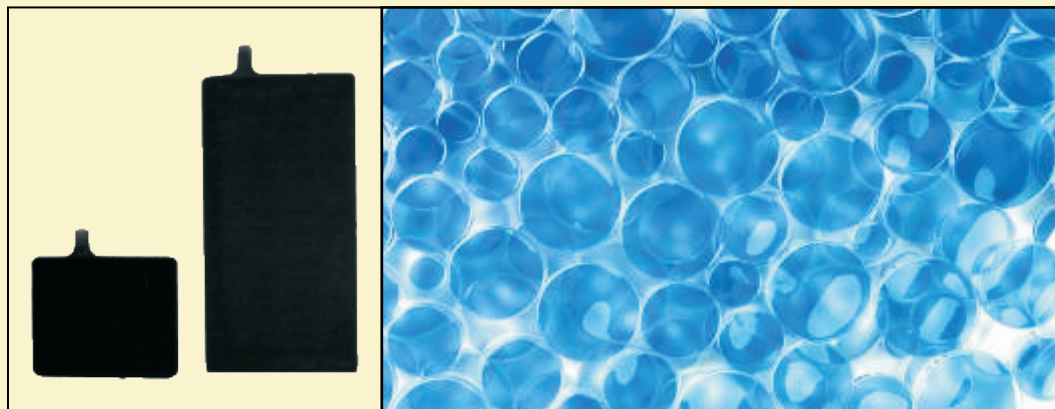




### Fast Cure Cum Binder : SLI & VRLA Positive electrode Paste Additive (For Automotive Positive Plate)



The positive plates in an SLI (Starting Lighting Ignition) lead-acid battery are made from lead-alloy grids pasted with active material. The active material on the positive plates is mainly a mixture of lead oxide and sulphuric acid. In order to achieve a

porous structure with a high surface area for the electro-chemical process, the pasted positive plates undergo a Paste preparation & curing process to transform the lead oxide and lead sulfate into basic lead sulfates – either Tribasic or Tetrabasic lead sulfate. There is however limitations due to the large size of the Tetra basic lead sulfate crystals. This can lead to a major disadvantage with Tetra basic lead sulfate namely a prolonged and higher electrical energy requirement for the formation of the positive plates and less surface area for the electro-chemical processes.

For Positive electrodes Fast Cure Cum Binder provides high energy density and high cycle lives suitable for in vehicles & other applications. It increases the conductivity flow from the positive active material to the current collector lead alloy. Fast Cure Cum Binder provides binding protective shell to paste while charge and discharge mechanism. The formation of a homogenous tetra-basic sulfate crystal structure in the positive plates of lead-acid batteries is well known to offer significant electro chemical improvements in battery performance in respect of improved cycling and battery life. A number of methods for obtaining the tetra-basic lead sulfate crystals by simply heating the pasted plates during curing to more than 80°C, for example during a short steam cure will generate a significant tetra-basic crystal structure although with a wide ranging crystal size distribution, sized of more than 50 microns being common. Therefore, figure 1 shows big sized tetra basic lead sulfate crystals formed after a steam cure step without any other additives.



Figure1 shows creating the tetra-basic structure is to control the crystal size distribution. Tetra-basic crystals, in comparison to tribasic crystals, are much harder to create. As the lead sulfate crystals develop there may be a limited number of developing crystal seed sites due to a higher activation energy compared to tri-basic and hence it is common to produce a relatively wide distribution across a plate with a number of very large crystals. These larger tetra-basic crystals lead to problems in the later formation of the plates as evidenced by an increased specific energy consumption and extended formation times when compared to tri-basic active materials.

By addition of Fast Cure Cum Binder a number of crystal seed sites are created, this leads to a large number of relatively even tetra-basic lead sulfate crystals. Trials carried out Fast Cure Cum Binder with approx. 4 to 5 micron particle size, shows some benefits with an improvement in the homogeneity of the crystal size distribution.

The main means of generating the crystals has in general been the heating of the pasted plates to more than 80°C in a steam cure process. By Use of Fast Cure Cum Binder, it has been found that only a relatively short treatment of 2 to 3 hours is required to fully develop the crystal structure. Figure 2 & 3 shows a tetra

basic lead sulfate structure formed after a steam cure step using 1 % of Fast Cure Cum Binder powder with a particle size of approx. 5 micron as a seeding crystal. Pilot trials with Fast Cure Cum Binder showed benefits in the curing and formation is SLI plate production related to process time reductions and energy savings. The Fast Cure Cum Binder was added as approx. 1%, of the lead oxide content in the batch. Some formulation, very often in the paste preparation of the acid-oxide ratio has been reduced to minimize the possibility of temperature spikes in the paste. These temperature spikes can lead to uncontrolled tetra basic crystal formation. With Fast Cure Cum Binder can follow regular paste preparation method or can increase acid-oxide ratios from 7 or 8 liters 1.400 sp. gravity per 100kg lead oxide giving higher porosity values for the paste.

### **Curing and Crystal Size Bonding**

There are two main ways of curing taking into account the different process steps and parameters available: the mixture of lead oxide and lead sulfate of the freshly manufactured positive plate is transformed into either Tribasic lead sulfate ( $\text{PbSO}_4 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$ ) or Tetra basic  $4/2$  lead sulfate ( $\text{PbSO}_4 \cdot 4\text{PbO} \cdot \text{H}_2\text{O}$ ). A Tetrabasic curing of  $4/2$  the plates is preferred versus a Tribasic curing because of the enhanced performance of the batteries. Batteries made from Tetra basic formed positive plates are known to last longer in all applications, compared to those made from Tribasic formed plates. The main disadvantage of the Conventional Steam Oven Tetrabasic curing process is the appearance of relatively large Tetrabasic lead sulfate crystals. The size/shape of the Tribasic as well as Tetrabasic lead sulfate crystals is controlled by temperature and humidity. Up to now it has not been possible to control precisely the size of the final Tetra basic lead sulfate crystals.

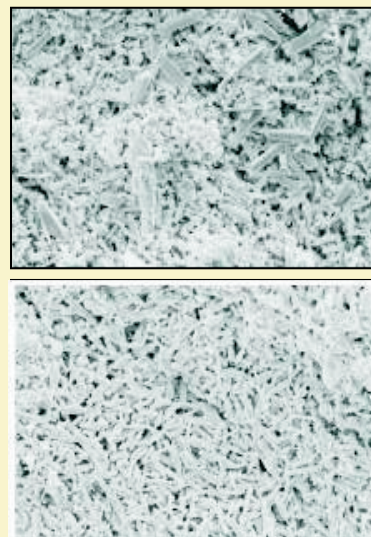
Nucleation theory explains the differences: Tri basic lead sulfate nuclei become stable at small sizes at low temperatures  $-50^\circ\text{C}$ . They are many in number and grow until the lead sulfate ions are exhausted. The result is a small sized Tri basic lead sulfate crystal structure.

Tetra basic lead sulfate nuclei became stable only at larger sizes. These sizes will be obtained only at higher temperatures,  $>60^\circ\text{C}$ , (by use of steam). Relatively few nuclei are generated and grow until the lead sulfate ions are exhausted. Because of the relatively low number of nuclei they tend to be large, around  $50\mu\text{m}$  and more influenced to some extent by the content of sulphuric acid in the paste preparation method. Even though the process time for curing to Tetra basic lead sulfate is shorter than for Tribasic lead sulfate the large crystals give rise to disadvantages with respect to formation and internal surface area.

The uncontrolled Tetra basic crystal growth leads to a reduction in the active surface of the plate. A high specific surface area is demanded for good battery performance with respect to high current discharge capability. The main feature of the Fast Cure Cum Binder is that size of the final Tetrabasic lead sulfate crystals can be controlled within the range from 3 to  $15\mu\text{m}$  by the paste preparation method, dependent on the amount of Fast Cure Cum Binder added to the lead oxide. Small crystals with a narrow distribution exhibit a larger specific surface in the plate thereby increasing the high current discharge performance of the plate with an advantageous Ah/kg ratio. Fast Cure Cum Binder allows the reduction of the curing time by use of steam and the small crystal size reduces the formation time. Consequently the use of FAST CURE CUM BINDER will reduce both the production costs and can lead to a significant reduction in working capital. Furthermore the improved cycling behavior of the batteries will improve the battery life.

It is a generally held belief that the reduction of the residual metallic lead is only achieved within such a curing step. It is easy to prove that the free lead reduction can place during the drying phase by ensuring that there is sufficient oxygen/air available. Nevertheless the appearance of large Tetrabasic lead sulfate crystals of  $50\mu\text{m}$  and above give problems during formation and reduce the specific surface area. It has been well tested that the addition of Fast Cure Cum Binder generates small and controlled sized Tetra basic lead sulfate crystals.

The Fast Cure Cum Binder additive is a very fine-sized and specially treated Tetra basic lead sulfate with Carboxymethylcellulose. Within the production process, an average grain size of  $0.5\mu\text{m}$  is obtained. The tendency of such small particles to re-agglomerate is avoided by addition. Fast Cure Cum Binder can use without any changes to the existing process. Generally it has been found that a short steam cure of 2 to 3 hours with more than  $80^\circ\text{C}$  on the plates leads to a very well developed tetra-basic crystal structure and helps



to improve the adherence of the paste on the grid, especially if the more corrosion resistant lead alloys are used. Thereafter, the plates are curing that was implemented to speed up the free lead reduction. It has also found to be important to have a good air circulation during the final drying to ensure the reaction of the small parts of residual free lead content below 1%. By use of Fast Cure Cum Binder effect of a homogenous crystal structure with a uniform and high porosity with good penetration of the acid into the active material provides an excellent positive plate for the lead-acid battery performance. It can be observed that the conventional methods come up with a lot of small sized crystals in the range of 0.05 to 3 micron. The tetra basic cured paste was adjusted to a crystal size of 8 – 13 micron by addition of 1 %.The applied high temperature curing converted more than 98 % of the sulfuric acid into tetra basic lead sulfate. Sulfuric acid as one of the construction materials is limiting the growth of the tetra basic crystals therefore it is possible to calculate the amount of seeds needed to adjust to a certain crystal size if the paste preparation method is validated. The results from the mercury high pressure porosimetry measurement are demonstrating the big difference of the pore size diameters and also of the pore areas and the porosity values.

As expected tri basic cured pastes have great pore areas but only a small part of this area is available for the electrical performance of the battery. Most of the small pores became clogged very soon during battery operation and therefore are not supporting the cold cranking capacity. At least the charge acceptance of the battery was reduced by clogging of the pores. By use of Fast Cure Cum Binder crystal sizes are able to withstand the clogging effect over a much longer period, because the pore diameter is bigger and supports the acid exchange within the pores. Porosity values of more than 50 % are indicating improved deep discharge performances due to the good acid transport within the whole paste.

**By the use Fast Cure Cum Binder Following Significant result would obtained :**

- The curing & drying time can be shortended to 1 day as compared with 2 to 4 days at present.
- By use of Fast Cure Cum Binder gives controlled crystal sizes of 3 to 15µm and narrow distribution of the Tetra basic lead sulfate crystals increasing the porosity.
- It assists the supply of acid to the positive active material on increasing the porosity of the paste to enhance diffusion. The addition of CMC was found to increase the water absorption of the paste with improved mechanical strength of the paste. This is due to the dispersion stabilizing properties of CMC. Vibration test shows marked improvement. It shows improvements in mechanical strength of active materials during all process and cycle life.
- It increases the water accumulating capacity of the paste & influence the crystallization of the mass lead into stabilizing the active mass structure.
- Formation is similar to that of regular process saves 10-15 % less electrical energy.
- No activation problems with dry-charged batteries. After being filled up with acid, dry charged batteries are operational without the need for additional charging.
- The battery performance is increased and the cycling behavior is improved due to the Tetra basic lead sulfate with residual alpha-PbO avoiding deep discharge. 2
- Due to increased porosity of the active the small crystal structure with higher surface area,it maintains high ionic conductivity, Better charge acceptance of deep discharged batteries due to higher alpha-PbO 2
- Fast Cure Cum Binder can be used with different kinds of lead oxide. It gives the same results for the crystal size for ball mill oxide and Barton pot oxide.
- By the use of FAST CURE CUM BINDER Stronger paste grid adhesion is achieved & More stable structure of the positive active material is obtained ultimately Shelf life of Lead Acid batteries is increased.

**Dosage :** 1.5 kg per 100 kg. of oxide material

**Available Packing :** 25 kg. HDPE Bag

**Storage :** Store in a cool & dry place

## Chemical Lab | Battery Testing Equipment

