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Selection of pre-blended expanders for optimum lead/acid battery performance

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Abstract

Expanders are an essential component of lead/acid batteries. They prevent performance losses in negative plates that would otherwise be caused by passivation and structural changes in the active material. The functions of the components of modern negative-plate expanders are described and data are presented to show how the capacity and life of the battery are affected by the type and amount of barium sulfate and lignin incorporated in the expander blend. The differences between expanders for automotive, deep-cycle and standby-power batteries are illustrated and typical formulations shown for each application. There are several ways in which expanders can be incorporated into negative plates. These range from adding the individual components to the paste mix to adding a pre-blended formulation. The benefits of pre-blending are more uniform distribution of expander in the plate, simplification of paste mixing, and improved quality control. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Without the use of expanders, the active material (sponge lead) in the negative plates of lead/acid batteries will lose performance rapidly when cycled. This performance loss is due to passivation which results from deposition of an impermeable film of lead sulfate on the lead substrate, and to loss of porosity caused by shrinkage of the lead sponge. Studies have shown [1–3] that there is considerable reduction in the surface area of the negative plate after relatively few cycles.

The above behaviour can be reduced significantly by the use of certain additives to the negative plate. These additives are usually called expanders but, more correctly, they act as anti-shrinkage agents. Modern expander formulations are usually a blend of barium sulfate, lignin derivatives and carbon black.

2. Functions of expander components

2.1. Barium sulfate

The function of barium sulfate is to act as a site for the precipitation of lead sulfate as the battery is discharged. It is extremely insoluble in sulfuric acid and is electrochemically inactive. These properties assure that it remains chemically unchanged in the negative plate, even after prolonged cycling. The ability of barium sulfate to act as a site for lead sulfate precipitation is due to the similar structure of the two compounds. Strontium sulfate has also been shown to be an effective expander [4].

Barium, strontium and lead sulfates are isostructural [5]. All belong to the orthorhombic space group and have similar R values and bond lengths, as shown in Table 1.

The inert barium sulfate provides a large number of sites for the precipitation of lead sulfate crystallites and, thereby, prevents its deposition as a thin, impermeable, passivating film. Barium sulfate is used in expanders in two forms: blanc fixe, which is precipitated from solution, and barytes, which is ground and purified mineral ore. Typically, blanc fixe has a median particle size of ~1 μm, while that of barytes is ~3.5 μm. Thus, barytes is

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Table 1
Structural characteristics of $BASO_4$, $SrSO_4$ and $PbSO_4$

	$BaSO_4$	$SrSO_4$	$PbSO_4$
R	0.043	0.053	0.067
Cation-O bond length (Å)	2.952	2.831	2.87
S–O bond length (Å)	1.478	1.474	1.490

much less effective than blanc fixe and can virtually be regarded as a filler. Whether barytes has the property of slowly breaking down into fine particles, and therefore acting as a slow-release agent, has not been settled.

2.2. Lignosulfonates

The lignin derivatives most often used in expanders are lignosulfonates. These are complex aromatic polyethers, as shown in Fig. 1 [6].

Lignosulfonates have the property of being strong anti-flocculents. As can be seen from their formula, they are composed of a large organic part (R^+) which is hydrophobic and a small inorganic fraction (SO_3^-) which is hydrophilic. They are soluble in water, i.e.,

$$RSO_3Na = RSO_3^- + Na^+ \qquad (1)$$

The hydrophobic part of the RSO_3^- anion will be adsorbed on the surface of the lead particles, and thus have the hydrophilic part of the anion facing out to the aqueous electrolyte phase. This results in an increase in the repulsion potential which prevents the particles from coalescing or sintering.

The most pronounced effect of lignosulfonates on battery performance is the improvement in low-temperature performance at high rates of discharge. Consequently, expanders formulated automotive batteries usually contain a high proportion of organic material.

Many different lignosulfonates have been employed as expanders, and these exert widely different effects on the performance of lead/acid batteries.

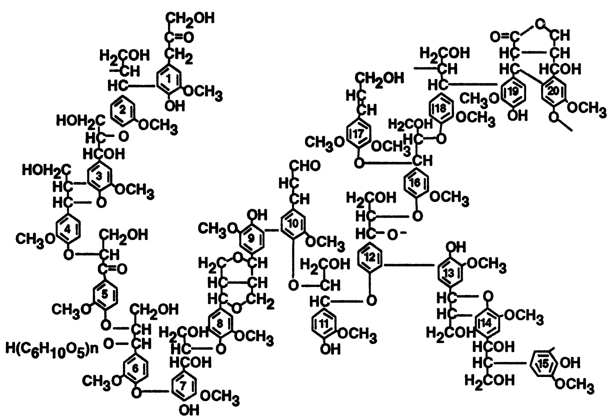

Fig. 1. Constitutional scheme of softwood lignin.

2.3. Carbon

Carbon black is added to the expander to improve the conductivity of the active material during deep discharges where the concentration of highly-resistant lead sulfate is high. It is usually added to the expander formula in an amount equal to the lignosulfonate.

3. Expander compositions for various battery applications

Generally, the applications for lead/acid batteries fall into three major categories. These are characterized by different operating conditions, discharge rates, and depths-of-discharge (DODS).

- Starting, lighting and ignition (automotive), where the battery experiences: low temperature, high discharge rates, shallow cycling, high under-hood temperatures.
- Motive powers, where the battery experiences: moderate temperatures, moderate-to-low discharge rates ($C_5/5$), deep cycling (80% DOD).
- Standby powers, where the battery experiences: moderate temperatures, low-to-high discharge rates, float charging (cell voltage uniformity).

Specific expander formulations have been developed for each of these three applications. Although there are a wide variety of minor differences in the formulae used by various battery manufacturers, the most widely employed today are shown in Table 2.

Occasionally, wood flour and soda ash are used in small amounts in motive-power battery expanders. The wood flour is assumed to act as a slow-release precursor of lignin. Expander is added to automotive battery negative plates at a rate of 0.5–1.0 wt.%, while 2 wt.% is generally recommended for industrial battery applications.

The principal difference in the expanders used in automotive and industrial applications is the ratio of barium sulfate to carbon. In automotive batteries, a high fraction of lignosulfonate (25–40%) is used while in industrial batteries a small percentage of lignosulfonate is employed (3–10%). The high percentage of lignosulfonate in automotive plates is necessary to produce the high cold-cranking amperes required by these batteries. On the other hand, the larger amount of barium sulfate in industrial plates prevents passivation during deep cycling and gives excellent durability.

Table 2
Typical expander formulations for different battery applications

	Automotive	Motive power	Standby
Barium sulfate (%)	40–60	70–90	90–95
Lignosulfonate (%)	25–40	3–10	0
Carbon (%)	10–20	5–15	5–10

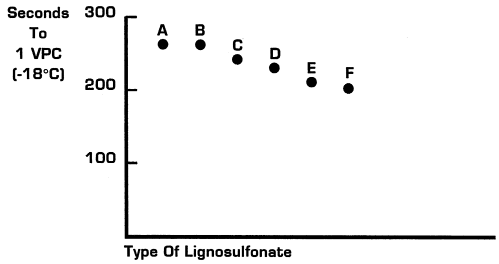

Fig. 2. Cold-cranking performance of various lignosulfonates (VPC = volt per cell).

For standby applications where uniformity of float voltages is important in long cell strings, lignosulfonate is often omitted from the expander. The reason for this is that the organic constituent has a strong effect on the hydrogen overpotential and, accordingly, can cause voltage variations from cell to cell and thus result in the cell string becoming unbalanced.

4. Effect of lignosulfonates and barium sulfate on the initial performance and life of automotive batteries

Both the type and amount of lignosulfonate, and the amount of barium sulfate used in a plate have a marked effect on its performance and life. The following results were obtained from simulated automotive cells that incorporated one negative and two positive plates. They were subjected to a cold-cranking test at 0.1 A cm^{-2} and then cycled using a modified SAE J240 protocol. During the cycle-life test, the cold-cranking test was repeated at 1000 cycle intervals. The effect of various lignosulfonates on the cold-cranking performance of the negative plates is shown in Fig. 2. These were incorporated into a standard commercial expander blend which is widely used in the USA. The effect of the various lignosulfonates is obvious. The effect of the same lignosulfonates on J240 cycle-life is demonstrated in Fig. 3. Major differences can be seen between them. Clearly, proper selection of the lignosulfonate is important to achieve maximum performance and durability from the plate. An important result of these experiments is that the same lignosulfonates that give the best cold-cranking performance also give good durability.

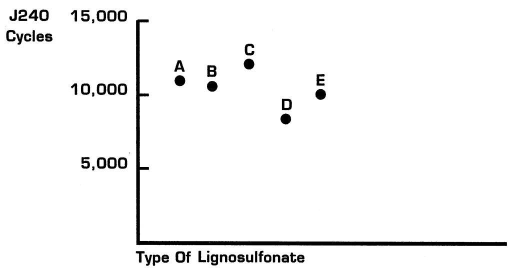

Fig. 3. Life-cycle durability of various lignosulfonates.

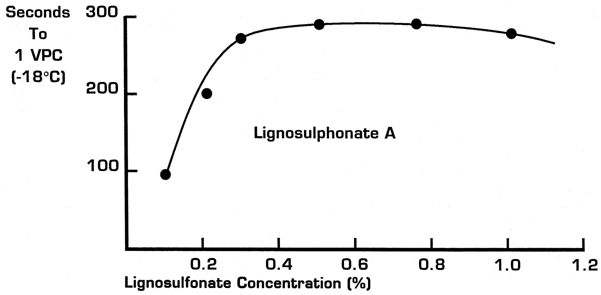

Fig. 4. Effect of lignosulfonate concentration on cold-cranking performance (VPC = volt per cell).

The effect of lignosulfonate concentration in the plate on the cold-cranking performance is given in Fig. 4. For this series of experiments, the amounts of barium sulfate and carbon in the plate were kept constant. The data show that the cold-cranking performance increases as the lignosulfonate concentration is increased up to 0.5 wt.%. Above this amount, the performance declines due to over-expansion of the plate and loss of electrical conductivity.

An important question is: to what extent is the cycle life of the plate affected by the amount of lignosulfonate? The data in Fig. 5 show that increasing the amount of lignosulfonate up to 0.5 wt.% results in an increased in J240 cycle life. At a concentration of 0.75 wt.%, there is no further improvement, while above this, over-expansion causes early failure. The concentration at which lignosulfonate yields the maximum cold-cranking and cycling performance (0.5 wt.%) is considerably higher than that usually employed in automotive batteries (0.25 to 0.40 wt.%). This indicates that there may be an opportunity to improve battery cold-cranking performance by using expander formulations with higher percentages of lignosulfonate.

The effect of increasing the amount of barium sulfate on the cold-cranking performance is shown in Fig. 6. The interesting and, perhaps, surprising result is that cold-cranking performance is independent of the amount of barium sulfate in the plate. It is generally believed that the principal function of the barium sulfate is to provide nucleation sites for the deposition of lead sulfate during discharge, thereby reducing passivation. The observation that the cold-cranking performance is independent of barium sulfate concentration indicates that passivation is not a serious limitation to performance at high discharge cur-

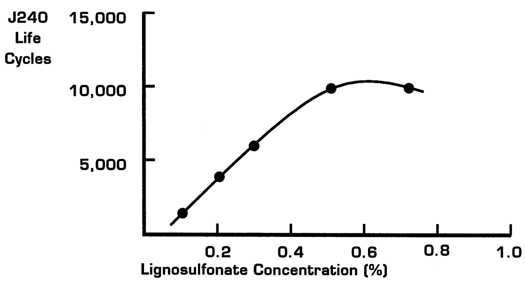

Fig. 5. Effect of lignosulfonate concentration on cycle-life durability.

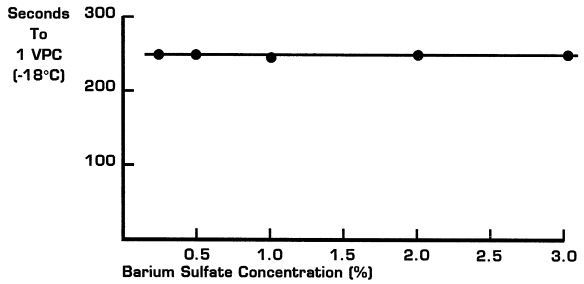

Fig. 6. Effect of barium sulfate concentration on cold-cranking performance (VPC = volt per cell).

rents and low temperatures. Limitation of ion transfer may be a more plausible explanation.

Barium sulfate does, however, exert a significant effect on cycle life, as shown in Fig. 7. The cycle life increases as the barium sulfate concentration is increased up to 1 wt.%. Above this concentration, the cycle life remains constant.

The following conclusions can be drawn from the above data, all of which need to be confirmed by tests on full-sized batteries in a normal operating environment.

(i) The correct choice of lignosulfonate is very important. Both the cold-cranking performance and the J240 cycle-life are significantly affected by the type of lignosulfonate. In general, the lignosulfonate which produces the greatest improvement in cold-cranking performance also yields the largest number of J240 cycles.

(ii) Increasing the amount of lignosulfonate in the plate increases both the cold-cranking performance and the cycle life. The greatest improvement in cold-cranking is achieved with 0.5 wt.% lignosulfonate, while the optimum cycle life is achieved with 0.75 wt.%. At concentrations higher than these, over-expansion becomes a significant problem.

(iii) The amount of barium sulfate in the plate has a negligible effect on initial cold-cranking performance.

(iv) The amount of barium sulfate in the plate has a significant effect on the J240 cycle life. A maximum is reached at 1% barium sulfate.

The results suggest that an increase in the amount of expander from the usual 0.75–1.00 wt.% level to the 1.25–1.5 wt.% level would be beneficial. Future work will concentrate on examining this in full-sized batteries in normal operating environments. This work has not examined possible interactions between the barium sulfate and lignosulfonate concentrations. These are being explored in further experiments on single plates.

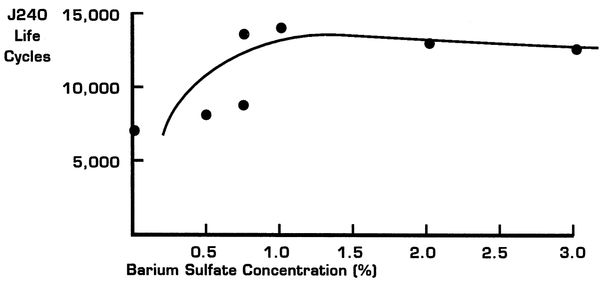

Fig. 7. Effect of barium sulfate concentration on cycle life.

5. Benefits of pre-blended expanders

It is still common in some parts of the world for battery manufacturers to add the individual expander ingredients directly into the paste mixer. It is a far better practice, however, to pre-blend and weigh the expander before it is added. The benefits are:

- precise control of the weights of the ingredients;
- precise control of the bag weights;
- bag weights are ‘customized’ to match the manufacturer’s addition rate and size of paste batch;
- every expander batch is tested for formula control;
- reduced inventory; three SKUs are replaced by one;
- reduced waste disposal;
- fewer paperwork transactions (purchase orders, receiving, record keeping, etc.);
- elimination of errors in paste mixing;
- better paste-mix uniformity;
- lower cost.

6. Conclusions

The expander exerts a profound influence on the performance and the durability of the negative plate. Different lignosulfonates have very different performance characteristics. Therefore, the correct selection of expander is very important. Thorough electrochemical testing is required to select from the many lignosulfonates that are available.

The correct expander blend of lignosulfonate and barium sulfate is important to achieve the optimum performance from the battery on its particular duty cycle.

Precise blending and control of batch weight are necessary to achieve uniformity and repeatability in plate characteristics. A pre-blended expander formulation is the best way to achieve the required level of control and consistency, and does this at the lowest cost.

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