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Manufacturing improvements in the processing of lead-acid battery plates and reduction in plate dusting with an active-material additive

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Abstract

Present-day plate processing offers ample opportunity for improvement within lead-acid battery plants. An inorganic, glass micro-fiber, active-material additive has been found to improve plate processing and lower cost in many of the various operations. This additive allows paste batches to be made with higher moisture contents that improve grid filling and paste texture through higher malleability and reduced resistance to flow. The additive also acts as a bulking agent to extend the plate yield of paste batches, which results in lower cost of active material per plate. Energy consumption and operation throughput in plate making is improved by lower flash-dryer temperatures on the pasting line and by a substantial reduction in curing time. Plates made with the additive have decreased paste pellet friability, which reduces battery assembly scrap. The additive also lowers plate surface dusting that results from handling and thus offers the battery manufacturer the opportunity of lowering lead-in-air emissions within the battery plant. Plates made with the additive have been found to have higher surface area and increased active-material utilization, which can enhance battery performance.

Keywords: Lead-acid battery; Micro-fiber additive; Paste mixing; Plate pasting; Lead-in-air emissions

1. Introduction

It is often said that the basic building block in the manufacture of the lead-acid battery is the preparation of the electrochemically active materials and subsequent application, or pasting, on to the positive and negative grids. This initial step also includes the use of active-material additives. These additives can affect the rest of battery manufacturing and also influence the performance of the battery. This paper focuses on the positive impact of a new, inorganic, active-material additive on the critical manufacturing steps of paste mixing, plate pasting, and curing.

The inorganic additive is described as a glass micro-fiber made with a borosilicate chemical composition that renders it highly resistant to attack in the harsh environment of the lead-acid battery. The hydrophilic nature of the new additive enables the paste mix to have higher moisture content without deviating from specified paste densities and rheological properties. Several practical production examples will be referenced of paste batches prepared with the addition of 0.5–1.5 wt.% of new additive to the positive and/or negative active-materials [1,2].

Pastes made with the additive have a higher plasticity than conventional pastes. Better pasting and a more complete grid fill is also achieved. Pasted plates with higher and more consistent paste moistures assure a more efficient oxidation phase in the curing process. The beneficial impact on the curing process of the additive is illustrated by the experience of two lead-acid battery manufacturers who are currently using the additive in production [3,4].

Benefits of the additive in subsequent battery manufacturing operations have also been observed and documented. The active materials adhere better to the surface of the grids and cohesion of the lead oxide particles appears to be improved with decrease in surface cracks and fissures.

Dust from cured plates can be a considerable source of lead-in-air emissions that contaminate the environment of the work place. The additive reduces the loose particulates on the plate surfaces and thus reduces the environmental hazard at its source. In addition, the specific surface-area of pastes, as measured by the BET technique, and the void volume in the plate structure and both increased due to the presence

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of the additive. These features offer the manufacturer the potential for improved battery performance.

This study demonstrates the impact of the additive on plate processing through real-life manufacturing examples gathered from various lead-acid battery manufacturers, world-wide.

2. Experimental

2.1. Description, usage, and applications

The new active-material additive is a glass micro-fiber that is designed and manufactured exclusively for lead-acid battery applications. The major characteristics of the additive are summarized in Table 1. The additive is composed of chemical-grade borosilicate glass that is used extensively in the manufacture of absorbent glass mat (AGM) separators [5]. The additive can be added directly to the paste mixer in much the same manner as other additives, such as negative-paste expander blends and inorganic flocks.

The additive has been evaluated in every major battery application, world-wide. The plant trials have provided a good understanding of its impact on the various process steps in battery manufacture.

The largest battery manufacturing sector is the automotive starting, lighting and ignition (SLI) application. Given the prominence of this application, about 55% of the more than 30 plant trials were conducted on automotive batteries. Industrial applications constitute the next largest use of lead-acid batteries. The industrial sector is divided into stationary and traction, the latter is also referred to as motive power. Both stationary (telecommunications and uninterrupted power supply (UPS)) and motive power comprised the balance of the trials (35 and 10%, respectively).

To provide a clearer understanding of the diversity of the trials, the batteries are grouped into the following four categories according to the manufacturing technology.

- *Technology A*: Utilizes continuous casting of both positive and negative grids. The grid is expanded or punched, and then processed on a continuous pasting machine. This technology represents the latest in manufacturing technology and is gaining wide acceptance due its impact in lowering the cost of plate production.
- *Technology B*: Conventional cast positive grids (book-moulds) pasted on a belt or orifice pasting machine. The negatives are produced by the continuous casting/pasting technologies described above (Technology A).
- *Technology C*: Both positive and negative are conventionally cast and pasted on a belt or orifice paster.
- *Technology D*: The positive plate is made by filling a tubular gauntlet with active material. The current-collector is a lead spine that is cast, sometimes by injection-casting techniques. The negative plate is conventionally cast and pasted. Technology D is widely used in the production of industrial traction batteries.

Table 1
New inorganic active-material additive

Chemical composition	Borosilicate chemical grade glass
Surface area	$0.5\,m^2\,g^{-1}$
Density	$2.4–2.6\,g\,cm^{-3}$
Average diameter range	3–5 μm
Length to diameter ratio	>5:1
Addition level	0.5–1.5% of oxide weight

Over 50% of trials were carried out with Technology C batteries. The distribution of plant trials by plate manufacturing technologies is shown in Fig. 1.

2.2. Evaluation of modified plate characteristics

Plates modified by the inclusion of the new additive have been analyzed with different techniques that quantify the changes the additive induces on the active materials throughout the mixing, pasting and curing processes.

Two key plate characteristics that are affected by the presence of the additive are cured plate strength and the degree of loose particulates on the plate surface (plate dusting). The method of evaluating these characteristics is to use a plate vibration tester that is commonly employed in battery production to measure grid-to-active material adhesion, as well as pellet strength. The tester vibrates at 60 Hz for a predetermined length of time (5 min) at an amplitude of 1.27 mm.

In addition, a measure of the propensity of a plate to dust was devised by a simple technique that consists of applying a plastic adhesive tape (Universal #91000 Clear Packaging tape, 3 in. wide) to the plate surface and then removing it. The particulates that are removed by the tape are only loosely held to the plate and are likely to dust off. This test is a quick and non-destructive method to give a measure of the amount of dust that can be released by a cured plate.

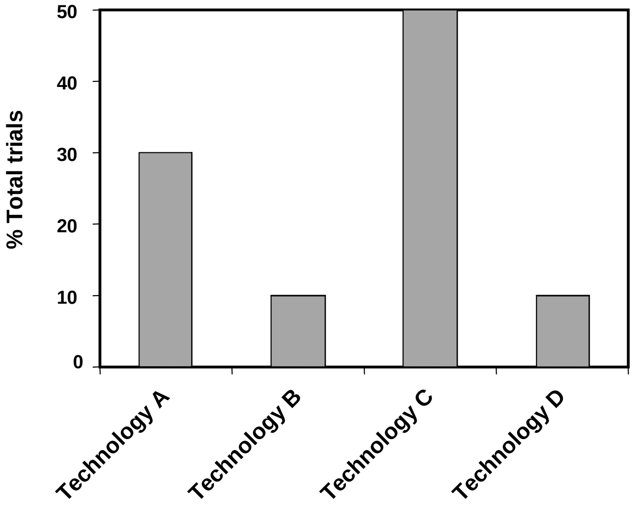

Fig. 1. Distribution of plant trials by plate-processing technologies.

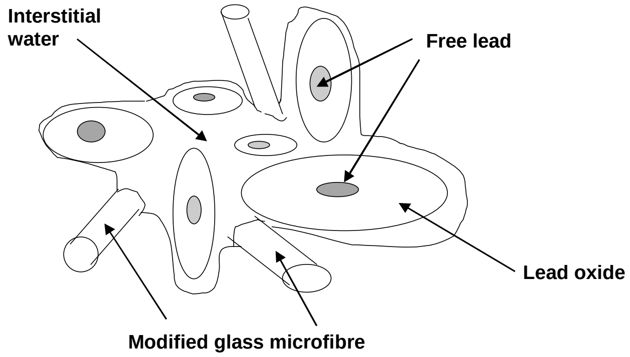

Fig. 2. Distribution of water added to lead oxide during paste mixing preparation in presence of additive.

3. Results and discussion

3.1. Impact on paste mixing

Preparing a paste batch with the inclusion of the new additive offers interesting possibilities and challenges to the battery technologist. As seen in Table 1, the additive is composed of borosilicate glass. It is well known that water has a zero contact angle with glass surfaces, which results in a very high affinity between the additive surface and water [5].

Paste rheology has been extensively studied [6,7]. In general terms, the amount of water added to the dry oxide will largely determine the density (cube weight) of the final paste. The other major contributor to paste density is sulfuric acid. Sulfuric acid reacts with the oxide to create lead sulfate. Thus, sulfuric acid causes bulking of the paste density.

When the paste mix contains the new additive, there will be competition for the water being added. The presence of the glass micro-fiber affects the total amount of interstitial water and allows the battery paste to be made with a greater amount of water, but still attain and retain the required paste density (cube weight) and plasticity (penetration) (Fig. 2). In the absence of additive, the additional initial water will be excessive for the paste, and therefore will adversely affect both the cube weight and penetration. Some values that were obtained with plant trials are given in Table 2. This additive is compatible with all mixing technologies and can be used in both dry- and wet-mixing methods.

Table 2
Differences in *mixing* parameters induced by the use of the glass micro-fiber active-material additive

	Technology A		Technology C	
	Positive	Negative	Positive	Negative
Additive (%)	0.5	1.1	1.0	1.5
Difference in initial water (%)	4.8	6.8	5.6	8.8
Difference in density (%)	0.7	0.9	0.7	0.3
Difference in penetration (%)	10	8	8	1.5

Table 3
Difference in *pasting* parameters induced by the use of the glass micro-fiber active-material additive

	Technology A		Technology C	
	Positive	Negative	Positive	Negative
Additive (%)	0.5	1.1	1.0	1.5
Difference in plate moisture (%)	8.2	11.8	13.6	12.5
Difference in pasting oven temperature (%)	n/a	n/a	10	10
Difference in plate count (%)	3	5	7	5

The impact of the additive is evident by the amount of initial water needed to prepare the modified batches. The initial water can be increased from about 5 to almost 10% over the specified amount, as dictated by the amount of additive. The extra water and the presence of the additive produce a very workable paste. The result is a more ‘fluid’ paste, which fills grids more completely and, thereby, reduces the scrap generated from incomplete grid fill.

3.2. Impact on plate pasting

The impact of the pasting process is presented in Table 3. An extensive number of trials has shown that this new additive is compatible with all known pasting technologies.

When plates containing the additive are being made, it has been observed that more plates are produced with minimal impact on cube weight. These additional plates (from 3 to as much as 10%) are a result of the presence of the additive, which is four times less dense than lead, as well as the additional water that is used to prepare the modified batch. The yield of additional plates will depend on the pasting criteria employed by a given manufacturer.

Another process improvement associated with the additive is lowering of flash-drying oven temperatures by 10% or more without risk of the freshly pasted plates sticking together. Since the modified paste contains more water and the pasting oven temperature is decreased, the result is a plate with 8–14% additional moisture content.

3.3. Impact on curing process

In the manufacture of lead-acid batteries, there are two key processes that cause changes to the chemical composition of the active materials, namely, curing (sometimes referred to as hydrosetting) and formation. Curing is the process that is vital to making plates of good quality that will ensure reliable battery performance [8]. The key change in curing is the oxidation of the metallic lead core of the particles of lead oxide in the paste. During paste mixing, sulfuric acid is added to the oxide particles that have been wetted with water. The sulfuric acid and lead oxide react to produce lead sulfate. This process also involves crystallographic changes

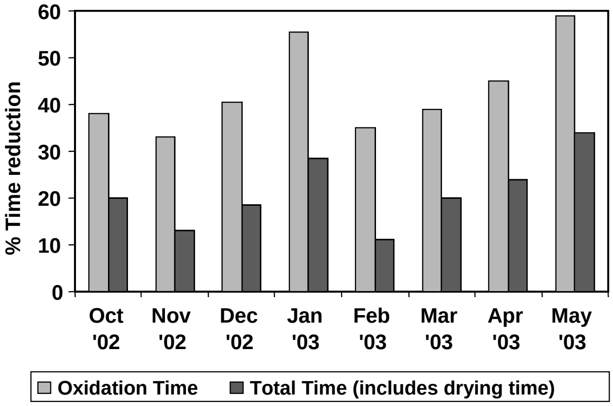

Fig. 3. Monthly curing improvement in a battery plant that uses the additive.

to the active materials. In the entire curing process water plays a critical role.

Water is the catalyst for the oxidation of residual lead. Once oxidation is accomplished, the water should be driven off as rapidly as possible. As discussed above, the new active-material additive allows for additional water during paste preparation. This, together with better water retention, results in modified plates that have a greater tendency to oxidize faster and more homogeneously. The presence of glass in the paste enhances gas transport and therefore aids in the removal of the water after oxidation.

An example from an application [3] that uses the active-material additive in the negative paste is shown in Fig. 3. The additive causes a consistent drop in both the oxidation time and the total drying time. Another application with the additive shows a decrease in both the oxidation and drying times of about 15% [4]. These latter trials have also resulted in a reduction in the micro-cracks in the pasted plates. Such cracks can have a detrimental impact in assembly lines in which vacuum-lift techniques are used, and can also degrade battery capacity.

Table 4
Test results of Technology C plate dusting

Plate type	Weight removed (g)	Difference (%)
1.4 mm standard positive	0.03	33
1.4 mm 0.5% modified positive	0.02	
2.5 mm standard positive	0.48	77
2.5 mm 0.5% modified positive	0.11	
5.0 mm standard positive	0.10	70
5.0 mm 1.0% modified positive	0.03	
6.4 mm standard positive	0.18	67
6.4 mm 0.5% modified positive	0.06	

3.4. Reduction in plate surface dusting of lead particulates

Reducing lead-in-air levels in the battery manufacturing plant is a constant challenge. Employers must provide a high-quality work environment and meet strict government standards. A major contributor to lead-in-air levels is the surface dust of cured pasted plates. The fundamental principle of workplace safety is to eliminate sources of danger and/or contamination at their source. An effective way to abate lead-in-air contamination is to reduce the amount of particulate that plates can shed. The tape test was used to measure the relative amounts of loose particulates and is

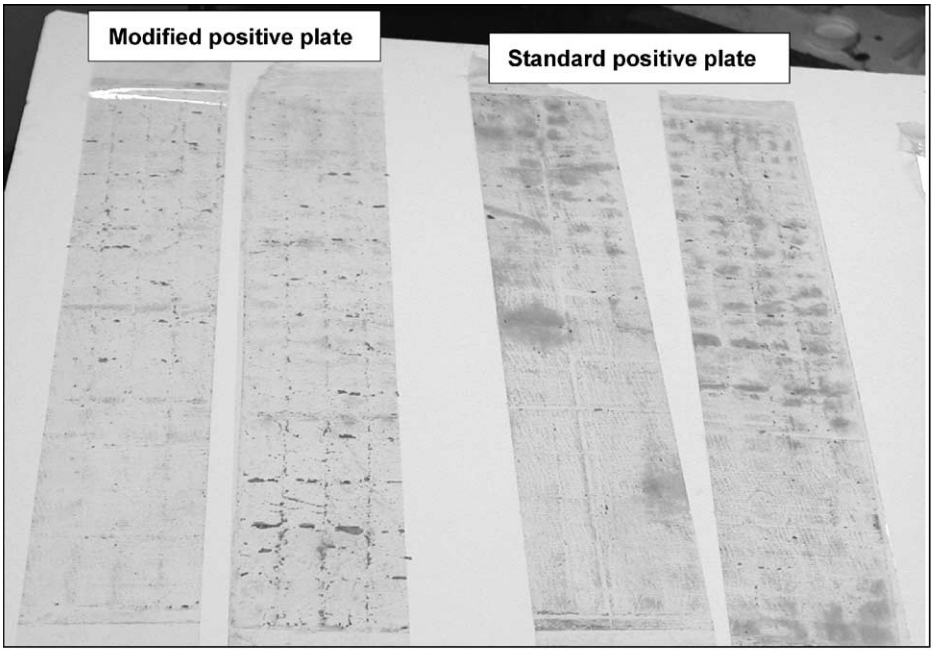

Fig. 4. Example of tape test for plate dusting.

Table 5
Results of plate vibration test

Technology level	Plate type	Average weight loss (%)	Plate thickness range (mm)	Difference (%)
A	Positive standard	0.88	1.20–1.30	34
	Positive modified	0.58		
B	Positive standard	0.79	1.40–2.29	6
	Positive modified	0.84		
C	Positive standard	0.23	2.29–6.35	43
	Positive modified	0.13		
A	Negative standard	0.09	1.02–1.14	44
	Negative modified	0.05		
B	Negative standard	0.40	1.14	0
	Negative modified	0.40		
C	Negative standard	0.23	1.52–2.03	13
	Negative modified	0.20		

illustrated in Fig. 4. The test was conducted on Technology C plates and the results (Table 4) show that the dust than can be liberated in routine plate-handling is greatly reduced by the presence of the active-material additive.

The mechanical integrity of the grid–active-material bond, as well as the cohesion of the active material itself, was evaluated by plate vibration testing. The results have verified the mechanical integrity of the modified plates. In general, the strength of these plates is comparable with standard formula plates, as shown in Table 5.

The active-material additive also appears to be a suitable replacement for the organic fiber flock when a pasting paper is used (Technologies A and B). This has been observed at addition levels as low as 0.5 wt.% [1,2]. For very thin positive plates without pasting paper, a flock still appears to be necessary at additive levels of less than 0.8 wt.%. For thicker positive plates (~2 mm or more) and all negative plates, the additive appears to provide adequate support at concentrations greater than 0.5% of oxide weight, which eliminates the need for the organic flock. Comparisons of modified plate strength to standard formula plates for positive and negative cured plates are shown in Figs. 5 and 6.

3.5. Improvements in battery assembly

The overall increase in the mechanical strength of cured modified plates is beneficial for battery assembly. One battery manufacturer who has used the new additive has reported a six-fold reduction in assembly line plate rejects through greatly reduced pellet cracking [4]. A factor that always leads to such scrap is loosely held pasting paper in Technology A and B batteries. Vacuum pick-ups will drop plates and create scrap when the pasting paper does not adhered well to the plate. The pasting paper on modified plates is more difficult to remove. This suggests that the higher moisture content in the modified pastes allows

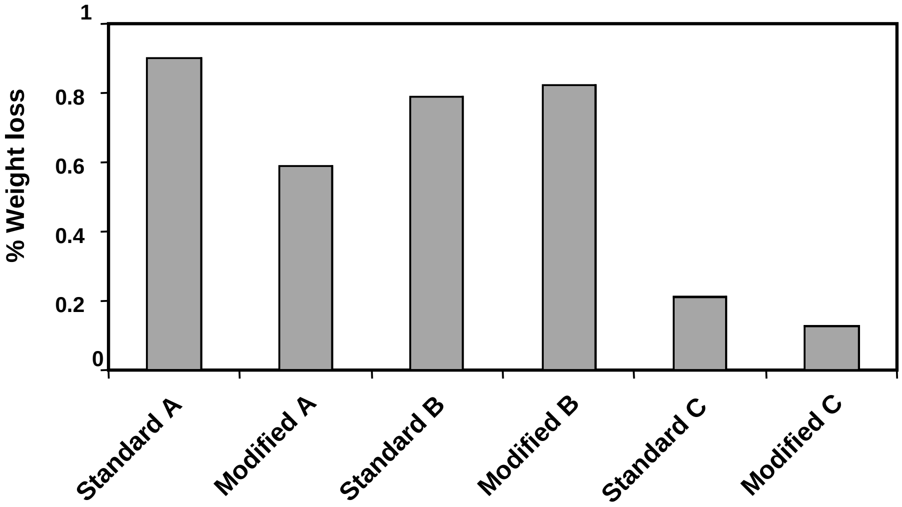

Fig. 5. Positive-plate vibration test results (A, B, C refer to plate technologies).

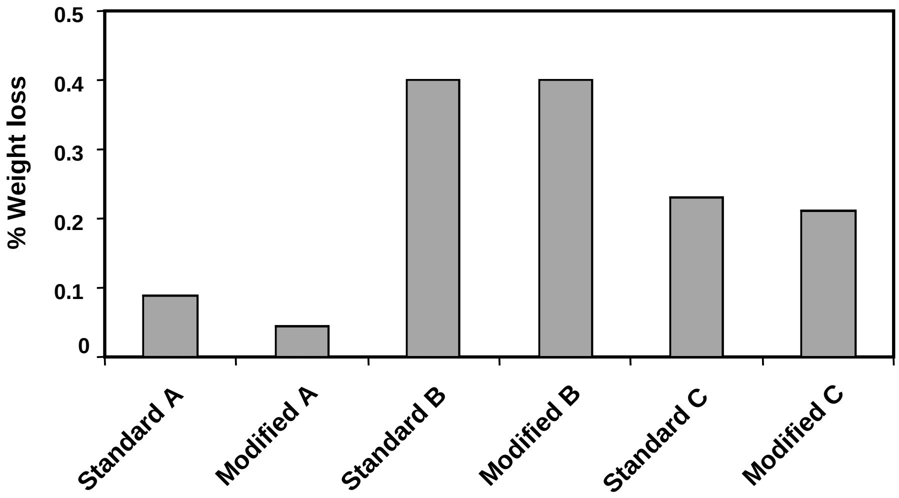

Fig. 6. Negative-plate vibration test results (A, B, C refer to technologies).

for better adhesion of the pasting paper. All these incremental improvements reduce overall plate scrap in the battery-assembly area.

3.6. Structural changes

Given the wide range of applications and the different plate-manufacturing technologies, it is reasonable to expect differences in the impact of an active-material additive. There are, however, some general observations that can be made. These are based on data gathered over dozens of plant trials in which the new additive has been evaluated. Results for cured modified plates (both polarities) that have been made according to the three major technologies used to prepare pasted plates are shown in Figs. 7 and 8.

The physical plate measurements presented in Fig. 8 clearly indicate that there is an increase in specific surface-area of positive cured plates which contain the additive. The average increase is around 30%, although there are cases where changes in the active material show a much greater increase in coarse particle structures. The impact of the additive on the cured negative plates is less clear. It was expected that fiber-modified negative plates would show a similar increase in specific surface-area, but this observation is confounded by the varying components and formulae of the expanders used by the various manufacturers.

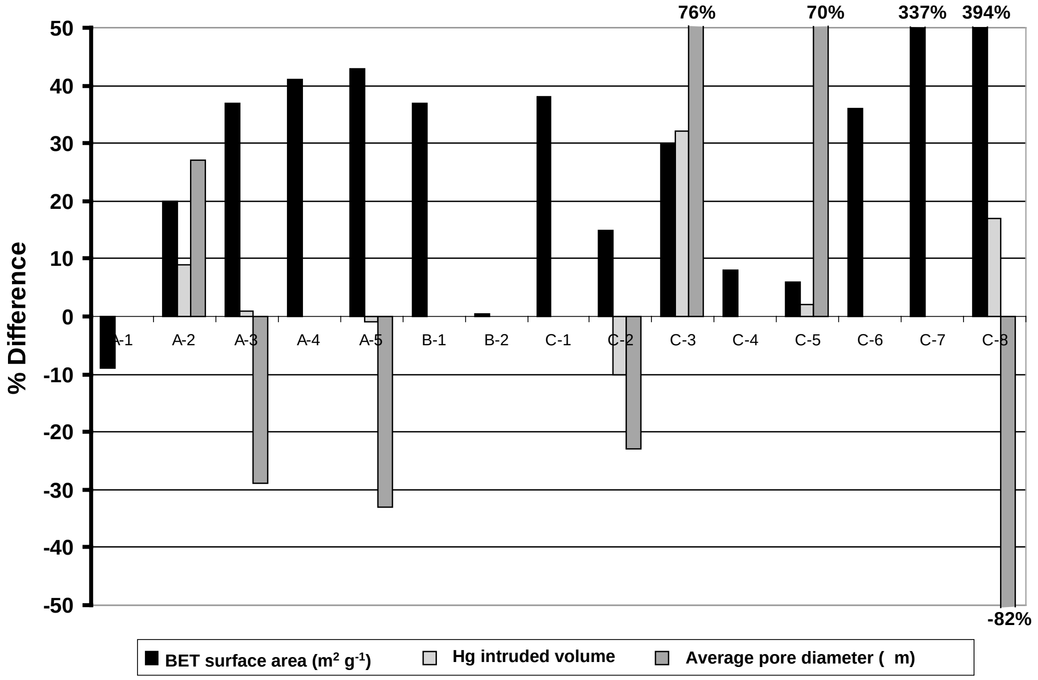

Fig. 7. Structural changes induced by active material to modified positive cured plates (A, B, C refer to plate-manufacturing technologies).

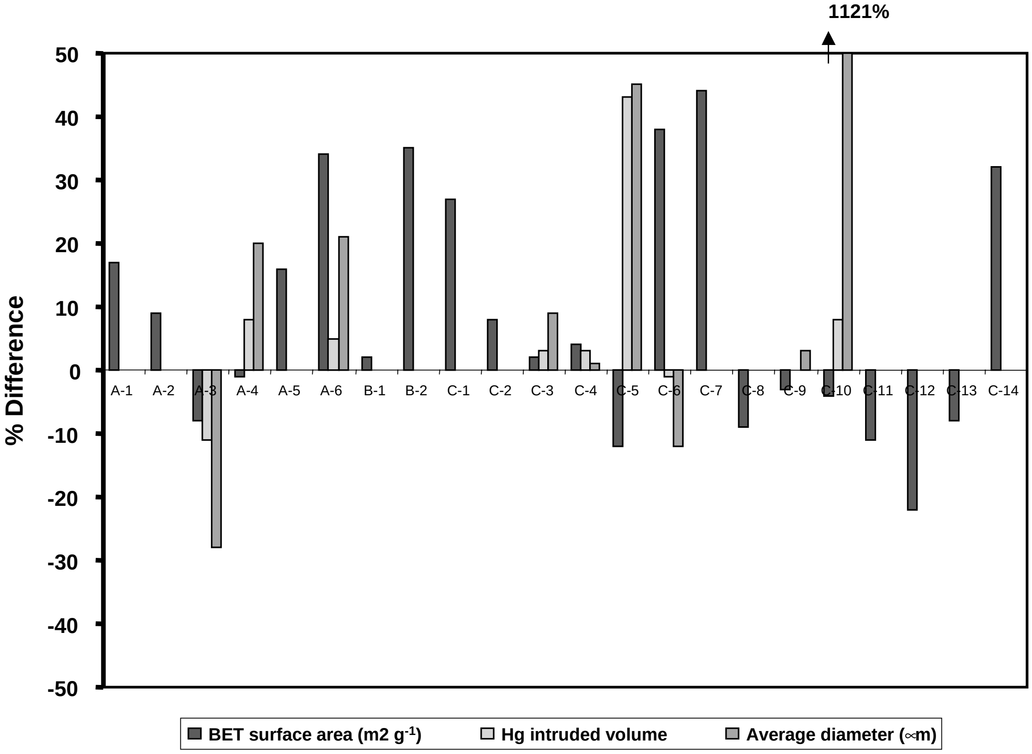

Fig. 8. Structural changes (% increase vs. control plate) induced by active material to modified negative cured plates (A, B, C refer to plate-manufacturing technologies).

The intruded volume measured by mercury intrusion porosimetry represents the void volume within the plate structure that is available for electrolyte. Increasing the void volume increases the electrolyte supply and, therefore, utilization of the active material. In general, the presence of the additive increases the intruded volume. Pore diameter, as measured by mercury intrusion, suggests a shift to larger pores in cured modified negative plates, but a shift to smaller pores in cured positive plates.

The structural changes induced to active materials that have been modified by the additive indicate greater activity of the active materials, which can improve battery performance [9–11].

4. Conclusions

A new, inorganic, active-material additive has been found to benefit key plate-preparation steps. Starting with paste mixing, the additive when added at 0.5–1.5% of oxide weight allows the preparation of modified pastes with higher moisture content. These pastes are easy to apply, provide for enhanced grid filling and surface finish, and decrease plate scrap. Another process advantage has been the consistent increase in the quantity of pasted plates.

The additive has minimal impact on paste density, yet allows sufficient bulking to generate an additional 3–10% plates per batch. Modified wet plates show an increase in excess of 10% moisture content. Given the highly hydrophilic nature of this additive, the plate surfaces have a lower tendency to stick. This allows lower temperatures to be used in pasting ovens, which lowers costs and conserves energy.

Beyond mixing and pasting, the impact of the new additive is seen in the critical transformation process of curing. The first step of curing is the oxidation of residual metallic lead. The oxidation is catalyzed by water and the process is accelerated in the additive-modified plates. The second step of curing is plate drying. This step is accelerated through improved gas transport. Commercial production data show that the time for the total curing operation is reduced by over 15%. More complete curing results in stronger plates, with lower surface cracking and reduced pellet loss. Again, this is a cost and energy saving advantage, as well as a tool to increase plate throughput and relieve potential bottlenecks.

Surface dusting is also reduced. Plate testing shows that surface dusting is abated by up to 70%. Less dusting means a cleaner work environment, as well as helping the battery manufacturer meet ever-stricter government environmental regulations.

Finally, the structural changes that account for all the process benefits that the new active material brings have been examined across a wide spectrum of battery applications and manufacturers. The data presented supports the concept that the new additive increases the specific surface-area of the active materials, thus rendering them more reactive with potentially higher utilization.

The additive is easily integrated into any pasting technology. It is a cost-effective method for improving key process steps in the manufacture of lead-acid batteries. The new patented additive is an additional weapon in the battery manufacturers' arsenal to combat lead-in-air issues.

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