

PATENT SPECIFICATION

938,354

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Improvements in and relating to Batteries.

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 ELLSWORTH GEORGE MUNCK and JOSEPH RANDOLPH TOMLINSON), 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 a method of encasing the cells of multiple cell batteries and to multiple cell batteries containing a novel encasing material therein, and it more particularly relates to the encasing of such cells with polyurethane foams.

In the past, manufacturers have secured the individual cells of multiple cell batteries in a variety of ways. Corrugated liners, fill-in pads of various types, and inner paper nests, waterproofed by wax or asphalt impregnation have been used to fix the position of the individual cells. Sometimes cathodic envelope and wafer cells are not put into containers as such, but are merely dipped in wax, asphalt, or other material to cover them and contain them in the appropriate size and relation to perform the task intended. A cathodic envelope cell is a cell the elements of which are wrapped into a cathode current collector film envelope such as a polyvinyl plastic film made conductive with carbon. A cell of this type is described in co-pending Application No. 2025/59 (Serial No. 912,911). In other instances, the external conductors must be fixed to the battery of cells by riveting or soldering. None of these techniques has been entirely satisfactory.

According to the present invention there

is provided a method of encasing the cells of a multiple cell battery which comprises introducing polyurethane resin into a container for the cells, foaming the resin, and curing the foam.

Polyurethane resins have been known for some time to the chemical industry. These resins are generally made by reacting a diisocyanate with an organic compound containing two or more hydroxyl groups per molecule, as for example, a glycol. This resin may be conveniently foamed by adding water to an excess of the diisocyanate. The foaming action may be catalyzed by introducing a tertiary aliphatic amine into the reaction mixture. The foam thus produced is either rigid, semi-rigid, or resilient, depending upon the amounts of various components employed. A cross-linking agent, such as castor oil for example, is generally used to increase the stiffness of the foam.

Foamed polyurethane resins are particularly suitable encasing materials for multiple cell batteries because they have relatively low curing temperatures, such as not to cause harm to the battery components, and short curing times, for example, about a half-hour at 125° F. being necessary for normal factory handling. A full strength cure takes place in about twenty-four hours at this temperature. These resins are further desirable because they are not acid, as are phenolics for example, and therefore do not short circuit the individual cells during curing. When properly formulated and cured, these resins are very useful since they adhere very well to both paper and metal, the materials principally used to make battery and cell containers. They are impact-, shock-, and vibration-resistant, and are relatively unaffected by high humidity.

[Price 4s. 6d.]

Because these resins may be foamed, a variety of densities, ranging from 1.0 to 30.0 pounds per cubic foot, are available to formulators thus providing a multitude of different density products having manifold uses. Good heat and electrical resistance, both essential to proper battery encasing materials, are provided by these resins at any of the densities available. In addition, when used in the proper formulation, such resins supply enough pressure, if foamed in an enclosed space, to insure good contact among a stack of cells of the wafer or cathodic envelope type. In the same operation, this foam will cause electrical leads in contact with the stack of such cells to become fixed in position, thereby removing the need for soldered or riveted connections.

This invention will be best understood with reference to the accompanying drawings in which:—

Fig. 1 is a perspective view of a battery utilizing the concept of this invention, part of the battery and container being broken away;

Fig. 2 is a perspective view of a different type of battery utilizing the concept of this invention, part of the battery and container being broken away; and

Fig. 3 is a plan view of a multiple cell battery in a container with encasing material therein according to this invention.

For some applications, it is desirable to provide an insulating container for a stack of cells and yet keep the stack under pressure to insure good electrical contact. A stack of cells suitable for such use may be placed in a mold under endwise pressure exerted through contact plates having electrical leads in contact therewith. A resin of the proper formulation is then introduced into the mold and allowed to foam in the confined space therein. The foamed resin is then cured to such a degree of stiffness that the cells under compression will be held that way and so the electrical leads will be fixed in the proper place.

A battery made in this manner is shown in Fig. 1 and comprises a stack of wafer type cells 10, an end plate 12 in contact therewith, electrical leads 16 and 18 in electrical contact with the stack of cells, and a foamed stiffened polyurethane resin 20 completely surrounding the stack of cells and the contact plates. This resin both holds the elements of this battery in proper relation and compression, and insulates all the elements thereof, except the electrical leads, from external contact.

Another type of battery made according to this invention is shown in Fig. 2. This battery consists of a stack of cathodic envelope cells 22 in a can 24. Electrical leads 26 and 28 extend through the cover 29 of the can 24 in order to facilitate con-

tact to the battery, and a stiffened polyurethane foam 30, inside the can 24 between a tray 32 which rests on the cells 22 and an insulator 34 adjacent the can cover 29, holds the cells in compression and fixes the leads in place.

This latter type of battery is made by placing a suitable number of cells in a coverless container, placing a tray on top of the cells, depositing the properly formulated resin in the tray, putting the suitably insulated cover on the container, inserting the electrical leads through the cover into contact with the cells, spinning down the cover so as to seal the container, and foaming the resin to fix the leads in place and provide sufficient pressure to hold the cells in the proper compression.

Referring now to Fig. 3, it is to be noted that the multiple cell battery container 40 has large cylindrical cells 42, flat cells 44 and small cylindrical cells 46 of the flashlight battery type, thus illustrating the adaptability of this invention to the encasing of various shape individual cells. The cells are insulated from the container 40 by a foam 48 of the encasing material above discussed. Each of the different types of cells is suitably connected to the proper terminals 50 in the battery container 40. Thus in using a multiple cell battery of the type shown, any of a variety of voltages and currents may be produced by connecting to the proper terminals 50.

It has been found that cells or batteries encased in polyurethane foam have excellent shelf life even under high humidity conditions. It has further been found that batteries made according to this invention are sufficiently resistant to shock, extreme vibration, and excessive compression to withstand rocket take off and flight. The excellent properties of the encased cells are believed to be derived from the fact that rigid polyurethane foam has: high surface resistivity at temperatures from -80°F. to 160°F. , even at humidities as high as 95% to 100%; excellent sealing properties thereby preventing moisture loss, electrolyte leakage, or short circuiting at temperatures from -80°F. to 160°F. ; and the ability to retain these properties even in the presence of small amounts of halogen gases.

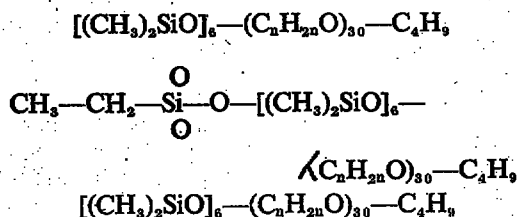
The following may be cited as specific examples of the practice of this invention;

EXAMPLE I.

A stack of 80 silver/silver iodide/vanadium pent-oxide cells was prepared and a contact plate placed at each end of the stack. Electrical leads were placed adjacent the contact plates and the whole assembly was placed in a mold. Pressure was exerted on the stack of cells through the contact plates during the time the assembly



was in the mold. A mixture of 100 parts by weight of a highly-branched polyester, derived from the reaction of adipic acid and a mixture of triols, which has a free hydroxyl number of 350 to 550, 0.3 parts by weight of a silicone resin, corresponding to the structural formula:—



wherein the group designated as $(C_nH_{2n}O)_{30}$ represents a mixture of oxyethylene units and oxypropylene units, the "n" being an integer from 2 to 4; 0.5 parts by weight water; 0.25 parts by weight anhydrous dimethylaminoethanol; and 100 parts by weight of a prepolymer composed of the reaction product of the polyester above disclosed and toluene diisocyanate having 34.2% free isocyanate functional groups was made. The mold was filled with 2 grams of this mixture which was allowed to foam therein thus fixing the respective electrical loads to the contact plates and fully enclosing the stack of cells in the foamed resin. The mold was then heated to 160° F. for 60 minutes to fully cure and stiffen the foam. The mold was then removed and the

stiffened foam held the stack in compression thus forming a completed battery.

EXAMPLE II.

A stack of 3 leclanche cathodic envelope cells was prepared and placed in an insulated battery can. A tray was placed on top of the cells inside the can and the insulated cover of the can placed in position but not fixed to the body of the can. Electrical leads were inserted into the can through apertures in the cover into contact with the appropriate cell terminals. A mixture of constituents identical with that described in Example I was made, and 30 grams thereof were metered into the tray. The cover was spun down to finish the battery can and the resin mix allowed to foam in the confined space inside the can. The foam was heated to 125° F. and cured at this temperature for 15 minutes. Upon the completion of the cure, the battery was tested and found to have been properly encased as shown by the output. The loads of the battery were found to have been fixed to the terminals without the necessity of riveting or soldering.

Batteries made according to this invention have been tested and found to have the proper output after having been pressurized with polyurethane foam. The results of tests conducted on batteries of silver iodide cells made according to this invention appear in Table I below:—

TABLE I.

Number of cells each 0.25 inch diameter and 0.005 inch thickness in battery	Voltage of cells before encasing	Voltage of cells after encasing
80	40	40
140	70	70
144	72	72

The results of these tests show that the encasing material set forth herein, stiffened polyurethane foam, is not detrimental to the output of a battery which utilizes this material. This fact, coupled with the improved shock and vibration resistance and simplified internal pressurizing made possible by the use of polyurethane foams make such the best material presently known for encasing multiple cell batteries.

EXAMPLE III.

A resin was prepared by mixing 25 parts by weight toluene diisocyanate, 80 per cent 2-4 isomer and 20 per cent 2-6 isomer, with 21 parts by weight castor oil, and 4 parts by weight polyethylene glycol 200. The catalyst was formed by mixing 5 parts of

triethyl amine with 1 part water. A blend of 16.7 to 1 resin to catalyst ratio by weight was made, metered into the bottom of a multiple cell battery container to a depth of 6 inches, and 4 stacks of 15 flat cells each and 7 round cells connected in series-parallel relation were placed on the mixture. Each cell used, both round and flat, was rated at 1.5 volts. Each flat cell stack was 4.75 by 1 by 1 inches and all these cells were connected in series to deliver 90 volts. The round cells were each 4 inches long by 1.25 inches in diameter and parallel connected to form an "A" battery. After the cells were in the proper place, the temperature was raised to between 80°—130° F. and the mixture allowed to foam. After foaming stopped, the foam was cured for



one-half hour at this temperature. The cells were then connected to the terminals provided in the container wall and the cover of the container placed thereon. The multiple cell battery thus completed was then

cured for twenty-four hours at this temperature. Batteries encased in accordance with the method of the present invention were tested for vibration and shock resistance by placing them on a bed which was capable of three directional perpendicular harmonic vibrations. That is to say, each battery was vibrated perpendicular to its terminal face and in the two other directions perpendicular to this direction. The bed was started at a frequency of vibration of 10 cycles per second and increased at the rate of at least 1 cycle per second per minute to a maximum of 60 cycles per second. The entire range of frequencies, from 10 to 60 and return to 10 cycles per second, was traversed in not less than 90 and not more than 100 minutes. The amplitude of the vibrations for those tests was 0.03 inches. The shock and vibration resistance of batteries tested in this manner is determined by measuring the open circuit voltage of the battery before and after each test. Batteries made according to this invention were subjected to this test about 15 hours after foaming the polyurethane resin. No voltage change was detectable in batteries encased with foamed polyurethane resins. However, asphalt encased batteries, those made according to conventional processes, failed completely upon being subjected to this very same test.

It should be noted, in the practice of this invention, that foaming of resins such as have been described above begins about one minute after they have been mixed with the tertiary amine catalyst. In order to insure the proper foaming action and adhesion, the individual cells should be placed on the resin-catalyst mixture less than 60 seconds after it has been metered into the battery container. It is to be further noted that the foam height may be regulated for any particular application by adjusting either the diisocyanate preparation or by varying the depth of resin-catalyst mixture initially metered into the battery container, since these control the amount of foaming and the quantity of resin available to be foamed.

In addition to the advantageous features referred to above, it is important to note that when cells are encased in polyurethane foam, the user thereof is protected against an occasional minor explosion which is sometimes caused by a build-up of gas pressure inside the cell. The foam acts to deaden the noise accompanying such explosion and also serves to absorb any of the liquid or gaseous material evolved. It

is, of course, understood that the teachings of this invention may be applied to any battery system, either primary or secondary. ~~best~~ include leclanche cells, regardless of the anode material employed; alkaline electrolyte cells; mercury cells; nickel-cadmium cells; and solid electrolyte cells. The method of the present invention may also be advantageously employed to encapsulate electrical circuits.

WHAT WE CLAIM IS:—

1. A multiple cell battery which comprises a multiplicity of individual galvanic cells and a foamed polyurethane resin holding the cells in position.

2. A battery as claimed in Claim 1, in which the cells are contained in a container and insulated from each other and from the container by the foamed polyurethane resin.

3. A battery as claimed in Claim 1 or 2 in which the cells are connected to each other and to terminals in the container.

4. A battery as claimed in Claim 1, in which the cells are in physical and electrical contact with each other, and electrical leads contact the cell terminals.

5. A battery as claimed in Claim 4, in which the cells are cathodic envelope cells stacked in series relation.

6. A battery as claimed in Claim 1, in which the cells are relatively thin galvanic cells stacked within a battery can, electrical terminals are in contact with the stack, and electrical leads contact the terminals and extend through the can.

7. A multiple cell battery substantially as hereinbefore described, with reference to and as illustrated in the accompanying drawings.

8. A method of encasing the cells of a multiple cell battery which comprises introducing polyurethane resin into a container for the cells, foaming the resin, and curing the foam.

9. A method as claimed in Claim 8, in which the cells are placed in the container before the introduction of the resin, and the resin is foamed in situ.

10. A method as claimed in Claim 8, in which the cells are placed in the container after the introduction of the resin.

11. A method as claimed in any of Claims 8 to 10, in which the foam is heated to 125° F.

12. A method of encasing cells of a multiple cell battery substantially as hereinbefore described with reference to the Examples.

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one-half hour at this temperature. The cells were then connected to the terminals provided in the container wall and the cover of the container placed thereon. The multiple cell battery thus completed was then cured for twenty-four hours at this temperature.

Batteries encased in accordance with the method of the present invention were tested for vibration and shock resistance by placing them on a bed which was capable of three directional perpendicular harmonic vibrations. That is to say, each battery was vibrated perpendicular to its terminal face and in the two other directions perpendicular to this direction. The bed was started at a frequency of vibration of 10 cycles per second and increased at the rate of at least 1 cycle per second per minute to a maximum of 60 cycles per second. The entire range of frequencies, from 10 to 60 and return to 10 cycles per second, was traversed in not less than 90 and not more than 100 minutes. The amplitude of the vibrations for those tests was 0.03 inches. The shock and vibration resistance of batteries tested in this manner is determined by measuring the open circuit voltage of the battery before and after each test. Batteries made according to this invention were subjected to this test about 15 hours after foaming the polyurethane resin. No voltage change was detectable in batteries encased with foamed polyurethane resins. However, asphalt encased batteries, those made according to conventional processes, failed completely upon being subjected to this very same test.

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WHAT WE CLAIM IS:—

1. A multiple cell battery which comprises a multiplicity of individual galvanic cells and a foamed polyurethane resin holding the cells in position. 80
2. A battery as claimed in Claim 1, in which the cells are contained in a container and insulated from each other and from the container by the foamed polyurethane resin.
3. A battery as claimed in Claim 1 or 2 in which the cells are connected to each other and to terminals in the container. 85
4. A battery as claimed in Claim 1, in which the cells are in physical and electrical contact with each other, and electrical leads contact the cell terminals. 90
5. A battery as claimed in Claim 4, in which the cells are cathodic envelope cells stacked in series relation.
6. A battery as claimed in Claim 1, in which the cells are relatively thin galvanic cells stacked within a battery can, electrical terminals are in contact with the stack, and electrical leads contact the terminals and extend through the can. 100
7. A multiple cell battery substantially as hereinbefore described, with reference to and as illustrated in the accompanying drawings.
8. A method of encasing the cells of a multiple cell battery which comprises introducing polyurethane resin into a container for the cells, foaming the resin, and curing the foam. 105
9. A method as claimed in Claim 8, in which the cells are placed in the container before the introduction of the resin, and the resin is foamed in situ. 110
10. A method as claimed in Claim 8, in which the cells are placed in the container after the introduction of the resin. 115
11. A method as claimed in any of Claims 8 to 10, in which the foam is heated to 125° F.
12. A method of encasing cells of a multiple cell battery substantially as hereinbefore described with reference to the Examples. 120

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