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Superiority and failure mode of automotive batteries insulated with polyethylene separators

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Abstract

For separator types used in North America and Western Europe the trend is towards microporous polyethylene (PE) materials. Battery industries in these regions have demonstrated the superiority of PE separators with respect to other types in terms of physical, electrical and chemical properties. Grace battery separator technical center (BSTC) in Hamburg (Germany) has analysed 53 failed batteries removed from field service and found only 11.3% of failures is related to PE separators. In explicit terms, separator-related failures are due to deep-discharge and subsequent charge of the batteries.

The shift towards polyethylene separators

The polyethylene (PE) separator was invented in the late 1960s by W.R. Grace & Co. It took nearly 10 years, however, to mature this product in the North American battery market. As shown in Fig. 1, the PE separator had less than 20% of the market share in North America in 1980. Nevertheless, within 10 years, the PE separator had wiped out its two major competitors – cellulosic and glass separators – to become the dominant design in North America.

In 1991, 82.7% of the total 84.4 million automotive batteries produced in North America were insulated with microporous PE separators (Table 1). It is anticipated

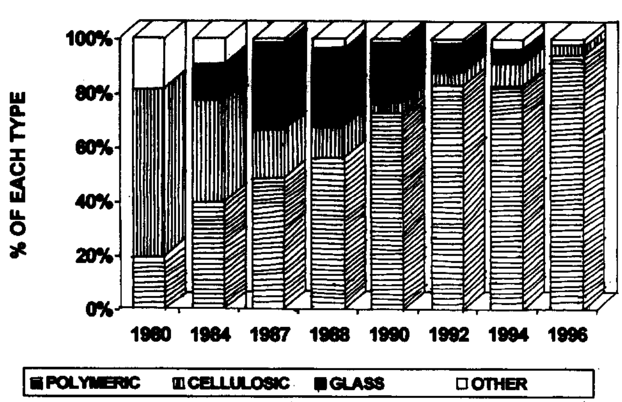

Fig. 1. Separator trends in North America (separator type: automotive batteries).

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TABLE 1

Market share of separator type in North America

Separator type	Market share (%)	
	1991	1995
Microporous polyethylene	82.7	92.0
Glass leaf	15.9	7.0
Cellulose	0.8	0.5
Miscellaneous	0.6	0.5

that the market share of PE separators will reach 92.0% in 1995. A similar trend has been observed in the Western Europe battery industry.

Why has the PE separator grown so fast? The two major reasons are as follows.

(i) The PE separator has a thermoplastic nature that is sufficiently flexible to allow the material to be enveloped by machinery. PE users in the industry have demonstrated that machine enveloping not only improves product quality, but also increases significantly productivity and reduces direct manufacturing costs.

(ii) The PE separator is out-performing its competitors in terms of physical, chemical and electrical properties. The PE separator has the smallest pore size and thus prevents dendrite formation. In addition, the electrical resistance is one of the lowest and this has a significant impact on the cold-cranking capability of the battery.

Effect of separator type on battery performance

A comparison of the properties of different types of separators is given in Table 2. It is clear that only the PE separator can be enveloped and can develop good sealability. It has low electrical resistance, sufficient porosity, small pore size, and great resistance to both shorting and corrosion. Batteries insulated with PE separators exhibit superior performance in terms of cold-crank capability and cycle life.

Table 3 shows the performance of batteries with different types of separators. The cold-cranking performance of batteries can be designed to meet specification with different types of separators. The PE separator, by virtue of its low electrical resistance, generally provides better cold-cranking performance.

For the cycle-life test according to the 40 C DIN schedule, all batteries met the required service of 5 weeks. Under the DIN 43539E-1980 test, however, where more severe cycling and a higher service temperature (50 °C) are required, significant differences appear between batteries with different types of separators.

Failure modes of automotive batteries

In the past, only a few articles have been published on the statistical analysis of the failure mode of automotive batteries and, in particular, on the role that PE separators play in these failure modes.

The European Division of W.R. Grace & Co. analysed 53 PE-insulated automotive batteries removed from field service during the last quarter of 1991. Each battery was

TABLE 2

Characteristic differences of various types of battery separator materials

Characteristics	Separator type				
	Rubber	Cellulose	PVC	Polymeric (PE)	Glass fibre
Envelopable (sealability)	Very poor	Poor	Sufficient	Very good	Very poor
Blocking (leaf)	Sufficient	Very good	Sufficient	Poor/sufficient	Very good
Electrical resistance	Very poor	Poor	Poor	Very good	Good
Porosity	Sufficient	Sufficient	Poor	Sufficient	Very good
Maximum pore size	Good	Poor	Sufficient	Very good	Poor
Resistance to shorting	Good	Poor	Poor	Very good	Poor
Corrosion resistance	Very good	Poor	Good	Very good	Good
Battery performance (Cold crank)	Poor	Sufficient	Sufficient	Very good	Good

TABLE 3

Performance of batteries with different types of separators

Separator type	Sintered PVC	Cellulosic	Resin fibre-glass	Resorcinol	PE Pockets
Separator electrical resistance					
(mΩ in²)	20	30	10	12	8
(Ω cm²)	0.129	0.193	0.064	0.077	0.051
Voltage (−18 °C, 30 s)	9.2	9.15	9.40	9.35	9.45
Cycle-life test (weeks)	>10	>10	>10	>10	>10
Accelerated cycle-life test DIN (43539E-1980) (weeks)	5	6	6	8	>10
Water consumption (g/Ah)	6	3–5	3	4	3–6

evaluated through a detailed procedure and was assigned to one of the eight failure modes listed in Fig. 2, and itemized as follows.

1. Eight batteries (or 15.1% of the total) were prematurely removed from field service. These batteries could be reused after charging.

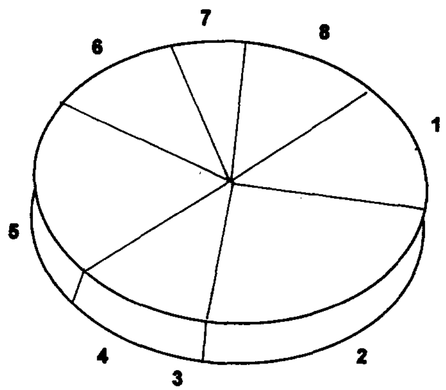

Fig. 2. Failure modes of PE-pocket automotive batteries.

Failure mode	%	
1	15.1	Needed recharge only
2	24.5	Manufacturing errors
3	3.8	Maintenance error
4	7.5	Mechanical damage
5	20.8	Positive grid corrosion
6	11.3	Positive material failure
7	5.7	Positive material failure and grid corrosion
8	11.3	Grown shorts due to deep discharge and recharging

2. Thirteen batteries (or 24.5% of the total) were classified as manufacturing errors that included improper group insertion, incomplete formation and bad intercell connections.

3. Two batteries (or 3.8% of the total) were due to maintenance error. It was even found that one battery was refilled with potassium hydroxide instead of sulfuric acid!

4. Mechanical damage accounted for four batteries (or 7.5% of the total).

5. Eleven batteries (or 20.8% of the total) suffered from positive grid corrosion.

6. Six batteries (or 11.3% of the total) exhibited positive material failure.

7. Three batteries (or 5.7% of the total) experienced a combination of failure modes 5 and 6, above.

8. The last failure mode was separator related, namely, short formation. Six batteries (or 11.3% of the total) failed because of cycling as a consequence of deep discharging and recharging.

In summary, positive-plate-related failures (failure modes 5 to 7) accounted for the most failures (37.8%), followed by failure mode 2 manufacturing errors (24.5%).

For failure mode 8, however, it must be emphasized that the automotive lead/acid battery is not designed to be utilized in any manner to allow deep discharge and to drop its acid density to a range near water. It is a well-known fact that lead sulfate ($PbSO_4$) is more soluble in water than in concentrated sulfuric acid. Deep discharge of the battery to a stage at which the electrolyte density is near to that of water would result in an order of magnitude increase in the solubility of lead sulfate. Subsequent recharging of the battery generates sulfuric acid at the plate surface. This would entrap and precipitate lead sulfate in the separator pores that, in turn, would cause the growth of micro-shorts. Based on this phenomenon, the failure mode of separator shorts should be classified as mishandling. In order to solve this problem, Grace has been working with a US battery company to develop a modified PE separator that will prevent the formation of lead sulfate in the separator pores.

The general appearance and conditions of the PE separators removed from the disassembled batteries were satisfactory. The majority had uniform colour, no damage (i.e., no tears or holes), and elasticity.

Characteristics of failed automotive batteries

Battery capacity

The 53 removed batteries had an average capacity of 54.4 Ah and a range of 30 to 92 Ah (Table 4). This represents a significant capacity increase compared with the 1984 US survey in which the average capacity was 43.8 Ah with a range of 36 to 88 Ah. The 24% growth (10.6 Ah) in the average battery capacity may be explained by the increased power demand by the automotive industry in the 1990s.

TABLE 4

Capacity distribution of automotive batteries, 1984–1992

Capacity (Ah)	1984		1992	
	No.	%	No.	%
30			3	5.7
32			1	1.9
34			1	1.9
35	3	4.8		
36	33	53.3	7	13.2
43			2	3.7
44	8	12.9	6	11.3
45	5	8.1	3	5.7
48			1	1.8
54	1	1.6	2	3.7
55	4	6.5	3	5.7
58			1	1.9
60	1	1.6		
62			4	7.4
63	1	1.6	4	7.5
64			1	1.9
66	3	4.7	3	5.7
68			1	1.9
72			7	13.2
77	1	1.6		
88	2	3.2		
92			3	5.7
Total	62	100	53	100

Average capacity 1984 = 43.8 Ah
1992 = 54.4 Ah

TABLE 5

Grid alloy vs. enveloping options

	Pb–Ca		Pb–Sb		Total	
	No. batteries	%	No. batteries	%	No. batteries	%
Negative pockets	11	78.6	29	74.4	40	77.55
Positive pockets	3	21.4	10	25.6	13	24.5
Total	14	100	39	100	53	100

Lead-calcium/lead-antimony grids

The increased demand for maintenance-free automotive batteries (minimal water consumption) has resulted in a shift in the lead–antimony/lead–calcium grid philosophy. In this survey, however, 39 (or 75%) of the total removed batteries still had positive lead–antimony grids. Only fourteen (or 25%) of the total batteries were equipped with lead–calcium plates.

Plate-enveloping options

Table 5 shows that the negative enveloped with PE separator outnumbers the positive plate by a factor of three. Forty batteries were found to have negative plates enveloped and thirteen batteries to have their positive plates enveloped. This three-to-one ratio does not seem to be affected by the type of grid alloy that was used. This may indicate that concern over premature positive material shedding seems to be smaller than assumed.

Conclusions

The following two conclusions can be drawn from this study.

1. The PE separator is not only the most popular separator in the developed countries, but also provides the best overall performance.

2. Positive-plate corrosion and shedding are the major failure modes of automative batteries. In most cases, the PE separator maintains better shape than the plates.

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