

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO LEAD-ACID STORAGE BATTERIES

(71) We, GOULD INC., a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 10 Gould Center, Rolling Meadows, Illinois 60008, United States of America, 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 lead-acid storage batteries.

In recent years, considerable attention has been directed to dry charge lead-acid storage batteries. It has therefore been proposed to form batteries, to remove the formation electrolyte, and in one proposal to wash the battery elements to remove any electrolyte residue, and then to dry and store them. Such batteries are ready for use merely by filling with electrolyte. The advantages are numerous; the cost of shipping such batteries is substantially less than "wet" batteries in which the electrolyte adds significantly to the weight of the battery. Also, shelf life is relatively long; and, accordingly, inventory control is facilitated.

The potential advantages of the dry charge battery have, however, not been fully realized because of the difficulties and the expense associated with washing and then completely drying the battery elements to remove the electrolyte used in forming and washing the elements. If not properly accomplished, chemical and electrochemical reactions can take place which adversely affect the initial battery performance. Thus, for example, oxidation of the negative plates can occur so as to significantly chemically discharge the plates, thereby adversely affecting the initial performance of the battery.

For the most part, hitherto proposed techniques for removing the formation electrolyte have been directed to thoroughly washing and drying the battery elements after formation or charging so as to prevent the battery from losing its charge during storage. Thus, U.S.

patent No. 2,880,520 uses a high velocity air stream. After drying the battery elements are installed into battery containers, electrically connected and a cover bonded onto the container. U.S. Patent No. 3,314,158 discloses installing the battery elements into the battery container and making the electrical connections prior to the formation, washing with water and drying steps. After the formation, a heated, non-oxidising gas is impinged onto the top of the battery elements.

A more recent technique, shown in U.S. patent No. 3,652,341, discloses assembling the battery elements into the container and making the electrical connections, filling the battery cells with a forming electrolyte and then charging the battery elements. About 70 to 97 weight per cent of the forming acid is then removed by applying an accelerative force, such as a centrifugal force, to the battery. According to this U.S. patent, a sufficient amount of forming acid should be removed from the battery elements to permit the achievement of the desired final specific gravity of the operating electrolyte after activation. When using the activation electrolyte employed for activating conventional dry charge batteries (i.e.—specific gravity of 1.265), this U.S. Patent states that removal of the forming acid so that the amount retained in the elements is about 8 to 15 per cent by weight results in a final electrolyte specific gravity of 1.246 to 1.255, after discharge and charge cycling.

However, while the application of the accelerative force obviates the necessity for completely drying the battery elements to remove all the residual formation electrolyte, the use of conventional activation electrolyte does not provide the result required. Thus, the use of conventional activation electrolyte does not result in the electrolyte, upon activation, reaching the industry accepted standard full charge specific gravity of 1.260 to 1.290, preferably 1.265, prior to service, due to the dilution of the activation electrolyte by the residual acid which remains in the

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battery during storage. While the utilization of activation electrolytes having higher specific gravities than those typically used can achieve the requisite full charge level, this is impractical since such electrolytes are not typically stocked by those actually carrying out the activation of the batteries. Moreover, and quite obviously, the stocking of odd types of activation electrolytes results in greater inventories when conventional dry charge batteries must also be activated.

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According to the present invention there is provided a method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically connected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being capable of being stored and thereafter activated by the addition of activation electrolyte, and, if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage, draining the formation electrolyte from the battery, treating the battery elements in a treatment step such that after said treatment step sufficient acid will be retained in the elements to provide, upon activation, including the addition of activation electrolyte having a specific gravity of about 1.265, a battery operating electrolyte having a specific gravity in the range of from 1.260 to 1.290, said treatment step comprising adding a development electrolyte and allowing the development electrolyte to diffuse into and saturate the battery elements and mix with the residual formation electrolyte therein, draining the battery leaving the battery elements substantially saturated, reducing the level of residual acid retained in the battery plates sufficiently below saturation that, on standing, the retained acid will not migrate to the outer surfaces of the battery elements to form liquid bridges between the plates and separators resulting in crystal growth and clusters of crystals creating internal shorts, and thereafter sealing the battery.

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The present invention also provides a method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically interconnected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being stored and thereafter activated by the addition of activation electrolyte, and, if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage,

treating the battery elements in a treatment step such that after said treatment step sufficient acid will be retained in the elements to provide, upon activation, including the addition of activation electrolyte having a specific gravity of about 1.265, a battery operating electrolyte having a specific gravity in the range of from 1.260 to 1.290, said treatment step being carried out by partially discharging the formed battery elements, draining the battery leaving the battery elements substantially saturated, reducing the level of residual acid retained in the battery plates sufficiently below saturation that, on standing, the retained acid will not migrate to the outer surfaces of the battery elements to form liquid bridges between the plates and separators resulting in crystal growth and clusters of crystals creating internal shorts, and thereafter sealing the battery.

The invention further provides a lead-acid storage battery comprising a container having a plurality of cell compartments and a plurality of battery elements consisting of a plurality of positive and negative plates with separators therebetween disposed in the cell compartments, the battery being sealed and the battery elements containing retained acid such that, upon activation by adding an activation electrolyte having a specific gravity of about 1.265, the resulting battery operating electrolyte has a specific gravity of from 1.260 to 1.290, the amount of retained acid being insufficient, upon standing, to allow acid to migrate to outer surfaces of the battery elements and form liquid bridges between the plates and separators which would result in crystal growth and clusters of crystals creating internal shorts.

In accordance with the present invention, it is preferred first to assemble a typical lead-acid battery, the battery elements, as conventional, consisting of a plurality of positive and negative plates with separators disposed therebetween. These are inserted into the cell compartments, and the electrical connections are then made.

The unformed, but fully assembled, battery can then be formed (viz.—charged). Formation electrolyte is added to the battery, and a current is applied thereto at a level and for times sufficient to achieve the desired end-of-charge voltage. As is well known, the concentration of the formation acid and the particular currents applied will vary with the type of forming employed and the battery-type involved. Typically, the formation electrolyte will be a sulphuric acid solution having a specific gravity ranging from 1.020 to 1.100. After the completion of the formation, the formation electrolyte is removed, as by merely inverting the container and dumping the electrolyte.

A treating step is then carried out by adding to the battery a development electrolyte of a

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vation with activation electrolyte alone, or upon activation with such electrolyte and charging.

5 In an alternative embodiment of the invention the treating step is effected to provide the requisite retained acid by partially discharging the battery plates after completion of the formation step. By suitable selection of the specific gravity of the formation electrolyte and the extent of the partial discharge, the amount of sulphate formed will combine with the retained acid to provide an acceptable initial specific gravity for normal operation after activation. This method is less desired since any extended period of storage will generally require that activation include suitable charging.

10 The extent of the partial discharge and the specific gravity of the formation electrolyte can be varied depending upon the battery size and type and the amount of the retained acid. For example, with a Group 24 automotive battery (81 Amp. Hr. capacity), wherein a formation electrolyte having a specific gravity of 1.060 is used, a partial discharge after formation to remove 10 Amp. Hrs., followed by draining and centrifuging or the like to remove 87.4 per cent by volume of the electrolyte, will allow operating electrolyte to have a specific gravity of 1.265 after activation with conventional activation electrolyte (1.265 specific gravity) and charging. With this same battery, the use of formation electrolyte of 1.100 specific gravity allows reaching the same battery operating electrolyte gravity with a 10 Amp. Hr. discharge when only 84.5 per cent by volume of the electrolyte has been removed.

35 If desired, the partial discharge can be preceded or succeeded by the addition of a development electrolyte as in the preferred embodiment. This is, however, usually unnecessary. Completion of the processing can then be carried out as has been described herein.

40 The present invention provides a ready method for forming dry charge-type batteries which can be activated by the use of conventional activation electrolyte, yet result in development of the industry accepted full charge electrolyte gravity level of from 1.260 to 1.290. The proper reduction of the retained acid in the battery elements ensures that the growth of crystals or clusters of crystals leading to internal shorts will be prevented.

55 Although the present invention is particularly described herein in connection with an embodiment wherein the treating step is carried out in a separate step following the initial formation, it should be appreciated that this step can be included in the formation step so that the residual sulphuric acid retained in the battery during storage has a specific gravity in the range of 1.260 to 1.290. This can be achieved by carrying out the

formation with a high gravity formation electrolyte, which will typically have a specific gravity of 1.100 or higher. Still further, while batteries are particularly described herein having battery elements which have been assembled and positioned in the container and the appropriate electrical connections made, the battery plates can be formed either before or after assembly into the typical battery elements.

WHAT WE CLAIM IS:—

1. A method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically connected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being capable of being stored and thereafter activated by the addition of activation electrolyte, and, if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage, draining the formation electrolyte from the battery, treating the battery elements in a treatment step such that after said treatment step sufficient acid will be retained in the elements to provide, upon activation, including the addition of activation electrolyte having a specific gravity of about 1.265, a battery operating electrolyte having a specific gravity in the range of from 1.260 to 1.290, said treatment step comprising adding a development electrolyte and allowing the development electrolyte to diffuse into and saturate the battery elements and mix with the residual formation electrolyte therein, draining the battery leaving the battery elements substantially saturated, reducing the level of residual acid retained in the battery plates sufficiently below saturation that, on standing, the retained acid will not migrate to the outer surfaces of the battery elements to form liquid bridges between the plates and separators resulting in crystal growth and clusters of crystals creating internal shorts, and thereafter sealing the battery.

2. A method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically interconnected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being capable of being stored and thereafter activated by the addition of activation electrolyte, and if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage, treating the battery ele-



sufficiently high specific gravity that after emptying out the development electrolyte, sufficient acid, in one form or another, is retained within the battery elements to yield a battery operating electrolyte with a specific gravity in the range of from 1.260 to 1.290, preferably about 1.265 for automotive and light commercial-type batteries, upon activation with standard activation electrolyte with specific gravity of about 1.265, and charging if necessary. The specific gravity of the development electrolyte will vary depending on the element size; however, it is generally suitable to utilize development electrolytes having specific gravities in the range of from 1.265 to 1.350. The development electrolyte should be allowed to permeate the battery elements so that saturation will result. This can be accomplished, for example, by merely allowing the development electrolyte to stand in contact with the battery elements for about 10 minutes or even longer. This soaking is effective to allow the development electrolyte to diffuse and mix with the residual formation electrolyte retained within the elements. Alternatively, this may be accomplished by mechanically mixing the development electrolyte while in contact with the battery elements. Any conventional mechanical mixing means can be advantageously utilized.

After removal of excess development electrolyte, as by inverting and draining the battery, the amount of retained acid is reduced below the amount the battery elements are capable of retaining when saturated. Thus, if the retained acid amount is not reduced below saturation, extended periods of storage can result in the growth of crystals or clusters of crystals that can bridge between adjacent positive and negative plates to create internal shorts, thereby irreversibly damaging the battery. Accordingly, the amount of retained acid is reduced to the point where, on standing during extended periods of storage (e.g. —2 months or more), the residual acid will not migrate to the outer surfaces (particularly the bottom) of the battery elements so as to form liquid bridges (between plates and separators or between exposed areas of adjacent plates) that result in crystal growth and clusters of crystals creating internal shorts. The determination of whether the retained acid amount has been sufficiently reduced can be made by means such as a visual inspection. The reduction step can be carried out by any known means such as an accelerative force as shown in U.S. patent No. 3,652,341, vacuum drying or the like.

The particular means used for the reduction step should, of course, be coordinated with the treating step to insure that the gravity of the retained acid is as is required. For example, as is known, vacuum drying tends to preferentially remove the water (compared to the rate of removal of acid) from the ele-

ments which thus increases the gravity of the retained acid. Accordingly, if vacuum drying is utilized in the reduction step, the gravity of the development electrolyte should be lower than that when an accelerative technique, such as centrifuging, is employed.

Following the reduction of the acid to obtain the appropriate retained acid content in the battery elements, the battery can then be suitably sealed and stored. If desired, the battery can be completely sealed; however, it is preferred to only substantially seal the battery so that the ingress of air is substantially prevented. Thus, because batteries processed according to the present invention do retain residual electrolyte, there is some internal generation of gases such as hydrogen caused by self-discharge of the negative active materials during extended storage. If the batteries are totally sealed to protect against oxidation, there can be some bulging of the containers as a result of hydrogen or other gas build-up. This bulging can cause permanent deformation of the containers or ejection of vent covers which do not allow gas egress. For these reasons, it is therefore preferred to seal the battery in such a fashion that the ingress of air is substantially prevented while permitting the gaseous atmosphere within the battery, after a slight pressure build-up, to be vented therefrom.

This substituted sealing can be accomplished using the vented seal shown in Application No. 5288/76 (Serial No. 1534037. These vented seals include means communicating with the atmosphere, such as a suitably sized aperture or channel.

After storage, and when it is desired to activate the battery for service, activation is accomplished by the addition of conventional activation electrolyte, having a specific gravity of about 1.265, and charging if necessary. In view of the adjustment of the residual acid in the battery processing, the gravity level after activation will be in the required range, i.e.—from about 1.260 to 1.290.

In stating that the electrolyte of the battery, upon activation with activation electrolyte having a specific gravity of 1.265, has an acceptable initial specific gravity for normal operation, i.e. 1.260 to 1.290, it should be recognized that, during storage, the residual acid in the battery elements may be partially consumed in various reactions, depending upon the length of storage time. Thus, upon activation with activation electrolyte, the initial specific gravity of the battery may be somewhat less than the desired specific gravity of 1.260 to 1.290. However, charging the battery will reconstitute the electrolyte to the desired specific gravity level. Thus, there is sufficient acid in the battery elements in one form or another to ensure that the battery operating electrolyte will initially have the desired specific gravity level, either upon acti-

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vation with activation electrolyte alone, or upon activation with such electrolyte and charging.

5 In an alternative embodiment of the invention the treating step is effected to provide the requisite retained acid by partially discharging the battery plates after completion of the formation step. By suitable selection of the specific gravity of the formation electrolyte and the extent of the partial discharge, the amount of sulphate formed will combine with the retained acid to provide an acceptable initial specific gravity for normal operation after activation. This method is less desired since any extended period of storage will generally require that activation include suitable charging.

10 The extent of the partial discharge and the specific gravity of the formation electrolyte can be varied depending upon the battery size and type and the amount of the retained acid. For example, with a Group 24 automotive battery (81 Amp. Hr. capacity), wherein a formation electrolyte having a specific gravity of 1.060 is used, a partial discharge after formation to remove 10 Amp. Hrs., followed by draining and centrifuging or the like to remove 87.4 per cent by volume of the electrolyte, will allow operating electrolyte to have a specific gravity of 1.265 after activation with conventional activation electrolyte (1.265 specific gravity) and charging. With this same battery, the use of formation electrolyte of 1.100 specific gravity allows reaching the same battery operating electrolyte gravity with a 10 Amp. Hr. discharge when only 84.5 per cent by volume of the electrolyte has been removed.

35 If desired, the partial discharge can be preceded or succeeded by the addition of a development electrolyte as in the preferred embodiment. This is, however, usually unnecessary. Completion of the processing can then be carried out as has been described herein.

40 The present invention provides a ready method for forming dry charge-type batteries which can be activated by the use of conventional activation electrolyte, yet result in development of the industry accepted full charge electrolyte gravity level of from 1.260 to 1.290. The proper reduction of the retained acid in the battery elements ensures that the growth of crystals or clusters of crystals leading to internal shorts will be prevented.

50 Although the present invention is particularly described herein in connection with an embodiment wherein the treating step is carried out in a separate step following the initial formation, it should be appreciated that this step can be included in the formation step so that the residual sulphuric acid retained in the battery during storage has a specific gravity in the range of 1.260 to 1.290. This can be achieved by carrying out the

formation with a high gravity formation electrolyte, which will typically have a specific gravity of 1.100 or higher. Still further, while batteries are particularly described herein having battery elements which have been assembled and positioned in the container and the appropriate electrical connections made, the battery plates can be formed either before or after assembly into the typical battery elements.

WHAT WE CLAIM IS:—

1. A method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically connected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being capable of being stored and thereafter activated by the addition of activation electrolyte, and, if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage, draining the formation electrolyte from the battery, treating the battery elements in a treatment step such that after said treatment step sufficient acid will be retained in the elements to provide, upon activation, including the addition of activation electrolyte having a specific gravity of about 1.265, a battery operating electrolyte having a specific gravity in the range of from 1.260 to 1.290, said treatment step comprising adding a development electrolyte and allowing the development electrolyte to diffuse into and saturate the battery elements and mix with the residual formation electrolyte therein, draining the battery leaving the battery elements substantially saturated, reducing the level of residual acid retained in the battery plates sufficiently below saturation that, on standing, the retained acid will not migrate to the outer surfaces of the battery elements to form liquid bridges between the plates and separators resulting in crystal growth and clusters of crystals creating internal shorts, and thereafter sealing the battery.

2. A method of manufacturing a lead-acid storage battery, the battery including a container having a plurality of cell compartments and a plurality of electrically interconnected battery elements consisting of a plurality of positive and negative plates with separators positioned therebetween, the battery being capable of being stored and thereafter activated by the addition of activation electrolyte, and if required, charging, which method comprises forming the plates by bringing said plates into contact with a formation electrolyte and applying current thereto at a level and for time sufficient to reach a desired end-of-charge voltage, treating the battery ele-



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ments in a treatment step such that after said treatment step sufficient acid will be retained in the elements to provide, upon activation, including the addition of activation electrolyte having a specific gravity of about 1.265, a battery operating electrolyte having a specific gravity in the range of from 1.260 to 1.290, said treatment step being carried out by partially discharging the formed battery elements, draining the battery leaving the battery elements substantially saturated, reducing the level of residual acid retained in the battery plates sufficiently below saturation that, on standing, the retained acid will not migrate to the outer surfaces of the battery elements to form liquid bridges between the plates and separators resulting in crystal growth and clusters of crystals creating internal shorts, and thereafter sealing the battery.

3. A method according to claim 1 or claim 2, wherein the amount of residual acid in the battery elements is reduced by subjecting the battery to an accelerative force.

4. A method according to any preceding claim, wherein the treatment step is effected to provide a battery operating electrolyte having a specific gravity of about 1.265.

5. A lead-acid storage battery comprising a container having a plurality of cell compartments and a plurality of battery elements consisting of a plurality of positive and negative plates with separators therebetween disposed

in the cell compartments, the battery being sealed and the battery elements containing retained acid such that, upon activation by adding an activation electrolyte having a specific gravity of about 1.265, the resulting battery operating electrolyte has a specific gravity of from 1.260 to 1.290, the amount of retained acid being insufficient, upon standing, to allow acid to migrate to outer surfaces of the battery elements and form liquid bridges between the plates and the separators which would result in crystal growth and clusters of crystals creating internal shorts.

6. A lead-acid storage battery according to claim 5, wherein the retained acid allows a battery operating electrolyte having a specific gravity of about 1.265.

7. A lead-acid storage battery according to claim 5, wherein the battery elements are in a partially discharged state.

8. A method of manufacturing a lead-acid storage battery according to any of claims 1 to 4 and substantially as herein described.

9. A lead-acid storage battery which has been made by the method claimed in any of claims 1 to 4 and 8.

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