

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.

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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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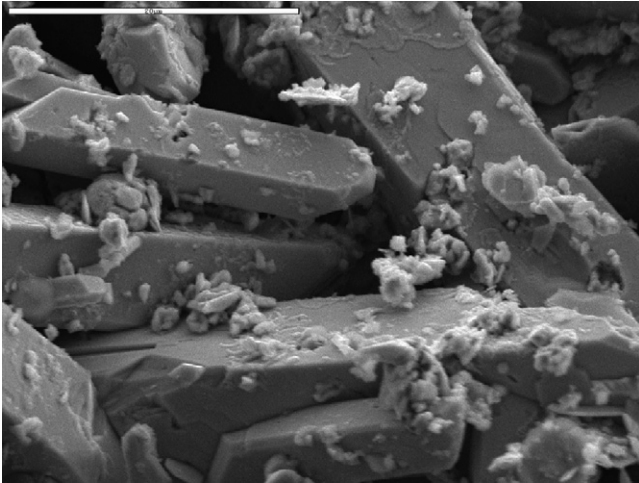


Fig. 1. A typical example of tetrabasic lead sulfate crystal morphology from conventional curing (magnification = 3000 and the scale bar = 20 μm).

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 $\sim 25\%$ 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

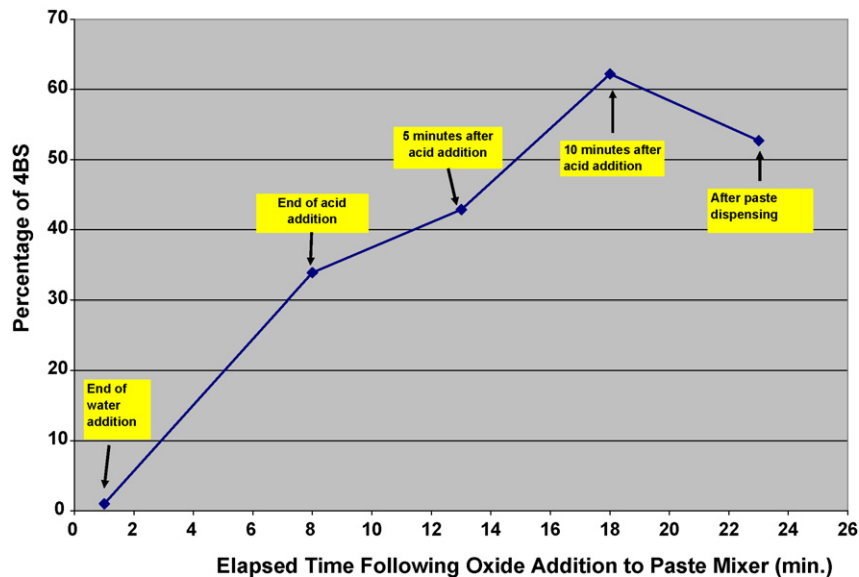


Fig. 2. Formation of 4BS during paste mixing with addition of 1%, 1 μm 4BS to oxide.

Table 1
Characteristics of oxides used in curing experiments

Properties	Conventional leady oxide	Low free lead leady oxide	Pure lead monoxide 1	Pure lead monoxide 2
Pb (%)	25	15	0.15	0.15
Tetragonal PbO (%)	70	70	–	–
Orthorhombic PbO (%)	5	15	99.85	99.85
Apparent density (g cm^{-3})	1.3	1.7	1.7	1.7
Acid absorption (mg g^{-1})	175	191	148	146
Median particle size (μm)	2.2	2.3	4.5	4.5

using leady oxides with lower than normal concentrations of free lead and also with lead monoxide having less than 0.2% free lead. One percent of pure 4BS with a median particle size of $1 \mu\text{m}$ was added to each paste mix (Hammond Lead Products SureCure® brand).

Table 1 shows the characteristics of the oxides used in these experiments.

The conventional oxide is typical of Barton oxide used for automotive battery production. The low free lead oxide (Pb = 15 wt.%) was also produced in a Barton reactor but at a higher operating temperature. This accounts for the higher concentration of orthorhombic PbO. The other two oxides were lead monoxides that were produced from the low free lead oxide by two different methods. Pure lead monoxide 1 was produced from conventional leady oxide by heating at 550°C for 6 h in a furnace equipped with rotating ploughs. Pure lead monoxide 2 was produced by an alternate method where the leady oxide is conveyed with heated high velocity air through a series of heated toroidal tubes. This produces lead monoxide with greater chemical reactivity. The lead monoxide samples were not milled resulting in larger average particle sizes and lower acid absorption values.

2.1. Experimental

Paste mixes were prepared in a laboratory scale paste mixer with the following formula:

- Oxide, 45.5 kg.
- Water, 5 l.
- Sulfuric acid (S.G. = 1.400), 3.6 l.
- Flock, 22.8 g.
- Tetrabasic lead sulfate, 0.455 kg.

The pastes were made by adding the oxide, 4BS and flock to the paste mixer and dry mixing for 1 min. The water was added and mixing was continued for 1 min followed by addition of the sulfuric acid over an 8 min. period. Peak paste temperatures were recorded. Mixing was continued until the pastes had cooled to $<49^\circ\text{C}$ at which point the densities were measured.

Paste properties are shown in Table 2. The pastes were hand pasted onto automotive battery grids having dimensions of 137.8 mm wide, 102.9 mm high and 1.34 mm thick and were stacked in groups approximately 13 cm high for drying in a Thermomax Model SM-8C environmental chamber. While loading the chamber the temperature and humidity were controlled at 54°C and 95% R.H., respectively. Loading could take as long

Table 2
Properties of positive pastes used in curing experiment

	Peak paste temperature ($^\circ\text{C}$)	Density (g in.^{-3})
Conventional leady oxide	72	4.20
Low free lead leady oxide	73	4.20
Pure lead monoxide 1	76	4.18
Pure lead monoxide 2	76	4.18

as 1 h depending on the number of plates pasted. Immediately after loading the plates were dried at 65.5°C and 75% R.H. until the water content was $<2\%$. Plates were extracted from the chamber at intervals to track the progress of 4BS formation by XRD, and free lead oxidation and water content by chemical analysis. Scanning electron microscope images of the dried plates were obtained.

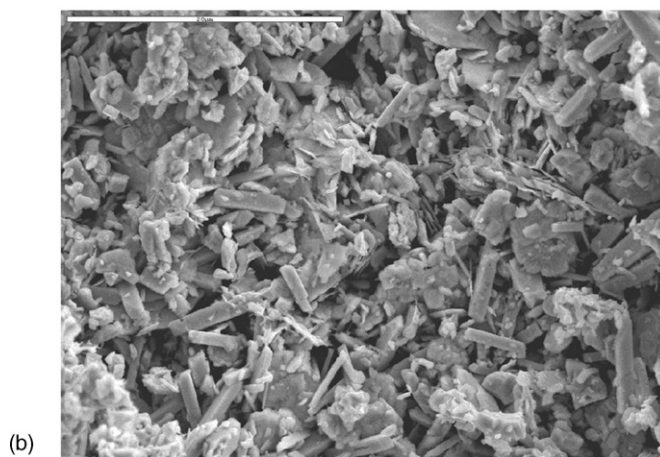
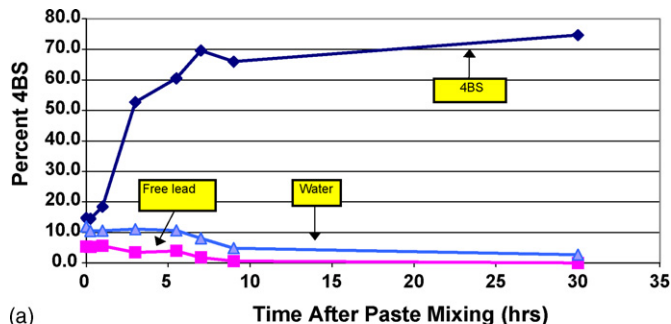


Fig. 3. (a) 4BS, free lead and moisture concentrations of plates produced from standard leady oxide during drying at 65.5°C and 75% R.H. (b) Scanning electron microscope image of dried plate produced from standard leady oxide (magnification = 3000 and the scale bar = $20 \mu\text{m}$).

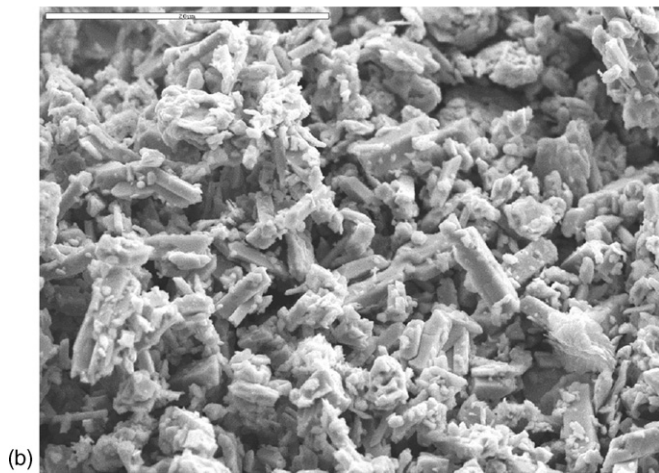
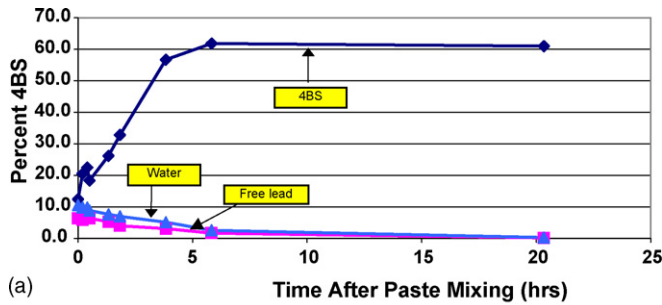


Fig. 4. (a) 4BS, free lead and moisture concentrations of plates produced from leady oxide with 15% free lead during drying at 65.5 °C and 75% R.H. (b) Scanning electron microscope image of dried plate produced from leady oxide with 15% free lead (magnification = 3000 and the scale bar = 20 μm).

The series of Figs. 3a–6a show plots of 4BS, free lead and water during the drying process for the four oxides and Figs. 3b–6b show the scanning electron microscope images of the dried plates.

3. Results and discussion

It can be seen that the rate of 4BS formation in the laboratory mixer (Figs. 3a–6a) was slower than in the Oxmaster battery plant mixer (Fig. 2). We believe that this is due to more rapid cooling of the paste mix in the laboratory mixer. However, during the drying process, all mixes produced high levels of 4BS in the plates within 5 h. Since it requires approximately 10 h to dry the plates under the conditions of these experiments we consider this to be a satisfactory result. After 5 h of drying the four mixes contained the following amounts of 4BS: standard leady oxide, 58%; leady oxide with 15% free lead, 60%; lead monoxide 1, 70%; lead monoxide 2, 74%. A higher concentration of 4BS is produced in the laboratory paste mixes with the pure lead monoxides 1 and 2, which contain greater concentrations of β -PbO. β -PbO is more reactive to sulfuric acid than α -PbO which results in a higher peak paste temperature and accelerated 4BS formation. We attribute the difference in 4BS formation with lead monoxides 1 and 2 to differences in oxide reactivity from the two manufacturing processes.

Free lead is oxidized during the drying process, requiring approximately 7 and 5 h, respectively, to achieve a concentra-

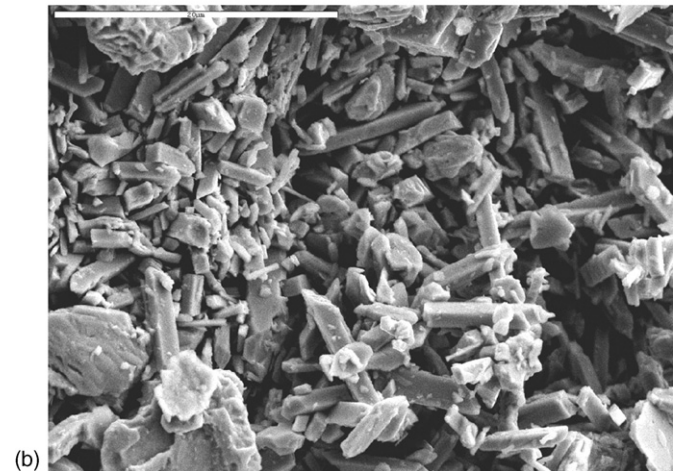
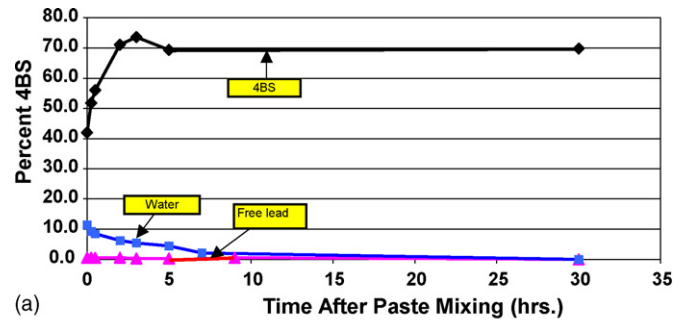
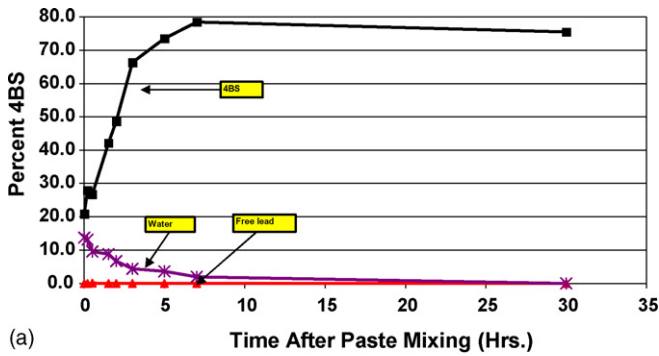


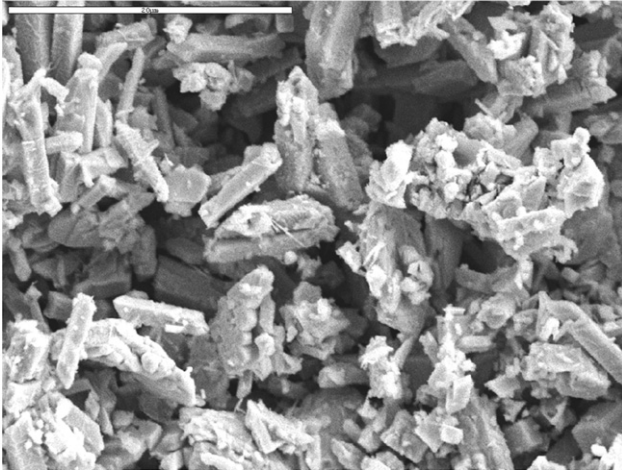
Fig. 5. (a) 4BS, free lead and moisture concentrations of plates produced from lead monoxide 1 with 0.15% free lead during drying at 65.5 °C and 75% R.H. (b) Scanning electron microscope image of dried plate produced from lead monoxide 1 with 0.15% free lead (magnification = 3000 and the scale bar = 20 μm).

tion of 2% with the standard and lower free lead leady oxides. Our data suggest that it should be possible to produce a cureless paste from either standard or reduced free lead leady oxides providing that 5–7 h of drying is allowed for oxidation of the residual free lead from paste mixing. This alone would be a considerable advance on existing curing technology. Since the pure lead monoxides contained only 0.15% free lead, none is detected in the finished paste or plates. In this case a cureless paste containing a high concentration of 4BS and with no residual free lead can be produced in the paste mixer and the plates can be used as soon as they are dried. This eliminates the curing process.

As we described earlier, conventional 4BS curing produces a crystal morphology that is undesirable since it yields a wide range of 4BS grain sizes with some larger than 50 μm in length. It would clearly be desirable to produce small, uniformly sized 4BS crystals with similar dimensions to the 3BS crystals formed in conventional paste mixing. Figs. 3b–6b show that the 1 μm 4BS additive readily produces such a structure. When the leady oxides with either 25% or 15% free lead are used the 4BS crystals range in length from 3 to 10 μm while with the pure lead monoxides the crystal sizes are slightly larger, with a range in length from 4 to 12 μm. The increased grain size with the lead monoxides is most probably due to their larger particle size. Both are a significant improvement over conventional processing.



(a)



(b)

Fig. 6. (a) 4BS, free lead and moisture concentrations of plates produced from lead monoxide 2 with 0.15% free lead during drying at 65.5 °C and 75% R.H. (b) Scanning electron microscope image of dried plate produced from lead monoxide 2 with 0.15% free lead (magnification = 3000 and the scale bar = 20 μm).

4. Conclusions

Our data indicate that conventional curing as it is carried out today can be eliminated as long as a 4BS seeding additive

is used in the paste mix. This promotes formation of a high level of 4BS in the paste and within 5 h of drying at 65 °C. It is no longer necessary to use high temperature steam curing to produce 4BS. A second, and very important benefit, is that the 4BS crystals are small and uniformly sized. When conventional leady oxides are used the residual free lead after paste mixing is oxidized during the drying cycle in 7 h when the initial free lead is 25% and in 5 h when the initial free lead is 15%. If lead monoxide is used to produce the paste, there is no free lead immediately after paste mixing and the plates can be used to assemble batteries as soon as they are dried. In our experiments, with drying at 65 °C and 75% R.H., this was approximately 7 h.

The following benefits have been obtained from this process:

- Formation of 4BS in the paste mix thereby eliminating the need for this in the curing process.
- Improved uniformity of 4BS crystal size.
- Elimination of the need for free lead removal.

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