Battery Materials

1970

Paul Conrad

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FOREWORD

This Electronics Materials Review presents techniques for producing battery materials, and is based on the U.S. Patent literature since 1960.

Electronics Materials Reviews are a series of comprehensive up-to-date studies of the technology of production and utilization of the materials used in today's and tomorrow's electronic devices. They represent the basic technology behind investment in such areas as: solid state lasers, magnetic recording media, thermoelectric devices, faster, more compact computers, improved solar cells, photoconductors for new copying processes, electroluminescent materials for color television, piezoelectric materials for ultrasonic devices, new and exotic batteries.

They are written from the practical, processing point of view giving specifics about material characteristics and construction of equipment as well as details of operating conditions. These volumes are of prime interest to managerial, research, engineering development, marketing personnel etc., in the broad range of industries producing and consuming electronic materials. Each Review includes a number of illustrations.

Electronics Materials Reviews are based primarily on the patent literature, supplemented by other commercial information and data to present as complete a picture as possible. The U.S. Patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

These Reviews are bound in paper in order to close the time gap between the "manuscript" and the "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

These Reviews are organized in such a way that the Table of Contents also serves as a subject index. Further, they are indexed by inventor, patent number, and company for the reader's convenience. Thus, they tell you quickly who is doing what today.

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INTRODUCTION

Batteries are devices from which chemical energy is converted into electrical energy by electrochemical processes occurring as current is withdrawn. Batteries are usually categorized as primary and secondary, or storage. The primary cells do not have practically reversible chemical reactions, that is, the cells cannot be recharged. The secondary or storage cells can undergo reversible reactions, and can be recharged by applying current to the electrodes in a reverse manner to the discharge cycle.

Fuel cells or other power generating cells which require separate external fuel or oxidant or electrolyte sources and pumps or auxiliary circulating systems are excluded from coverage in this volume.

AQUEOUS BATTERY SYSTEMS

LEAD-ACID BATTERIES

One general class of conventional storage batteries employ a lead-lead dioxide electrochemical couple and are commonly referred to as lead-acid batteries. Such storage batteries have found wide acceptance, particularly for starting in automobiles, but are not particularly desirable for use as a motive power source, as for traction purposes, where space and weight limitations are present. In this connection, lead-acid storage batteries have a low energy density, i.e., power output per pound of battery weight.

A conventional lead-acid storage battery has a theoretical maximum energy density of 76 watt-hours per pound of reactants and produces 5 to 20 watt-hours per pound of total battery weight in practice. The low power output per unit weight is primarily due to the high molecular weight of the reactants and the rather large excesses of anodic and cathodic reactants required, since all of the electrodes cannot be completely consumed during the discharge of the battery. The lead-acid battery's reversibility is dependent upon the physical position of the reactants and decomposition products and requires the use of highly porous electrode plates to provide sufficient surface for the solid-solid reactions to take place.

Accumulatoren-Fabrik AG

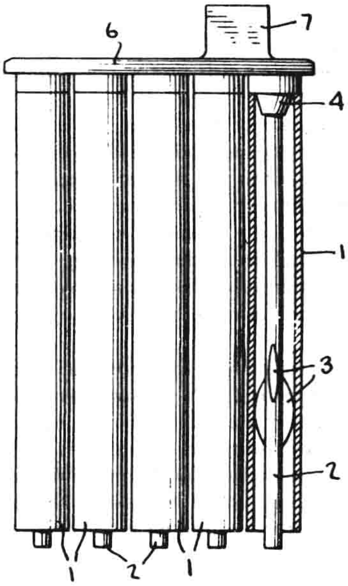
A battery developed by D. Evers, H. Gumprecht and M. Rasche (U.S. Patent 3,011,007; November 28, 1961; assigned to Accumulatoren-Fabrik AG, Germany) is a lead-acid storage battery with positive plates consisting of vertical tubes containing the active material, which makes full use of the advantageous aspects of a phosphoric acid addition to the electrolyte in respect to preventing sulfation and increasing the battery life due to reduction of washing out of the active material without, however, sacrificing the capacity of the battery.

It has previously been proposed to add phosphoric acid to the electrolyte of lead-acid batteries with positive grids or large-surface positive plates. The main purpose of this additive was the prevention of harmful sulfation, another advantage being the solidification of the active mass. This inhibited the active material from being washed out and thus increased the battery life. On the other hand, the phosphoric acid addition reduced the capacity of the storage battery by 10 to 15%. Phosphoric acid has heretofore not been added to the electrolyte of lead-acid batteries with positive plates consisting of active material-containing tubes because the capacity loss was considered highly disadvantageous and a solidification of the active material seemed unnecessary with the generally used slotted hard rubber tubes for enclosing the material. It has been held that phosphoric acid additions in such batteries were not useful because the active material was securely held in the hard rubber tubes in contrast to the grid plates where the active material is self-supporting.

Improved operation is obtained with this battery design by using an active material having a porosity of at least 65%, i.e., a pore volume of 65% of the total mass, preferably 75%, and enclosing tubes of a microporous material for the active material, the electrolyte, after charging, having a phosphoric acid content of 3 to 10 grams per liter, preferably 5 grams per liter. The microporous material for the tubes may be a woven or nonwoven sheet material of synthetic or glass fibers.

The structure of the lead-acid battery may be conventional and the positive plate as used in this battery design is shown in Figure 1, as illustrated on the following page. In the drawing, the microporous tubes of the plate are indicated at 1, the tube at the extreme right of the figure being shown in section. The tubes are mounted in a framework comprising lead spines 2. Spacers 3 which are alternately mounted at right angles to each other, center the tubes about spines 2. The tubes are held by a frustoconical element 4 at one end of the spines and all spines are connected by lead bar 6 provided with lug 7. Unexpectedly, the usual capacity loss caused by the addition of phosphoric acid to the electrolyte of lead-acid batteries has been practically completely eliminated by the use of an active material of very high porosity

FIGURE 1: SECTIONAL VIEW OF LEAD-ACID BATTERY WITH TUBULAR POSITIVE PLATES CONTAINING ACTIVE MATERIAL



Source: D. Evers, H. Gumprecht and M. Rasche; U.S. Patent 3,011,007; November 28, 1961

and microporous enveloping tubes having a very small contact area with the active material while presenting a high cross-section of passage for the electrolyte. Taking advantage of the solidification effect of phosphoric acid on the active material, it has been possible to use enclosing tubes of larger mesh size, thus further increasing the effectiveness of the active material and simultaneously saving tube material. Adding to all of these advantages, it has also been found unexpectedly that the phosphoric acid additive greatly reduces corrosion of the current collector and conductor. Depending on the alloy used for the terminal, the corrosion decreases as much as 30 to 50%.

The solidification of the active material by the phosphoric acid also offers the possibility of using finer particles for the production of the active material cores, which further increases the efficiency and capacity of the battery. Thus, instead of using red lead with a major portion of particles between 15 and 20 microns, as has been the custom, red lead with a major portion of particles between 4 and 10 microns can be used. The use of microporous tubes has been found advantageous to reduce the contact areas between the tubes and the active material they enclose to a minimum and to increase the passage area for the electrolyte to a maximum. For this purpose, woven and nonwoven glass fiber webs or mats, woven synthetic fiber fabrics, microporous rubber, or microporous plastics have been found satisfactory. In contrast to slotted hard rubber tubes, these materials produce notable surface irregularities and fragmentation in the active material cores, which also contributes to the higher efficiency and greater capacity of batteries according to this process.

The microporous tubes may be made of a nonwoven glass fiber web the fibers of which are bonded together with a polyvinyl chloride binder or a polystyrene dispersion. According to another embodiment, a woven, knitted or reticulated synthetic fiber web may be used as tube material, polyvinyl chloride, polyester and acrylic fibers, as well as copolymers or blends of any of these synthetic resins, being useful for this purpose, by way of example. The fibers may be monofilaments or staple fibers. Preferably, the synthetic resin fibers or the webs produced therefrom are subjected to a heat treatment at a temperature from 100° to 200°C. which causes them to shrink to the desired final dimensions and imparts to them a high acid-resistance and resistance to anodic corrosion.

Lead-acid storage batteries according to this design may be produced in a variety of ways. For instance, phosphoric acid in the form of a dry phosphate, for instance, lead phosphate, zinc phosphate, or alkali metal phosphates may be added to the active material powder, such as litharge or red lead or a suitable mixture thereof. The dry mixture can be intimately mixed in any suitable dry mixer, such as a Werner-Pfieiderer mixer, a Simplex mixer, or a ball mill with porcelain balls, for instance. As is known, the battery plate tubes are filled with such lead oxide powders by vibration or shaking, for instance, these oxides being formed electrolytically in the battery by anodic oxidation into lead dioxide, which is the active material. If a lead oxide paste is used to be molded about the current collector and conductor, liquid phosphoric acid may be added to the active material paste. The paste may be any conventional paste and dilute phosphoric acid, for instance, of a density of 1.2 to 1.8 is added, the amount having been established by simple experiments to yield the desired concentration of phosphoric acid in the electrolyte, after the battery is charged. It is also possible to immerse the unfinished multiple tube plates in a sulfuric acid solution to obtain sulfation, as hereinabove mentioned in connection with the production of highly porous active material. If desired, the sulfuric acid, preferably having a density of 1.15, may contain phosphoric acid, for instance, 40 grams per liter. To prevent dilution of the phosphoric acid content in the positive plate during the subsequent formation, the formation acid must contain between 5 and 10 grams per liter of phosphoric acid, preferably 8 grams per liter.

Finally, phosphoric acid may be added to the electrolyte after a conventional battery of this type has been put into operation. In this case, it is desirable to add the phosphoric acid slowly between a series of charge and discharge cycles of the battery. This is done by adding 5 grams per liter of phosphoric acid to the electrolyte of an operating battery cell. The battery is then discharged, charged again, and an equal addition of phosphoric acid is made again. When this cycle is repeated three times, the electrolyte usually contains about 5 grams per liter of phosphoric acid in the charged state of the battery, the excess phosphoric acid remaining in the positive plate, as hereinbelow explained. If the acid analysis of the cell should show that the electrolyte does not contain the desired minimum amount of phosphoric acid, more phosphoric acid is added in one or more additional cycles.

However the phosphoric acid is added, it is essential that the phosphoric acid content of the positive plate be larger in the charged state of the battery than the phosphoric acid content remaining in the electrolyte and that the latter does not exceed 10 grams per liter, being at least 3 and preferably 5 grams per liter. Whether added in a dry or wet state, the total phosphoric acid content in the positive plate after charging is preferably about 25 to 35 grams calculated per liter of electrolyte. With such a phosphoric acid content in the positive plate, the electrolyte will contain less than 10% of phosphoric acid. If the phosphoric acid content in the electrolyte exceeds 10 grams per liter, a spongy, conductive mass is produced at the positive plate and deposited on the negative plate, which causes short circuits at the plate and thus destroys the cell.

Generally speaking, the active material in the positive plate will contain 3 to 4 times as much phosphoric acid as the electrolyte because the desired phosphoric acid concentration in the electrolyte could otherwise not be maintained. During discharge, a portion of the phosphoric acid moves from the positive plate into the electrolyte and is returned during the charging cycle. If the positive plate would not contain an excess of phosphoric acid, the active material in the positive plate would be loosened during the discharge.

Accumulatorenfabrik Sonnenschein

A process developed by O. Jache (U.S. Patent 3,449,116; June 10, 1969; assigned to Accumulatorenfabrik Sonnenschein GmbH, Germany) for producing filling materials for grids of batteries or accumulators is one in which pulverized reaction material, such as ball-milled lead powder, is introduced into a reaction vessel to form a bed at the bottom of the vessel, sulfuric acid is sprayed onto this bed, and compressed air is simultaneously fed from the bottom of the vessel through the bed. The lead and sulfuric acid react to generate heat which changes the water in the reaction material and that in the sulfuric acid into steam. The compressed air drives off the steam through an outlet in the top of the vessel. Heat can be supplied from the outside to the vessel if necessary.

In the production of accumulator plates it is known to use lead monoxide, such as red lead and litharge or lead powder, which consists of fine pieces of lead monoxide and lead, as the starting material. The starting material is introduced for the reaction either dry or mixed with water displaced by dilute sulfuric acid so that a pasty mass is produced which attachedly is housed in a lead grid. For effecting the designated reaction as a mixing process there has been used previously mechanical mixers which either operate continuously or in a batch process.

By examination of the pasty masses produced by the known process it has been determined that the mechanical apparatus employed, such as a mixing or a kneading flap, a radial mixer, mixing screws, edge runners, etc., do not suffice to attain the mixing in which the single components are uniformly distributed, especially if large amounts have been added to the sulfuric acid. This leads therefore to the conclusion that the mixing speeds attainable in the production of the pasty masses during or at least at the end of the process are very much smaller than the reaction speed between lead monoxide and sulfuric acid. For the attainment of a satisfactory homogeneity the pasty masses therefore must be united in the reaction phase for more or less lengthy postmixing time.

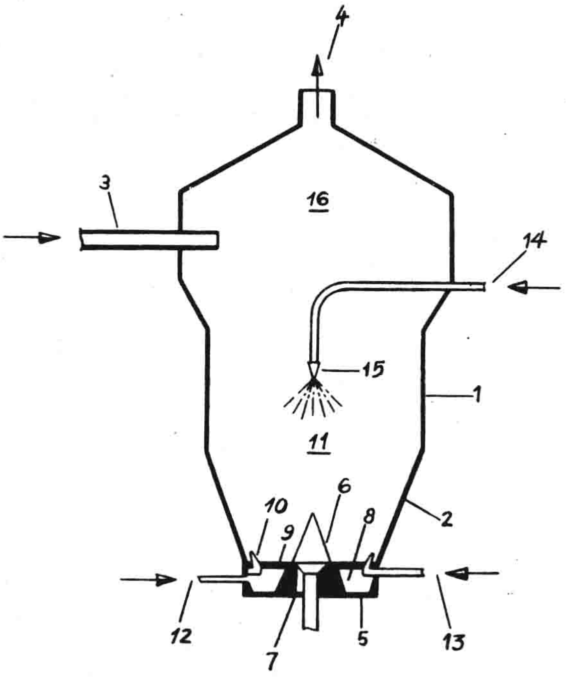
In the hitherto known process difficulties arise also in the removal from the reaction zone of the heat generated, for example, by the reaction between the lead monoxide and the sulfuric acid, since with mechanical mixing the heat only can indirectly dissipate from the walls of the mixing holder or the mixing devices. Localized overheating in the pasty mass leads, especially with additions of large amounts of sulfuric acid, unavoidably to the building up of agglomerates through which the originally provided particle size of the lead dust is deranged. The consequence of building up agglomerates are crumply or granular masses with poor pasty characteristics. The removal of the built-up agglomerate requires considerable shearing power and only succeeds with difficulty and incompletely with the additional use of edge runners and long mixing times. The pasty masses produced by the hitherto known processes must be worked immediately, since if they stand for even a short period, as is not avoidable with the batch process, physical and chemical changes take place in the pasty masses, which influence disadvantageously the subsequent paste condition, especially with use of high speed machines. Changes in the chemical composition and in the physical characteristics are not excluded by use of continuous mixing, especially with interruptions in the machines disposed for the paste production. Prior conditioning of the pasty mass is thus not possible. The problem has now been solved by a process which is characterized by the fact that all the reactive material mixed in powdered or mist form state is introduced at the dew point to the reaction, and thereby the steam is carried out in a gas stream and then a pulverized reaction product is attained.

In this process, the building up of a pulp or a paste is avoided, since the transposition and mixing of the lead powder with the sulfuric acid is carried out under such conditions that the water existing as a result of the reaction and the water carried in a given case with the sulfuric acid is immediately evaporated. The evaporated water is immediately removed through introduction to or conduction of a gas stream, preferably an air stream, through the reaction mixture. The reaction temperature can in any case be held solely by the heat freed by the reaction to a suitable value since the reaction between the lead monoxide and the sulfuric acid is heavily exothermic and also in any case further exothermic reactions take place, for example, oxidation of the metallic lead. In case the heat generated in the reaction is not sufficient, additional heat must be added from the outside, for example, through use of a heated air stream.

Whether the dew point is exceeded or not depends at a given temperature upon the shared water and air quantities, that is, upon the temperature and moisture content of the air used for carrying away the steam. Through suitable measurement of the parameters influencing the dew point the reaction is so controlled that it exceeds the requirements based upon the dew point. For carrying out the process, mechanical, preferably pneumatic, mixers are used. The sulfuric acid is sprayed on the mechanically or pneumatically moved mixing bed. The steam is carried off through introduction of an air stream into the mixing bed.

The pulverized filler material obtained by the process can be used for tilling from tubes or table plates and then in known manner an aftertreatment, such as dipping and drying, or handling with superheated steam is applied. The powdered form of material obtained can also be brought to paste form by addition of water and in the usual manner can be formed into a grid electrode. The production of the paste can be carried out in a continuously operating mixer to which the pulverized filling mass is conveyed by a feeding apparatus. The feeding apparatus and the continuously operating mixer can be controlled by the machine serving for introduction of the paste into the grid plate. Figure 2 shows an intermittently operating pneumatic mixer for the conduct of this process.

FIGURE 2: INTERMITTENTLY OPERATED PNEUMATIC MIXER FOR PRODUCING FILLING MATERIAL FOR LEAD-ACID BATTERY PLATES

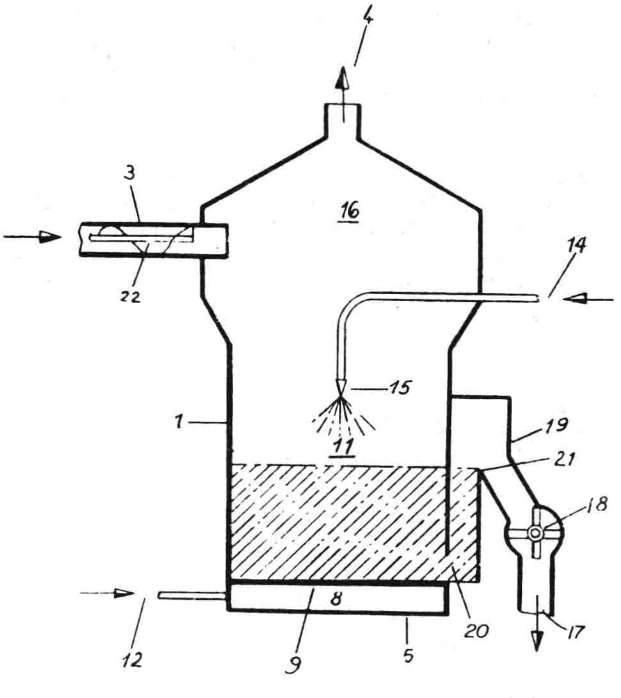


Source: O. Jache; U.S. Patent 3,449,166; June 10, 1969

The mixer illustrated consists of a mixing vessel 1 which is conical at its lower end and into which the pulverized reaction material can be fed through a pneumatic duct 3. In the upper part of the vessel an exhaust opening 4 is provided. For removal of the reaction product there is provided in the center of the base 5 of the mixing container an exhaust opening 7 normally closed by a valve or a conical closure 6. The opening 7 is surrounded by an annular space 8 which communicates through a porous annular cover plate 9 and/or annularly arranged nozzles 10 with the chamber 11 of the mixing container 1.

The annular space 8 is supplied by a duct 12 with compressed air. The nozzles 10 can be supplied with compressed air, if occasion arises, by its own duct 13. The fluid starting material is fed by a duct 14 to a nozzle 15 which is disposed in the chamber 11 of the mixing container over the exhaust opening 7. The compressed air introduced through the porous plate 9 and/or nozzle 10 is released in the widened upper part 16 of the mixing holder 1 so that the pulverized material carried with it can again sink to the bottom, and dissipates finally through the outlet opening 4 and an adjacent dust filter (not shown) to atmosphere. Figure 3 shows a continuously operating pneumatic mixer for the conduct of this process. Parts corresponding to one another in the figures are designated by the use of the same reference numerals.

FIGURE 3: CONTINUOUS PNEUMATIC MIXER FOR PRODUCING FILLING MATERIAL FOR LEAD-ACID BATTERY PLATES



Source: O. Jache; U.S Patent 3,449,166; June 10, 1969

Instead of the exhaust opening 7 which is closed by the conical seal 7 in the intermittent mixer design, a port 17 is provided for the continuous removal of the mixing goods which contains a rotary, partitioned valve 18 which is connected with the container 1 by a side outlet 19 provided over a porous plate 8. The height of the mixing bed 20 is determined by an overflow baffle 21. The pulverized starting material is introduced continuously with the help of the conveyor screw 22 provided in the forwarding duct 3. The following is a specific example of the conduct of this process using the intermittent mixer design shown.

The starting product was ball-milled lead powder with the following characteristic data: PbO content, 64%; bulk weight, 2.07 kg./l.; water capacity, 158 ml./kg.; particle size over 100 microns, 24.8% and particle size over 40 microns, 65.2%. 50 kg. of this lead powder, which in this case was used for the preparation of a positive electrode mass, was fed to the mixing chamber 11 by the pneumatic lead powder filling duct 3. This lead powder was fluidized then through introduction of compressed air at 3 to 4 atmospheres through the porous annular bottom 9 of the container chamber in order that a standing lead powder flow bed of about 2/3 of the container height may build up until it was the height of the spray nozzle 15. For control of the compressed air nozzles 10 which operate at an air pressure of

6 atmospheres gusts of the air at uniform intervals of 2 seconds were supplied to the chamber thereby providing the existing flow bed with rhythmic whirls. The lead powder highly whirled in this manner, through this arrangement is supplied into very fine particles into contact with the acid spray nozzles 15.

The accumulator sulfuric acid used for the production of the described mixture with a specific gravity of 1.40/20°C. was now provided in an amount of 4.30 liters at a pressure of 5 atmospheres by the duct 14 and the spray nozzle 15 delivers the whirling lead powder during a period of 10 seconds. The elevated reaction temperature achieved by this operation attains a maximum value of 66°C. The steam built up exhausts with the exhausting compressed air through the exhaust duct 4 and a filter attached thereto of about 3.5 qm. filter surface. After uninterrupted spraying of the sulfuric acid the mixing was resumed for 3 minutes time, then the compressed air was stopped and the mixed material is emptied through the bottom valve 6 in the container. In consequence of the complete dryness of the mixed material it is in a sprinkleable stage whereby a quick and complete emptying of the mixing container is possible. The total used working time for preparation of the above described 50 kg. charge of the accumulator mass comprises 15 minutes.

In a battery developed by O. Jache (U.S. Patent 3,257,237; June 21, 1966; assigned to Accumulatorenfabrik Sonnenschein GmbH, Germany), the electrolyte is formed by a thixotropic hydrogel constituting a colloidal solution of an additive in a diluted acid. This additive is formed by a finely dispersed material which while insoluble in the diluted acid is capable of forming a colloidal solution therewith which constitutes a thixotropic hydrogel, i.e., a gel which, when agitated, becomes liquid and congeals again after the agitation has ceased.

Preferably, an oxide insoluble in sulfuric acid, such as silica or alumina, may be used as the gel-forming additive. The particles of this finely dispersed material should have an average size of less than 0.1 micron and preferably between 0.01 and 0.02 micron. These small particles of silica or alumina, added to the electrolyte, immobilize the electrolyte within the battery owing to their ability to agglomerate thereby converting it into a hydrogel of a surprising stability. The particle size of the additive should be limited to a maximum of 0.1 micron which while sufficient to form the thixotropic hydrogel within the space between the electrodes will not form the gel within the pores of the active material of the electrodes, as it is desirable that the pores of the active material be filled by the liquid phase of the colloidal solution only. This will be enhanced by using porous active material having an average size of its pores which is substantially smaller than the colloidal agglomerations so as to substantially prevent sulfuric acid within the pores from forming a hydrogel.

This hydrogel produces the surprising effect that the gel-forming agglomerations even if their concentration in the electrolyte is insufficient to form a coherent stable gel are too big to be able to enter into the pores of the active material even though the average size of its pores amounts at any rate to more than 0.1 micron and preferably amounts to between 0.5 and 2 microns. Owing to this effect, the electrolyte only which is outside of the pores of the electrodes will be converted into a gel, whereas the electrolyte within the pores of the active material will remain liquid and freely movable. Where the additive is formed by a finely dispersed silica having a particle size of 0.01 to 0.02 micron, the quantity of the additive may amount to 3 to 10% by weight, preferably to 6% by weight, of the electrolyte. A quantity of the additive smaller than 3% results in a colloidal solution which takes an unduly extended time to form a coherent hydrogel, whereas a quantity of the additive exceeding 10% by weight of the electrolyte results in a gel subject to excessive ageing and liable to reduce the volume of the electrolyte to an objectionable degree. Use of such an electrolyte gives a battery which is capable of operation in any position, its housing being normally sealed so as to prevent leakage.

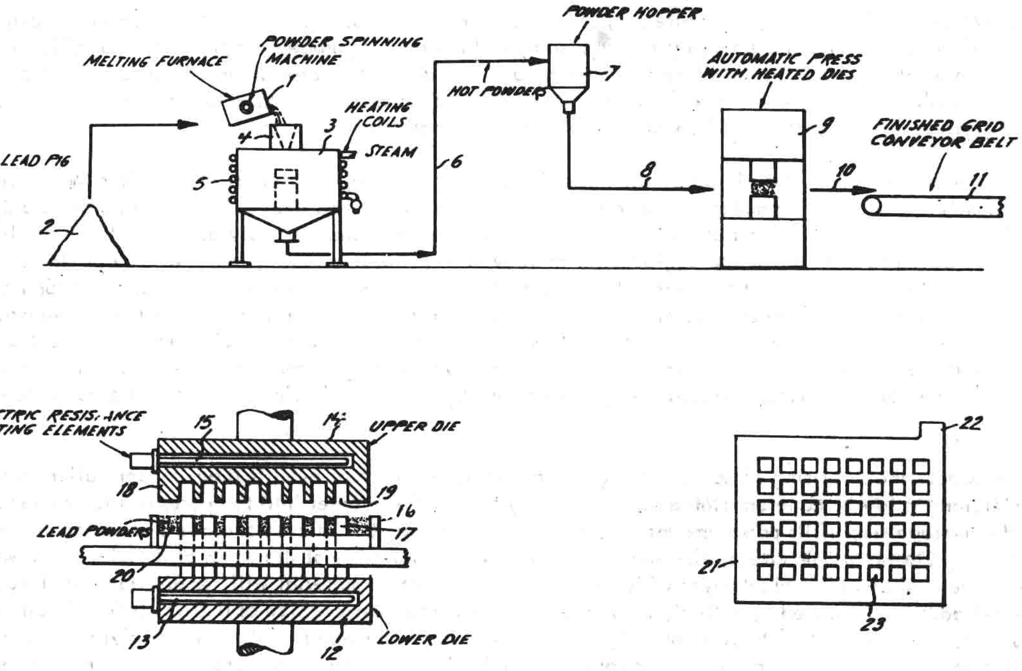
Alloys Research & Manufacturing Corp.

A process developed by S. Storchheim (U.S. Patent 3,153,590; October 20, 1964; assigned to Alloys Research & Manufacturing Corporation) yields an improved method of manufacturing grids for lead-acid storage batteries. In the past such grids were made by melting lead and casting it into suitable molds. It was found that such grids, while having excellent corrosion resistance to sulfuric acid, did not have sufficient strength to withstand the stresses encountered in service and they did not exhibit good resistance to creeping. To overcome these deficiencies it was customary to alloy the lead with antimony, about 7% thereof. While this increased the strength of the grids, the alloying materials were costly and special precautions were necessary in the fabrication thereof. Also, distortion was likely to occur.

This process is intended and adapted to overcome the difficulties and disadvantages encountered in the prior art, it being among the objects thereof to devise a process of making lead grids for storage batteries which does not require the use of alloys of lead to produce satisfactory grids. It is also an object to provide a method of making battery grids, so that the product will have high strength or resistance to stress and also have excellent resistance to corrosion by sulfuric acid. It is further among the objects of this process to devise a method which eliminates the necessity of melting and casting the lead, which is simple and does not require complicated or expensive apparatus, and which lends itself to operation on a continuous or semicontinuous basis.

In the practice of this process, lead in the form of powder is used. Instead of melting the lead, it is pressed in a suitable mold or die under selected conditions, whereby a strong, compact, and corrosion resistant grid is formed. These conditions including the molding at elevated temperatures, about 300°C., are commercially feasible for the purpose. In the case of lead powder from certain sources, the film of oxide on the granules may be too heavy to produce a grid of satisfactory strength, in which case there is provided a pretreatment which reduces the thickness of the oxide film to an extent which permits the formation of excellent grids. Figure 4 is a diagrammatic view of a plate for the manufacture of lead battery grids by the hot pressing of lead powders, in a continuous operation. The detail at the lower left of the figure is a diagrammatic view partly in section of a press adapted to carry out the process. The finished grid is shown in the detail at the lower right of the figure.

FIGURE 4: DIAGRAM OF PLANT FOR MANUFACTURE OF LEAD BATTERY GRIDS BY HOT PRESSING OF LEAD POWDERS



Source: S. Storchheim; U.S. Patent 3,153,590; October 20, 1964

The apparatus includes a melting furnace, into which pig lead 2 is fed. The molten lead is introduced into the powder spinning machine 3 through hopper 4, the machine being suitably heated to 100°C. or over as by steam coils 5. Hot powder 6 from spinning machine 3 is transported to hopper 7 from which it is fed at 8 into press 9. From the press, which is preferably of the automatic type, the finished grid is passed at 10 to conveyor belt 11. As shown in the detail at the lower left of the figure, the press includes a lower platen 12 heated to the desired temperature by electric resistance heating elements 13, and an upper platen 14 also heated by electric heating elements 15. A lower die or mold 16 has a plurality of upstanding projections 17 and an upper die or mold 18 has a plurality of recesses 19 in alinement with and corresponding to projections 17. Lead powder 20 is introduced into lower die 16 and is consolidated to form a dense body by the usual operation of the press.

The basic units required are a powder production unit and a compacting press. The powder production unit shown is a melt spinning apparatus. Molten lead is poured into a metal container having perforated walls. When the container is rotated at speeds up to 1,000 rpm, the molten metal is forced through the perforations and a fine dispersion of lead is obtained. The hot lead powders are conveyed to the hopper which feeds the automatic compacting press provided with heated platens. The pressure, duration and temperature during the pressing cycle is such that material having optimum properties is produced. A typical set of conditions would be a pressure of 20 tsi (tons per square inch), a temperature of 300°C. and a time under pressure of 1/2 minute. The completely finished grids are ejected from the die onto the conveyor belt and the cycle is repeated automatically.

Referring to the detail at the lower right of the figure, the finished grid may be of the usual configuration consisting of a frame 21 having a terminal 22 and a series of openings 23 which are to be filled with the active storage battery elements. Impure or waste or scrap lead may be used, as well as lead containing alloying metals. For example, an alternate feed material for the plant may be lead made by chemical reduction processes. Satisfactory grid material has been produced, for example, from lead obtained as a by-product in the manufacture of tetraethyl lead used in motor gasolines. Such lead in the as-received condition is coated with a heavy oxide film. Thus when this material is hot pressed the resultant plate does not have optimum mechanical properties, the oxide films preventing satisfactory bonding between the particles.

A method of pretreating the lead has been devised, however, which permits removal of the surface oxide films thus rendering such powders satisfactory as a feed material for the manufacture of battery grids. The pretreatment of the tetraethyl lead by-product involves heating the contaminated lead powders in hydrogen at a temperature in excess of the melting point of lead. The oxide skins on the lead particles contain the molten lead and thus prevent them from fusing together into a coherent mass. Thus tetraethyl by-product lead powders have been treated at 500°C. for 1 hour in hydrogen. Powders so treated remain in the form of discrete particles. The treatment also renders the powder more metallic looking, evidence of the fact that the surface films have been partially removed. Hot pressing of such material yields plate of much higher strength and ductility. As compared to prior methods of making such grids, this process has many advantages, among which are the following:

(1) It permits the use of unalloyed lead in battery grids that are normally cast of a lead-antimony alloy containing 7% antimony. Alloyed lead is normally used because pure lead is not strong or creep resistant enough. Battery grids fabricated from pure lead powders have much higher strength than pure cast lead, are more creep resistant and have a higher modulus of elasticity. Thus lead powder fabricated grids manufactured as described here are strong enough for handling and for withstanding the stresses imposed upon them during service. They are also creep resistant so that distortion of the grid does not occur during normal operating conditions at room temperatures or at the higher temperatures encountered during charging.

(2) High grid mechanical strength without the need for using costly alloyed materials. The strength of plate fabricated by hot pressing various lead powders is highly satisfactory. Powder particle size or more specifically surface area to volume ratio, is particularly important as regards the strength of powder-fabricated plate. Thus as the surface area to volume ratio, i.e., SA/V, of a powder particle increases, the tensile strength of plate fabricated from that powder also increases. Perhaps the correlation can best be understood from the fact that the surface of a powder particle is not a perfect mosaic but rather is composed of a variable number of crystalline discontinuities, forcibly bonded to each other. This type of mismatch bonding, in turn, creates numerous localized coherency stresses. Therefore as the SA/V ratio increases, the number of discontinuities per unit volume increases and the amount of surface area available for bonding also increases.

This is in agreement with the oxide dispersion theory in that the greater the surface area per unit volume exhibited by a certain type particle, the greater is its oxide content. When particles are compacted, their oxide films are ruptured. This facilitates the dispersion of oxide inclusions throughout the metal matrix and inhibits the movement of dislocations through the matrix. Strength is thereby increased and very notably at high temperatures. The oxide content of powder-fabricated plate as such does not adversely affect room temperature ultimate tensile strength but has quite a pronounced effect on the ductility of powder-fabricated plate. Thus, as the oxide content of a given powder product increases, its ductility tends to decrease while its ultimate tensile strength remains virtually unchanged.

Hot consolidation of lead powders also results in a remarkable improvement in high temperature mechanical properties, particularly creep resistance. +140 mesh and -140 mesh powder-fabricated lead strip were subjected to creep testing at 300°F. at a stress level of 300 psi for a 500 hour period. The data obtained revealed that the majority of deformation occurred during the primary stage of creep. This was true of both the +140 mesh and -140 mesh strip. Minimum creep rates for the powder-fabricated lead strip in the secondary creep stage are given below. Also given is the creep rate of chemical lead. The chemical lead was tested at a temperature of only 150°F., in contrast to 300°F. for the powder-fabricated product. The superior elevated temperature properties of the powder-fabricated lead product permits its use in structural applications where the cast-wrought material could not be used.

Type of Lead Strip	Creep Rate, %/Year
+140 mesh powder fabricated	0.24
-140 mesh powder fabricated	1.26
Cast-wrought chemical	43.8

(3) Excellent corrosion resistance to sulfuric acid. This is of great importance in a lead battery grid because if the grid corrodes excessively, the active material it holds will be lost and the battery will no longer function properly. By hot pressing lead powders, superior corrosion resistance to that of cast alloyed lead has been obtained by unalloyed lead.

Thus, battery grids fabricated from hot pressed powders have a longer life. The corrosion rates for cast alloy battery grids and powder-fabricated grids are compared as follows:

Material	Corrosion Rate in 98% Sulfuric Acid, Mils/Year
Conventional cast alloy battery grid	46
Lead granules pressed at 300°C. and 10 tsi	31.8

The excellent corrosion resistance of the powder-fabricated plate is attributed to the oxide films originally surrounding individual powder particles. Such films tend to limit corrosion by serving as more or less continuous protective barriers about relatively small volumes of metal in the matrix so that any corrosion which does occur is localized.

(4) Grids may be made at lower cost by the technique described in this process because the materials used are lower in cost. Conventional battery grids are fabricated of a lead alloy containing 7% antimony. Since lead is much cheaper than antimony, the cost of a battery grid fabricated from pure lead powders is also cheaper. Note that the cost of making lead powder from pure lead is low enough so that there is still a considerable saving in cost when pure lead powders are used for grid manufacture instead of lead-antimony alloy. Furthermore, less capital investment is required for the fabricating equipment since a conventional automatic press is substituted for a specially designed continuous casting machine.

Bell Telephone Laboratories

A battery design developed by L.D. Babusci, B.A. Cretella, D.O. Feder and D.E. Koontz (U.S. Patent 3,434,883; March 25, 1969; assigned to Bell Telephone Laboratories, Inc.) is a totally new cell design which represents a significant departure from that of existing commercial batteries. Secondary batteries of the lead-acid type have traditionally been constructed in a regular hexahedron form or box-like configuration, with vertically disposed rectangular plates. This design has an attractive shape from several standpoints and the flat planar plate is attractive from a manufacturing standpoint. The vertically disposed plates are ideal for permitting gases formed on the plates to bubble off out of the active battery region.

In view of these advantages and the absence of any recognized shortcomings, there has been, until now, no significant reason to consider design changes. However, recent studies of the failure mechanisms of commercial lead-acid batteries have provoked inquiries into the soundness of this design and have resulted in a battery configuration with accompanying detailed features which present radical departures from the classical box receptacle and rectangular plate. A significant use for commercial lead-acid batteries is for standby power in telephone plant locations which represents an investment of several hundred million dollars. Such cells are characteristically operated on a float basis, i.e., the cells are maintained in a fully charged state by virtue of line charging which maintains the battery at an overpotential of several hundred millivolts. In such a floating scheme, where power is required in a rare emergency, the life expectancy of the batteries is significantly greater than that of batteries which are used for primary power and regularly cycled. Batteries designed for this purpose should have a useful life of considerably more than 10 years.

However, recent experiences with battery failures indicate that the expected battery lifetimes are not being realized. A thorough investigation of the failure mechanisms has revealed that many of these premature failures can be attributed to the physical design and structural shape of the battery receptacle and particularly the battery plates. The prevalent causes of failure of lead-acid cells of the conventional design in float service are consequences of excessive growth of the battery grid assembly on aging. The positive grids and associated support structures expand in size due in part to electrolytic formation of an insoluble species of lead oxide on the positive grid. Ultimately the grid becomes so severely distorted that the ribs of the grid no longer retain the active material which falls away from the plate thus reducing the charge capacity of the cell.

In studying the manner in which the positive grid grows, it has been found that the rectangular grid construction is an undesirable structure from this standpoint. The stresses which form in the interior portions of the grid radiate to the edges but, since the grid extremity is rectangular in shape, the stresses developed are nonuniform. Furthermore, in the conventional grid design there is little structural strength provided by the grid itself to counteract the effect of these stresses. These factors result in a grid which deforms readily on aging and deforms in an unpredictable manner. The grids may buckle together, shorting through the separators; the corners often tend to separate due to the concentration of stress at that point, and in extreme cases, the battery receptacle may rupture due to the strain of containing the growing members. The seal between the connecting posts and the cover of the receptacle is particularly vulnerable as corrosion of the grid assembly places stresses on the connecting posts.

The reevaluation of the rectangular plate design occasioned by these battery failures, resulted in other observations suggesting that this is a poor design. In particular, the current distribution, that is, the feeding and collecting of