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Benefit of increasing the organic expander dosage on the high temperature performance of the negative electrode of lead–acid batteries

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Abstract

Organic expanders function in the negative electrode of lead–acid batteries to promote the development of fine crystal sponge lead upon formation and to preserve this high surface area structure by preventing coarsening of crystals upon cycling. Organic expanders also serve to protect the negative active material from passivation during discharge or on open circuit by preventing the formation of an impervious non-conducting film of lead sulfate. The deleterious effect of a high temperature service environment on the life of the lead–acid battery and the negative electrode is well known. In this paper, we investigate the effect of Vanisperse A organic expander content on the capacity and life of the negative electrode of flooded lead–acid SLI batteries designed to be negative electrode limiting. The low rate capacity and cold cranking performance of batteries designed to be negative electrode limiting remained essentially unchanged upon increasing the organic expander dosage from 0.25 to 0.50% on weight of lead oxide in a negative mixture. Battery life, however, when tested according to the SAE J240 protocol, increased 25% at 41 °C, and 20% at 75 °C. When tested according to the SAE J2185 protocol at 50 °C, battery life increased 15%. No adverse effects were observed. This work shows that increasing the Vanisperse content has a beneficial effect on the high temperature service life of the negative electrode.

Keywords: Organic expander; Lead–acid battery; Negative electrode; Capacity; Cycle life

1. Introduction

Organic expanders function in the negative electrode of lead–acid batteries to promote the development of fine crystal sponge lead upon formation and to preserve the high surface area structure upon cycling [1–6]. The deleterious effect of high temperature service environment on the life of the lead–acid battery and the negative electrode is well known [7]. Improving the performance of the negative electrode is of great importance to the lead–acid battery industry and the future of the lead–acid battery as an electrical energy storage device for high temperature service.

2. Experimental

The organic expander employed in this study was Vanisperse A, an oxy-lignin manufactured by Borregaard LignoTech, in Sarpsborg, Norway. The batteries were a flooded SLI Group 24 design and were manufactured by formerly GNB, now Exide Technologies, Table 1. The design variable was the organic expander dosage of Vanisperse A with the low level at 0.25% and the high level at 0.50% based on the weight of lead oxide in a negative mixture. Normal amounts of precipitated barium sulfate and carbon black were used with each organic variable. Ten identically matched batteries of each factor were manufactured. The batteries built and tested in this study were specifically designed to be negative limited so as to accentuate the effect of the negative electrode and its additives. Thus the batteries do not represent standard GNB production. In each cell six common heavy-duty truck positive plates were mated with five lightweight SLI negative plates containing the expanders yielding, a positive active mass (PAM) to negative active mass (NAM) ratio of 1.5:1. The cast positive grids were lead–calcium–tin–silver alloy. The negative grids were continuous expanded lead–calcium–tin alloy. Batteries with a Group 24 size and a nominal rating of 500 CCA and 85 min of reserve capacity (RC) were assembled and one-step formed according to standard manufacturing practices.

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Table 1
Battery design

Manufacturer	GNB, now Exide Technologies
Group	24; nominal capacity: 500 CCA/85 RC
Grids	Negative: continuous expanded lead–calcium–tin; positive: heavy-duty cast lead–calcium–tin–silver
Plate ratio	6:5; positive to negative
Active mass ratio	1.5:1; PAM to NAM
Organic expander	Vanisperse A—sodium salt of partially desulfonated oxidized and purified lignosulfonate. Manufacturer: Borregaard Lignotech, Sarpsborg Norway
Organic expander dosage	0.25 or 0.50% based on weight of lead oxide in negative mixture
Battery design	Flooded
Carbon black and barium sulfate	Standard levels
Formation	Standard manufacturing practice—one-step formation

Note: Batteries were designed to be negative limited to accentuate the effect of the negative electrode and its additives and therefore do not represent standard GNB production.

The low rate capacity and cold cranking of the 20 batteries were tested according to both SAE and DIN protocols. For the SAE, the reserve capacity (RC), the time in minutes, to discharge the batteries at 25 A to 10.5 V was measured. For the SAE Cold Cranking test, the voltage after 30 s of discharge at 500 A and −18 °C was measured with an additional extension of the discharge to determine the time in seconds to reach 6.0 V. For the DIN capacity the batteries were discharged to 10.5 V at the C20 rate of 2.75 A. For the DIN cranking performance, a discharge current of 285 A at −18 °C to a cut-off voltage of 6.0 V was arbitrarily chosen since there was no DIN rating for this battery. Cycle life was evaluated according to the following protocols: SAE J240 at 41 °C, SAE J240 at 75 °C, and SAE J2185 at 50 °C, which was modified to give the current density of a battery twice its size. The test population was three batteries per life test protocol. To monitor capacity during the life tests, one battery from each test group and for each life test protocol was discharged to 6.0 V during the high rate discharge portion of the life tests.

After failure and before further testing, the batteries were charged at 3 A until the battery voltage stabilized. This was followed by an ambient high rate discharge at 500 A where the voltage and time to 5.0 V was measured to assess remaining high rate capacity. To assist in establishing cause of failure and to verify whether the negative electrode was in fact the limiting electrode, the half-cell voltage of both the negative and the positive end cells were monitored relative to a cadmium reference electrode. After recharge, an SAE reserve capacity was performed, the batteries were recharged, then the batteries were dissected, and the condition of the positive electrodes, the negative electrodes and the separator were noted. The negative plates were collected and the NAM was analyzed for apparent density, pore volume, BET surface area. In addition, the residual organic expander was estimated by extracting NAM pellets with 1N sodium hydroxide and measuring the absorbance on an ultraviolet spectrophotometer.

3. Results and discussion

The initial low rate capacity and cold cranking data measured according to both the SAE and DIN protocols are presented in Table 2. The data indicate doubling the Vanisperse A concentration did not significantly affect these performance values. For the various performance parameters, the results for the two groups were generally within 2% of each other. The lone exception was the second SAE cold crank where the difference was 4.8%. This data suggests that for initial performance, little or no significant benefit is realized by increasing the organic expander dosage beyond 0.25%.

It is interesting to note that both test groups exceeded the SAE cold cranking specifications, voltage greater than 7.2 V after 30 s, but exceeded only one of the two specifications for the DIN Cold Cranking test. Both test groups exceeded 9.0 V at after 30 s specification, but neither group achieved a voltage greater than 6.0 V after 150 s required by the test. This suggests the DIN cold cranking performance is more related to the capacity of the negative electrode. Since this battery design was not previously rated for the DIN Cold Cranking test, selecting the DIN discharge rate was arbitrary and the data indicate the rate selected was too high. In any case, the performance values were nearly identical.

3.1. Standard SAE J240 life test (41 °C)

The results for measuring cycle life according to the SAE J240 protocol at 41°C are presented in Table 3. The values represent the average life of the three batteries for each test group. The data indicate a substantial increase in cycle life was realized when the dosage of Vanisperse A was increased from 0.25 to 0.50% based on weight of lead oxide in a

Table 2
Summary of capacity and cold crank performance according to SAE and DIN protocols

Vanisperse A dosage[a]	0.25%	0.50%
First SAE reserve capacity (min)	95.9	97.3
Second SAE reserve capacity (min)	101.0	104.7
First SAE cold crank: (voltage at 30 s)	7.61	7.62
Second SAE cold crank: (voltage at 30 s)	7.69	7.72
First SAE cold crank: (seconds to 6.0 V)	58.8	60.1
Second SAE cold crank: (seconds to 6.0 V)	56.1	58.5
DIN capacity at 20 h rate (Ah)	55.3	54.2
DIN cold crank: (voltage at 30 s at 285 A)	9.40	9.50
DIN cold crank: (seconds to 6.0 V at 285 A)	107.6	108.1

[a] Percentage based on weight of lead oxide in negative mixture.

Table 3
Summary of cycle life tests according to SAE J240 protocols

Vanisperse A dosage[a]	0.25%	0.50%
SAE J240: standard (41 °C)	2293	2867
SAE J240: high temperature (75 °C)	1433	1720

[a] Percentage based on weight of lead oxide in negative mixture.

negative mixture. On average batteries containing the higher dosage of Vanisperse A lasted 25% longer than batteries containing the lower dosage. This is evidence of a significant beneficial dosage effect of the organic expander prolonging the service life of the negative electrode. In Fig. 1, the capacity of one battery from each test group is plotted as a function of cycles. In this instance, the data indicates the two batteries possessed comparable capacity and life during the course of the test.

3.2. High temperature SAE J240 life test (75 °C)

Cycle life as measured according to the SAE J240 protocol at 75 °C is presented in Table 3. The values represent the average life of the three batteries for each test group. Once again, the life of batteries containing the higher dosage of Vanisperse A exhibited significantly longer life than batteries containing the lesser amount. On average batteries containing 0.50% Vanisperse A lasted 20% longer than batteries containing only 0.25%. In Fig. 2, the capacity of one battery from each test group is plotted as a function of cycles. The data indicate the battery with the greater dosage of Vanisperse A possessed greater capacity throughout the duration of the test and yielded longer life than the battery containing the lesser dosage.

3.3. Heavy-duty service life test—SAE J2185 (50 °C)

SAE J2185 is a life test for heavy-duty storage batteries normally meant for truck service. It tests heavy-duty applications by subjecting the battery to deeper discharge cycles than those encountered in typical SLI protocols. The test simulates occurrences where the total electrical load exceeds the alternator output or when the battery system supplies the electrical load when the engine is not operating. Because this test is normally meant for those batteries with reserve capacities over 200 min (approximately equivalent to 100 Ah) and the test batteries possessed approximately 100 min of reserve capacity, each of the rate parameters

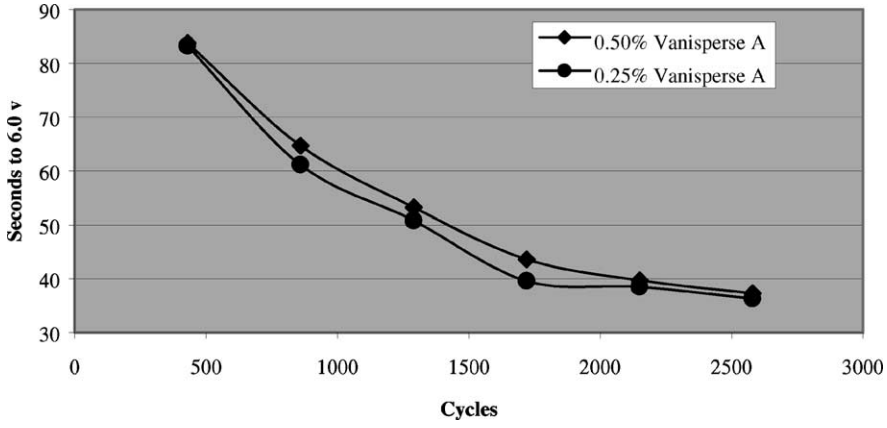

Fig. 1. High rate discharge results for one battery from each group cycled according to SAE J240 life test at 41 °C.

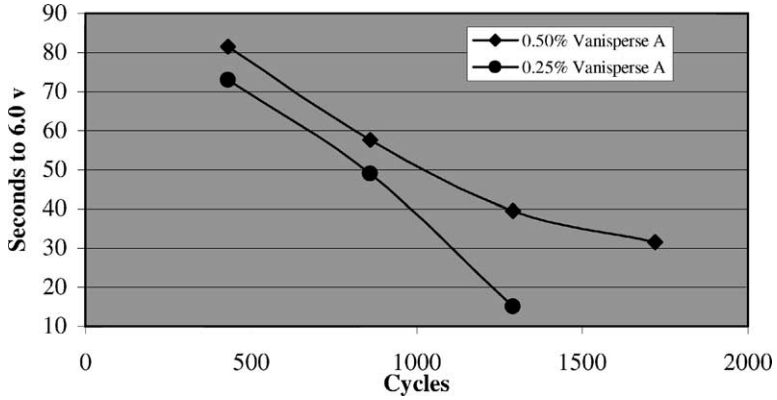

Fig. 2. High rate discharge results for one battery from each group cycled according to SAE J240 life test at 75 °C.

Table 4
Summary of SAE J240 and J2185 life test protocols

Test	Charge	Discharge	Cycles/week	Temperature (°C)	Failure: high rate discharge
Standard SAE J240	10 min at 25 A, 14.8 V max	4 min at 25 A	430	41	Voltage at 30 s < 7.2 V (500 A)
High temperature SAE J240	10 min at 25 A, 14.8 V max	4 min at 25 A	430	75	Voltage at 30 s < 7.2 V (500 A)
Heavy-duty SAE J2185	2.5 h at 12.5 A, 14.8 V max	1.0 h at 12.5 A	26	50	Voltage at 50 s < 7.2 V (500 A)

for charging and discharging were reduced by half to simulate the current density of a larger battery capable of being tested. A comparison of the normal J2185 and J240 cycling portion of the life tests are presented in Table 4. In SAE J240 protocol, the charge and discharge times are 10 and 4 min, respectively, while for the SAE J2185 they are 2.5 and 1.0 h, respectively, but at half the ampere rate in the modified test, 12.5 A. Consequently, for the SAE J240, 430 cycles are completed per weekly test period compared to only 26 cycles for the SAE J2185. Also the SAE J240 test is conducted at 41 or 75 °C, while the SAE J2185 test temperature is 50 °C. The failure determination is also different. With respect to the high rate discharge, the SAE J240 stipulates a failure when the voltage at 30 s is less than 7.2 V, while for the SEA J2185 the discharge time parameter is longer. The failure specification for SAE J2185 is when the voltage at 50 s is less than 7.2 V. The batteries 500 CCA rate was used for the high rate discharge portion of the SAE J2185 life test.

The average cycle life measured according to the SAE J2185 protocol is presented in Table 5. Under the SAE J2185 protocol, simulating heavy-duty cycling, the batteries containing the higher dosage of Vanisperse A exhibited significantly longer life than batteries containing the lesser amount. On average batteries containing 0.50% Vanisperse A lasted 15% longer than batteries containing only 0.25%. In Fig. 3, the capacity of one battery from each test group is presented as a function of cycles. Once again the battery with the greater amount of Vanisperse A yielded consistently greater capacity during the test and yielded the longer cycle life than the battery containing the lesser dosage.

Table 5
Summary of cycle life tests according to SAE J2185 protocol

Vanisperse A dosage[a]	0.25%	0.50%
SAE J2185: heavy-duty (50 °C)	169	195

[a] Percentage based on weight of lead oxide in negative mixture.

In summary, the results of three life tests consistently indicate that there is a significant beneficial effect of prolonging the life of the negative electrode by increasing the organic expander dosage. Specifically, from 0.25 to 0.50%. This benefit was observed for life tests conducted at 41, 50 and 75 °C and encompassing both shallow and deep type cycles.

3.4. Post mortem observations and analyses

3.4.1. High rate discharge

The change in the negative half-cell voltage for cell 6 relative to a cadmium reference electrode during the high rate discharge suggests the capacity of the negative electrode was largely the limiting factor. Discounting initial polarization, the negative electrode voltage decay accounted for 87–100% of the high rate voltage loss of the J240 test failures. In the J2185 test, a lesser amount of capacity loss, 56–87%, is attributable to the negative electrode. This agreed with observation of the degradation of the positive electrodes. This negative capacity domination was observed for both test groups containing 0.25 or 0.50% organic expander.

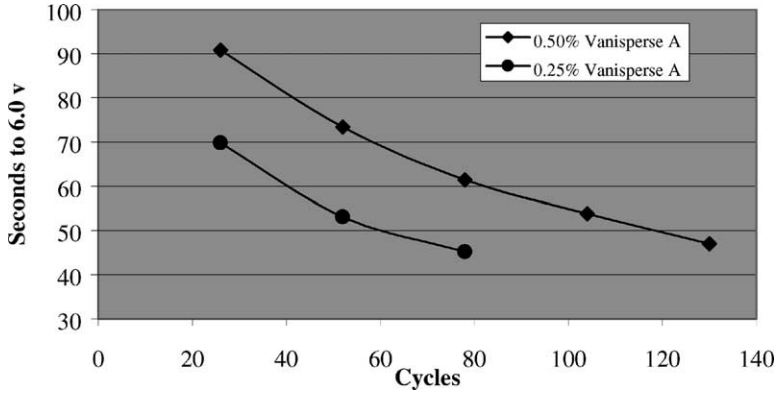

Fig. 3. High rate discharge results for one battery from each group cycled according to SAE J2185 life test at 50 °C.

Table 6
Reserve capacity (RC) after cycling

Vanisperse A dosage[a]	0.25%	0.50%
Test	RC	RC
J240 41 °C	40.2	43.2
J240 75 °C	37.1	41.8
J2185 50 °C	51.2	52.9

[a] Percentage based on weight of lead oxide in negative mixture.

3.4.2. SAE reserve capacity after cycling

The reserve capacity was greatly diminished as a result of cycling. Data are presented in Table 6. The batteries retained 47–51% of the original reserve capacity rating after the J240 at 41 °C life test, 44 and 49% after the J240 at 75 °C life test and 60 and 62% after the SAE J2185 at 50 °C life test for batteries containing 0.25 and 0.50% Vanisperse A, respectively. Reference electrode values indicated this was also dominated by the negative electrode, except in the J2185 test. The data demonstrate that both high and low rate capacity suffer upon cycling.

3.5. Tear down observations for life tests SAE J240 at 41 and 75 °C

Densification of the NAM was evident in batteries tested according to J240 life test at both 41 and 75 °C. Densification was evident by the many shrinkage cracks in the negative active material (NAM). The size of the cracks and their distribution did not vary with the organic expander dosage. Some sulfation was observed as a band approximately 1.5 cm along the bottom of the plate. Pellets from this region were hard and gritty, not typical of sponge lead. This suggests stratification of electrolyte, which is a common phenomenon with bench life tests with limited voltage and overcharge.

For batteries tested according to SAE J240 at 41 °C, the positive active material (PAM) exhibited limited surface shedding and was in overall good condition. Some sulfation was evident in the bottom 2.5 cm. Positive grids were in good shape and flexible. There was good adhesion between the PAM and the grid structure.

For batteries tested according to SAE J240 at 75 °C, there remained very good adhesion between the PAM and the grid structure. The grids were more brittle than grids recovered from the J240 at 41 °C, but they were still intact with adequate integrity. A small amount of sloughing of the PAM was observed but not an excessive amount.

3.6. Tear down observations for life test SAE J2185

In general, the observations suggest the cause of failure was more bimodal, attributing loss of capacity of both the positive and negative electrodes. Regarding the NAM, signs of shrinkage were absent. In fact the NAM was expanded in the lower two-thirds of the plate for both battery groups. Expansion of the NAM is common for deep cycle applications. Though there was expansion, none of the batteries in this study failed due to shorts caused by growth of dendrites even for the high organic expander dosage. Again, there were signs of stratification in the bottom 1.5 cm as in the shallow cycle tests. The PAM appeared to be well worked. It had softened with very little integrity remaining and had poor bonding to the grids. Grids were brittle but intact.

3.7. NAM apparent density, porosity and BET surface area

Apparent density, porosity and BET surface area measure the gross morphology of the NAM and by comparison can reveal structural changes that have taken place during cycling. The data are presented in Table 7. The pore volumes and apparent densities were comparable for the two test groups within each of the test protocols. However the values vary between test methods and this suggests the structural changes are different for the various test methods. For both test groups, relative to the uncycled control, the porosity decreased during the SAE J240 at 41 °C life test. The porosity also decreased during the SAE J240 at 75 °C life test, but the decrease was on a smaller scale than observed for the former test. Meanwhile, the porosity increased during the SAE J2185 life test. The apparent density increased during both the SAE J240 at 41 and 75 °C but decreased somewhat during the SAE J2185 in line with the porosity data.

3.8. BET surface area

With respect to the batteries containing 0.25% Vanisperse A, relative to the uncycled control, the BET surface area diminished for all three life tests. The decrease was most pronounced in the high temperature J240 test. The values decreased from the control at 0.58–0.45 m^2/g for the standard J240, 0.36 m^2/g for the high temperature J240 and 0.43 m^2/g for the SAE J2185. The BET surface area differed between the two groups of batteries. Within a given life test, batteries with the higher dosage organic expander consistently had

Table 7
Pore volume, apparent density and BET surface area of NAM

Vanisperse A dosage[a]	Control, uncycled	SAE J240 at 41 °C	SAE J240 at 75 °C	SAE J2185 at 50 °C
Pore volume (%)				
0.25%	55.9	47.0	54.1	61.5
0.50%	58.2	48.5	52.0	59.0
Apparent density (g/ml)				
0.25%	4.1	4.9	4.8	4.0
0.50%	4.0	4.9	4.6	3.6
BET surface area (m^2g)				
0.25%	0.58	0.45	0.36	0.43
0.50%	0.61	0.57	0.44	0.53

[a] Percentage based on weight of lead oxide in negative mixture.

greater BET surface area. This suggests the organic expander is key to preserving the surface area necessary to maintain capacity even though other gross structural changes are taking place.

The structural changes can be summarize as follows: during the J240 at 41 °C, the pore volume decreases as the NAM becomes denser and the reactive surface area decreases. Capacity as reflected in high rate run time is significantly reduced. During the J240 at 75 °C, the NAM also densifies but perhaps not as much as in the J240 at 41 °C while the surface area decreases to a greater extent than in the J240 at 41 °C. It is probable that the reduction of surface area is the dominant factor in the capacity loss. Finally, during the SAE J2185, the pore volume actually increases, but, again, the surface area decreases leading to a loss in negative capacity.

3.9. Residual organic expander content

Negative active material pellets were recovered from negative plates or electrodes during various phases of the battery life. The Vanisperse A was extracted from the pellets using boiling 1N sodium hydroxide and the amount contained therein was estimated by the solution's ultraviolet absorbance at 280 nm and an absorbance coefficient determined from a Vanisperse A solution treated in like manner. The amount of Vanisperse A recovered as a percentage of the initial amount added to the negative mixture is presented in Table 8. The data indicate that for both test groups the largest decreases in extractable Vanisperse A occurred in formation, before the batteries were cycled. After formation and open circuit stand, as represented by the uncycled controls, the extractable amount is reduced to only about 32% of the initial amount added. It is generally known that the method employed to form the battery can dramatically affect the amount of organic expander expelled from the negative paste, with one-step formations such as the one used in this experiment being the most severe.

The further reduction in extractable organic expander that occurs upon cycling according to the three life tests was much smaller. After cycling according to the J240 at 41 °C, the amount of extractable organic expander decreased little or not at all compared to the uncycled control batteries. The amount of extractable organic expander after J240 at 75 °C life test, decreased from about 32% for uncycled controls to about 21% for both test groups, after the J2185 life test, it decreased to about 27% for both test groups.

That the amount of extractable organic expander did not change after the J240 at 41 °C life test suggests further degradation or loss of the organic expander does not lead to the coarsening of crystals. Rather, it suggests that crystal coarsening is a natural process that is retarded but not prevented by the presence of the organic expander, and according to the life tests, increasing the organic expander dosage further retards the rate of coarsening. Indications are that once crystal coarsening with the loss of reactive surface area occurs, it cannot be readily reversed.

Table 8
Recoverable organic expander from NAM pellets

NAM sample	Organic expander recovered (%)[a]	
	0.25%[b]	0.50%[b]
Control, uncycled	34	30
J240 41 °C	30	31
J240 75 °C	21	22
J2185 50 °C	28	27

[a] Based on initial amount added to negative mixture.
[b] Vanisperse A dosage (in percentage) based on weight of lead oxide in negative mixture.

4. Conclusion

The post mortem examination verified that we achieved our battery design criteria. Specifically, the design active mass ratio of 1.5:1 PAM to NAM was successful in effecting the negative electrode to be the capacity limiting element. This was true for all cycling protocols. Thus the performance tests and cycling protocols were a true measure of the effect of the organic expander dosage on the capacity of the negative electrode.

Increasing the organic expander dosage from 0.25 to 0.50% did not significantly affect the low rate capacity or cold cranking performance. This finding was true whether the performance parameters were measured via SAE or DIN protocols.

The most important finding was the strong beneficial effect increasing the organic expander dosage exerted on lengthening the life of the negative electrode. The study suggests the higher organic expander dosage effects longer life by preserving the surface area and hence the capacity of the NAM upon cycling. The improvement was observed in all three life tests covering both standard and high temperature conditions as well as both shallow and deep cycles. When the Vanisperse A dosage was doubled from 0.25 to 0.50% the life increased 25, 20 and 15% for protocols J240 at 41 °C, J240 at 75 °C and J2185 at 50 °C, respectively. Therefore, when designing batteries for high temperature service, establishing the optimal organic expander dosage is key to obtaining the most service life from the negative electrode. The cost to realize the improvement is minimal relative to the overall cost of the battery. For a battery of Group 24 rating the cost is about 1.2 cents per battery.

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