Interactions between lignosulphonates and the components of the lead acid battery. Part 2. Interactions with the electrolyte and lead sulphate growth

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Abstract

Several lignin based expanders underwent various physical and chemical tests. The results were compared with life time measurements for batteries with the same expanders. The aim was to gain understanding of the interactions between the expanders and the other components in the lead acid battery, and also, if possible, to find a quick and reliable screening test for the life time of batteries. The low pH of the sulphuric acid electrolyte will give both hydrolysis of the lignins and condensation. Hydrolysis seems to be detrimental to the performance. The lignosulphonate expanders seem to promote a dissolution–precipitation mechanism for lead sulphate formation.

1. Background

Expanders in lead acid batteries influence the size and shape of the lead sulphate particles formed during discharge [1–7]. In previous work [8] we looked at the interactions between the lignosulphonate expander and the different solid phases present in a lead acid battery. In this work we will look at the interaction with the electrolyte, that is sulphuric acid, and the lead ions dissolved in the sulphuric acid.

The expander greatly improves the performance of starter, lightning and ignition (SLI) batteries. The cold cranking ability is greatly improved, and the life time of the battery is several times longer than without the expander. Many natural and synthetic organic compounds have been used for this purpose [1]. Lignosulphonates have proven to be very well suited as expanders [1, 2, 9].

The construction and testing of batteries is a time and energy consuming process. Several simple tests to screen the expander have been suggested. In this work we investigate whether simple properties of the expander can be used to predict to expander performance, and thus speed up the development time for new expanders. Understanding of the mechanism responsible for the performance of the expanders is also needed.

2. Experimental

2.1. Surface tension

The surface tension was determined by a Cenco de Nouÿ tensiometer with a platinum ring. The solutions used were 0.01–5% lignin in a phosphate buffer at pH approximately 6, or in unbuffered sulphuric acid solutions. The temperature was 23 °C. The values given are the average of three measurements. The experimental uncertainty is less than 0.2%. The surface tension is a measure of the surface activity of the lignins.

2.2. Precipitation pH

The precipitation pH was determined by dissolving the lignosulphonates in water and adding sulphuric acid until a precipitate or cloudy solution formed. Solutions with lignin in 6% sulphuric acid were filtered and the molecular weight distribution determined for the soluble fraction in this acid.

2.3. High temperature stability

The high temperature stability was determined in two different ways. 2500 ppm of the lignosulphonates were dissolved in sulphuric acid at three different strengths, e.g. pH 1, pH 3 and pH 5. The solutions were kept at room temperature, at 65 °C, and at 105 °C. The molecular weight distributions were checked at different times.

The high temperature stability was also determined in a solution of 4.16 g lead oxide, 17.17 g sodium sulphate and 14.95 g 36% sulphuric acid diluted to 1.0 l. The pH of this solution was 1.88. About 1.0 g of each of the lignosulphonates were dissolved in 20 ml of this solution and heated to 65–70 °C for 5 days. The samples were
filtered off, dried and weighed. The percentage insoluble material was calculated. This gives a measure of the survival of the lignins in a battery environment.

2.4. Molecular weight distribution

Molecular weights were determined on a Jordi Glucose DVB 10000 Å column. The mobile phase consisted of 10% DMSO in water buffered to pH 10.5 with a sodium hydrogen phosphate buffer and 0.1% SDS added. A Spectra System AS3500 sampler, P4000 pump, and UV2000 detector were used. The software allows the calculation of the different molecular weight averages \((M_n, M_w, M_z\) and \(M_{z+1}\)) as well as polydispersity. The molecular weights are given relative to two in-house standards with \(M_w\) of 68 000 and 8300 Da, respectively. The relative values of the different lignosulphonate fractions are accurate to ±2000 Da, while the absolute values depend on the accuracy of the standards. For the purpose of this study, the absolute molecular weights are of less importance.

2.5. Changes in the lignins

In some cases, it was necessary to look in more detail at the changes in the expanders. Standard methods for characterising lignosulphonates were employed. Details of these methods have been given earlier [10]. Details of the composition of the expanders are given in Table 1.

2.6. Particle size distribution

The particle size distributions of the substrates were determined on a Microtrack X100 particle size analyser. Water was used as the fluid carrier. Each result is the average of three measurements. The suspensions were dispersed by ultrasound for 60 s before measurements.

2.7. Chemicals used

Sulphuric acid was a technical grade supplied by Borregaard Base Chemicals. All other chemicals were of analytical grade.

Lead oxide was from Alfa. The carbon black used was Cabot Elftex 460. Sodium sulphate, sodium dihydrogen phosphate, potassium chloride, sodium hydroxide, and acetic acid were all from E. Merck.

The lignosulphonates are commercially available (Vanisperse A) or experimental products from Borregaard LignoTech. Details of the expanders’ compositions and performances are given elsewhere [10].

2.8. Crystal growth

22.32 g (0.1 mol) lead oxide in 90 ml water and 0.056 g lignosulphonate in 10 ml water were mixed and heated to 80 °C with stirring. 46 ml 34% sulphuric acid was added drop wise. The solution was left standing for 4 h. The crystals were dried at 105 °C overnight before particle size determination.

3. Results and discussion

3.1. Precipitation pH

Sulphuric acid makes up the bulk of the volume of lead acid batteries. The lignins contain several functional groups that can be ionised. The most important are phenolic hydroxyl, carboxylic acids and sulphonic acids. The \(pK_a\) values of these groups are \(\approx 10, \approx 4, \approx 1.5\), respectively. This means that the number of dissociated groups, and thus the solubility, will be strongly pH dependent for the lignosulphonates. If the pH is lowered the solubility decreases, at some pH the lignins will precipitate out of solution. In Figure 1 the precipitation pH for a number of lignins are given as a function of their organic sulphur content. About 1% organic sulphur is in the form of unknown groups, while the rest is from sulphonic acid groups. We see from Figure 1 that with a high sulphonic acid content the lignosulphonates are soluble over the pH range found in a lead acid battery. More details about these expanders can be found elsewhere [10].

The solubility was also determined directly in gram per litre at three different pH values. The results are

<table>
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<th>Expander</th>
<th>(M_n) kDa</th>
<th>(M_w) kDa</th>
<th>–OMe %</th>
<th>S %</th>
<th>COOH %</th>
<th>–CHO %</th>
<th>CO %</th>
<th>–OH %</th>
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