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Comparison of methods for adding expander to lead-acid battery plates—advantages and disadvantages

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Abstract

Expanders are an essential component of the negative plates of lead-acid batteries. They increase the surface area and stabilize the structure of the negative active material. They can be added to the negative paste mix in a number of ways and each of these has advantages and disadvantages. The individual components can be added to the paste mixer during paste preparation or they can be pre-mixed before addition. This pre-mixing can be done by the battery manufacturer or by companies that specialize in expander manufacture. This paper reviews the different ways in which expander can be added to negative paste mixes and discusses the consequences of each method. It concludes that the simplest, lowest cost and most risk-free option is to purchase pre-blended expander from a recognized supplier.

Keywords: Barium sulfate; Carbon black; Lead-acid battery; Lignosulfonate; Negative plate; Pre-blended expander

1. Introduction

Expanders are materials that are added to the negative plates of lead-acid batteries to improve their performance and life. They are generally composed of three principal ingredients, viz., barium sulfate, lignosulfonate and carbon black, each of which has a specific function in the negative plate [1,2]. For example, barium sulfate acts to provide sites for nucleation of lead sulfate during battery discharge. Barium sulfate has similar unit cell dimensions to lead sulfate, as shown in Table 1. This similarity of structures facilitates the formation of small crystals of lead sulfate in the negative active-material in preference to the formation of large crystals that are difficult to recharge.

The lignosulfonate is strongly adsorbed on the surface of the active material and induces a fine, porous crystal structure. An example of this behaviour given by a widely-used lignosulfonate is shown in Fig. 1. The lignosulfonate increases the specific surface area from $\sim$0.2–0.8 $m^2 g^{-1}$. The effect of a number of lignosulfonates on the specific surface area of negative active-material is shown in Fig. 2. This increase in surface area reduces the effective current density during discharge and thereby, increases utilization of the active material. This effect is particularly important at low temperatures and at high rates of discharge and is the principal reason why automobile battery expanders use a high dosage of lignosulfonate.

The function of the carbon black is to increase the conductivity of the negative active-material to assist in the initial charging of the battery (formation). Until recently, it has been thought that once the active material has been charged (lead sulfate converted to lead), the carbon has little influence on its behaviour. This belief has recently been challenged by the discovery that high levels of carbon and/or graphite in the negative plate have a beneficial effect on battery life [3–5].

2. Methods of adding expander to negative plates

Expanders are always introduced into the negative active-material during the paste-mixing process. They were first developed in the 1940s and at that time the separate components were weighed and added to the paste by hand at the paste-mixing station. Variants of this were sometimes used where the components were placed in a bucket and slurried with water before being added to the paste. There are still battery manufacturers using these procedures today.

In some factories, systems have been installed that automatically mix the components with water and add them to the paste mixer. These can be as simple as continually agitated tanks to which the solids and water are added and

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Table 1
Structural characteristics of barium and lead sulfates

	$BaSO_4$	$PbSO_4$
Cation–O bond length (Å)	2.952	2.87
S–O bond length (Å)	1.478	1.490

from which the contents are dispensed, or dry mixing either by ball mills or ribbon blenders after which the material is packaged into bags for use in the paste-mixing process.

3. Benefits of pre-blended, packaged expanders

The principal reasons why battery manufacturers have adopted pre-mixed expanders is that this simplifies the process and reduces the risks and cost associated with the earlier methods.

4. Manufacturing technology

The most important processes in expander manufacturing are mixing and packaging. In the mixing operation, the individual components are usually blended in a ball mill or high intensity ribbon blender. Both methods produce acceptable expanders; the type of carbon black in the expander determines which method is used. Ball milling is always chosen when granulated carbon black is used because an aggressive attrition between the grinding medium and the material is required to break down the granules. High intensity ribbon blending can be employed when powdered carbon is selected. Important factors in ball milling are accurate batching, the correct ratio of grinding medium to components, the speed of rotation and the time of milling. When ribbon blending, the principal requirements are accurate batching and blending time. The objective is to achieve a homogeneously blended material that is identical from batch to batch. Examples of a ball milling and a high intensity blending operation are shown in Fig. 3a and b.

Pre-blended expanders are packaged in bags that contain the exact amount of material required for a customer's paste mix. It is essential that the bag weights are extremely repeatable. Because battery manufacturers use a variety of paste-mix weights and formulae, the packaging system must be flexible as well as accurate. A typical packing station is shown in Fig. 4.

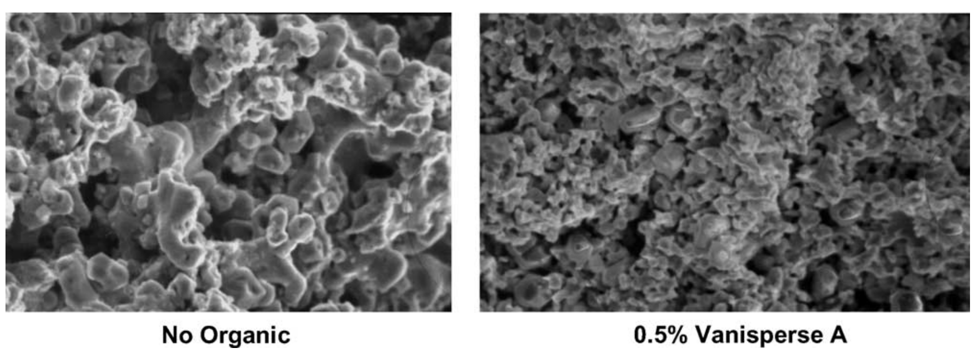

Fig. 1. Effect of lignosulfonate on structure of negative active-material.

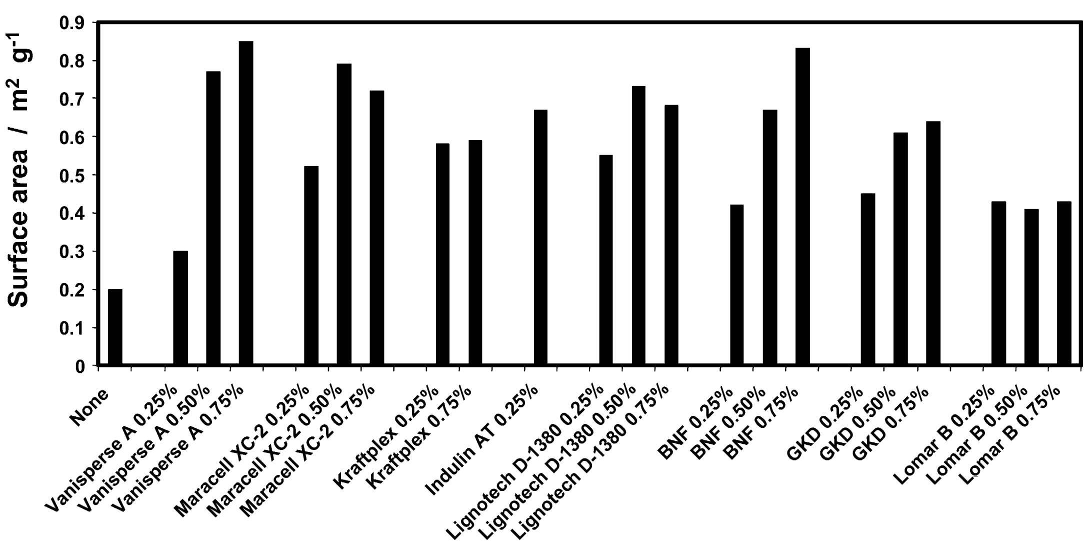

Fig. 2. BET surface-area of formed negative active-material with various organic additives (additions are in wt.%).

(a) (b)

Fig. 3. (a) Ball mill used for expander blending and (b) high intensity of ribbon blender used for expander production.

5. Cost factors

Since expander manufacturers purchase materials in much greater quantities than individual battery manufacturers, they can obtain the materials at lower cost. Large-volume manufacturing also reduces the cost per kilogram of expander produced. Adding individual components or a slurry to the paste mixer is also inherently more expensive than adding the contents of a bag.

The total cost of adding expander materials or making expander in the battery plant includes many actions.

- Several materials have to be purchased, namely: (i) carbon black; (ii) various types of lignosulfonate; (iii) different types of barium sulfate, e.g. blanc fixe, barytes and (iv) wood flour.
- This adds cost for: (i) purchasing; (ii) receiving; (iii) storage; (iv) inventory control; (v) space and (vi) administrative paperwork.
- Mixing the materials or adding them to the paste at the mixing station also adds cost for: labour, e.g. handling, weighing, equipment maintenance, waste disposal; (ii) capital; (iii) energy and (iv) replacement parts.

Fig. 4. Packing station for expanders.

6. Quality factors

The most important issue is the increased risk of errors involved with self-mixing. The most diligent workers will inevitably make mistakes and the best maintained equipment can malfunction. This introduces the possibility that the amounts of individual components or the total amount of expander may be variable from mix to mix. Since it is not possible to test the expander before it is added to the paste mixer, these errors will not be detected until after the batteries are produced. They may not even be detected until the batteries have been placed into use, which would result in customer dissatisfaction and warranty claims. This is the most frequently cited reason for using pre-blended expanders in customer satisfaction surveys.

Pre-blended expanders eliminate most of these costs and risks. Most of the administrative costs are removed because only one stock-keeping unit has to be purchased. The expander is supplied in bags containing the exact weight of material for a paste mix and, therefore, the only manufacturing operation is to open the bag and empty the contents into the paste mix. This considerably simplifies the paste-mixing process by eliminating the need to weigh and blend materials in the battery plant. Clearly, this gives savings in both labour and equipment costs.

The risk and uncertainty associated with expander addition are also eliminated since pre-blended expanders are tested for both composition and weight before they are shipped. Most expanders are shipped with a certificate of conformance that verifies that the expander meets the specified composition and weight.

7. Quality assurance testing

A variety of tests are carried out to verify composition. These include:

(i) ash content following incineration; this gives an overall indication of conformation to the formula;

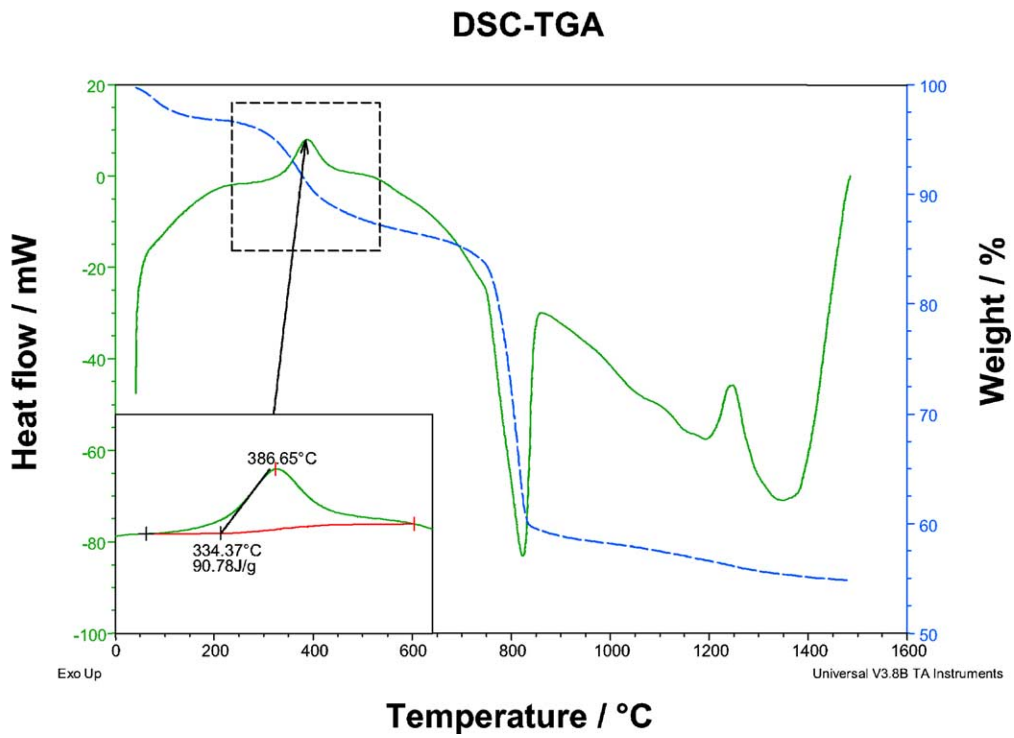

Fig. 5. Typical DSC−TGA data for an expander.

(ii) UV spectrophotometry for determination of lignosulfonate content;
(iii) differential scanning calorimetry (DSC) coupled with thermogravimetric analysis (TGA) to determine the concentrations of the individual components;
(iv) inductive coupled plasma for metallic impurities.

A typical DSC−TGA graph taken from an expander composed of lignosulfonate, barium sulfate and carbon is shown in Fig. 5.

Expander manufacturers also provide assistance with expander selection. After years of working with battery manufacturers in all applications, they have developed proven formulae for every type of battery and all battery applications. These expanders are used by most battery manufacturers world-wide and are proven by experience. In addition to their own proprietary formulae expander manufacturers custom blend materials for clients who prefer to use their own compositions. Expert advice is also available to assist battery manufacturers with selection, application and problem solving.

8. Electrochemical testing

A further benefit from working with a recognized expander manufacturers is that they maintain well-equipped laboratories for electrochemical testing, as well as for research and development. All expanders are tested electrochemically before they are released for use by the industry.

Table 2
Examples of expander electrical tests

Automotive	Industrial
Cold-cranking	Capacity
Reserve capacity	Cycle-life
Charge acceptance	Float behaviour
Gassing	
Life cycle	
SAE J537 (USA)	
BS 3911 (UK)	
DIN 43539 (D)	
JIS 5301–1991 (Japan)	

These tests are conducted for single cell, i.e. during the research and development phase, through to large-scale battery tests. Equipment is available to perform all the common automotive and industrial battery tests. Examples of the tests that are routinely conducted are shown in Table 2.

Expander technology is not static. At present, more expander work is being undertaken than at any time in the past. This is because the battery industry is pursuing improvements to existing products and is developing new products for emerging markets such as electric and hybrid electric vehicles.

9. Conclusions

Battery manufacturers use a number of methods to add expander to negative paste mixes. Adding materials directly to the paste mixer, or mixing the ingredients in the battery plant before addition, involves unnecessary costs and risks. Purchasing pre-blended expanders from a specialist supplier is the simplest, most cost-effective and most risk-free option.

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