



Technique to improve performance of flooded and VRLA batteries

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Abstract

A technique is presented here to enhance key characteristics of flooded and VRLA batteries. This technique relies on the use of an inorganic additive that is added to the active materials of either or both of the electrodes. The addition is done while the active materials are being prepared.

The inorganic additive is described as a modified glass microfiber with a borosilicate chemical composition that renders it highly resistant to attack in the highly oxidative environment of the lead acid battery. The impact of this inorganic additive on the process of manufacturing the battery plates is also described. The very hydrophilic nature of the new additive enables a higher degree of moisture control management in the paste mixing and plate processing steps.

The impact of the presence of the modified glass microfibers on the structure of both unformed and formed active materials is analyzed and reviewed for different types of plate designs and applications.

This patent pending technique of adding modified glass microfibers to the active materials of lead acid batteries has a significant impact on the high rate performance, particularly cold cranking discharges of automotive batteries. High rate discharge enhancement through the use of special glass microfibers is also reported for UPS monoblocs (VRLA-AGM technology). The dramatic improvement in high rate performance leads one to attribute the action of this inorganic additive as one of *ion flow enhancement*.

Charge acceptance is another key battery performance that is markedly improved with this technique. Direct evidence is provided for both flooded and VRLA batteries. As a consequence of improved charge acceptance, one sees an improvement in deep cycle performance of VRLA monoblocs designed for the UPS and cycling applications. Modifying active materials by the inclusion of this inorganic additive is also seen to have an impact on float currents. Here, telecom monoblocs were built with modified plates and the impact on float current is analyzed and discussed.

Overall, this paper presents the description and an explanation for the activity of this modified glass microfiber additive. The impact of this new additive is amply illustrated by data gathered from lead acid batteries from a variety of designs and applications.

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1. Introduction

The evolution of the lead acid battery technology has been driven by the introduction of new materials and new manufacturing processes and machinery.

The awareness that purity played such a key role in the performance of the battery directed the early battery technicians to specify ever purer raw materials. This trend has culminated in the ultra pure requirements for the manufacture of today's highly performing stationary batteries [1].

In tandem with the trend for increasing raw material purity, there were large scale efforts to make more efficient electrodes, elements and all other battery components. The move towards improved battery components was paralleled with ever improving manufacturing technologies.

Another major strategy used by battery technologists to obtain better battery performance and also to improve the process of making these devices, has been to use appropriate additives, particularly active material additives.

The role of these additives has been reviewed and it is generally accepted that modern batteries could not function effectively without the extensive use of additives [2].

In this paper, we shall introduce a new material additive and briefly review its impact on the battery making process, as well as on the electrical performance.

This new inorganic additive has a noticeable impact on key processes of battery making, namely the mixing of the pastes that make up the electrode and also the process of making the battery electrode (battery plates) themselves. The impact on these process steps is largely due to the very hydrophilic nature of the inorganic additive.

The surface chemical composition of the inorganic active material additive as well as its geometry and how it interacts

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with the surrounding active material structures help us to understand its impact on battery performance. This impact is mostly seen on the better charge acceptance and high rate discharge characteristics of the battery.

The impact is universal and it cuts across manufacturing technologies and battery designs. The use of this new inorganic additive holds much promise for the next round of battery development.

2. New active material additive

In this section, the new additive is described. Along with this description, questions concerning its availability and impact on the battery making process are also addressed.

2.1. Description and usage

The inorganic active material additive that we are describing is a modified glass microfiber that was designed and manufactured exclusively with the lead acid battery application in mind.

The major characteristics of this new active material are summarized in Table 1.

It is available in industrial quantities and is shipped to its final destination in pre-weighed plastic bags. It can be added directly to a paste mixer in much the same manner that expanders are added in most lead acid battery manufacturing plants. Normal precautions needed when one handles fine particulate are recommended, i.e. light facial mask, gloves and appropriate garments.

As one can glean from the above description, this active material additive is totally compatible with the electrochemistry of the lead acid battery. Chemical grade borosilicate glass is extensively used in the lead acid battery in the form of very absorbent separators that act both as separators and acid reservoirs in one important segment of the valve regulated type of lead acid batteries [3].

2.2. Impact on process

Preparing a paste batch with the inclusion of this new additive offers interesting possibilities and challenges to the battery technologist.

As seen in Table 1, the surface of this additive is borosilicate glass, it is well known that water has a zero contact

angle with glass surfaces, this means that there is a very high affinity between the additive surface and water.

Battery paste preparation proceeds by two possible routes:

- *Dry mixing*: Where the oxide and additives (dry ingredients) are blended dry prior to being wetted by water and sulfuric acid, and
- *Wet mixing*: Where water floods the mixer before the addition of the dry ingredients. The acid is added to the wet oxide mass.

The rheology of paste mixing is a rather complex and studied area of battery technology [4]. 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 large contribution to paste density is the addition of sulfuric acid. Sulfuric acid reacts with the oxide to create lead sulfate. Thus sulfuric acid impacts paste density by bulking it.

When the paste mix includes the new additive, there will be competition for the water being added. The presence of the modified glass microfiber impacts the total amount of interstitial water. This means that the battery paste can be made with a greater amount of water in it and yet retain the required paste density (cube weight). Once this modified paste is used to paste battery plates, one gets pasted plates with a slightly higher amount of water in them and with an additive that is more hydrophilic than the particles of oxide.

The physical model for the interaction of oxide particles and modified glass microfibers can be visualized as a blending of spheres and rods. The free volume of packing of spheres is dramatically modified by the presence of rods [5].

When plates containing the modified glass microfiber additive are being made, it has been observed that more plates are produced. These additional plates are a result of the presence of the additive that is four times less dense than lead and also of the additional water that was used to prepare the modified batch.

3. Experimental: impact on battery performance

The impact brought about by adding very tiny inorganic microfibers to the active materials of different types of lead acid batteries is demonstrated in this section. Both flooded and VRLA designs are included in this evaluation. An attempt has also been made to get a cross-section of applications, starting off with the very important SLI or automotive application, deep cycling and floating type of stationary batteries are included in this study.

3.1. SLI flooded and VRLA batteries

Since over 60% of all lead acid batteries are destined for the SLI or automotive application, it is natural that this application should come under scrutiny in the present

Table 1
Description of new inorganic active material additive

Chemical composition	Borosilicate chemical grade glass
Surface area (m ² /g)	>0.3
Density (g/cm ³)	2.4–2.6
Average diameter range (μm)	0.25–10
Length to diameter ratio	>5:1
Addition level	1–3% of oxide weight

evaluation study. Thus both flooded and VRLA battery designs were selected to participate in the study.

The flooded battery type used was a Gr. 31 having a cold cranking rating of 750 A and a reserve capacity of 180 min. The batteries tested in this study were made by a well-known manufacturer in the USA and are good representatives of the present technology being used to produce flooded automotive batteries.

The automotive VRLA battery selected for this evaluation was the high performance spiral wound design manufactured in Europe. This battery has been modified to take on deep cycle functions. It was this latter variation that was used here. The spiral wound battery has a cold cranking rate of 750 A and a reserve capacity of 95 min.

3.1.1. Enhanced charge acceptance

The impact on the charge acceptance of SLI batteries (flooded and VRLA) of the new inorganic active material additive was investigated. The results are presented below in Table 2.

Charge acceptance was tested under two regimes, the one specified in the SAEJ537 and the EN50432 European

Standard. Improvements are significantly higher with the VRLA battery testing.

The improvement in charge acceptance is a key performance enhancement, particularly when this enhancement is measured to be well in excess of 25%. This means that the battery can be brought back from a discharged state significantly faster.

3.1.2. Improved cold cranking

Cold cranking is the most significant performance criteria for SLI batteries; this is a particularly critical requirement in temperate climates. The impact on cold cranking of adding the new additive to active materials is very significant and is reproducible in both flooded and VRLA battery types. It is an enhancement that is tied to the design of the battery, this means that the addition of the new additive will have a greater impact over the performance of the limiting electrode.

Cold cranking test results are tabulated in Tables 3 and 4 for flooded Gr. 31 batteries. It is clear from these results that this type of battery greatly benefited from a modification of the negative plates. The improvement in discharge time to 7.2 V is quite significant (over 50%) when the battery is

Table 2
Charge acceptance results of SLI batteries (flooded and VRLA)

Group	SLI Gr. 31 flooded SAEJ537 (spec. 22.5 A) (A)	Deep cycle SLI Gr. 34 VRLA-spiral wound	
		SAEJ537 (spec. 24 A) (A)	EN50432 (spec. 9.6 A) (A)
Std +/Std –	39.2	36.8	8.8
Std +/HV –	44.8 (+14) ^a	43.4 (+18) ^a	11.2 (+27) ^a
Std +/SG – graphite	N/A	44.4 (+21) ^a	10.7 (+22) ^a
HV +/Std –	N/A	50 (+36) ^a	12.3 (+40) ^a

Values in parentheses are percent values.

^a Percentage difference from control (Std +/Std –).

Table 3
Cold cranking results of flooded Gr. 31 batteries

Group	750 A discharge		850 A discharge	
	Volt 30 s (V)	Time to 7.2 V (s)	Volt 30 s (V)	Time to 7.2 V (s)
Std +/Std –	8.10 (112)	46 (153)	7.16 (99)	33 (110)
Std +/HV –	8.37 (114)	66 (220)	7.78 (108)	48 (160)
HV +/HV –	8.10 (113)	52 (173)	7.41 (103)	39 (130)

Average of six batteries per group (values in parentheses are percent values).

Table 4
Cold cranking results of VRLA spiral wound deep cycle Gr. 34 batteries

Group	SAEJ537 cold cranking @ 800 A (10 s V = 7.5 s)		EN50342 cold cranking @ 800/480 A C = 9.6 A	
	Volt 10 s (V)	Time to 7.2 V (s)	Volt 10 s (V)	C 6.0 V (Ah)
Std +/Std –	7.93 (105)	23 (77)	7.65 (102)	8.5 (89)
Std +/G – (G = graphite)	7.98 (106)	24 (80)	7.78 (104)	7.0 (73)
HV +/Std +	8.12 (108)	31 (103)	8.15 (113)	10.6 (110)
Std +/HV –	8.01 (107)	27 (90)	8.00 (106)	9.2 (96)
HV +/HV –	8.18 (109)	31 (103)	7.94 (106)	9.7 (101)

Average results of two batteries per group (values in parentheses are percent values).

Table 5
Initial performance values for Gr. U1 (35 A) 12 V monobloc used in UPS applications

Group	1 min 171.4 A (2.9 A) (Ah)	5 min 102.3 A (8.5 A) (Ah)	2 h 11.7 A (23.7 A) (Ah)	5 h 5.5 A (27.5 A) (Ah)	20 h 1.8 A (35 A) (Ah)
HV +/HV –	6.2	12.7	28.2	31.7	35.1
Std +/HV –	6.5	13.4	28.7	32.4	35.5
HV +/Std –	5.7	12.4	27.5	31.3	34.7
Std +/Std –	5.3	11.3	26.4	31.1	35.1

Average results of two batteries of each group.

cranked at its nominal value, and is remains equally significant when the battery is cranked at the higher current of 850 A. Basically, when the negative plates of this type of battery are modified, the battery easily exceeds the higher cranking requirements.

The cranking results of the deep cycle version of the spiral wound Gr. 34 battery show that the modified positive plates gained the most from the addition of the new inorganic additive. Here, the gains are in the range of 20% for the discharge time to 7.2 V and higher (over 30%) when one examines the cold cranking capacity requirement of the EN50342 specification.

It is interesting to note that the addition of fine graphite particulate to the negative electrodes of this type of battery do not impart any additional cold cranking performance.

These results will be explained in Section 3 in terms of the structural changes to the active materials induced by the addition of the new inorganic additive.

3.2. Stationary VRLA (AGM) batteries

Another important step in evaluating the impact of the new additive on the performance of lead acid batteries. Given the vast array of such type of battery, two representative applications were selected, the uninterrupted power supply (UPS) and the telecom batteries. Both of these applications call for VRLA batteries using the absorbent glass mat (AGM) technology of electrolyte immobilization.

In the present evaluation, three characteristics are examined, first the initial performance and deep cycling of the UPS batteries and the floating characteristics of a type of telecom monobloc.

3.2.1. Initial performance and deep cycling of UPS monoblocs

The results reported in this section were obtained with Gr. U1 (35 A) 12 V monoblocs. There was also extensive work, not reported here done with Gr. 24 (65 A) 12 V monoblocs. The overall trends in both sets of results are very similar. The initial performance profile of modified U1 batteries is shown in Tables 5 and 6. It is clear that the impact of adding the new additive is limited to the higher discharge rates, where the performance enhancement is significant.

The deep cycling of these 12 V monoblocs was done according to a special regime that stresses them and hence

Table 6
BET test results of plates removed from SLI–VRLA Gr. 34 batteries

	Plates				
	Std +	HV +	Std –	HV –	SG –
Unformed (m ² /g)	1.66	2.34	2.23	2.58	2.22
Difference (%)	+40	+40	+15	+15, –4	–4
Formed (m ² /g)	5.30	5.58	0.83	1.29	N/A
Difference (%)	+5	+5	+55	+55, N/A	N/A

accelerates their potential failure modes. This regime consisted of the following steps:

- *Step 1:* Discharge to 10.5 V at the 5 h rate.
- *Step 2:* First constant current recharge at the C5 rate for 5 h or to 15 V limit.
- *Step 3:* Second constant current recharge at 10% of C20 for 15 h.
- *Step 4:* Floating at 2.27 V per cell for 12 h.

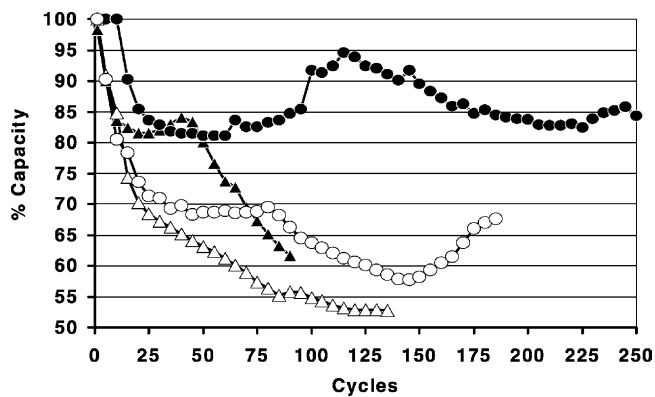
The results of the cycling can be seen in Fig. 1A–C. The picture that emerges from these graphs is that when the negative plates modified by modified glass microfiber additive are used in conjunction with standard positive plates, cycling is greatly enhanced. When the recharge data is examined, one sees that the recharging of the batteries with modified negatives is faster and more efficient than the batteries with standard negatives. At the present additive loading, the new additive in the positives seems to have an adverse impact on the cycling of the positive plates in this type of battery. However, additional cycle performance testing will be done at a lower loading.

3.2.2. Floating of telecom monoblocs

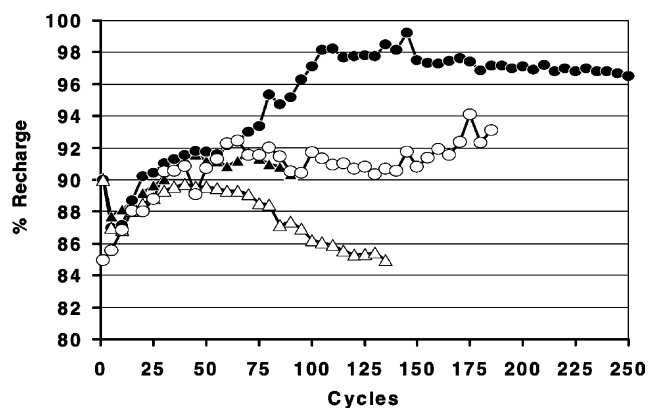
While the cycling behavior of the 35 A 12 V monobloc confirms that the impact of the new additive on the negative active material enhances its recharge ability, the impact on floating 100 A 12 V monoblocs may fill in an additional piece of information.

Fig. 2 shows the float current profile for the first month of floating at room temperature (27 °C) of eight telecom batteries, divided into four groups.

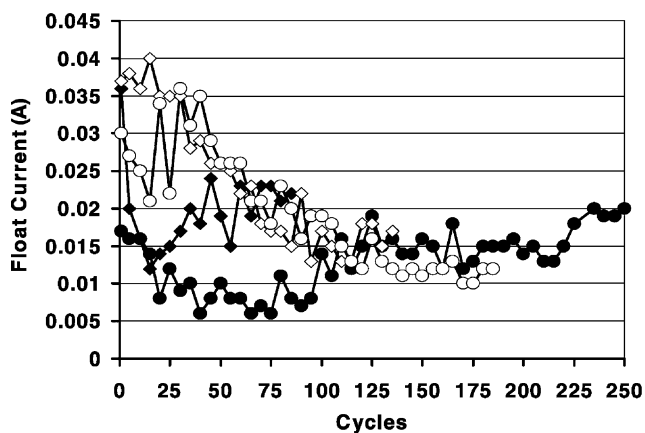
These telecom monoblocs were specifically designed to achieve very low float currents. The plate design and the special absorbent separator composition used in these



(A)



(B)



(C)

Fig. 1. (A) Capacity profile of U1 (35 Ah) VRLA-AGM 12 V monoblocs. (B) First constant current recharge at 5 h rate to 100% Ah capacity return. (C) Cycling of Gr. U1 (35 A) VRLA-AGM 12 V monoblocs. Profile during 12 h floating step at 2.27 V per cell.

batteries assures a float current in the range of 0.015–0.020 A when floating at 2.27 V per cell at room temperature. This low float current consumption is typical of ultra pure advanced designs [1].

These very low float currents are seen on the monoblocs that were assembled with standard negative plates. How-

ever the float currents of test batteries with modified negative plates are radically different. Here the float current is noticeably higher, the modified negative batteries float in the range of 0.050–0.060 A. This is not an unreasonable float current consumption [6]. However, it does point out that the modification of the negative electrodes has upset the design floating equilibrium of these telecom batteries.

The higher current consumption is inferring a more active internal oxygen cycle, hence a higher oxygen generating current. This means that there is a possibility that these batteries will recharge faster when the negative plates are modified by the new additive. This faster recharge would be due to reduced negative plate potential under a constant voltage limited recharge regime.

From Tafel studies it is clear that it takes more current to bring the negative electrode to the gassing point. Higher float current is not necessarily a higher corrosion rate, especially in this type of efficient stationary battery that has a very large grid surface area. This stationary battery has a large grid surface area that is three of six times larger than conventional designs [7].

As a follow up to this study, similar batteries have been assembled with standard and modified plates and also with different absorbent separators with different compositions. This future study, will investigate the role of separator composition and saturation on the impact of modifying the negative plates by the addition of the special inorganic microfiber.

4. Discussion: active materials structural changes

The performance characteristics reported in the previous section, are due to the structural changes induced to the active materials of the batteries under investigation by the addition of the new additive.

The investigation tools that are used to look into these structural changes are very widely employed in this field and even though additional analytical methods were employed, for the sake of brevity only the most pertinent results are reported here. Also given the scope of this work, only selected active materials were tested to explain a specific effect.

In this manner, BET (specific surface area) analysis of formed and unformed plates is reported here, the results of this analysis help to explain the great high rate results obtained with SLI batteries.

The increased activity of the negative plates is also easier to understand when one examines the results of the X-ray diffraction (XRD) analysis of cycled negative plates.

4.1. BET measurements

The specific surface area of active materials is greatly impacted by the raw materials employed as well as by the

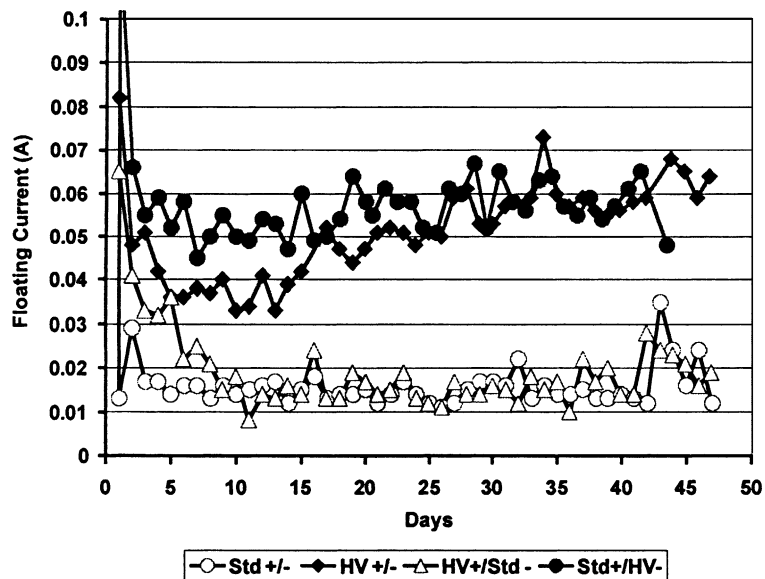


Fig. 2. Floating profile of telecom 100 A 12 V monobloc.

methods of manufacturing of the electrodes [4]. Thus, BET testing measuring the specific surface area of active materials, accurately predicts many of the key characteristics of the battery. High rate discharges in particular are highly dependent on high specific surface area values.

Table 5 shows the values of BET measurements done on unformed and formed plates removed from Gr. 34 spiral wound SLI–VRLA batteries. From that table one can deduce that the impact of the addition of the new additive to the formed negative active material is quite considerable (55% gain in specific surface area). The gain in the formed positive is less significant (only 5%). However it should be mentioned that the gain in the BET values of the unformed positive is much greater than the positive (about 40%). This result may be a consequence of the particular requirements of the deep cycle version of this advanced SLI battery design

and the radical differences in pore structure of the positive and negative plates.

4.2. X-ray diffraction analysis

This analytical technique gives us a glimpse into the chemical composition and the crystallography of electrode surfaces. With this in mind, following a reserve capacity discharge, one battery from each of the four test groups of Gr. 31 flooded SLI batteries was torn down. The plates from the 3rd cell were removed and the negative plates were washed free of acid and air-dried. The plates were then analyzed for their XRD spectra.

In Fig. 3 one sees the spectrum of standard negative plates superimposed on the corresponding XRD spectrum of modified negative plates. The picture that emerges is that the lead

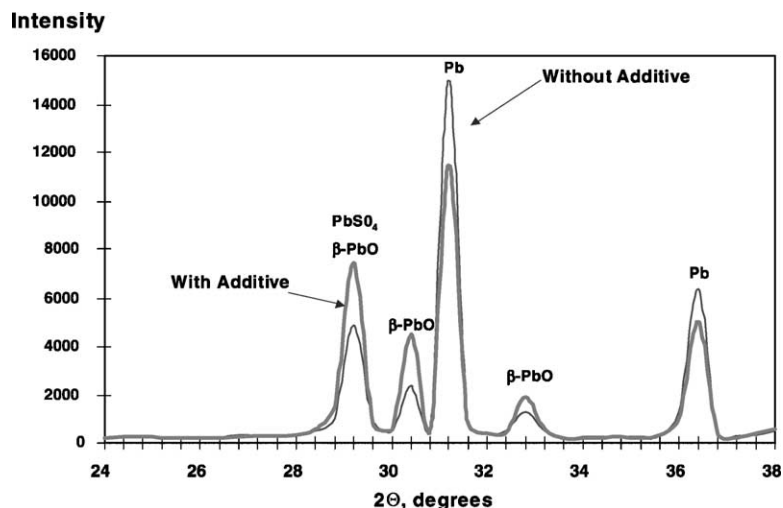


Fig. 3. XRD spectra of partly discharged negative plates removed from cycled Gr. 31 flooded SLI batteries.

oxide peaks are more intense on the modified plates and there is a decrease of the pure lead lines in these modified plate spectra. This is an indication that these plates oxidized more readily than the standard plates when exposed to the oxygen in the atmosphere.

Because these modified plates contain hydrophilic modified glass microfiber in their structure and since water catalyses the oxidation of lead, this finding is not unexpected. It also predicts that modified negative plates would be capable of having more sites for a more vigorous internal oxygen cycle in VRLA batteries.

The results of plate analysis, using the techniques outlined here, point out that the active material structure is greatly impacted by the inclusion of the new additive. The active material becomes more reactive due to the micro openings that are created. Of particular note is the large increase in the specific surface area of formed negative plates. Since all electrochemical reactions rely on fast ion transport, and given the observation that the new inorganic microfiber additive impacts the active material structure to facilitate electrolyte penetration, this new additive can be known as *ion flow enhancing additive*.

5. Conclusions

- New active material additive is a *modified glass micro-fiber*.
- Allows for better moisture control management of paste mixing and pasting.
- Significant improvement in charge acceptance and cold cranking performance of SLI flooded and VRLA batteries.
- Early studies indicate improvement to life cycling and floating characteristics of stationary VRLA batteries.
- Performance enhancement due to active material structural changes: higher active materials specific surface area.
- XRD and other analysis show more reactive structures with micro gaps where electrolyte can quickly more active material, hence new additive acts as *ion flow enhancing additive*.

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