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Formation of wrought lead–calcium batteries for consistency

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Abstract

Consistent and optimum formation is critical to performance and durability of lead/acid batteries. Delco Remy's approach to formation consistency includes conformance to process, material and product requirements, and the accommodation of model mix variables in the plant. An overall process model for formation control is presented. Specially designed charge tables, air-moving equipment, and optimized procedures are utilized to achieve control of formation results. The influence of battery design variables on optimum current schedules is reviewed. Use of computer-generated schedules for coordination of process and design factors to achieve predictable and consistent product characteristics is suggested.

Introduction

Consistent and optimum formation is important to the performance and durability characteristics of lead/acid batteries which contain wrought lead–calcium grids. In this paper, the technology difference between Delco Remy's wrought grids and conventional lead–calcium grids is emphasized.

Figure 1 characterizes the wrought lead principle. This operation takes a 25 mm slab of lead through a multi-pass rolling process that reduces the thickness to about 1.25 mm and, thereby, causes a mechanical refinement of the grain structure to a finely layered composite. The coils are then expanded into wrought calcium grids. Cast calcium grids, on the other hand, are generally cast to the required grid thickness and grain refinement is achieved by an alloy modifier. Our work indicates that the wrought process provides improved tensile and corrosion characteristics.

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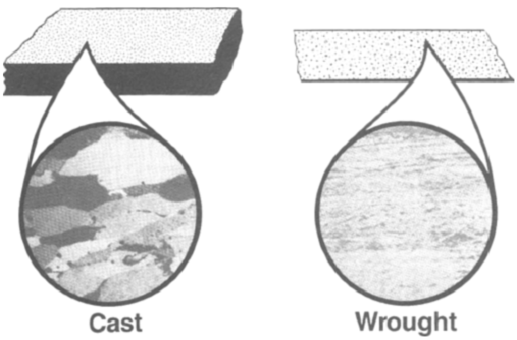

Fig. 1. Lead microstructure.

Formation characteristics

Delco Remy's approach to formation consistency includes optimization and control of plant processes and accommodation of model mix variables. With the complexity of lead/acid battery processes and variations found in the plant process, it is sometimes difficult to establish consistent formation schedules. The following characteristics insure proper product: (i) chemical composition of the positive and negative plates, to insure complete electrochemical reactions, (ii) porosity in both plates, to insure that the design parameters give rise to the desired performance requirements; (iii) adhesion of the active mass to the grid in the positive electrode and cohesion of the positive active mass, to insure good electrical conductivity and plate strength (which is verification of the plate curing process); (iv) crystal morphology of the positive plate, as shown in Fig. 2. The crystal morphology of a positive

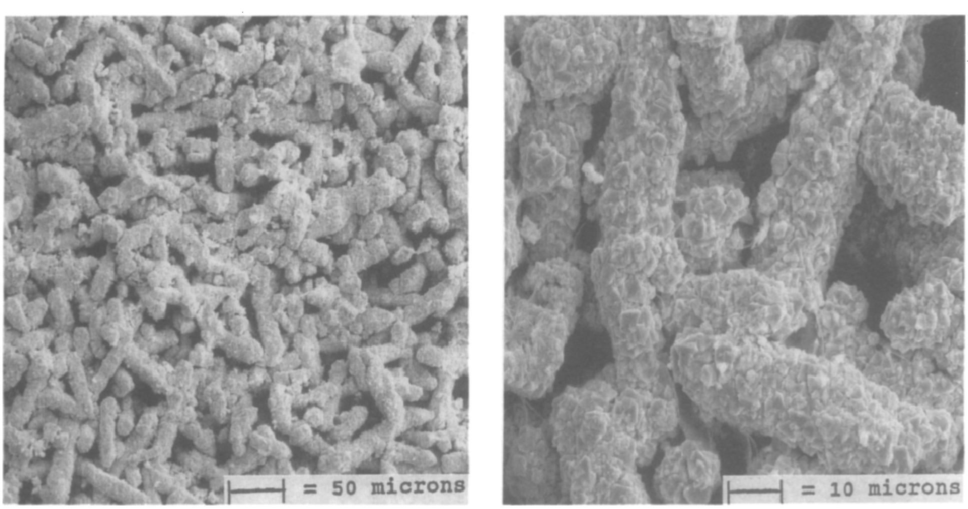

Fig. 2. Positive plate crystal morphology.

plate is observed in order to verify both the crystal integrity and the α-PbO_2 and β-PbO_2 contents. Like other investigators, we find α-PbO_2 gives lower capacity and initial performance than β-PbO_2, but on the other hand, we see longer laboratory cycle-life with increase in the α-PbO_2:β-PbO_2 ratio. These contrasts in battery chemistry lead to compromises in battery designs and processes.

Delco Remy formation procedures and equipment

Delco Remy uses an in-the-case formation that is considered appropriate for high volume automotive battery production at the Sarreguemines plant in France. The approach to formation consistency is heavily based on the equipment used in the formation process. It is also based on adherence to statistical process control principles. These reduce variation and aid control to target specification means in order to satisfy customer requirements and to meet formation objectives. The formation process is shown schematically in Fig. 3, as part of the overall electrochemical and materials conversion process from cured plates to formed material in cells having the proper full charge or operating electrolyte. Each of the ellipses focusing on the formed material must be under control or there will be unwanted variation in both the formed material and the degree of formation. The process is complex and involves interactions among materials, equipment, procedures, and model mix.

The formation equipment was designed to give consistent-quality formation of the lead–calcium batteries, as well as to provide a work area that is

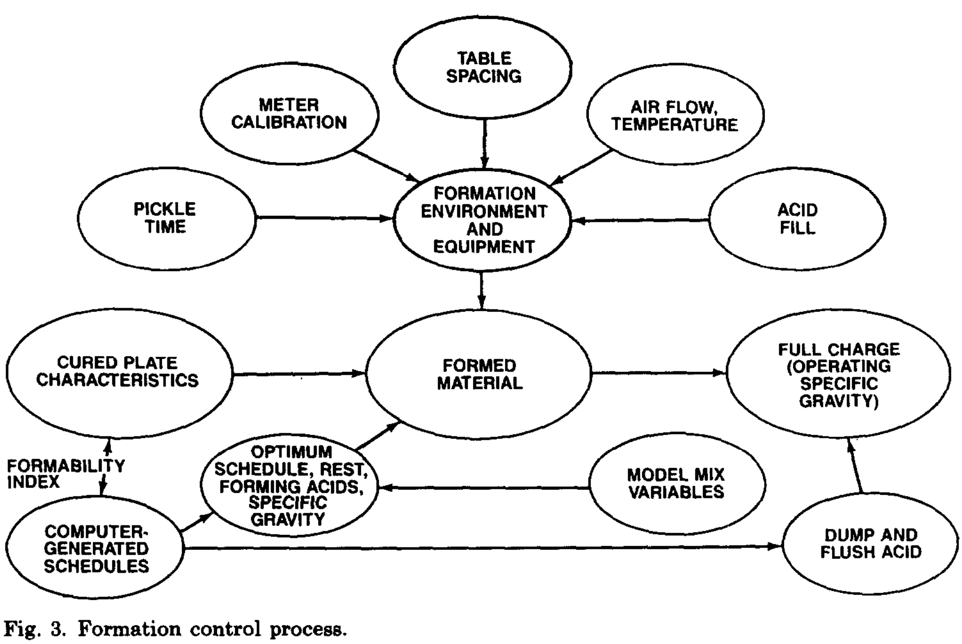

Fig. 3. Formation control process.

environmentally safe and pleasant for employees. The following is a short review of the formation equipment used for battery production.

The acid-fill stations provide proper fill level; this is critical for the benefit of chemical reactions and heat management. The stations are automatic and can accommodate various battery sizes. The materials used in construction are polypropylene plastic and stainless steel. Use of these materials assists not only equipment durability and corrosion resistance, but also helps to maintain acid purity.

The charge tables are designed to control battery temperature and acid mist. The batteries are properly spaced, and the tables contain openings to provide air flow around each unit. Air is drawn down over the batteries and through the table at a rate of 15 000 to 20 000 $ft.^3 min^{-1}$, depending on the size and the spacing of the batteries. The air is then drawn through mist eliminators that condense and remove the acid droplets to provide a clean air discharge. The formation of automotive batteries is completed within a 24-h period.

The acid dump is a partial rollover, 120° tilt facility. Homogeneity of acid concentration within each cell and minimization of cell-to-cell variations are major objectives of this operation. The station is constructed from plastic materials for corrosion resistance. The dump station is angled and timed to give the correct final gravities. The line speed, battery tilt and battery cover design allow for proper discharge of the forming acid.

The rectifiers used in production are thyristor controlled, 20 to 30 A, constant-current, a.c. to d.c. units. Automatic timers provide proper current usage and a formation rest period, as required by the specifications. Temperature control is monitored by visually reading thermometers placed in the batteries.

Formation schedules and conditions must be optimized to meet basic formation objectives. The following criteria are monitored:

(i) chemistry of positive and negative plates;

(ii) active material crystal structure, specifically in the positive electrode;

(iii) grid/active-material interface (both adhesion and cohesion);

(iv) electrolyte operating specific gravity;

(v) purity level of electrolyte (to maintain maintenance-free characteristics).

Both process factors and product-design factors must be considered in arriving at optimum formation schedules. Typical process factors are: forming acid specific gravity; pickle time, or the time between acid fill and current start; operating schedule including currents, time and rests. Additional process factors are: formation aids; cooling conditions affecting temperature control; acid specific gravity used to refill after formation.

Product design factors are important because of the many models that must be formed over a period of time. Typical design factors considered include: plate thickness; positive/negative active-material ratio; acid/material ratio; total surface area per cell. Also considered are density of active material and grid-mesh parameters. Studies have shown that a finer grid mesh promotes formation efficiency.

The achievement of consistent results from model to model and from day to day requires considerable understanding of the influence of these variables and a formation control strategy. A limited analysis of our understanding and approach to controlling some of the key factors is as follows.

Control of formation parameters

As mentioned earlier, air-moving equipment is utilized to provide basic *cooling* at several velocities. *Current density* adjustment linked to *acid/material ratio* is utilized as the *temperature control* method. Tests on effects of temperature during formation show the following results.

High formation temperatures (above 80 °C):

- produce higher β-$PbO_2 \rightarrow$ poor battery life (shedding of positive active material).
- reduce negative material capacity → poor cold-rate capacity
- increase positive grid corrosion → poor battery life

Low formation temperature (below 60 °C);

- produce higher α-$PbO_2 \rightarrow$ poor initial reserve capacity
- lower formation efficiency → longer formation times
- more durable crystal structure → longer battery life

Sulphuric acid specific gravities of 1.180, or lower, are found to increase the formation efficiency and also produce a higher α-PbO_2 content, which is good for cycle-life. Figure 4 shows the α-PbO_2 content dropping from about 60% in a 1.100 specific gravity forming acid to about 25% in acid of 1.190 specific gravity. Initial reserve capacity, expressed as percent of rating, and total PbO_2 content are slightly lower over the 1.100 to 1.190 range. There is, however, a compromise to be made in choosing the specific gravity for specific designs because lower acid gravities could increase the possibility of positive grid corrosion.

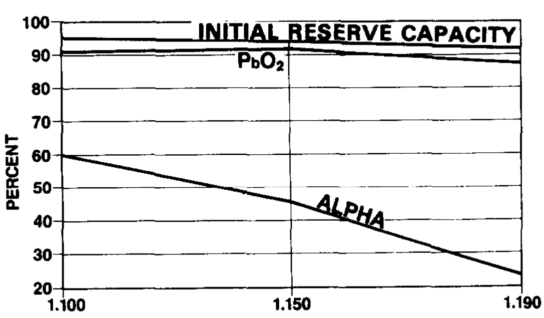

Fig. 4. Effect of forming acid.

TABLE 1

Plate pickling process: $PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$ (both plates)

Pickle	Plate composition (wt.%)					
	Positive			Negative		
	PbO	PbO_2	$PbSO_4$	PbO	PbO	$PbSO_4$
Start	86	–	12	88	–	10
End	62	–	36	68	–	30

Table 1 shows the reaction that takes place during pickling and the effects on both the positive and negative plate. What does pickling do? Based on the number of plates and plate density, a sufficient amount of time is required to: (i) fill the pores of the plate, to increase electrical conductivity throughout the plate; (ii) wet the plate material, to initiate the formation of lead sulphate ($PbSO_4$); (iii) decrease the pH of the liquid around the grid wire, to reduce positive grid corrosion. We restrict pickling times to a specific range below 2 h, depending on battery design variables.

Figure 5 illustrates a typical formation profile in the production of a wrought lead–calcium battery. The curves portray the temperature and voltage profiles in the formation process. A two-step current density process is used. Lower current densities are employed in the second step in order to minimize negative plate overvoltage and gassing, and to improve positive conversion efficiency. Between the two steps, a rest period is included to: (i) reduce battery temperature prior to the second step; (ii) depolarize for increased current efficiency in the second step; (iii) reduce battery self-discharge after formation. The theory behind the last comment relates to the unreacted lead oxide that reacts with sulphuric acid during the rest period and the $PbSO_4$ is then more easily formed into lead dioxide in the second step of formation.

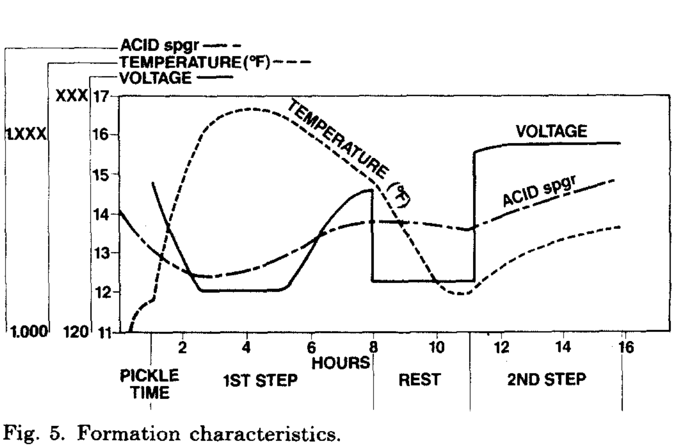

Fig. 5. Formation characteristics.

Battery formation is positive-plate limiting. As a consequence, the total formation ampere hours are determined by design and process factors, such as the total positive paste weight per cell, positive paste density, grid design, and initial formation acid specific gravity.

In order to facilitate the use of low specific gravity forming acid and to aid operating specific gravity control across all cells, batteries are drained of the forming acid and refilled with *flushing acid*. As indicated in the process control chart earlier (Fig. 3), the selection of the proper flushing specific gravity is based on model design factors coupled with feedback empirical data on operating specific gravity.

Computer generation and validation of formation schedules

As indicated in the previous section, it is a complex task for the electrochemical engineer responsible for formation process specifications to generate schedules for the model mix, and to incorporate process variables that will give consistent formation results. We have developed a computer model that will calculate a schedule to meet the formation objectives, such as degree of formation and finish chemistry and structure, control of maximum temperature to specified range, and interface integrity.

Inputs to the formation schedule model include *total surface area per cell, acid volume, paste density, paste weights*, and *grid opening or mesh structure*.

The schedule output includes *first- and second-step current levels, a rest point, total ampere hours*, and *flushing acid specific gravity*. Tables 2 and 3 show a printout of data from a given battery design.

The model operates from basic relationships that utilize the input parameters. For example, since maximum temperatures must be controlled to specified limits, current densities are adjusted in relationship to acid/material ratio. Fill acid specific gravity is inversely varied with acid/material ratio to avoid grid corrosion potentials during formation.

Table 4 shows characteristics of three different designs from an early model development test. The designs differed in paste density, paste weight, surface area, and acid/material ratio. Current schedules for each design were predicted by a computer model using previous experience on current density and acid/material ratios.

The current density versus acid/material ratio relationship is given in Fig. 6. Maximum formation temperatures achieved are shown below the

TABLE 2

Formation information

	1st step (20 A/11h)	Rest (3 h)	2nd step (12 A/13h)
Initial calculated A h	220		156

TABLE 3

Formation information

	Acid sp.gr.	
Initial fill	1.190	
Formation drop	1.066	
End of formation	1.249	
Flush and fill	1.280	
Ship	1.270	
Electrolyte volume (l)	6.06	
Total lead weight (kg)	14.84	
Acid/material ratio	0.60	
State-of-charge	**Acid sp.gr**	**Open-circuit voltage (V)**
1.000	1.270	12.72
0.800	1.232	12.49
0.600	1.191	12.24
0.400	1.144	11.96
0.200	1.096	11.67
0.000	1.045	11.37

TABLE 4

Design

	X	XX	XXX
Plates/cell	9	15	8
Positive $PbSO_4$(%)	6	14	10
Positive paste/cell (g)	725	392	252
Positive density ($g\ cm^{-3}$)	3.9	3.4	3.64
Acid/material ratio	0.64	0.80	1.27
Fill acid (sp. gr.)	1.17	1.17	1.17
Surface area/cell (cm^2)	1312	2148	1025

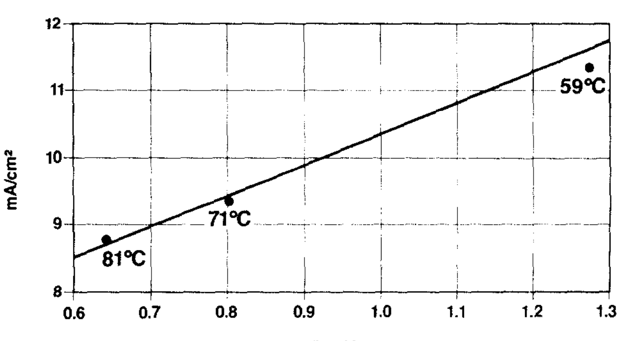

Fig. 6. First step of formation (current density vs. acid/material ratio).

curve and varied from 59 to 81 °C. The current density is proportional to the acid/material ratio, and we have since shifted the slope (in the model) to reduce maximum temperature variation. Results after formation showed good plate chemistry, clearing and interface conditions. We are continuing to evaluate all designs that are built and will make adjustments to correct particular conditions. An important feature of the model approach is that it allows fine-tuning of the relationships among the factors as additional tests on formation development are conducted.

As shown in the earlier formation process control diagram, the use of an input ampere-hour modifier or formability index across plants for fine-tuning the degree of formation is suggested. Even though we feel that the raw materials' production and plate-making are under control in each of our nine worldwide plants, there are slightly differing ampere-hour requirements across the plants.

Summary

Consistency in formation conditions for batteries using lead–calcium wrought grids may be critical and complex, but formation was critical before the advent of such grids. How much of the equipment and process we now use came about because of a special need for lead–calcium grid batteries versus consistency and general formation control objectives is not known. We, believe that our process operation is sufficient to get the most from the wrought lead–calcium maintenance-free product.