

PATENT SPECIFICATION

(11) 1285 413

DRAWINGS ATTACHED

- (21) Application No. 46523/70 (22) Filed 30 Sept. 1970
 (31) Convention Application Nos. 35820, 35821 and 35822
 (32) Filed 24 April 1970 in
 (33) Japan (JA)
 (45) Complete Specification published 16 Aug. 1972
 (51) International Classification H01M 9/02
 (52) Index at acceptance
 H1B D1 D6 D8C D8L S1A8 S1D3 S3A1 S3A2 S4E S4F



(54) LEAKPROOF BATTERY AND METHOD OF MANUFACTURING THE SAME

(71) We, YUASA BATTERY COMPANY LIMITED, a Japanese Corporation, of 3—1, Hakubaicho, Takatsuki-City, Osaka Prefecture, Japan, 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 leakproof battery, and more particularly to a storage battery and a method of manufacturing the same. Conventionally included under means for rendering immobile the electrolyte of a battery are a method of using an acid resisting porous body such as glass mat, a sheet made of animal fiber and vegetable fiber, non-woven feltlike fabric pumice powder, diatomaceous earth, as an electrolyte holding body and disposing the porous body in the interstice between electrode plates and around a plate group and also a so-called colloidal battery produced by adding sulphuric acid to sodium silicate or commercially obtainable silica sol, stirring the mixture and pouring the same into a battery and gelatinizing it into a porous electrolyte holding body. But the former has disadvantages; it cannot rid itself of a fluid electrolyte namely, if there is a fluid electrolyte present in the battery, there is a possibility of the electrolyte leaking from a filling hole, a vent hole or jointed portions when the battery falls or because of the gas produced at the end of charging the battery; the electrolyte that leaks may sometimes corrode appliances and implements, and in such an instance where the battery is used with toys, users of the battery are children and accordingly the battery is handled carelessly, and hence the electrolyte tends to leak, and should it leak, there is a fear of the children being subject to burns and accordingly such a battery is very dangerous and there leaves much to be desired in point of safety in the battery. On the other hand, the latter is not free from disadvantages either; namely, colloid in the form of an electrolyte holding body is very weak, and a

decrease in the liquid made by an increasing number of charges and discharges cleaves the colloid and causes capacity deterioration.

A primary object of the invention is to obtain a leak-proof battery that is free from leak of electrolyte from the battery container.

Another object of the invention is to obtain a battery of high performance free from reduction in the porosity of silica gel and having a liquid absorbable porous body high in porosity.

Still another object of the invention is to provide a battery very simple in assembling and inexpensive.

Yet another aspect of the invention is to render the electrolyte immobile by means of a liquid absorbable porous body and to satisfactorily fix electrode plates and prevent active material from falling off the electrode plates.

According to one aspect of this invention a method of manufacturing a leak-proof battery comprises disposing, a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around an electrode plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the electrode plate group, said liquid absorbable body being impregnated with an electrolyte and thereafter received in a battery container.

According to another aspect of this invention a method of manufacturing a leak-proof battery comprises disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around an electrode plate group formed so as to provide spaces between plates by interposing separator bodies therebetween, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an

electrolyte and thereafter received in a battery container.

According to a further aspect of this invention a method of manufacturing a leak-proof battery comprises inserting an electrode plate group in a battery container, disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around said plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an electrolyte.

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings of which:—

Figure 1 is a perspective view of an electrode plate group;

Figure 2 is a perspective view showing a mould which is the same in size and shape as a container for receiving therein the plate group shown in Figure 1 and into which mould mixed powder for constituting a liquid absorbable porous body is poured;

Figure 3 is a perspective view showing the mould of Figure 2 disassembled;

Figure 4 is a longitudinal sectional front view showing the composition shown in Figure 3 placed in the container after the composition has been treated;

Figure 5 is a perspective view of a set of plates, a positive and a negative plate between which a special separator is used; and

Figure 6 is a longitudinal sectional front view of the plate group of Figure 4 packed in a bag and received in the container.

EXAMPLE 1:

This is a method of integrating an electrode plate group and a liquid absorbable porous body by the use of a moulding frame. As a material for the liquid absorbable porous body for covering and fixing the plate group was used a composition 6 of the mixture of 1 part by weight of high density polyethylene powder (50—500 mesh) with 3 parts by weight of hydrated silica gel powder (50—300 mesh and having a water content of 70% by weight). As shown in Figures 1 to 3, a plate group 4 having an acid resisting separator 3 interposed between each lead dioxide positive plate 1 and adjacent lead negative plate 2 was enclosed by a collapsible metallic moulding frame which was made of four plates 5 and which was of the same size and shape as the battery container. Then, said powdered composition 6 was filled between the plate group 4 and the inner surfaces of the moulding frame 5. In this case the interstice between the plate group and the moulding frame was rapidly filled by imparting slight vibration to the moulding frame. The moulding frame 5 filled with the

powdered composition 6 was left in saturated steam at a temperature of more than 100°C at a pressure of 5—9 kg/cm² at. for $\frac{1}{2}$ —2 hours, and when the polyethylene in the composition had melted, the mold frame was taken from the saturated steam so as to solidify the resin and transferred into the ambient atmosphere where the frame was collapsed as shown in Fig. 3, whereupon a plate group covered with a body having a porosity of 70—80%, requiring no surface active agent treatment, being excellent in absorbability and mechanically strong was obtained. The plate group covered with the liquid absorbable porous body obtained by the method described was dried in hot air below 100°C and thereafter was dipped in a specified electrolyte, for example a dilute sulphuric acid bath of specific gravity of 1.240 to impregnate the porous body with the electrolyte. The porous body thus treated was taken up and placed in a battery container 7 having a lid 9 with a filling plug 8 (Fig. 4).

EXAMPLE 2:

This is a method of integrating an electrode plate group and a liquid absorbable porous body in a battery container. In this example is described a method of using no molding frame in order to obtain more efficiently the plate group covered with a liquid absorbable porous body. The plate group was beforehand placed in a battery container 7 formed of thermoplastic resin, thermosetting resin, or ebonite that can resist saturated steam of a temperature of over 100°C for $\frac{1}{2}$ —2 hours, and a composition of the powdered mixture described in Example 1 was filled between the plates and between the interstice of the plate group and the container and was left in saturated steam at a temperature which was above 100°C and which melted the synthetic resin. Thus a battery in which the plate group, the liquid absorbable porous body and the container are formed integral was obtained. The plate group was dipped in an electrolyte so as to impregnate the porous body with the electrolyte. In this method, as there is no necessity of using any particular molding frame, a battery can be manufactured at low cost. Also, as it can save labor, it is suitable for mass production.

EXAMPLE 3:

This is a method of using no U-shaped separators between the electrode plates. As shown in Fig. 5, a plate group was formed by parallelly disposing several sets of assemblies each comprising a U-shaped separator 3 placed between a lead dioxide positive plate 1 and a lead negative plate 2, and was placed in the molding frame in the same manner as in Example 1, and then a composition 6 of a mixture of 1 part by weight of powdered polyethylene with 2—3 parts by weight of powdered hydrated silica gel was filled

between the plate group members and the molding frame and between the plates while vibration was imparted to the frame, and the molding frame thus filled with the composition 6 was left in saturated steam of a temperature of over 100°C for $\frac{1}{2}$ —2 hours, heated, and was then taken out into the atmosphere so as to solidify the resin. The battery manufactured in this manner had a liquid absorbable porous body formed between the plates without the use of the platelike separators. Accordingly, such a battery has the advantage that it is capable of being impregnated with a larger quantity of electrolyte.

EXAMPLE 4:

This is a method of covering an integral combination of an electrode plate group and a liquid absorbable porous body with a bag 13 as shown in Fig. 6. Accordingly to the method, a plate group 4 was placed in a suitable molding frame or container, and the composition 6 of a mixture of 1 part by weight of powdered polyethylene with 3 parts by weight of powdered hydrated silica gel was uniformly filled in the space surrounding the plate group and in the interstice between the plates and was heated in saturated steam at a temperature of over 100°C and a pressure of 4—5 kg/cm² at. and solidified to form a liquid absorbable porous body with the plate group, and was dried and thereafter dipped in the electrolyte for about $\frac{1}{2}$ —1 hour under reduced pressure and then taken up from the electrolyte. Thereafter, a cover plate 12 made of an acid resisting, oxidation resisting rubber or synthetic resin was placed on the top of the plate group, said cover plate having a gas vent 10 and holes 11 for passing there-through the battery poles. Next, the assembly was put into a bag 13 of heat-shrinkable synthetic resin, for example vinyl chloride, poly-

ethylene or silicon resin, and was externally treated with hot water or hot air to shrink the bag 13 so that it is closely covered the liquid absorbable porous body 6. The bag 13 serves to prevent leakage of the liquid electrolyte. If, in this case, an adhesive agent is previously applied to the surface of the cover plate 12, such application will prove more effective since adhesion between the bag and the cover plate assists the prevention of leaking into the container 7.

In the invention, a composition of a mixture of hydrated silica gel with powdered thermoplastic synthetic resin is disposed around the plate group, heated in saturated steam of a temperature above the softening temperature of resin and solidified to obtain a liquid absorbable porous body. Since the composition is heated above the softening temperature of resin, resin particles are melted and chained in a threadlike manner along the points of contact of silica gel powder, while on the other hand the water in the hydrated silica gel is evaporated, but because the hydrated silica gel is heated in saturated steam, the hydrated silica gel, unlike drying effected in the normal hot air, makes little or no volume shrinkage, and accordingly the molten polyethylene is interrupted by the silica gel and is chained in a narrow threadlike manner along the points of contact between silica gel particles. The resin does not agglomerate and does not completely envelop the silica gel. This is a strong physical characteristic brought about by heating in saturated steam. Moreover, continuous fine pores of about 30 μ are uniformly formed in the silica gel, and a general porosity of about 70% can be obtained.

The types of synthetic resins of the liquid absorbable porous body used in the invention and the mixing ratio of the synthetic resins to silica gel are shown in the following table.

45

50

55

60

65

70

75

80

85

TABLE

No.	Type of synthetic resin	Percentage (by weight) of Hydrate Silica gel	Mixing ratio (part by weight)		Atmosphere at time of heating	Porosity of porous body %	Properties of porous body
			Resin	Silica gel			
A	Polyethylene	70	2	4	in saturated steam	69	hard
B	Polyethylene	70	2	5	"	72	"
C	Polyethylene	70	2	10	"	79	soft, easily pulverizable
D	Polyethylene	40	2	5	"	64	hard
E	Polyvinyl chloride	70	3	2	"	55	"
F	ABSS	70	2	2	"	49	"
G	ABS	70	2	3	"	59	"
H	Polypropylene	70	2	4	"	63	"
I	Polypropylene	70	2	5	"	91	"
J	General-purpose styrol	70	2	5	"	73	"
K	High impact styrol	70	2	2	"	51	"
L	Low-pressure polyethylene	70	2	5	"	71	"
M	Polyamides resin	70	2	3	"	61	"

The determination of porosity can be made by the following formula

$$P = \frac{W_1 - W}{W_1 - W_2} \times 100\%$$

in which W represents the weight of a porous body; W_1 the weight of the porous body having the pores thereof completely filled with water; W_2 the weight of the porous body in the water; and P represents porosity (%).

In the table shown, A—M show the properties of a porous body according to the invention. The porosity and strength shown can be freely selected by changing the mixing ratio of hydrated silica gel to thermoplastic resin over the range of 1—5 parts of hydrated silica gel to 1 part of thermoplastic resin. Heating conditions may vary with synthetic resins, but are above the softening temperature of the respective resins. The liquid absorbable porous body of the invention is high in porosity and capable of holding a large quantity of electrolyte. Even if the electrolyte comes out in bubbles on the surface of the porous body in proportion to the gas generated within the battery, the bubbles break immediately and the electrolyte is reabsorbed by the porous body, and hence there is no possibility of the bubbles bursting into a fluid electrolyte. Accordingly, the porous body of the invention makes it unnecessary to particularly improve the structure of a battery but can be advantageously used in an ordinary type of a battery container. Furthermore, it is another advantage of the invention that, since the plate group is covered and firmly fixed by the liquid absorbable porous body, the battery is protected against damage by hard vibration and shocks and falling of the active material is prevented.

Also, whilst in a conventional type of battery it takes trouble to lay plates, separators and glass mats one over another, this invention can advantageously simplify the assembling step of the battery as by resorting to the method shown in Example 3.

It should be understood that this invention has been described with reference to the examples of a lead acid storage battery but the invention is not limited thereto but can be applied to various other batteries such as an alkaline storage battery without departing from the scope of the invention.

WHAT WE CLAIM IS:—

1. A method of manufacturing a leakproof battery comprising disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around

an electrode plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the electrode plate group, said liquid absorbable porous body being impregnated with an electrolyte and thereafter received in a battery container.

2. A method of manufacturing a leakproof battery comprising disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around an electrode plate group formed so as to provide spaces between plates by interposing separator bodies therebetween, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an electrolyte and thereafter received in a battery container.

3. A method of manufacturing a leakproof battery comprising inserting an electrode plate group in a battery container, disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around said plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an electrolyte.

4. A method of manufacturing a leakproof battery according to claim 1 characterised in that the liquid absorbable porous body is covered with a bag made of heat-shrinkable synthetic resin before being received in the battery container.

5. A method of manufacturing a leakproof battery according to claim 1 characterised by the use of a powder composition of a mixture of 1 part by weight of thermoplastic synthetic resin powder with 2—4 parts by weight of hydrated silica gel powder.

6. A leakproof battery manufactured in accordance with the method of any one of claims 1—5.

7. A method of manufacturing a leakproof battery, substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

8. A leakproof battery, manufactured in accordance with the method of claim 7.

WITHERS & SPOONER,

Chartered Patent Agents,

148—150 Holborn, London, E.C.1.

Agents for the Applicant.

The determination of porosity can be made by the following formula

$$P = \frac{W_1 - W}{W_1 - W_2} \times 100\%$$

in which W represents the weight of a porous body; W_1 the weight of the porous body having the pores thereof completely filled with water; W_2 the weight of the porous body in the water; and P represents porosity (%).

In the table shown, A—M show the properties of a porous body according to the invention. The porosity and strength shown can be freely selected by changing the mixing ratio of hydrated silica gel to thermoplastic resin over the range of 1—5 parts of hydrated silica gel to 1 part of thermoplastic resin. Heating conditions may vary with synthetic resins, but are above the softening temperature of the respective resins. The liquid absorbable porous body of the invention is high in porosity and capable of holding a large quantity of electrolyte. Even if the electrolyte comes out in bubbles on the surface of the porous body in proportion to the gas generated within the battery, the bubbles break immediately and the electrolyte is reabsorbed by the porous body, and hence there is no possibility of the bubbles bursting into a fluid electrolyte. Accordingly, the porous body of the invention makes it unnecessary to particularly improve the structure of a battery but can be advantageously used in an ordinary type of a battery container. Furthermore, it is another advantage of the invention that, since the plate group is covered and firmly fixed by the liquid absorbable porous body, the battery is protected against damage by hard vibration and shocks and falling of the active material is prevented.

Also, whilst in a conventional type of battery it takes trouble to lay plates, separators and glass mats one over another, this invention can advantageously simplify the assembling step of the battery as by resorting to the method shown in Example 3.

It should be understood that this invention has been described with reference to the examples of a lead acid storage battery but the invention is not limited thereto but can be applied to various other batteries such as an alkaline storage battery without departing from the scope of the invention.

WHAT WE CLAIM IS:—

1. A method of manufacturing a leakproof battery comprising disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around

an electrode plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the electrode plate group, said liquid absorbable porous body being impregnated with an electrolyte and thereafter received in a battery container.

2. A method of manufacturing a leakproof battery comprising disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around an electrode plate group formed so as to provide spaces between plates by interposing separator bodies therebetween, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an electrolyte and thereafter received in a battery container.

3. A method of manufacturing a leakproof battery comprising inserting an electrode plate group in a battery container, disposing a composition of a mixture of a thermoplastic synthetic resin powder with hydrated silica gel powder around said plate group, heating the composition in saturated steam at a temperature of over 100°C to melt the resin and then allowing the composition to solidify to form a liquid absorbable porous body integral with the plate group, said liquid absorbable porous body being impregnated with an electrolyte.

4. A method of manufacturing a leakproof battery according to claim 1 characterised in that the liquid absorbable porous body is covered with a bag made of heat-shrinkable synthetic resin before being received in the battery container.

5. A method of manufacturing a leakproof battery according to claim 1 characterised by the use of a powder composition of a mixture of 1 part by weight of thermoplastic synthetic resin powder with 2—4 parts by weight of hydrated silica gel powder.

6. A leakproof battery manufactured in accordance with the method of any one of claims 1—5.

7. A method of manufacturing a leakproof battery, substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

8. A leakproof battery, manufactured in accordance with the method of claim 7.

WITHERS & SPOONER,

Chartered Patent Agents,

148—150 Holborn, London, E.C.1.

Agents for the Applicant.

