other suitable conductive carrier grids include conventional expanded metal.

The thickness of the conductive carrier grid should be sufficient to provide electrodes which are strong and at the same time highly flexible. Generally, a grid thick-

ness in the range of from 0.02 inch to 0.1 inch is suitable for cylindrically formed electrodes of the type used in nickel-cadmium batteries, for instance. The number of openings in the grid is important in respect to maintaining a high electrode capacity, approximately one hundred openings per square inch of grid being suitable in most instances. The conductive grid should, of course, be inert to the battery system in which it is used; for example, in nickel-cadmium batteries, the grid may be composed of nickel.

An essential feature of the present invention is the compression of both the conductive carrier grid and the dry powder 12 of active material. It is this combined compression which makes it possible to mechanically lock the dry powder 12 in the grid openings so that when the electrode is shaped into cylindrical form the dry powder will not become loosened and dislodged. Furthermore, since the dry powder 12 is initially compacted into the grid openings and then compressed together with the conductive grid, a high powder density and electrode capacity is achieved.

Depending on the particular type of conductive carrier grid employed, the compression necessary to reduce the grid thickness a sufficient amount to lock the dry powder 12 therein will generally vary. It has been found that a compression of between 5 per cent and 60 per cent of the original grid thickness is suitable for most types of presently available grids. A preferred compression is approximately 25 per cent of the thickness of the grid.

Figs. 8 and 9 show an electrode in accordance with the invention employing the preferred conductive carrier grid previously described. It will be noted that the grid openings 44 are substantially entirely filled with the dry powder 12 of active material, and that the grid strands 40 and junctures 42 are compressed and flattened out along the longitudinal direction of the grid as indicated at 46.

In the practice of the present invention, the dry powder 12 may be of any convenient particle size or shape so long as it can be uniformly fed, compacted and compressed into the conductive carrier grid. The particle size is not critical, anywhere from sub-micron up to 35 mesh screen sizes (U.S. standard sieve) having been used successfully. The dry powder 12 may consist of metallic or nonmetallic materials or mixture of both, such as a mixture of  $\text{Ni}(\text{OH})_2$ , Ni and Cd metal powders for producing the positive electrodes of nickel-cadmium batteries. It may also be desirable to employ a binder in powdered form or in the form of relatively short fibers (1/16 inch or less), as for example Dynel fibers, (DYNEL is a Trade

Mark), or a conductive material, such as powdered or fibrous graphite.

In addition to the foregoing, a great many active materials have been employed for producing electrodes in accordance with the invention. For instance, a number of electrodes have been made for primary batteries using dry powders of manganese dioxide, silver oxide and zinc.

An important advantage of the invention resides in the use of a dry powder of an active material which makes it possible to produce electrodes for secondary batteries of the alkaline type without the costly procedures of impregnation as previously required in the manufacture of sintered electrodes. Furthermore, since the porosity of the electrodes can be easily controlled in carrying out the process of the present invention, the use of a dry powder eliminates the necessity for electrode formation, i.e., the continuous charging and discharging of the electrodes to build up the porosity to a desired level. It may also be mentioned that since the composition of the dry powder can be easily varied to produce electrodes in most any condition of charge, it is entirely possible to construct batteries which are fully charged, discharged or partially charged when manufactured.

Although the present invention has been described herein with particular reference to cylindrically formed electrodes for use primarily in secondary batteries of the alkaline type, it will be understood that the present electrodes may be used in primary batteries and in the form of substantially flat plate-like bodies.

#### WHAT WE CLAIM IS:—

1. A flexible electrode comprising dry powders of active material embedded within, and pressure bonded to, a conductive carrier grid, wherein the grid is a continuous web of expanded metal composed of a plurality of metal strands interconnected at bond joints and defining a network of open pockets within which the dry powders of active material are embedded, the grid traversing the cross section of the electrode from one surface to the other such that edge portions of the bond joints are exposed at the electrode surfaces, the carrier grid and the powder being compressed along the plane of the electrode surface so as to physically bond the dry powders of active material within the open pockets of the grid.

2. An electrode as claimed in claim 1, in which the grid pockets are square shaped.

3. An electrode as claimed in claim 1 or 2, in which the grid contains one hundred openings per square inch of said grid.

4. An electrode as claimed in any one of claims 1 to 3, in which the grid has a thickness of from 0.02 to 0.1 inch.

example by a simple locking slide mechanism (not shown) into which the metal sheet 32 is clamped.

5 Fig. 4 shows an adjustable shim means composed of a single sheet 32a, the leading edge of which is contoured to direct a maximum amount of dry powder 12 into the center and longitudinal edges of the grid 28.

10 Another adjustable shim means is shown in Fig. 5 wherein two metal sheets 32b, 32c are provided, each of which is separately movable into the compression zone for varying the effective contour, and hence the powder flow into the grid 28. The use of the two contoured sheets 32b, 32c may be preferred where the flow characteristics of a specific powder composition require it.

20 Continuous strips of paper 34, 36 are preferably fed into the compression zone and pressure gap 18 from underneath the metal sheet 32 and the roll cover 22 in order to aid the compression of the dry powder 12, i.e., the paper strips 34, 36 provide a rough surface which increases the coefficient of friction of the pair of horizontal rollers 14, 16. The presence of the paper strips 34, 36 also prevents the surfaces of the resulting electrode from becoming polished or glazed by the pair of rollers 14, 16. In addition, the comparatively soft paper strips 34, 36 serve to recess the dry powder 12 into the grid openings and to ensure that substantially all of the dry powders are contained within the grid. Furthermore, the paper strips 34, 36 shield the surfaces of the rollers 14, 16 so as to keep them clean, and also are sufficiently porous to permit egress of some air as the dry powder 12 is compressed. A soft porous paper having a thickness of approximately 0.003 inch has been found suitable in the process of the present invention.

50 The finished electrode strip 38 emerges from the pressure gap 18 between the pair of horizontal rollers 14, 16 together with the continuous strips of paper 34, 36 which are then withdrawn therefrom. Suitably, the electrode strip 38 is cut into individual lengths or is fed to a take-up roll, not shown, for storage or subsequent treatment.

55 Preferably the continuous strips of paper 34, 36 are maintained under slight tension in order to prevent buckling as they are fed into the pair of rollers 14, 16. Although not shown, the paper strips 34, 36 are suitably fed from a supply roll and similarly wound on take-up rolls for disposal or possible reuse. In a similar manner, the continuous strip of conductive carrier grid 28 is fed from the supply roll and is maintained under substantially constant tension by any suitable means desired.

Generally, the dry powder 12 of active material should be kept at a relatively constant level above the compression zone as the grid 28 is fed therethrough. Further, a fixed force may be applied to the dry powder 12 to assure a more uniform powder distribution. The speed (rpm) of the pair of horizontal rollers 14, 16 essentially determines the grid feed rate since the grid 28 is actually drawn through by the rollers 14, 16 as it is continuously fed into the dry powder 12. A grid feed rate of approximately 8 to 30 feet per minute has been used successfully for different powder compositions. Although the dry powder 12 is preferably fed vertically from a hopper 10 as shown in Fig. 1, it may be convenient to use another arrangement, as for example a horizontal feed screw of a conventional design.

Referring now to Figs. 6 and 7, a preferred conductive carrier grid for use in the invention is shown. The preferred grid comprises a continuous web of expanded metal having a plurality of strands 40 integrally joined as at 42. In the direction of feed of the grid, the strands 40 are joined atop one another at the junctures 42 in a somewhat co-linear fashion as best shown in Fig. 7.

In comparison to conventional expanded metal wherein the grid openings are elongated or "diamond" shaped, the preferred grid structure of the present invention is composed of a plurality of substantially square openings or "pockets" 44, these openings providing larger regions bound by the grid to contain the dry powder 12 with a minimum of grid material per unit volume. To achieve this structure, it is necessary to stretch the grid to a greater amount than in the manufacture of the conventional expanded metal, i.e., an amount generally sufficient to form co-linear junctures 42. It should also be noted in Fig. 7 that the junctures 42 are disposed at an angle to the direction of feed (approx. 45 to 90 degrees) so that as the grid passes into the compression zone, the grid openings 44 are "up and open" to receive the dry powders 12 and to actually draw them into the grid as before described.

It will of course be understood that almost any conductive carrier grid may be used in the practice of the present invention so long as it can be compressed a sufficient amount to lock the dry powder 12 in grid openings. In addition to the preferred grid structure, other suitable conductive carrier grids include conventional expanded metal.

The thickness of the conductive carrier grid should be sufficient to provide electrodes which are strong and at the same time highly flexible. Generally, a grid thick-



5. An electrode as claimed in any one of claims 1 to 4, in which the active material is manganese dioxide, silver oxide or zinc, or a mixture of nickel hydroxide, nickel and cadmium.
6. An electrode as claimed in claim 5, in which the active material contains a binder, or a conductive material.
7. A flexible electrode substantially as hereinbefore described and shown in Figs. 6 to 9 of the accompanying drawings.
8. A process for producing a flexible electrode as claimed in any one of the preceding claims, which comprises continuously feeding a conductive carrier grid together with a dry powder of an active material to a pair of horizontal rollers, spaced from each other at a distance less than the thickness of the grid to define a pressure gap therebetween and provided with roll covers extending in close proximity to said pressure gap and defining a compression zone thereabove, passing the grid between the roll covers and through the dry powder to fill the openings in the grid with said powder, passing the filled grid through the compression zone to compact the dry powder in the grid openings, pulling the filled grid through the pressure gap and compressing said grid to between 5 per cent and 60 per cent of its original thickness.
9. A process as claimed in claim 8, in which the grid is fed along the surface of one of the roll covers at a tangent with respect to the corresponding roller.
10. A process as claimed in claim 8 or 9, in which continuous strips of paper are fed into the compression zone and the pressure gap over the surface of each of the rollers.
11. A process for producing a flexible electrode, substantially as hereinabove described and shown in Figs. 1 to 5 of the accompanying drawings.

W. P. THOMPSON & CO.,  
12, Church Street,  
Liverpool, 1.  
Chartered Patent Agents.

B. K

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