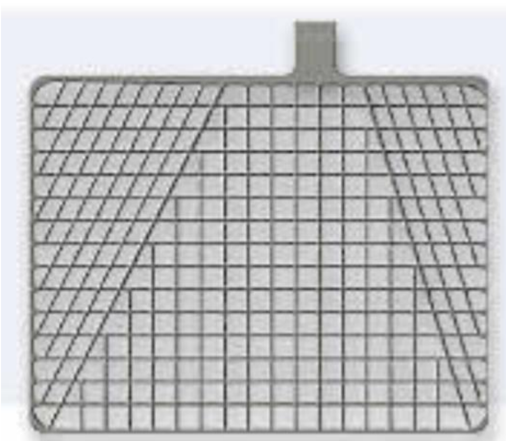
GELCOservices Pty. Ltd.

Battery Grid Construction Comparisons

A Technical Report - lead acid battery grid construction & comparisons.

Author: Robert J. Gell



GELCOservices
Automotive Industry Consultants

May 2013

Lead Acid Grid Construction Comparisons

Abstract:

This technical report outlines the differences in the most commonly used lead acid battery grid forms and constructions. The features and benefits of each grid type are outlined and a summary and conclusions are presented. Some of the chemistry effects of various grid builds are discussed and commentary is given in regard to each grid type. Technical references are acknowledged at the end of the text.

Essentially the grids contained within the lead acid battery are fundamental to the design purpose of that battery and form the "heart" of the planned battery longevity and electrical / chemical performance.

Battery Construction:

The automotive starter battery (SLI)* is a highly developed piece of electrochemical engineering. It contains in excess of 68% lead and lead alloys by weight, tolerates operational and temperature extremes and is required to perform faultlessly for around 48 months.

The following illustration depicts the components of an SLI battery.

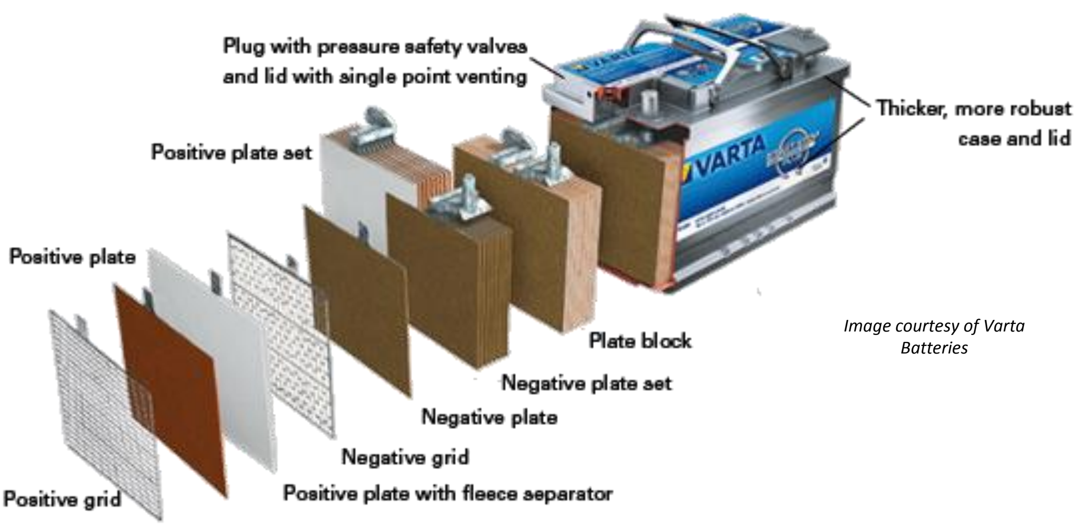


Image courtesy of Varta Batteries

Lead-acid storage batteries typically comprise several cell elements which are encased in separate compartments of a container containing sulfuric acid electrolyte. Each cell element includes at least one positive plate, one negative plate, and a porous separator positioned between each positive and negative plate. The positive and negative plates each comprise a lead or lead alloy grid that supports an electrochemically active material.

* SLI: Starting-Lighting-Ignition

Lead Acid Grid Construction Comparisons

The active material is a lead based material (i.e., PbO, PbO_2, Pb or $PbSO_4$ at different charge/discharge stages of the battery) that is pasted onto the grid. The grids provide an electrical contact between the positive and negative active materials which serves to conduct current.

Battery Grids – background and evolution:

The SLI battery positive grid and the negative grid are – in many cases – designed and manufactured in a different form as the positive grid essentially delivers the electrical energy and suffers a differing level and type of corrosion to the negative grid.

It is well known that by increasing the adhesion between the paste mixture and the grid, formation efficiency can be improved. Among other things, the increased adhesion between the grid and the paste provides for improved interfacial contact between the grid and paste thereby improving current flow between the grid and paste. Accordingly, certain efforts to improve battery formation efficiency have focused on improving the adhesion between the battery grid and paste.

It is also recognized that improved adhesion between battery paste and the grid can increase the service (cycle) life of a battery. It is known that lead-acid batteries will eventually fail in service through one or more of several failure modes. Among these failure modes is failure due to corrosion of the grid surface.

Electrochemical action corrodes the grid surface and reduces the adhesion between the active material and the grid. In most instances, failure of the battery occurs when the grids are no longer able to provide adequate structural support or current flow due to the separation of the active material from the grid. Therefore, there have been efforts to improve the service life of a lead-acid battery by increasing the adhesion of the grid material to the active paste material.

- In one method, a lead-calcium alloy substrate is coated with a layer of a tin, lead-antimony, lead-silver or lead-tin alloy. The layer of metal on the surface of the grid promotes better adhesion of the active material paste to the grid.
- Another similar method is described wherein a layer of a lead-tin-antimony alloy is roll-bonded to a grid base formed of a lead-calcium alloy. It is stated that the surface layer of the lead-tin-antimony alloy enables the battery active material to be retained for a long period of time. The increased adhesion of the paste to the grid serves to improve the cycle life of the battery.
- Yet another similar method is described in Japanese Patent Publication No. 10-284085 which discloses a method wherein a coating of a lead-antimony-selenium alloy is fused to a lead-calcium-tin alloy strip and the strip is punched and/or expanded to form battery grids. The grids formed by this process are believed to increase battery life.

Lead Acid Grid Construction Comparisons

Thus, it can be seen that the adhesion between a battery grid and battery active material may affect, among other things, battery formation processes and battery service life. Accordingly, various methods, such as those mentioned above, have been proposed to improve the adhesion between a battery grid and battery active material.

While these methods may provide satisfactory solutions to the problem of inadequate paste adhesion, they do have certain disadvantages. For example, each of these processes requires the incorporation of an additional material into the grid manufacturing process. In certain processes, the grid must be treated with an additional chemical (e.g., a persulfate or perborate solution, or an oxide).

In other processes, an additional layer of a dissimilar metal or alloy must be deposited on the grid by chemical (e.g., electroplating) or mechanical (e.g., roll-bonding) means. It can be appreciated that the additional process steps and materials required in these methods can significantly increase the cost of manufacturing the battery grids. As a result, certain battery manufacturers may be reluctant to incorporate these methods into a production facility.

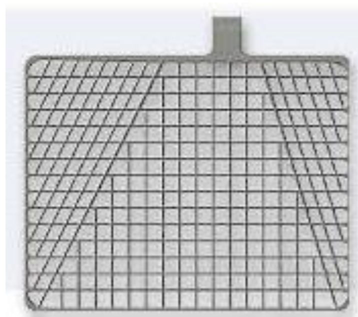
It is apparent that previous attempts at improving paste adhesion have focused on the compatibility problems between battery paste materials and the alloys or coatings at the surface of the battery grid. Accordingly, proposed solutions to the problems of paste adhesion have involved the application of a dissimilar metal or coating to the grid surface.

However, it has been discovered that another source of the problem of inadequate paste adhesion may be the ***configuration of the grid***. Consequently, the effect of different battery grid making processes on paste adhesion has been further examined.

As detailed above, grids for lead acid batteries provide structural support for the active material therein, and serve as a current collector during discharge and a current distributor during recharge. Known arts of lead acid battery grid making include:

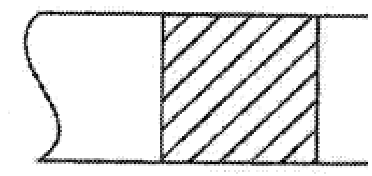
(1) batch processes such as book mold gravity casting; and

(2) continuous processes such as strip expansion, ***strip stamping***, continuous casting, and continuous casting followed by rolling. Grids made from these processes have unique features characteristic of the process and behave differently in lead acid batteries, especially with respect to the pasting process.



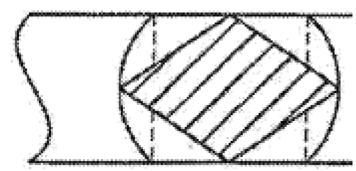
In the book mold casting process, molten lead is poured into a grid mold and cooled to form a grid. The surface of the grid made from book mold casting is somewhat rough and the geometric shape of the cross-section of the grid wires is usually oval with a sharp angle formed at the plane where the book mold closes. Book mold casting is a batch process and its productivity is much lower than other processes that are continuous in nature.

In the strip expansion process, a cast or wrought lead strip is pierced, stretched above and below the strip plane, and then pulled or expanded to form a grid with a diamond pattern. The surface of the wires perpendicular to the plane of the strip is smooth and the cross-section of the wires is rectangular.



Stamped grids also have smooth surfaces and a rectangular cross-section in the wires.

For continuous casting, the surface of the grid can be rough on the mold side and is smooth on the belt/air side. The geometry of the cross-section of the wires produced by continuous casting can be a triangle, a trapezoid, a section of an arc or a semi-circle, depending on the mold design. If the grids are rolled after casting, the surfaces become smooth and the cross-section of the grid wires become rectangular.



When applying battery paste to a grid, an oval-shaped wire, such as that in a book mold cast grid, allows the paste to flow around the wire. The rough surface and the sharp angle of the wires provide a mechanical graft and interlock of paste particles. Therefore, the contact between the grid and the battery paste is good and the plate is strong.

With rectangular wires, on the other hand, it is much more difficult to make good contact between the battery paste and the surface of the wire moving in a direction perpendicular to the direction in which the paste is applied because the flow of paste must change in a 90 degree step. This is similar to the situation where water flows down a 90 degree cliff, and the surface right below the edge of the cliff is not contacted by the falling water. With a grid wire orientation other than 90 degrees, the change of paste flow is gradual and continuous and therefore, provides better paste coverage.

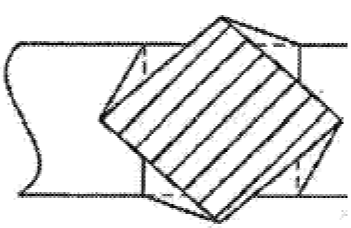
When the battery paste is cured and dried, it will shrink and generate tensile force at the paste/grid interface. The tensile force at the paste/grid wire interface is at a maximum when the wire surface is perpendicular to the grid surface and at a minimum when the wire surface is parallel to the grid surface. As a result, a gap is formed between the grid wire and the paste at the location where the tensile force is the maximum. This type of plate is weak and the paste will fall off easily. Because of a lack of contact between the paste and the grid, a battery made with this type of plate is much more difficult to form, performs poorly in certain reserve capacity tests, and does not exhibit satisfactory cycle life.

Lead Acid Grid Construction Comparisons

Therefore, there continues to be a need in the battery manufacturing field for alternative methods for improving the adhesion of battery paste active material to the battery grid. More particularly, there is a need for a method that can increase the adherence of battery active material to a battery grid produced by a continuous process, such as strip expansion, strip stamping, or continuous casting, without the need for additional materials such as treatment chemicals or metal coatings.

A method that increases the formation efficiency of a battery by enhancing the adhesion between the battery paste material and the battery grid, along with a method that can modify the wires of a battery grid made from a continuous process to mimic the wire shape observed in a book mold gravity cast battery grid so that the paste can flow around the grid wires to improve the plate strength, will give an ideal outcome for the total battery performance.

It is an objective to provide a method of making battery grids that allows a battery manufacturer to take advantage of a low cost continuous grid making process eg; stamping or punching, without the drawbacks associated with inadequate paste adhesion such as reduced formation efficiency and reduced cycle life.



The grid wires of the battery grids produced by the stamping process are deformed such that the grid wires have a cross-section other than the rectangular cross-section produced by the stamping process. The nodes and the opposed ends of each grid wire that are attached to each node retain a generally rectangular cross-section so that the grid surface retains a planar configuration.

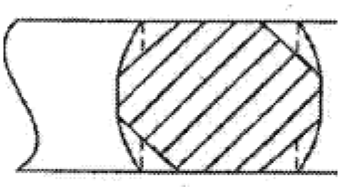
While this method of manufacture is advantageous when applied to individual battery grids, it is particularly advantageous when employed as part of a continuous battery plate making process.

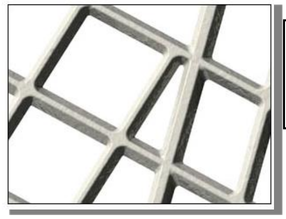
The cross-section of the intermediate portion of the stamped grid wire may be any number of shapes including diamond, rhomboid, hexagon, octagon or oval. All these basic shapes will give maximum active material adhesion and ease of formation.

After the punching operations form a strip having interconnected grids, the battery grid wire sections of the strip are processed in a stamping station. The stamping station is used to deform or coin the grid wires so that the grid wires have a cross-section similar to one of the coined grid wire cross-sections shown above.

Lead Acid Grid Construction Comparisons

For instance, the stamping station may include a die that deforms the rectangular cross-section of the grid wires of the punched grid into an octagonal cross-section as shown here. .





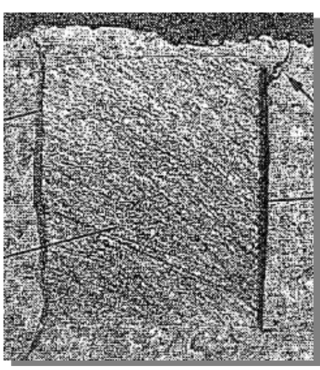
Actual cross section of stamped and coined grid wires.

While it is preferred that the nodes remained undeformed, in certain circumstances it may be advantageous to deform or coin the nodes in the stamping station. Since coining of the nodes as well as the grid wires will tend to make the grid strip non-planar, pasting operations which tend to apply paste more thickly to one side of the plate than the other can benefit from this effect. The grid strip can then be oriented so that paste can more readily flow to the surface which is thinly pasted, i.e., fed into the pasting machine so that the concave side faces the direction that otherwise would be thinly pasted, typically the bottom.

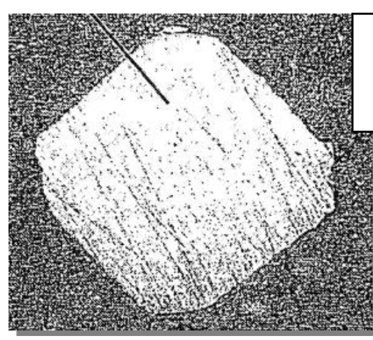
Batteries made of conventional stamped grids and grids prepared in accordance with the coining process as described were cycled in accordance with the SAE J240 life test procedure at a temperature of 167° F. to measure the service life.

Fourteen batteries having grids prepared in accordance with coining of node edges and ten control batteries having conventional stamped grids were tested. The average number of cycles for batteries having grids prepared in accordance with coining process was 2.7 times the average number of cycles for the control batteries.

This demonstrates that batteries including grids made in accordance with the coining of wires and node edges will have better cycle life performance than batteries including conventional grids.



Rectangular wire form showing gaps in active material adhesion



Coined stamped wires showing improved active material adhesion

Lead Acid Grid Construction Comparisons

Stamped Grid Manufacturing Summary:

The process detailed above provides a method that can increase the adherence of battery active material to a battery grid produced by a continuous process, such as strip stamping, or punching without the need for additional materials such as treatment chemicals or metal coatings.

The process of coining the node edges increases the cycle life of a battery by enhancing the adhesion between the battery paste material and the battery grid. The process to modify the wires of a battery grid made from a continuous process to mimic the wire shape observed in a book mold gravity cast battery grid so that battery paste can flow around the grid wires to improve the plate strength after pasting ensures the active material adhesion.

As a result, a battery manufacturer can take advantage of a low cost continuous grid making process without the drawbacks associated with inadequate paste adhesion.

Grid Metallurgy:

The basic differences in metallurgical characteristics of grid materials and alloys can be seen in the table below.

Lead Calcium Grid (PbCa)	**Vs**	**Lead Antimony Grid** (PbSb)
Cold Wrought - Punched		Heat cast (formed in a book mold)
Fine, uniform surface grain		Course surface grain
Resists corrosion		Accelerate corrosion

Lead with a small percentage of calcium (0.03-0.05%) is preferred to deliver grid rigidity across a broad range of operational temperatures.

Lead Calcium grids perform well under the punching process and molecular integrity is retained.

Gradual corrosion is a normal occurrence during the service life of a SLI battery and it is the primary enemy of the positive grid. Corrosion begins on the grid surface at grain boundary sites (places where the grain touches and bonds) and penetrates into the interior of the grid along the grain boundaries. This corrosive effect is more prevalent in batteries with course grained grids.

Corrosion principally takes place at the positive grid, and the process is more pronounced in batteries that routinely experience overcharging.

With punched grids the corrosive effect is well resisted by the much improved molecular structure over a cast or expanded metal grid.

Lead Acid Grid Construction Comparisons

Summary & Conclusions:

From the scientific appraisals detailed above it can be seen that the best by far method of volume production of grids is by the punched or stamping technology.

The improvement in active material adhesion – after the coining of nodes and grid wires ensures maximum resistance to corrosion and greater formation control. All of which relate to an expected longer battery service life.

Benefits of a punched and coined grid form are:

- Greater active material adhesion
- Improved structural integrity
- Ease of current flows
- Improved CCA and RC
- Resistance to corrosion
- Lower potential plate height – improved electrolyte saturation
- Ease of high volume manufacture – less cost to produce
- Improved electrical performance over time
- Improved ability to recover from deep discharge than conventional expanded (non coined) or cast grids
- Potentially longer service life

Some battery makers tend to combine a cast positive grid with a punched negative grid. This method is still quite satisfactory, but less than the total battery life expected from a punched positive and negative grids. In the case of a calibrated Ca/Ca stamped grid battery the Electrical Power Management (EPM) system can be specifically designed to maximize the ICE fuel savings as the reserve capacities of a stamped grid calibrated Ca/Ca battery are easy to identify by various temperatures and thus design a charge regime and algorithm to manage the delivery of energy from the vehicle alternator.

In conclusion the author thoroughly recommends the significant benefits to be gained by the introduction of punched or stamped grids with coined wire modification to ensure maximum active material adhesion.

Report Author: Robert J. Gell *SAE-A (AM), IAME, AFAMI*

Date: Friday May 31st 2013 *(revised)*

GELCOservices Pty. Ltd.
16 Dawson St.,
Fullarton SA 5063
AUSTRALIA
www.gelcoservices.com.au

References: *AtlasBx – Korea US Patent Application – Battery Grid WIPO Patent – Lead Acid Grid Plates Varta Batteries AC Delco Batteries Lindens Handbook of Batteries Oxford Dictionary of Chemistry*