

SureCure[®]—A new material to reduce curing time and improve curing reproducibility of lead–acid batteries

David P. Boden^{*}, Daniel V. Loosemore, G. Dean Botts

Hammond Lead Products Division, Hammond Group Inc., 2323 165th Street, Hammond, IN 46320, USA

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Abstract

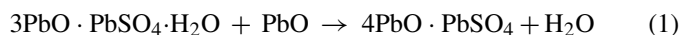
This paper introduces a technology that considerably reduces the time to cure the positive plates of lead–acid batteries. In each of several full-scale trials at automotive and industrial battery manufacturers, the simple replacement of 1 wt.% of leady oxide with finely-divided tetrabasic lead sulfate (SureCure[™] by Hammond Group Inc.) is shown to accelerate significantly the conversion of tribasic lead sulfate (3BS) to tetrabasic lead sulfate (4BS) in the curing process while improving crystal structure and reproducibility. Shorter curing times result in reduced labour and energy costs, as well as reduced fixed (curing chambers and plant footprint) and working (plate inventory) capital investment.

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Keywords: Curing time; Capacity; Lead–acid battery; Tetrabasic lead sulfate; Tribasic lead sulfate; SureCure[®]

1. Introduction

The curing of positive plates for lead–acid batteries is a critical operation. During this process, the chemical and physical structure of the active-material is established and the plates develop the strength that is required for subsequent mechanical handling. When a paste mix is prepared by conventional methods, the primary compounds present are tribasic lead sulfate (3BS) ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O} = 3\text{BS}$), unreacted lead oxide (PbO), and free lead. It has become apparent to battery manufacturers that a high concentration of 3BS in the positive plates improves the life of batteries. This is the case for both automotive and industrial products. Therefore one of objectives of curing is to convert the 3BS ($4\text{PbO}\cdot\text{PbSO}_4 = 4\text{BS}$) formed during paste mixing to tetrabasic lead sulfate (4BS). The other important goal is to oxidize residual free lead in the active material to lead oxide, i.e.,



These reactions take place under different conditions. In conventional curing, the conversion of 3BS to 4BS is effected by heating the pasted plates for several hours at a temperature of about 80 °C (176 °F) in air that has having a relative humidity of about 95%. Following this, the temperature and humidity are both reduced to allow the plates to dry slowly. During this stage, air enters the porous structure of the plate and reacts with the free lead to produce α -PbO. It is important not to let the relative humidity decrease too quickly because once the moisture content of the active material falls below 5 wt.% the oxidation rate of the free lead reduces appreciably. Large curing chambers capable of holding a shift's worth of plates or more are typically used in battery plants. These have controls to adjust temperature and humidity over wide ranges. Battery manufacturers employ a variety of temperature–humidity–time profiles and it is not uncommon for the curing process to take several days.

Despite numerous refinements to curing chambers over the years, curing remains the last completely un-automated process in battery manufacturing. In addition, numerous other problems exist with this process, namely, i.e. energy, labour and capital intensive, curing times are frequently uncertain, and the chemical characteristics of the plates are variable. Battery plants may require tens of curing chambers to handle plates, and these occupy space that could be more profitably used for more productive purposes. Large numbers of plates quarantined in curing

^{*} Corresponding author. Tel.: +1 219 989 4060; fax: +1 219 989 4071.
E-mail address: dboden@hmdexpander.com (D.P. Boden).

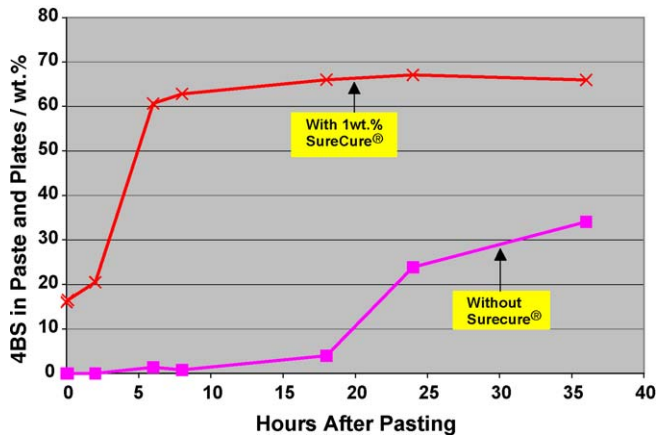


Fig. 1. Effect of 1 wt.% SureCure[®] (median particle size = 0.8 μm) on curing of automotive positive paste and plates—Company A.

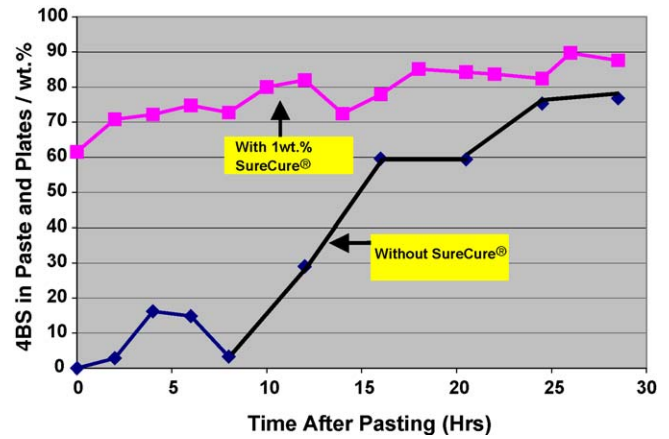


Fig. 3. Effect of 1 wt.% SureCure[®] (median particle size = 0.8 μm) on curing of industrial battery paste and plates—Company C.

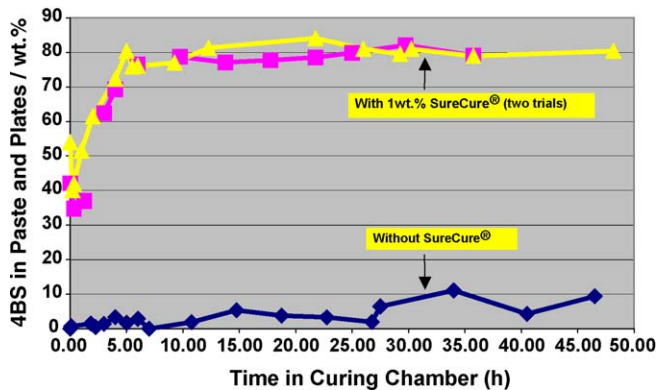


Fig. 2. Effect of 1 wt.% SureCure[®] (median particle size = 0.8 μm) on curing of automotive battery positive paste and plates—Company B.

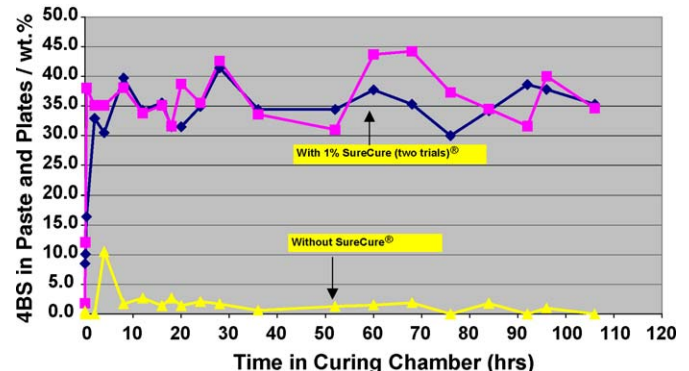


Fig. 4. Effect of 1 wt.% SureCure[®] (median particle size = 0.8 μm) on curing of industrial paste and plates—Company D.

chambers increase working capital. Clearly, considerable economic benefits would result from an improved process.

2. The SureCure[®] process

A new technology for curing has been developed and involves the use of finely-divided 4BS (median particle size < 0.8 μm) as an additive to the paste mix. This is a bright white dry powder with a 3BS content greater than 95% and has been given the trade name SureCure[®]. It has been found that 1 wt.% of SureCure[®] (by weight of oxide) in the mix is sufficient to cause significant amounts of 4BS crystals to be formed in the paste before curing

and in the plates during curing. The amount formed prior to curing depends on the paste temperature. The 4BS is added to the paste batch with the other solids and in all other respects the paste-mixing procedure is unchanged. The small addition of 4BS does not affect either the density or the plasticity of the paste and therefore pasting operations are unaffected.

The small 4BS crystals act as nucleation sites for the formation of more 4BS during paste mixing and accelerate conversion of 3BS to 4BS during curing. By eliminating energy of nucleation, 4BS readily grows on the existing particles rather than expending the energy required to form new crystals.

Table 1
4BS concentrations (wt.%) in plates from multiple curing trials using 1 wt.% SureCure[®] in the paste mix

Trial no.	Paste mix	Pasted plate	Curing time (h)					End of cure
			2	6	8	18	24	
1	19.8	14.3	21.8	60.7	66.3	66.1	69.9	67.2
2	12.2	15.9	17.8		64.3	64.3	69.3	64.0
3		14.3	18.4		56.9	64.7	61.8	68.6
4		21.4	24.1		62.6	68.9	67.4	64.0
5					63.7			
Avg.	16.0	16.5	20.5	60.7	62.8	66.0	67.1	65.95

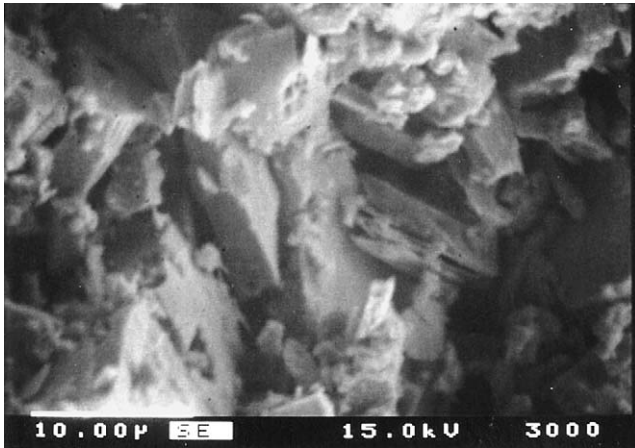


Fig. 5. Scanning electron microscope image of positive active material after conventional curing. Magnification = 3000.

A number of full-scale trials with this material have been conducted in automotive and industrial battery plants. In every case, the time required for formation of 4BS has been shortened appreciably and the uniformity of the cured plates has been considerably improved. Typical automotive and industrial paste mixes were made using conventional commercial paste mixers. To these pastes was added 1 wt.% of 4BS with a median particle size of around $0.8\ \mu\text{m}$. The standard paste mixing and curing processes used by the battery manufacturers were followed and the plates were pasted and tunnel-dried by conventional pasting machines and driers, respectively. The automotive plates were generally stacked on pallets, while the industrial plates were either stacked or racked depending on the manufacturer's preference. The plates were cured in standard commercial curing chambers following the manufacturer's normal procedure.

To evaluate the results of the additive, samples of paste were taken at the end of the mixing process and samples of the pasted plates were collected both at the take-off station and at intervals during the curing process. Active material was removed from the plates, immediately placed in a freezer at $-18\ ^\circ\text{C}$ ($0\ ^\circ\text{F}$) and subsequently vacuum dried. The material was then analyzed by X-ray diffraction to determine the phases present using a Rigaku Miniflex X-ray analyzer with software adapted for calculation

of concentrations of phases in battery plates. Scanning electron microscope images were also obtained at a magnification of 3000 to determine crystal size. In some cases, BET specific surface-area and porosity measurements were made.

3. Automotive battery plate paste-mixing and curing

A summary of the data obtained from trials carried out with two automotive battery manufacturers is shown in Figs. 1 and 2.

Company A and Company B employed different curing processes and equipment, although in both cases the plates were placed on pallets in stacks of approximately 20 cm high. In the case of Company A, the process was intended to produce 4BS by employing a schedule in which the curing temperature was low initially and then increased with time to $80\ ^\circ\text{C}$ ($176\ ^\circ\text{F}$). At Company B, the curing chamber temperature was maintained at $54\ ^\circ\text{C}$ ($130\ ^\circ\text{F}$) throughout the process. In both companies, the relative humidity was maintained at $>95\%$ until the drying cycle was started.

It is clear that the addition of only 1 wt.% 4BS to the paste mix accelerated conversion of 3BS to 4BS. In the case of Company A, some conversion took place in the paste mixer and virtually complete conversion had taken place after 6 h in the curing chamber. Without the additive, no conversion occurred until after 18 h in the curing chamber. At the end of the curing cycle, the untreated plates contained only 35% 4BS compared with 66% in the treated plates.

In the case of Company B, a significant amount of 4BS had formed in the paste mixer before the plates were pasted. The reason for this is that the peak paste-mixing temperature was approximately $63\ ^\circ\text{C}$ ($145\ ^\circ\text{F}$), i.e., $5\ ^\circ\text{C}$ ($9\ ^\circ\text{F}$) higher than those of Company A. This small increase in peak paste temperature was sufficient to accelerate formation of 4BS in the paste mixer. The paste contained 40–50% 4BSLS before it was dispensed into the pasting machine hopper. The 4BS levels in the plates of Company B were also higher than in these of Company A. This was because Company B employed a higher sulfation level in its paste.

The plates that contained 4BSLS were also very reproducible. This is shown in Table 1 which provides data from several separate trials carried out at Company A. These data yield some important conclusions:

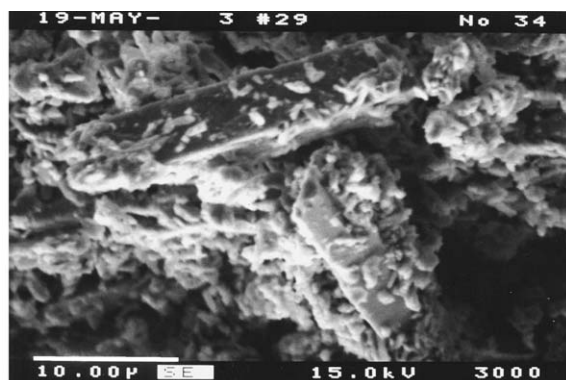
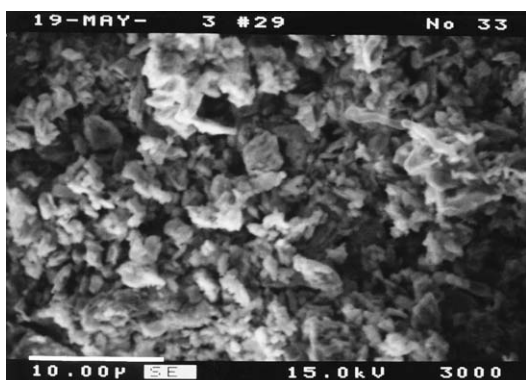


Fig. 6. Crystal structure of positive plates taken from different locations in the curing chamber after conventional curing.

- (i) Addition of 1 wt.% of finely-divided 4BS to the paste mix accelerates the conversion of 3BS to 4BS in the curing process.
- (ii) 4BS can be formed in the curing chamber at a temperature of 54 °C (130 °F).
- (iii) 3BS conversion to 4BS takes place in the paste mixer at a peak pasting temperature above 63 °C (145 °F).
- (iv) Conversion of 3BS to 4BS does not take place at these temperatures in the absence of the finely divided TTBLs additive.

4. Industrial battery plate paste-mixing and curing

Results from trials performed in industrial battery plants are shown in Figs. 3 and 4. As in the trials on automotive plate curing, the two companies used different curing processes. Consequently, different results were obtained in each case. Nevertheless, in all tests the formation of 4BS was considerably enhanced when the additive was used. In the case of Company C (Fig. 3) the plates were placed on notched racks and the curing profile began with a slow ramp up in temperature from ~54 °C (130 °F) to ~77 °C (170 °F), followed by several hours at the higher temperature. Without additive, no 4BS was present in the paste and only began to form 9 h after the curing cycle had commenced. This coincided with the end of the ramp up to high temperature. After 24 h, when the drying phase of the curing process was started, the 4BS concentration was ~75 wt.%. By contrast, inclusion of the additive caused considerable conversion of 3BS to 4BS (60 wt.%) in the paste mixer. Over 70 wt.% 4BS was obtained after only 2 h in the curing chamber while the process was still in the ramp-up phase. In summary, these data show that the additive promotes the formation of 4BS in the paste mix and that conversion of 3BS to 4BS can be achieved during curing at temperatures between range 55 and 60 °C (130–140 °F).

The investigation at Company D was conducted to determine whether it was possible to achieve good conversion of 3BS to 4BS at much lower temperatures by use of the additive. The plates were stacked on pallets and the curing room was held at ~50 °C (125 °F) with a relative humidity >95%. The peak paste-mixing temperature was 60 °C (140 °F). Under these conditions, the untreated paste and plates developed very little 4BS, even after 100 h in the curing chamber (Fig. 4). By contrast, the treated paste contained about 5 wt.% 4BS and this rapidly increased to 30–35 wt.% after 1 h in the curing chamber. Complete conversion took place after about 5 h. These data confirm that the additive enables the development of 4BS to occur at temperatures well below those traditionally used by the battery industry.

5. Crystal size and uniformity

The size and uniformity of the 4BS crystals are very important. Large crystals will result in longer plate formation times. Uniformity is also essential for all crystals to be converted to active material at the same rate and thus ensure that plates are reproducible. Wide variations in crystal size can cause signif-

icant changes in charge acceptance and variable performance from plate to plate. In conventional curing it is common for the crystal size of 4BS to vary considerably, due to the difficulty in initiating the conversion of 3BS to 4BS. As mentioned earlier, the latter requires high temperature and humidity, but

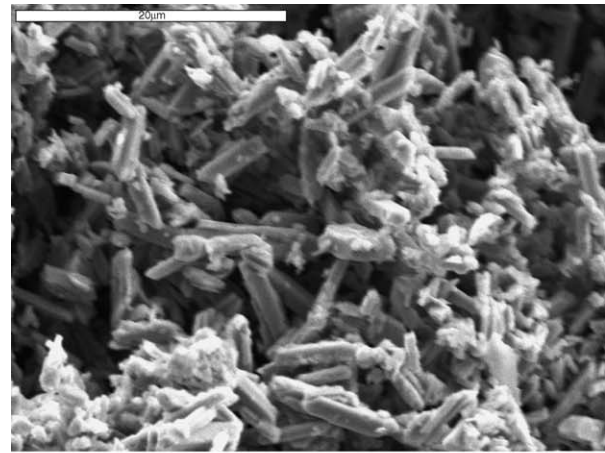


Plate at take-off station

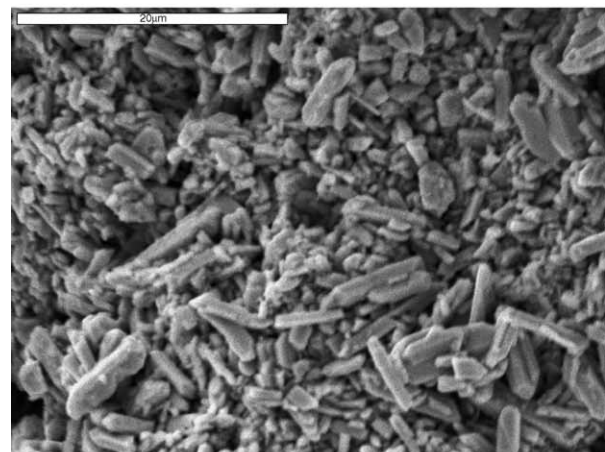


Plate After 2 h in curing chamber

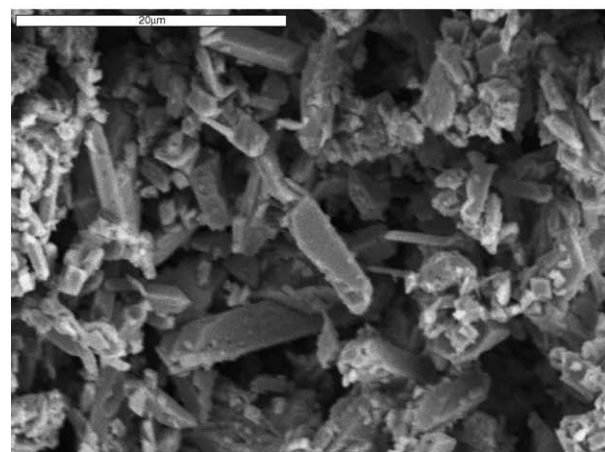


Plate at end of curing process

Fig. 7. Scanning electron micrograph of positive active material (1 wt.% SureCure® added) at different stages of curing.

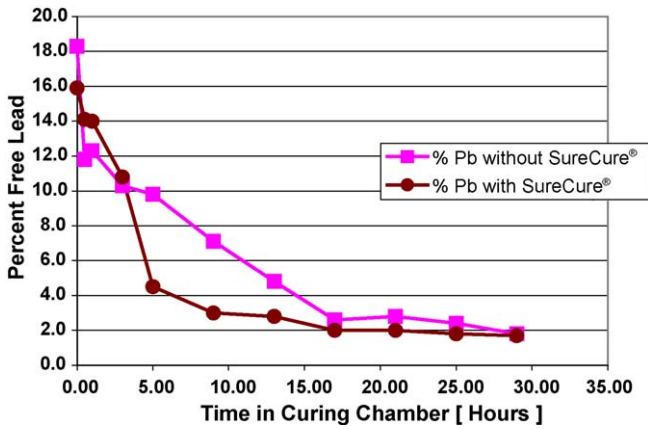


Fig. 8. Effect of 1 wt.% SureCure® (median particle size = 0.8 μm) on free-lead oxidation in positive plates during curing.

once the reaction has started 4BS crystals form quickly and can grow to a large size within a short time. Because of varying thermodynamic conditions from place to place in the curing chamber, and the influence position of plates on the racks or stacks, 4BS crystal growth does not begin simultaneously in all the plates. Therefore, crystal growth can be variable from plate to plate and from place to place within the plate. This situation is improved by the use of a 4BS nucleation additive because the energy of crystallization is decreased. Consequently, crystal growth is facilitated at a lower temperature and takes place uniformly on the 4BS ‘seeds’ distributed in the active material.

A scanning electron micrograph of typical positive-plate active material at the end of conventional curing is shown in Fig. 5. The large, angular crystals are 4BS and they exhibit a wide variety of crystal sizes. Further examples of variability in 4BS crystal development are given in Fig. 6, which presents micrograph of positive active-material collected from plates at different locations in the chamber after conventional curing. Differences in crystal morphology will lead to variations in charge-acceptance during plate formation (large crystals charge more slowly) and in the initial capacity of batteries. Differences in battery life may also eventuate since batteries made from

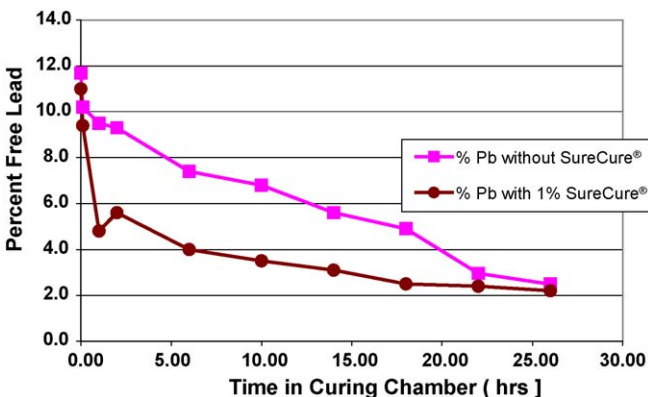


Fig. 9. Effect of 1 wt.% SureCure® (median particle size = 0.8 μm) on free-lead oxidation in negative plates during curing.

plates with poor crystal development will suffer from premature softening and shedding of active material. With as little as 1 wt.% SureCure® added to the positive paste mix, the crystal structure is improved markedly. This is illustrated in Fig. 7 which shows electron micrographs at 3000 magnification of positive active-material from the plate take-off station, after 2 h in the curing chamber, and at the end of the curing process. The plate at the take-off station has a high concentration of 4BS (~60 wt.%) that increases to approximately 70 wt.% after 2 h in the chamber and to 85 wt.% at the end of curing. This demonstrates that the presence of SureCure® promotes formation of 4BS in the paste mix before the plates are pasted. The implications of this are very significant since it shows that the crystallization phase of the curing process can be shortened or even eliminated. The crystal uniformity is also noteworthy and the crystal size changes very

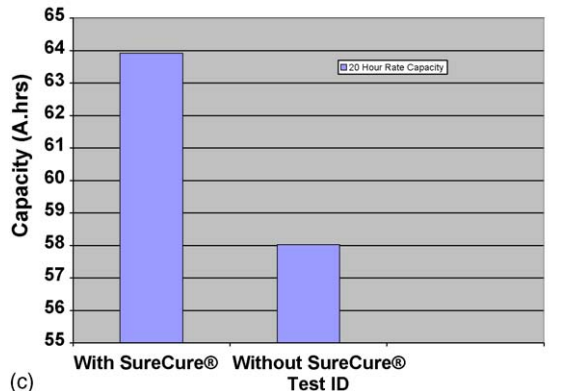
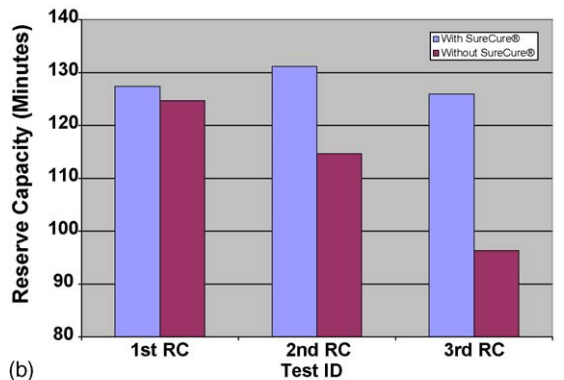
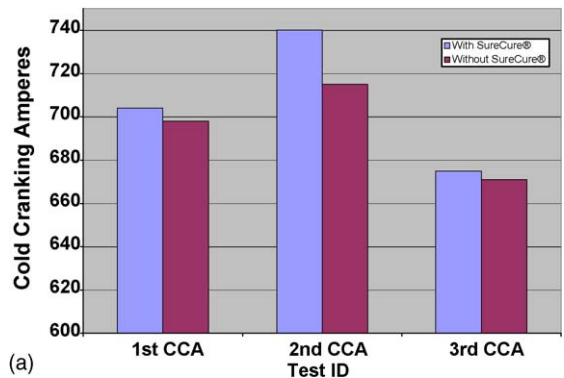


Fig. 10. Effect of 1 wt.% SureCure® on (a) cold-cranking amperes, (b) reserve capacity and (c) 20 h rate capacity of automotive batteries.

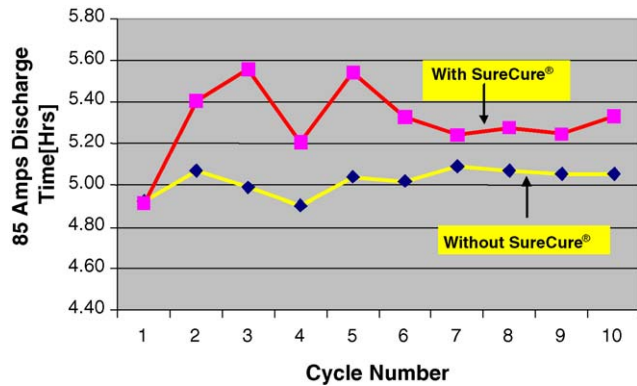


Fig. 11. Effect of 1 wt.% SureCure® (median particle size = 0.8 μm) on initial capacity of motive-power batteries.

little from pasting (~5–7 μm) to the end of curing (~10 μm). These features will improve both the charge acceptance and the consistency of plate formation. Consequently, more efficient formation will occur and the variation in initial capacity will be reduced.

6. Free-lead oxidation

The curing process serves to oxidize free lead in addition to the development for of the crystal structure. It has been found that use of SureCure® speeds up the oxidation of free lead in both positive and negative plates. By way of example, data obtained from industrial positive and negative plates subjected to a curing profile at 80 °C and 95% relative humidity are presented in Figs. 8 and 9, respectively. For positive plates, the times required to achieve a free-lead concentration of the usually accepted 2 wt.% is about 18 h and 28 h with and without SureCure®, respectively. For negative plates, the reduction in

free lead to 4 wt.% is achieved in 8 h with the additive while 18 h are required without additive. The time required to obtain 2 wt.% free lead is approximately 26 h in both cases.

7. Initial capacities of batteries

Initial capacity testing has been carried out on both automotive and motive-power batteries, and life testing is in progress.

7.1. Automotive batteries

Data from cold-cranking, reserve capacity and 20 h capacity testing are given in Fig. 10. In all of these tests, the batteries that contained SureCure® in the positive plates give improved performance.

7.2. Industrial batteries

Results from initial capacity tests on motive-power batteries are presented in Fig. 11. Compared are the first 10 cycles from two 12 V-425 Ah batteries. The battery with 1 wt.% 4BS yields a higher capacity.

7.3. Life testing

As noted above the principal reason for producing batteries with 4BS in the positive plates is that this increases life, particularly in cycling applications. Unfortunately, life testing takes a considerable amount of time and in this study it has yet to be completed. Nevertheless, data exist for golf-car batteries up to 550 cycles, as shown in Fig. 12. These tests were carried out on two full golf-car battery sets that were charged and discharged by conventional Lester dischargers and chargers.

It can be seen that at this point batteries with SureCure® have given higher capacity than the standard product throughout the

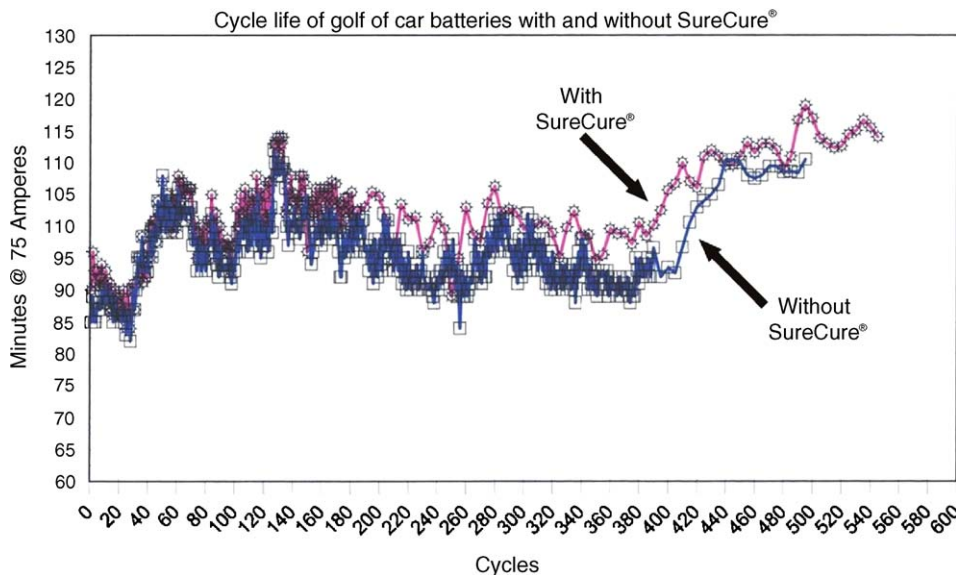


Fig. 12. Cycle-life of golf-car batteries with and without SureCure®.

test. (Note, in other respects the compositions of the cured pastes of the two sets was the same.)

8. Conclusions

SureCure[®] has been found to be a remarkably effective additive for both positive and negative plates. The following observations are made:

- (i) The additive causes formation of 4BS in the paste mix and this reduces the need to develop this material during the curing process.
- (ii) Where low paste-mixing temperatures are used that result in reduced 4BS formation in the paste mix, the additive promotes rapid conversion of 3BS to 4BS in the curing chamber at temperatures above 55 °C (130 °F).

(iii) The additive also:

- improves the uniformity of the 3BS to 4BS conversion
- improves crystal size uniformity
- prevents the formation of very large, difficult to form, 4BS crystals
- shortens the time for free-lead oxidation in both positive and negative plates
- increases the initial capacity of industrial batteries
- increases the cold-cranking amperes, reserve capacity and 20 h rate capacity of automotive batteries
- maintains capacity increase for more than 500 deep cycles.

These benefits give a significant reduction in curing times and improved performance from batteries.