

MECHANISMS BY WHICH ORGANIC EXPANDERS IMPROVE THE PERFORMANCE OF LEAD/ACID BATTERIES*

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Introduction

The role of the organic expander in modern lead/acid batteries was discussed during the Second Asian Battery Conference [1]. In particular, attention was paid to the development, manufacture and performance of expander materials. Other workers have carried out extensive research on the influence of expanders on the electrochemical [2], electrical [3 - 5], morphological [6, 7] and chemical [8, 9] properties of the battery. Nevertheless, relatively few of the recent studies have been devoted to understanding the action of expanders on the dimensional structure of the formed porous negative paste. This is surprising given the fact that the role of the expander is vital to the performance characteristics of the battery. Investigations of the electrode structure have concentrated [10, 11] mainly on the problem of the growth of lead sulphate crystals during the discharge of the battery. By contrast, far too little concern has been shown over the complex problems of the particle distribution in the negative material prior to the pasting process, the structure (or formation) of the 'sponge' in the negative plate, or the influence of the expander during the mixing operation of the negative-paste components.

Given the basic requirements of maximum homogeneity and an as even as possible distribution of the component particles in the negative paste, it is essential to avoid the development of agglomerates of these components during plate processing. Agglomerates both reduce the relative surface area and weaken the adhesive bond between particles. The former decreases the plate capacity, whilst the latter impairs its mechanical strength and hastens the disintegration of the negative material. Thus, a closer study must be made of the behavior of the negative-paste components in terms of their distribution and dispersion. The ability of the expander to control such parameters is examined in this paper.

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Experimental procedure

Simple systems serving as representative examples of battery paste were prepared separately from individual samples of lead, lead oxide, or water-insoluble inorganic and organic compounds. The particle-size range was below 10 μm . The dispersions were prepared in water containing various concentrations of selected dispersants; strong mechanical stirring was applied. In these experiments, the term 'dispersing power' was defined as the concentration of a given dispersant that was required to produce a given apparent viscosity (or plasticity) of a certain type of material at a constant concentration in water. A range of dispersants potentially applicable as battery expanders was examined. The dispersing tests were conducted with a high speed ATO-Mixer and the apparent viscosity was measured with a Brookfield viscosimeter. Random samples were subjected to optical microscopic examination in order to determine the degree of agglomerate formation.

Results

Initial dispersion tests showed that carbon black was the only component of the negative paste that was difficult to disperse. The remaining components were not, therefore, subjected to further examination. Rather, because of the strong tendency of carbon black to form large agglomerates in water (Fig. 1(a)), work was directed towards methods for dispersing this component. To this end, carbon black of differing quality was dispersed in water (at concentrations: 15 wt.% to 35 wt.%) by the stepwise addition of expanders (dispersants).

The viscosity of the carbon black dispersions exhibits a rapid fall in value when the dispersant dosage reaches a certain level (Fig. 2). Following this, a dramatic change is observed in the consistency. Repetition of this experiment with different carbon black types of known relative surface area revealed a linear relationship between the surface area and the optimum dispersant addition that causes the sudden reduction in viscosity.

A commonly accepted simple model of dispersion, or deflocculation, assumes that the hydrophobic endings of the dispersant molecules that are

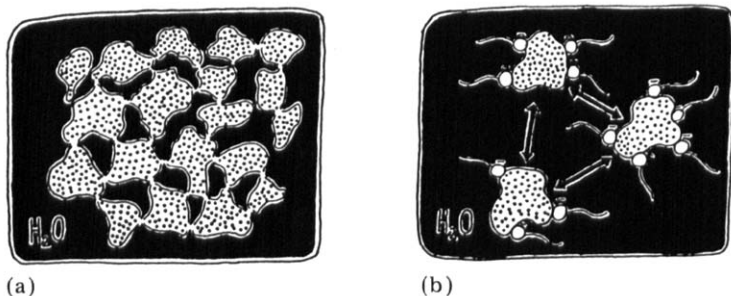


Fig. 1. (a) Agglomerate formation of carbon; (b) agglomerate-free dispersion.

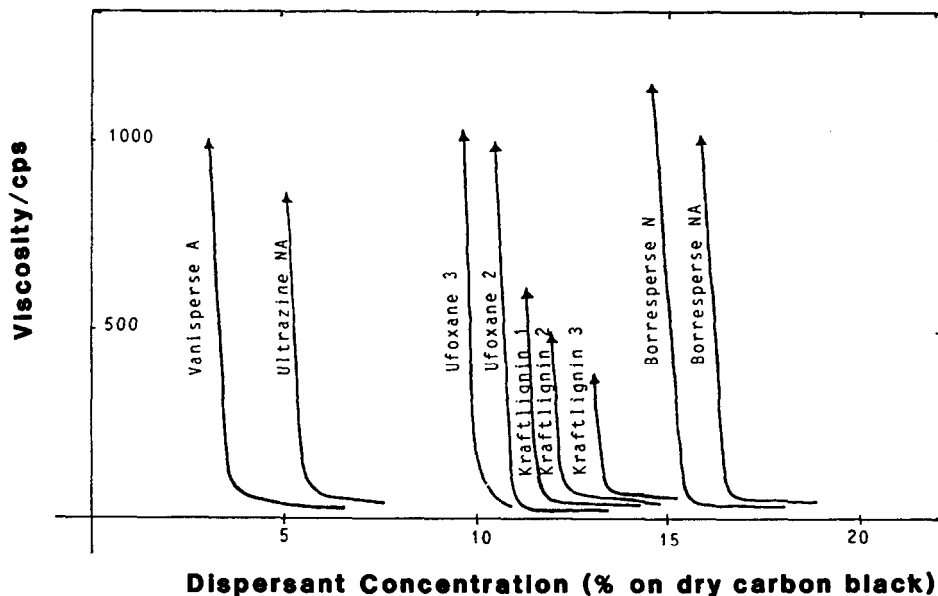


Fig. 2. Dispersion of Statex R carbon black (30 wt.%) in water by expander materials as indicated.

attracted to the solid particles and the hydrophilic endings that are oriented towards the surrounding humidity will, as a result of the forced movement caused by the agitation, cover the surface of the solid particles with a film of the dispersant. In the case of the anionic dispersants investigated here, the particles receive a negative electrostatic charge and are forced apart from each other. Since the film of dispersant molecules adsorbed on the particle surface is assumed to be elastic, and collisions between elastic film-covered particles maintain a certain Brownian movement, the stability of the dispersion is assured.

The film-covered particles in a deflocculated system of low water content of the type found in a battery-plate paste cannot be truly characterized as a 'dispersion'. More correctly, the paste should be described as a deflocculated plastic body. The consistency of such a body is more difficult to measure than the apparent viscosity of a fluid. There are a number of consistometerers available for industrial applications, most of them are constructed for a specific purpose. Although these instruments can control the production to within narrow maximum/minimum values, the Brookfield viscosimeter is more acceptable as a general purpose measuring instrument. In summary, it is concluded that an optimally dispersed system consists of single particles, each covered with a monomolecular film of the dispersant. The system remains optimally deflocculated, or plastified, even when a considerable reduction in the water content produces a plastic body.

Discussion

Values of the dispersing power of the tested expanders are plotted in Fig. 2 for comparison purposes. Noticeable differences in dispersing action are found between quite similar products. The most remarkable of these is exhibited by Vanisperse A and Borresperse NA which are both sodium lignosulphonates. Small improvements in the quality (*e.g.*, the purification) of the lignosulphonate can yield appreciable enhancement of the dispersing power. The ranking of the organic expanders according to dispersing power is the same as that found by other authors [3, 6, 9, 12, 13] from comparative tests in which electrical capacity, cold-start capacity, cycle life and other vital parameters of the battery were investigated with expanders of different grades of purity and sophistication.

A few random tests to determine the dispersing power of huminates (van Dyke Brown, Kasseler Braun) and tannins (Quebracho, Mimosa, Chestnut extract) did not reveal any measurable effects. As stated by Brennan and Hampson [3], these and similar products 'have now been superseded by expanders based on lignosulphonic acid'.

In the case of lignosulphonic acid derivatives, a study of the influence of different cations on the electrical parameters of the battery was considered to be of value. The results showed, in agreement with Mahato [13], that sodium exerts 'by far' the strongest effect on the dispersing power.

Conclusions

An expander must provide the negative paste with a perfectly deflocculated, agglomerate-free structure. In addition, it is obvious that the mixing equipment and process control must be adequate to produce a battery of high quality. The dispersing power test shows that the high purity Vanisperse A expander is the best material for negative plates. This sodium lignosulphonate is obtained from Norwegian Spruce and is a low molecular weight fraction of the original lignin compound. Vanisperse A is probably the most widely used organic expander in the battery industry. The second best group of lignosulphonates is the Ultrazine and Ufoxane products purified by ultrafiltration. More modest dispersing power is shown by the common Borresperse desugared, unmodified sodium lignosulphonates. The efficacy of North American Kraftlignin products falls between the ultrafiltrated and the desugared lignins.

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