

New MOLECULAR REBAR[®] Solutions To Address Corrosion/Adhesion-Based Failure

Enhancing the Corrosion Layer by Modifying the Active Mass Structure

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Who We Are

Black Diamond Structures[™] is a global nanotechnology leader with the mission to help manufacturers create the next generation of world-class batteries.

Our unique products, based on proprietary **MOLECULAR REBAR**[®] technology, together with our team of world-class nanomaterial experts alter your battery's "DNA", unlocking its full potential... fast.

Our teams work directly with our customers to find solutions that enhance your battery's mechanical and electrochemical properties to meet market challenges for decades to come.





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Our Joint-Venture Partners



MOLECULAR REBAR®: The Nano-Connector

• Molecular Rebar products provide nanoscale reinforcements which:

- Act to bring the active material together, reinforcing plate structure \rightarrow Enhanced robustness
- Alter crystal packing to enhance surface area and modify pore structure -> Improved electrical performance
- Restrict the growth of large, insulating lead sulfate crystals → Consistency of performance



Molecular Rebar Products Change the "DNA" of Your Battery



Molecular Rebar: Successful Against Corrosion

CONTROL

Failure Mode = NAM sulfation, Positive Plate Corrosion



Pb2300N + Pb2300P Life Cycle Improvement = +150%



• Previous Molecular Rebar PAM products:

- Commercially adopted mostly in Deep Cycle and AGM/VRLA applications
- Some anti-corrosion properties are seen in Automotive and Flooded

BDS required better understanding to develop a targeted product:

- Tailored our DNA-changing technology to focus on corrosion mitigation
- Explored our own mechanism of action, using it to drive product development
- Performed joint-development work on formation and curing impacts
- Targeted cost-to-value of any new solution

INTRODUCING PbAC SERIES OF PRODUCTS!



Corrosion: A Necessary Evil



Fig. 210. Disintegrated Positives



Fig. 206. Weak and Cracked Positives

• Corrosion is unavoidable and fundamentally required for Lead-acid battery function

- Controlling it has always been a challenge
 ex. Ford "Model A" Manual from 1922
- Made more difficult by higher operational temperatures in the engine compartment
- Increasingly difficult test standards intensify corrosion failure



5 A Witte. The Automobile Storage Battery; Its Care and Repair. 1922

Mechanism of Corrosion



Acid Alloy Components

6

- Acid attacking the grid
- Corrosion Layer (CL) is built during curing/forming and is the 1st line of defense against further damage
- Defects and gradual wear of CL allow acid access to alloy
- Releases alloy components to PAM/NAM; weakens the grid and active mass
- Escaping metals aggravate gassing, ex. Sb poisoning

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- **Field Conditions that Exacerbate Corrosion:**
 - Temperature
 - Over-charge
 - Over-voltage

Advanced NAM Solutions Can Increase Corrosion

PAM Comparison Following 10 Weeks of KLT* (75 °C) After Key Life Test, Plates are Dropped Once from 1m and Photographed



High Carbon Sample 95% Active Material Lost Intensified Grid Breaks (O) Low Carbon Sample 80% Active Material Lost Few, Small Grid Breaks (O)

Industry has been Negative Plate-focused

- Charge Acceptance has been a dominant market driver for the last 10 years due to Start-Stop technology
- Industry research concentrated on NAM improvements since that electrode is typically charge limiting
- NAM advancements increase the occurrence of PAMrelated failures, primarily due to grid corrosion
 - Seen heavily in current technical specifications
 - eg. SAE J2801, SAE J240, JIS 5301D LLE, others
 - H₂O loss-induced acid concentration speeds corrosion
 - High-temperature operation intensifies corrosion
 - Decreased NAM polarization in charging overworks PAM

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^{*}IEC/EN proposed "Key Life Test" or KLT

Present Solutions to the Corrosion Challenge







Inside-Out approach (grid changes)

- Implementation of new grid manufacturing technology
- Increased Tin (Sn) in alloy
- Specialty alloys

Outside-In approach (paste changes)

- Increased [H₂O]_{plate} during cure sticky plates, increased cure time, optimization
- High temperature or steam curing
- Exotics compounds
- Solution must be balanced to avoid Premature Capacity Losses (PCL), often due to Poor Grid-to-Mass Adhesion
 - PCL 1 & 2 First identified in switch to Pb/Ca alloys
 - PCL (1) insulating material or poor adhesion between grid and active material

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• PCL (2) active material softening

Our Approach: Build An Improved Corrosion Barrier

- New PbAC Products are designed to modify the Corrosion Layer to improve plate robustness
- PbAC technology changes cured PAM "DNA"
 - Uniformly affects the active material
 - KEY TO ENABLEMENT
 - Discrete, uniformly distributed MR
- During formation, PbAC is a sacrificial agent
 - Initially, energy goes to PbO/PbSO₄ and MR oxidation
 - Tempers energy delivery to system
- A lasting effect on Corrosion Layer after formation
 - Thinner, denser, more uniform
 - Improved Grid-to-Mass Adhesion
 - Changes persists through life
 - Shield grid from acid to prolong life



FORMED/CYCLED



Acid

Alloy Components Molecular Rebar







Corrosion Layer becomes More Uniform

- Analysis shows a quantifiably thinner, more uniform corrosion layer with PbAC utilized in the positive plate
- Sampling technique selected to provide representative data
 - Chose 4 plate locations for "whole-plate" analysis (yellow circles)
 - Grid samples are carefully excised to prevent active material loss and bathed in epoxy mounting liquid
 - Epoxy sections are cut, polished, sputter-coated with platinum, and imaged (JOEL)



Enhanced Corrosion Layer Delays Corrosion-based Failure

• PbAC generates a superior corrosion layer to improve cycle life >25% (SAE J2185 post life image below)

- PbAC layer is thinner, denser, more uniform, and as a monolayer instead of a bilayer
- An effect of altered acid access, improved grid/mass adhesion, likely changed electrochemistry



Ca/Sn, Cast, Formed

Enhanced Corrosion Layer Delays Corrosion-based Failure

- PbAC enhancements are obvious even directly after Formation
- CON grid
 - Shows 2 distinct corrosion layers
 - Thick, less uniform than PbAC
 - Less dense, "fluffier"
 - EDS shows corrosion layer as slowly increasing O%, slowly dropping Pb%

PbAC grid

- Shows 1 corrosion layer
- Thin, more uniform than CON
- More dense, tighter, more robust
- EDS shows corrosion layer as quickly increasing O%, quickly dropping Pb%



Dramatic Improvements Seen in Full-scale Testing

SAE J240 Cycling (75 °C)

Sb, Cast

- Implementation of PbAC results in an enhanced Corrosion Layer
- This new corrosion layer protects grid from further degradation and improves battery life where corrosion is the main failure
- Effects confirmed with:
 - Grid Alloys
 - Ca/Sn, Ca, Sb
 - Grid Types
 - Cast, Expanded, Punched
 - ...and counting!!



JIS D5302 Cycling (45 °C)

100% improvement using PbAC to delay corrosion





SAE J2185 Cycling (50 °C)

PbAC delayed corrosion and acid decolorization



Maximize PbAC Benefits By Working Together

Let Us Be Your Nano Connection!!

• The Collaborative BDS Approach:

- Joint evaluation of needs and current challenges
- Joint review of negative and positive grid/plate design
- Joint analysis for formation procedures under use
- BDS recommends PbAC product loading and other implementation considerations
- BDS on-site to support trial
- Joint analysis of formation data and confirmation of corrosion layer modification
- Further validation in lab or field
- Application Development Engineers stand ready in all geographies to assist you!!
 - Leverages over 100 years of entrenched lead-acid battery experience
 - In constant communication with US-based R+D Team



Summary

• NEW PRODUCT RELEASE: PbAC Series for Corrosion Resistance

- Improves the corrosion layer to protect the grid and enhance life in corrosion-limited applications
- Easy adoption, no capital expense, application-development teams available to assist in implementation
- BDS uses a collaborative approach and our Application Development Teams stand ready to support you
- Cost reduction and/or performance improvements accessible with existing Molecular Rebar products:
 - Pb1100 Series Light and Heavy Duty SLI
 - Pb1200 Series Enhanced Flooded Batteries
 - Pb2x00 Series Deep Cycle (Flooded and VRLA)
 - ... and many more!!
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