Ni-Cd Battery Separator Improvement
Based upon Mr. Paul Scardaville’s research and Crane testing

DSCR and NAVAIR Sponsored program to develop a Ni-Cd battery separator system that will increase battery safety and life to highest levels
Ni-Cd Battery Separator Improvement

2009 Joint Service Power Expo
New Orleans, LA
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OUTLINE

• Background: Problems that prompted program

• Tests:
  – Gurley airflow (time to pass air volume)
  – Rewet-ability in KOH (soak15%, rewet 30%)
  – Temperature-Rise & Float Charge (TR&F)

• Comparisons: Results of TR&F
  – Wetting agents
  – Absorbers
  – Gas barriers
Background

• Production Battery Performance began to decrement
  – Celgard increased average porosity of gas barrier by tightening tolerance toward high porosity limit
  – Kimberly-Clark (KC) dropped melt-blown polypropylene (mbPP) absorbers.*
  – As manufacturers reached end of their KC supply, battery performance decrement accelerated.
    (Reason: “Wayfos A” no longer available)
Type M81757/16, KC mbPP Absorber

• Celgard gas barriers with Celgard standard wetting agent
  – One with 37 Gurley-second (G-s) porosity
  – One with Celgard 3400 (24 G-s)

• Both performed essentially same in TRF & Life Cycling.

• No difference in post life capacities
Sulfur Contamination

Sulfur in electrolyte was believed to cause a permanent decrement in capacity.

Source of the sulfur was determined to be from water-soluble dispersants that were used to apply the wetting agent to the mbPP absorber.
Surfactants Suspected

- Dissections exhibited separator dryout and poor rewet ability in production batteries made after the 1980’s
- Investigated why wetting agent appeared to leaving gas barrier
- Determined Celgard Inc was applying a wetting agent that was fugitive
Surfactant Comparisons

Performed a wetting agent rewet-ability using membrane with Celgard’s & 2 candidate W.A.s* from Mr. Paul Scardaville’s search

Test: Samples soaked in 15% KOH solution, air dried and returned to 30% solution for rewet.

Results of soak durations to 12 months

A) Celgard 3400: Lost rewet ability in 1 day
B) Surfonic L24-4 (alcohol/ether): Rewet
C) Deforest HP-739* (anionic ester): Rewet

*HP-739 is a clone of 1970-2000 Wayfos A & has same CAS #
Baseline Testing

Type M81757/16 batteries with Celgard 37 G-s porosity gas barrier

Separators:

#1: Manufacturer’s absorber & gas barrier with fugitive wetting agent (N3400G1-P)
#2: Grafted H&V MBPP and N3400G1-P
#3: Grafted H&V MBPP and nonsoluble wetting agent on gas barrier, DePHOS HP 739 (CAS # 12645-31-7)
Baseline Conclusions

• Porosity in 20-40 G-s range has large impact on charge stability*

• Wetting agents
  – Nonionic (Huntsman) was unusable
  – Fugitive afforded no safety*
  – Dispersant residues were generally harmful

• Coated & grafted absorbers have same performance

*Influenced by wetting agent transfer
TR&F Cycling Test
Type M81757 35Ah Batteries

• Initial charge: 2-Step CC with water addition

• TRF cycles:
  – Stabilize battery in Chamber @ 120ºF
  – 315A discharge to 14.4V or 5 minutes
  – 24-hour CP @ 28.5V
  – Repeat -315A and CP charges (M–F)
  – Sat AM: Rest open circuit and return to amb.
  – Sun PM: Repeat sequence above
  – Water additions: As needed
Effects of Gas Barrier Porosity and Applied W.A. on Safety

• 35Ah Batteries using Woven Nylon absorber and different gas barriers
  – 3400: 24G-s porosity and fugitive wetting agent
  – A519: 37G-s porosity & insoluble wetting agent DePHOS HP 739 (CAS # 12645-31-7)
Charge Current TR&F Cycling
W.N. & A519 VS. W.N. & 3400

Charge Current (Amperes)
Charge Time (Hours)

Distribution Statement A: Approved for Public Release; Unlimited Distribution
Battery Temperature TR&F Cycling
W. N. & A519 VS. W. N. & 3400

Charge Time (Hours)

Degrees Fahrenheit

- A519 T1
- A519 T2
- A519 T3
- 3400 T1
- 3400 T2

Distribution Statement A: Approved for Public Release; Unlimited Distribution
Wetting Agent Mobility
Effect on gas barrier performance

• Gas barrier (N3400G1-P)
  – Porosity: 37G-s
  – Wetting agent: Fugitive - Celgard proprietary

• Absorbers
  – Grafted mbPP
  – Coated mbPP (CAS # 12645-31-7)
TR&F Charge Current (PL)
Grafted Absorber, N3400G1-P

Charge Current (amps)

Charge Time (Hours)

- Current 1
- Current 2
- Current 3
TR&F Charge Current (PL)
Coated Absorber, N3400G1-P

Charged Time (Hours)

Charge Current (amps)

- Current 1
- Current 2
- Current 3
TR&F Charge Temperature (PL)
Grafted Absorber, N3400G1-P

Degrees Fahrenheit

Temp #1
Temp #2
Temp #3

Charge Time (Hours)
TR&F Charge Temperature (PL)
Coated Absorber, N3400G1-P
TR&F Conclusions

• Gas barrier porosity does not control charge stability if wetting agent is absent.

• Anionic wetting agent (CAS 12645-31-7) on absorber “caused" charge stability. It appears W.A. can transfer from absorber to the gas barrier.

• The wetting agent in the pores IS the gas barrier.
How Good is Good?

- Type M81757/16 battery with GSS was subjected to continuous TR&F cycling

- Results:
  - Battery’s charge stability remained completely stable throughout test.
  - Testing was terminated after 226 days on test and completing 150 TR&F cycles
TR&F Cycling Comparisons
EOC Currents

EOC Current (Amps)

/16wGSS
/16wGF&3400
/9-3wKC&3400*

Cycle Number
TR&F Cycling Comparisons
EOC Battery Temperatures

 Degrees Fahrenheit

 Cycle Number

/16wGSS
/16wGF&3400
/9wKC&3400

Distribution Statement A: Approved for Public Release; Unlimited Distribution
Battery Temperature
Individual TR&F Cycles
Specifying a Separator System

• Wetting agent
  – Anionic
  – Unaffected by charge V using special test cell
  – Insoluble in electrolyte
  – Dispersant must leave no residue that can disperse into electrolyte
Specifying a Separator System

• Gas Barrier
  – Polyolefin membrane
  – Thickness: 1mil ± 0.1 mil
  – Maximum Resistance: 18-milliohm-sq. inch
  – Porosity (35 to 40 G-s)
    • High enough for low resistance
    • Low enough to keep wetting agent in pores.
Specifying a Separator System

Absorber:

- Hydrophilic (W.A. coated preferred)
- Highly absorbent
- High tortuosity for better protection (mbPP)
- Weight: Governed by performance
Any Questions?
Speaker POC Info

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