May 11, 1954 A. F. DANIEL 2,678,343

DEPOLARIZER MATERIAL FOR PRIMARY CELLS

Filed Sept. 5, 1951

FIG. 1

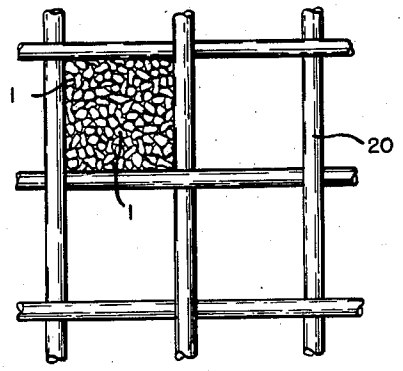


FIG. 2

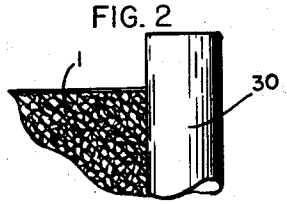


FIG. 3

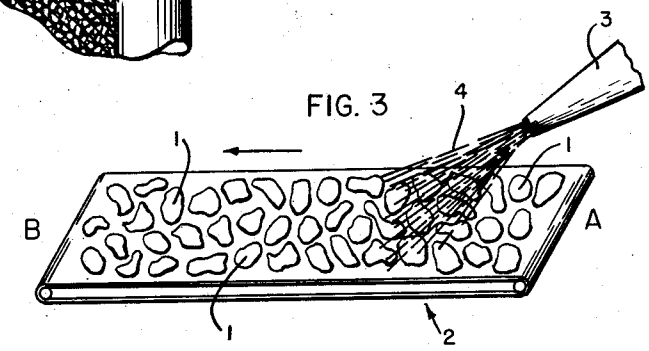


FIG. 4

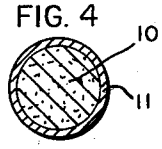


FIG. 5



FIG. 6

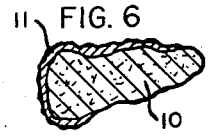
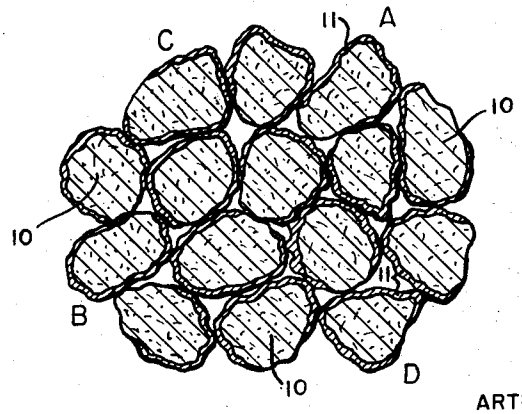


FIG. 7



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DEPOLARIZER MATERIAL FOR PRIMARY CELLS

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5 Claims. (Cl. 136—136)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment of any royalty thereon.

This application is a continuation-in-part of my application Serial No. 172,000, filed July 3, 1950, now abandoned.

In primary and secondary batteries, depolarizers such as manganese dioxide, mercuric peroxide, silver peroxide or lead peroxide, which are more or less non-conductive, are mixed with relatively large amounts or carbon black, graphite or other finely ground conductive materials to provide the degree of conductivity necessary for satisfactory performance of the cell. All such conductive materials must fulfill a number of conditions as, for instance, great purity, very small particle size (not much in excess of 38 millimicrons) and a certain dispersibility lying between the two extremes of clumping together and complete isolation of the particles. The depolarizers and the conductive powder must be thoroughly mixed preferably by grinding them together for a considerable length of time. Even if the best conductive materials and the best mixing procedures are used most of the particles of the finished mix will show on their surface not a continuous film but several disconnected patches consisting of clumps of the conductive material used. Only if excessive amounts of the conductive powder have been used, the particles of the depolarizer will have their surface covered by a continuous but relatively very thick film of the conductive material. In the later case, however, the absorbency of the depolarizer particles for the electrolyte will be markedly decreased which impairs the electrical characteristics of the cell. Another disadvantage of carbon black or graphite as conductive materials lies in the fact that the mix made with such materials has to be formed under relatively high pressure.

It is an object of the invention to avoid the use of carbon black or graphite as well as grinding operations in making the depolarizing material conductive. A further object is to obtain a depolarizer material which can be formed under relatively low pressure.

Another object of the invention is to cover the surface of the particles of the depolarizing material with a continuous extremely thin metal film in such a manner that after the coated particles are pressed together innumerable conductive paths of considerable length are formed throughout the compressed mass in all directions while leaving the mass sufficiently bibulous for quick absorption of electrolyte.

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Briefly stated, this and other objects of the invention are accomplished by surface coating the particles with a continuous, extremely thin, metal film before they are pressed together to form the depolarizing electrode, and then compressing the coated particles into the desired shape.

The invention and its objects will be apparent by reference to the following description of specific embodiments of the inventive idea taken in connection with the accompanying drawing wherein—

Fig. 1 is an enlarged elevational view of a portion of a wire screen used as a grid-type positive battery electrode, one opening of which has been filled with depolarizing material according to the present invention,

Fig. 2 is an enlarged, partly sectional view of a portion of the bobbin of a Leclanché type cell,

Fig. 3 is a schematic view of an apparatus for spraying a metal film on to particles of depolarizing material,

Figs. 4, 5 and 6 are further enlarged cross-sectional views of different forms of individual depolarizing particles coated according to the present invention, and

Fig. 7 is a similarly enlarged cross-section of particles coated according to the invention and then pressed together.

The depolarizer may be any suitable, electrolytically reducible, oxidizing type of compound such as manganese oxides, lead oxides, mercuric oxides or silver oxides, and various metals may be used as conductive surface coatings for these depolarzing materials.

In particular, manganese oxides may be coated with metallic silver, gold, nickel, chromium, manganese or titanium; lead oxides with metallic lead, silver or titanium; mercuric oxides with metallic iron or nickel and silver oxides with metallic silver.

The thin metal coating may be deposited on the depolarizer particles in a number of ways well known in the art of metal plating; choice of the method will depend on the specific depolarizer material to be coated and the specific metal to be used as coating material.

The thin metal coating may, for instance, be formed on the particles by a spray process or by electroplating or sputtering or metal vaporizing or by any other means which is capable of producing a continuous, very thin metal coating on the particles of depolarizing materials.

For sprayed metal coatings the metal is first melted in oxyacetylene or oxyhydrogen flames then atomized and finally forced against the particles. The most common and simplest type of

spray gun for this procedure consists of a nozzle with three concentric openings. Metal in the form of wire is fed through the central opening at a constant rate. As it comes out of the opening, it passes into the flame, where it is fused and pushed into the compressed-air blast by the force of the flame gases. The compressed-air blast then atomizes the liquid metal and forces it at a high velocity against the base material.

Fig. 3 of the accompanying drawing shows schematically and in simplified form the arrangement of the essential parts of an apparatus for coating the depolarizing particles by the method of metal spraying. An endless conveyor belt 2 receives the uncoated depolarizer particles 1 at A and as the conveyor belt moves in the direction of the arrow from A to B, the particles are coated by a metal spray 4 which is forced out of the spray gun 3. The thickness of the metal coating thus deposited on the particles may be regulated by controlling the speed of the conveyor belt, the distance of the spray gun from the conveyor belt and the conditions in the spray gun itself. If the conveyor belt moves only in the direction from A to B the particles will remain uncoated at the side with which they lie on the belt. If, however, the belt is allowed to vibrate while moving, the whole surface of the particles will be coated.

Fig. 4 shows an enlarged cross-sectional view of a spherical particle consisting of a porous depolarizer material 10 the surface of which is completely coated with a very thin metal film 11. For the sake of clearness, the thickness of the film is exaggerated in the drawing.

Fig. 6 shows an irregular shaped particle consisting as in Fig. 4 of a porous depolarizing material 10 the surface of which, however, is coated only partly with the thin metal film 11.

The coated particles as shown in Fig. 4 and Fig. 6 are now compressed into the desired form to obtain the depolarizer electrode. Even if the particles are completely covered with a continuous metal film 11 as shown in Fig. 4, the deformation of the particles due to the exerted pressure in forming the electrode will crack or rip the film in spots and thus expose parts of the porous depolarizing mass of the particle in the manner shown in Fig. 5 and thus make the original completely covered particle absorbent for the electrolyte.

The particles may be compressed to form any desired depolarizing electrode. They may, for instance, be pressed into a suitable wire screen as shown in Fig. 1 which wire screen is made of wire 20 of copper, nickel or any other suitably coated or uncoated metal. One opening of the wire screen shown in Fig. 1 is filled with compressed particles 1 of depolarizing material having a coating of very fine metal film (not shown in Fig. 1). The depolarizing material according to the invention may, of course, be pressed into any other suitable type of grid.

Fig. 2 shows an enlarged view of a portion of the bobbin of a Leclanché type cell. The carbon rod 30 is surrounded by a bobbin of depolarizing material which has been compressed from particles 1 coated with a thin metal film (not shown) according to the invention.

Generally speaking, the surface coating of the depolarizer electrode after the particles have been compressed into the desired shape should be not less than 25% and not more than 75% of the free surface of the depolarizer particles.

After the depolarizer particles have been compressed the metal films 11 will form innumerable irregularly shaped conductive paths of considerable length throughout the compressed mass in all directions as indicated in Fig. 7. In following the metal film 11 from one particle to another it can be seen that there exist electrical connections between almost all of the particles in any one direction. For instance, there is a continuous path of metal film from point A to point B and also from point C to D.

To achieve optimum cell function there should be at least 25% of the surface of the depolarizing particles open for the absorption of the electrolyte. For specific depolarizers the best percentage of surface coating of the particles has been found to be about 25% for silver particles, 40% for mercuric peroxide and 75% for manganese dioxide.

All known methods of surface coating with metals may be adapted for the purpose of the present invention.

Particularly advantageous effects have been achieved with cathode sputtering which has found much practical application for obtaining metal films on glass (see, for instance, "Procedures in Experimental Physics" by J. Strong, Prentice-Hall, Inc., N. Y. 1942, chapter 4). Sputtering can be carried out successfully under a wide variety of conditions with pressures of the glow discharge ranging from 1 down to 10^{-2} mm. For the purpose of the present invention, the metal with which depolarizer particles are to be coated is made the cathode while the particles themselves are made the anode. The glow discharge is preferably produced by a direct potential ranging above 1000 volts. Since the sputtering rate can be easily controlled any desirable thickness of the metal coating is obtainable.

The evaporation method for producing thin metal films on non-metals is also very well known and simple both in its mechanism and in its practical application. (See the above cited book by Strong, chapter 4.)

A piece of the metal with which the particles are to be coated is simply heated in a high vacuum until its vapor pressure is about 10^{-2} mm. of mercury or greater whereupon the metal emits molecular rays. The degree of vacuum required for successfully carrying out the process is such that the mean free path of the molecules is larger than the diameter of the vacuum container. Therefore, molecular rays propagate from their source without disturbance until they impinge on the walls of the vacuum or some object within them. If, therefore, the depolarizer particles to be coated are exposed to those molecular rays, they condense on it to form the desired metal film.

The depolarizing particles may also be electroplated by making them the cathode in a bath of an ionizing salt of the metal which is to form the coating. Preferably, a tumbling barrel will be used to plate the particles.

The particles may also be coated with thin metal films by chemical deposition. There are two widely used methods known for chemical silvering; i. e., the Brashear method and the Rochelle salt method. The latter method is better suited for the purpose of the present invention since very thin silver coats can be achieved with it. In case silver peroxide particles are used as depolarizer material a thin silver coat may also be obtained by reducing the surface of these particles in well known manner to silver.

The conducting material used as coating should be of such a nature that it will not adversely af-

fect the characteristics of the cell. Excellent results have been achieved with films of iron or nickel on the mercuric peroxide powder in the alkaline zinc mercuric peroxide cell, and with manganese on the manganese dioxide particles in the Leclanché type cell.

The depolarizing electrodes made according to the invention possess much higher electric conductivity than any other type of depolarizing electrode while being at the same time of very high absorbency for the electrolyte. Another advantage lies in the fact that the particles coated according to the invention need less compressing than the known mixtures of depolarizing particles with carbon or graphite.

It is apparent that while the invention is shown and described in particular applications, many changes and modifications may be made without departing from the spirit of the invention as sought to be defined in the following claims:

What is claimed is:

1. In a method of producing depolarizer electrodes by compressing finely divided depolarizer material into the desired electrode form in the absence of any conductive carbon material comprising completely coating the individual particles of the depolarizer with an extremely thin continuous metal film and then compressing the coated particles to cause the metal film to crack due to the deformation of the depolarizer particles whereby the cracked metal film forms innumerable conductive paths of considerable length thruout the compressed mass while the remaining parts of the surfaces of the depolarizing particles become exposed and free for the direct action of the electrolyte.

2. In a method of producing manganese dioxide electrodes by compressing finely divided manganese dioxide into the desired form in the absence of any conductive carbon material comprising completely coating the individual particles of the manganese dioxide with a continuous extremely thin film of a metal selected from the group consisting of silver, gold, nickel, chromium, manganese and titanium, and then compressing the coated particles to cause the metal film to crack due to the deformation of the manganese dioxide particles whereby the cracked metal film forms innumerable conductive paths of considerable length thruout the compressed mass while the remaining parts of the surfaces of the manganese dioxide particles become exposed and free for the direct action of the electrolyte.

3. A method of producing lead-peroxide depolarizer electrodes comprising coating individual particles of lead-peroxide with a member of the group consisting of lead, silver and titanium and then compressing said particles of lead-peroxide to form the depolarizer electrode.

4. A method of producing mercuric oxide depolarizer electrodes comprising coating individual particles of mercuric oxide with a member of the group consisting of iron and nickel and then compressing said particles of mercuric oxide to form the depolarizer electrode.

5. A method of producing silver peroxide depolarizer electrodes of electrical cells comprising coating individual particles of silver peroxide with metallic silver and then compressing said coated particles to form the depolarizer electrode.

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