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Short communication

A technology for production of a "Cureless" paste containing a high concentration of tetrabasic lead sulfate and a low concentration of free lead

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Abstract

The conventional paste used to produce plates for lead-acid batteries comprises a mixture of leady oxide, water and sulfuric acid. Fibre and other additives, such as expander in negative plates, are added to improve paste properties and battery performance. Following pasting of the plates, they have to be cured to provide the correct chemical composition and crystal morphology, and to oxidize any residual free lead metal to lead monoxide. The desired result of the curing process is a positive plate with a high concentration of uniformly sized tetrabasic lead sulfate (4BS) crystals and with both positive and negative plates having a low concentration of free lead. Curing is a time-consuming and expensive process, which requires large numbers of chambers capable of being heated to 85 °C and containing an atmosphere with a relative humidity greater than 95%. This process adds significant cost to the battery.

Keywords: Lead-acid batteries; Positive plates; Curing; Pasting; Crystal morphology

1. Introduction

Curing is one of the most critical processes in the production of plates for lead-acid batteries. During this operation the correct chemical composition and crystal morphology of the active material are established and residual free lead from the precursor leady oxide is oxidized to lead monoxide. It is now generally accepted that the chemical composition of the positive plate should comprise a high concentration of tetrabasic lead sulfate (4BS) with small residual concentrations of tribasic lead sulfate (3BS), unreacted lead monoxide and free lead. The total concentrations of the basic sulfates are, of course, dependent on the amount of sulfuric acid added to the paste mix. The reason why a high concentration of 4BS is preferred is that it produces a durable formed positive plate structure that resists cycling-induced degradation leading to longer battery life. 4BS is not considered necessary in negative plates because the formed active material is lead metal, which unlike the positive plate, is protected from structural breakdown by expander.

4BS is difficult to produce and requires use of chambers maintained at approximately 85 °C and >95% relative humidity. A common problem with the conventional process is that the chemical composition of the resultant plates is frequently not uniform yielding variable amounts of 4BS and also a wide range of 4BS crystal sizes ranging from 10 to 50 μm. A typical example of positive plate morphology from conventional processing is shown in Fig. 1.

The wide range in size of the 4BS crystals is easily seen. The large crystals have a low surface to volume ratio, which results in high current density during formation. This reduces formation efficiency resulting in increased time. The variable crystal sizes lead to variable charge acceptance with subsequent variability in initial battery performance. This is the principal reason why it is a common belief that it is more difficult to form a plate composed primarily of 4BS than one with a corresponding concentration of 3BS (where the average crystal size is of the order of 5–10 μm). However, past comparisons involved both chemical and crystal size differences and the latter may be the principal reason for

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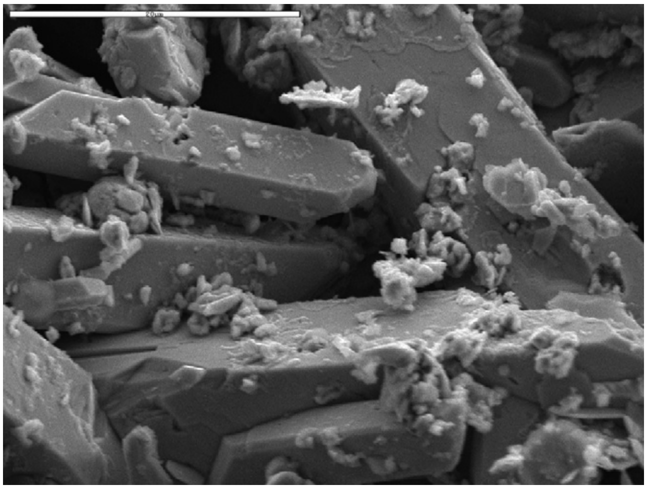

Fig. 1. A typical example of tetrabasic lead sulfate crystal morphology from conventional curing (magnification = 3000 and the scale bar = 20 μm).

the different degrees of charge acceptance. This may not be the case if the crystals are the same size.

Other common problems include the time to complete the curing process, sometimes as long as 5 days. This creates a need for large numbers of curing chambers and, consequently, high capital and energy costs. Overall, the curing process is labor, capital and energy intensive and the composition of the plates is frequently variable which leads to reduced reproducibility in batteries made from them.

Development of a plate making process that eliminates curing would clearly be of great value to the lead-acid battery industry. This requires that the pasted plates have the desired chemical composition and crystal morphology immediately after pasting so that they only require drying before assembly. To achieve this it is necessary to produce a paste that contains high 4BS and low free lead concentrations. In this paper we will report on progress towards development of such a "cureless paste" for positive plates. It provides plates having a high concentration of 4BS and a low concentration of free lead immediately after pasting and which only require drying to be ready for assembly. The process is described and data will be presented that demonstrate how formation of 4BS and elimination of free lead take place.

2. Experimental

There have been previous attempts to produce a cureless paste from use of pure 4BS as a positive paste material [1] and by a variety of methods to produce 4BS *in situ* during paste mixing [2–8].

In previous papers [9,10] we have shown that 4BS can be produced in the paste with use of a 4BS nucleation additive without the need to change conventional paste mixing processes or equipment. Fig. 2 shows an example of 4BS formation in a typical automotive battery paste with the addition of 1% of SureCure® (4BS with a median particle size of 1 μm) during the mixing process. These data were obtained from a battery plant using an Oxmaster paste mixing system. It can be seen that 4BS forms rapidly following sulfuric acid addition with a concentration between 50% and 60% in the finished paste. Further formation occurs after the paste is dispensed into the feeder and during pasting and tunnel drying. At the end of the pasting line 4BS concentrations of the order of 70% are achieved which, for the amount of sulfuric acid in the paste mix, represents full conversion. This formation of 4BS in the pasted plates eliminates the need for high temperature curing chambers.

The remaining obstacle to production of a cureless plate process is the removal of free lead. A finished paste produced from Barton leady oxide having a free lead concentration of ∼25% will have free lead in the range of 10–14%, showing that approximately half of the free lead is oxidized during paste preparation. It is reasonable to assume that precursor oxides with a decreased amount of free lead would exhibit lower amounts of free lead in the finished paste. A number of experiments were carried out

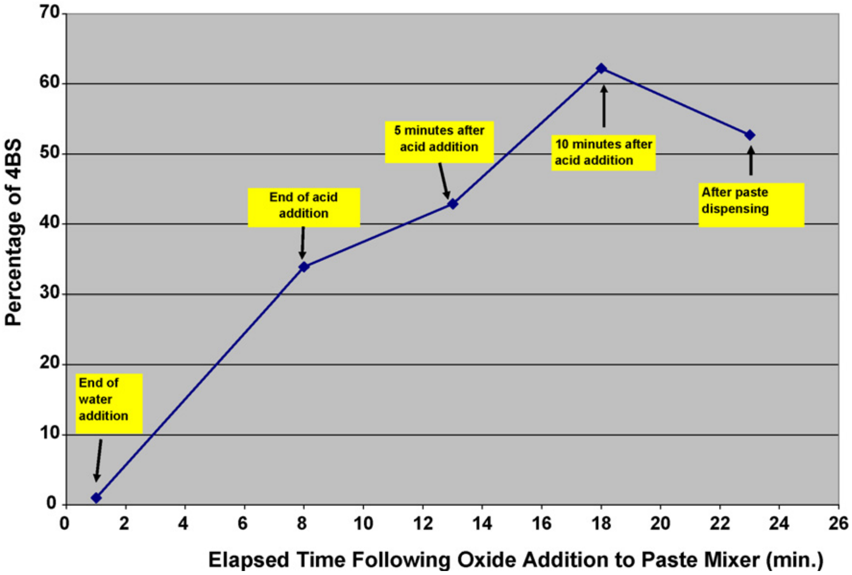

Fig. 2. Formation of 4BS during paste mixing with addition of 1%, 1 μm 4BS to oxide.