SureCure – the science behind the time savings

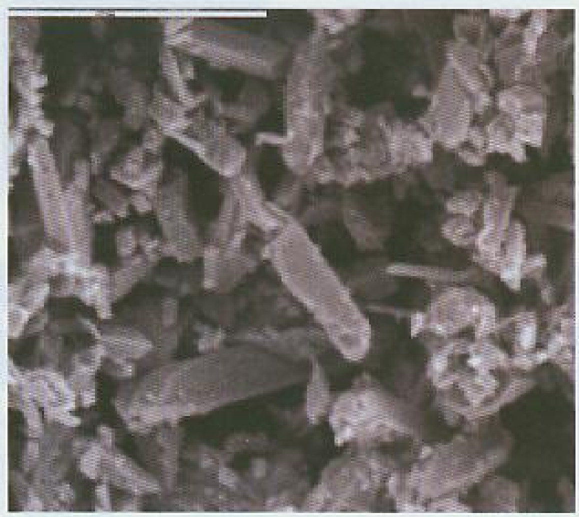
David P. Boden and Benjamin Labovitz of Hammond Lead Products explain how the addition of just a little leady oxide and tetrabasic lead sulfate can save so much time in curing.

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 required for subsequent mechanical handling. When a paste mix is prepared by conventional methods, the primary compounds present are tribasic lead sulfate (TRBLS), unreacted lead oxide (PbO) and free lead. It has become apparent to battery manufacturers that a high concentration of tetrabasic lead sulfate (TTBLS) in the positive plates improves the life of batteries. This is the case for both automotive and industrial products. Therefore one of the principal objectives of curing is to convert the tribasic lead sulfate (TRBLS) formed during paste mixing to TTBLS. The other important goal is to oxidize residual free lead in the active material to lead oxide.

$$3PbOPbSO_4.H_2O + PbO > 4PbOPbSO_4 + H_2O$$

$$Pb + 1/2O_2 > PbO$$

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



Watch that tetrabasic lead sulfate grow – what Surecure does, in just a few hours.

Despite numerous refinements to curing chambers over the years, curing remains the last completely un-automated process in battery manufacturing. Numerous other problems exist with this process. It is energy, labor 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 their plates, occupying space that could be more profitably used for more productive purposes. Large numbers of plates quarantined in curing chambers increase working capital. Clearly, considerable economic benefits would result from an improved process.

The improved process

The process involves use of finely divided TTBLS (median particle size <1μ) as an additive to the paste mix. This is a bright white dry powder with a TTBLS content greater than 95%. This has been given the trade name SureCure. We have found that one percent of SureCure (by weight of oxide) in the mix is sufficient to significantly accelerate formation of TTBLS crystals in the paste before curing and in the plates during curing. This material is added to the paste batch with the other solids and in all other respects the paste mixing procedure is unchanged. This small amount of TTBLS does not affect either the density or plasticity of the paste therefore pasting operations are unaffected.

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

A number of full-scale trials with this material have been carried out in battery plants involving automotive and industrial battery plates.

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In every case the time required for formation of TTBLS 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 Oxmaster and SMS commercial paste mixers. To these pastes was added 1% by weight of TTBLS having a median particle size of around 0.8μ. The standard paste mixing and curing processes used by the battery manufacturers were followed and the plates were pasted and tunnel dried by MAC pasting machines and driers. Automotive plates were generally stacked on pallets while industrial plates were either stacked or racked depending on the manufacturer's preference. The plates were cured in standard commercial curing chambers following the battery manufacturer's normal procedure.

To evaluate the results of the additive, samples of paste were taken from the paste mixer at the end of the mixing process and samples of the pasted plates were taken 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°C (0°F) and subsequently vacuum dried at ambient temperature. This 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.

Automotive battery plate pasting andc uring

A summary of the data obtained from trials carried out with two automotive battery manufacturers is shown in Figures 1 and 2 on page 86.

Company A and Company B employ different curing processes and equipment. In the case of Company A the curing temperature is low initially and is increased with time to a higher value. In the case of Company B the curing chamber temperature is kept at a low value throughout the process. In both cases the relative humidity is maintained at >95% until the drying cycle is started.

It is clear that addition of only 1% TTBLS to the paste mix accelerated conversion of TRBLS to TTBLS. In the case of Company A some conversion took place in the paste mixer and virtually complete conversion had taken place after six hours in the curing chamber.

Without the additive no conversion of TRBLS to TTBLS took place until after 18 hours in the curing chamber. At the end of the curing cycle the untreated plates contained only 35% TTBLS compared to 66% in the treated plates.

In the case of Company B a significant amount of TTBLS had formed in the paste mixer before the plates were pasted. The reason for this is that the peak paste mixing temperature was approximately 2.8°C (5°F) higher than that of Company A. This small increase in peak paste temperature was sufficient to accelerate formation of TTBLS in the paste mixer. The paste contained 40% – 50% TTBLS before it was dispensed into the pasting machine. Complete conversion to TTBLS had taken place after only 5 hours in the curing chamber. The TTBLS levels in Company B's plates were also higher than Company A's. The reason for this is that Company B uses a higher sulfation level in its plates than Company A.

Industrial battery plate paste mixing and curing

Results from three trials carried out in industrial battery plants are shown in Figures 3, and 4.

As with the automotive plate curing trials the three companies used different curing processes. Consequently different results were obtained in each

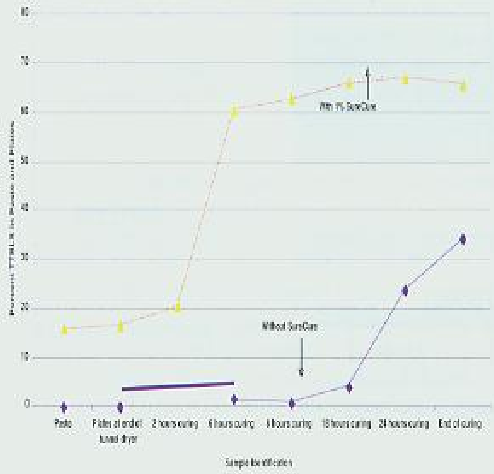

Figure 1: Effect of 1% SureCure on Automotive Paste and Plate Curing. Company A

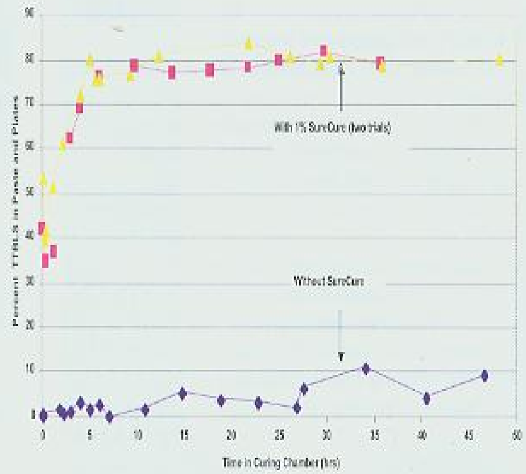

Figure 2: Effect of 1% SureCure on Automotive Battery Paste and Plate Curing. Company B

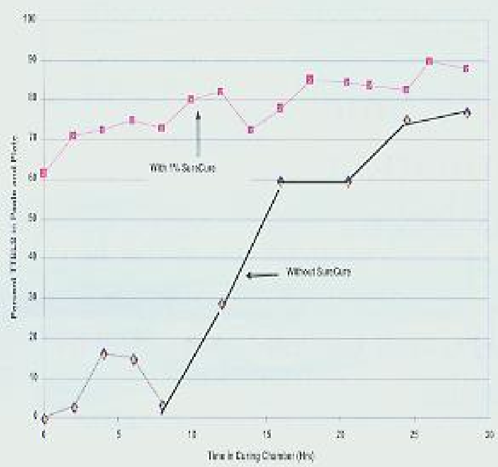

Figure 3: Effect of 1% SureCure on Industrial Paste and Plate Curing. Company C

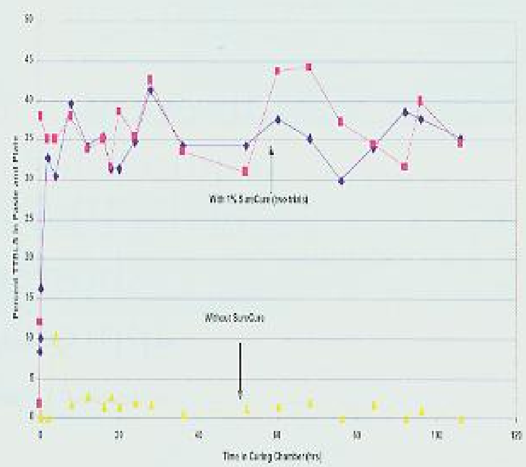

Figure 4: Effect of 1% SureCure on Industrial Paste and Plate Curing. Company D

case. However, in every case, formation of TTBLS was considerably enhanced when the additive was used. In the case of Company C the plates were placed on notched racks and the curing profile began with a slow ramp up in temperature from -55°C (130°F) to -77°C (170°F) followed by several hours at the high temperature. Without the additive no TTBLS was present in the paste and TTBLS began to form 9 hours after the curing cycle had been started. This coincided with the end of the ramp up to the high temperature. After 12 hours, when the drying phase of the curing process was started, the TTBLS concentration was +/-20%. In contrast, with the additive, the paste contained over 70% TTBLS indicating that the additive had caused considerable TRBLS to TTBLS conversion in the paste mixer. Complete conversion occurred after only 4 hours in the curing chamber while the process was still in the ramp up phase. These data show that the additive promotes formation of TTBLS in the paste mix and that complete conversion from TRBLS to TTBLS can be achieved in the curing process at temperatures in the range 55°C – 60°C (130°F – 140°F).

The trial at Company D was carried out to verify that it was possible to achieve complete conversion from TRBLS to TTBLS at much lower temperatures by use of the additive. In this case the plates were stacked on pallets and the curing room was held at -50°C (125°F) with a relative humidity >95%. Peak paste mixing temperatures were 60°C (140°F). Under these conditions the untreated paste and plates developed very little TTBLS even after 100 hours in the curing chamber. On the other hand, the treated paste contained about 5% TTBLS which rapidly increased to 27% after 1 hour in the curing chamber. Complete conversion took place after about 4 hours. These data confirm that conversion of TRBLS to TTBLS takes place at much lower temperatures than previously believed when the additive is used.

These data clearly show with use of the SureCure additive:

1. That it is possible to produce TTBLS easily in the paste mix with peak paste mixing temperatures in the range of 60°C - 63°C (140°F - 145°F).

2. Conversion of TRBLS to TTBLS is significantly accelerated during the curing process.

3. Plate composition is very uniform and reproducible.

Crystal size and uniformity

Size and uniformity of the TTBLS crystals is very important. Large crystals are more difficult to form and will require longer formation times that small crystals. Uniformity is also important so that all crystals in the plate form at the same rate assuring that all plates are reproducible. Wide variations in crystal size can cause significant changes in charge acceptance and variable performance from plate to plate. In conventional curing it is common for the crystal size of TTBLS to vary considerably. The reason for this is that it is difficult to initiate conversion of TRBLS to TTBLS; as mentioned earlier this requires high temperature and humidity. However, once the reaction has started, TTBLS 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 position of plates on the racks or stacks, TTBLS crystal growth does not begin simultaneously in all the plates. Therefore crystal growth can be variable from plate to plate. This situation is improved by use of a TTBLS nucleation additive because energy of crystallization is eliminated. Consequently, crystal growth is facilitated at a lower temperature and takes place uniformly on the TTBLS "seeds" distributed in the active material.

Figure 5 is a typical scanning electron microscope (SEM) image of positive plate active material taken at the end of a conventional curing process.

The large angular crystals are TTBLS. It is easy to see the wide variety of crystal sizes in this photograph. It is easy to see the differences in crystal morphology. These differences will lead to variations in formation charge acceptance (large crystals charge more slowly) and in the initial capacity of batteries. There may also be differences in life since batteries made from plates

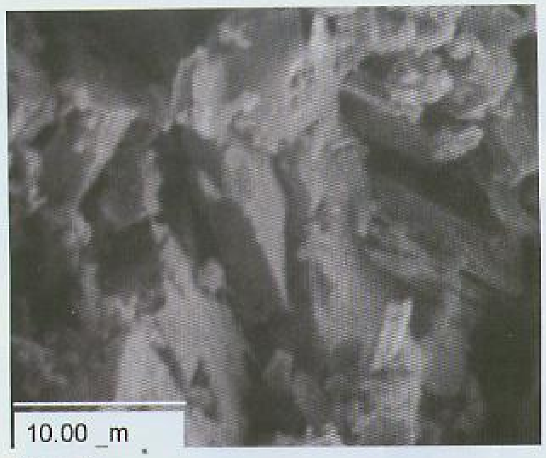

Figure 5.

with poor crystal development will suffer premature active material softening and shedding.

With as little as 1% SureCure added to the positive paste mix the crystal structure is improved markedly. This is illustrated on the first page of this article which shows SEM images at 3,000 magnification showing the increased concentration of TTBLS risng to 85% at the end of the curing cycle.

This shows that the presence of SureCure promotes formation of TTBLS 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 eliminated.

The crystal uniformity is also very noteworthy. Crystal size is very uniform and changes very little from pasting (~5-7 microns) to the end of curing (~10 microns).

This grain size uniformity will improve formation charge acceptance and consistency. Consequently more efficient formation will occur and initial capacity variation will be reduced.

Free lead oxidation

The curing process also serves to oxidize free lead in addition to formation of crystal structure. We have found that use of SureCure speeds up oxidation of free lead in both positive and negative plates. For positive plates the time required to achieve a free lead concentration of the usually accepted 2% was about 18 hours and 28 hours with and without SureCure respectively.

For negative plates the reduction in free lead to 4% was achieved in 8 hours while 18 hours was needed to achieve 2% free lead. In this work an additional grade of SureCure with a larger median particle size (3.5μ) was also tested. This is known as SurecureLD. The results show that SureCure LD is more effective in accelerating free lead oxidation than standard SureCure.

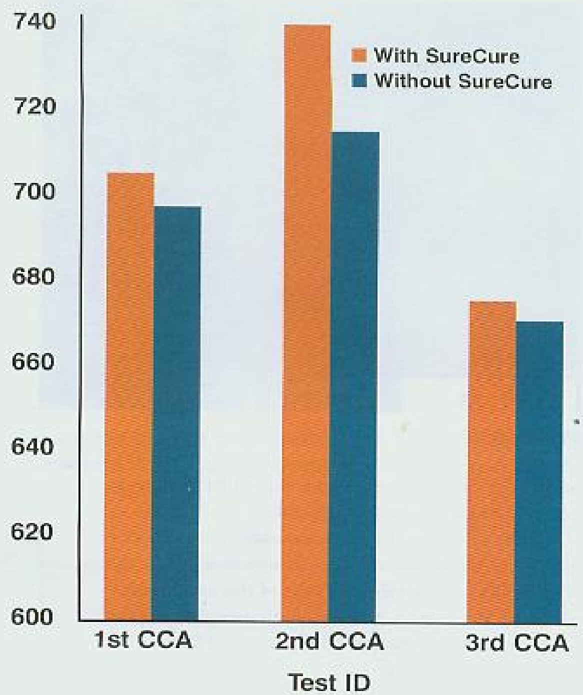

Figure 6: Effect of 1% SureCure on Cold Cranking Amperes.

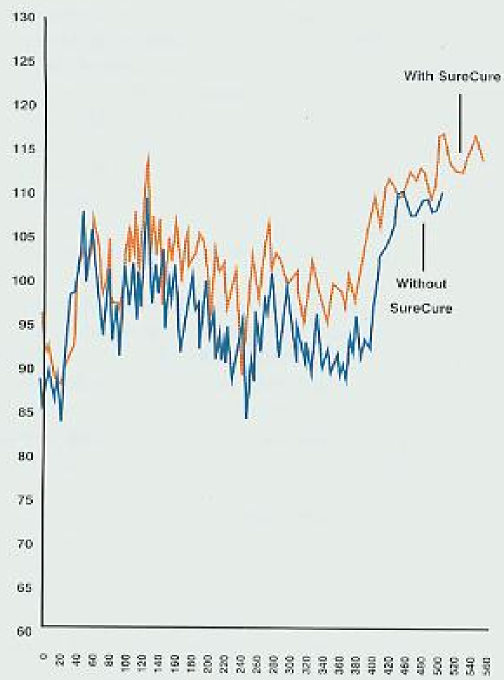

Figure 7: Cycle life of golf car batteries with and without SureCure. 1% SureCure added to positive plate.

Initial capacities of batteries

Initial capacity testing has been carried out on both automotive and motive power batteries.

Figure 6 shows the results from cold cranking. In all of these tests the batteries that contained SureCure in the positive plates showed improved performance.

Life testing

As we have discussed previously the principal reason for producing batteries with TTBLS in the positive plates is that this increases life, particularly in cycling applications. Unfortunately, life testing takes a considerable amount of time therefore it has not yet been completed but data exists for golf car batteries up to 550 cycles as shown in Figure 7. 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 test.

Conclusions

SureCure has been found to be a remarkably effective additive to both positive and negative plates.

- It causes formation of TTBLS in the paste mix obviating the need for this in the curing process.
- Where low paste mixing temperatures are used resulting in reduced TTBLS formation in the paste mix, it causes rapid conversion of TRBLS to TTBLS in the curing chamber.
- It improves the uniformity of the TRBLS to TTBLS conversion.
- It improved crystal size uniformity.
- It prevents formation of very large, difficult to form TTBLS crystals.
- It shortens the time for free lead oxidation in both positive and negative plates.
- It increases initial capacity in industrial batteries.
- It increases cold cranking amperes, reserve capacity and 20-hour rate capacity in automotive batteries.
- In deep cycle batteries the capacity increase is maintained over more than 500 cycles.

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