

# Advances in manufacturing systems for the production of pastes for lead/acid battery plates

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## Abstract

The aim of this paper is to highlight the key considerations in preparing a high-performance paste for lead/acid battery plates, especially one that contains a high proportion of tetrabasic lead sulfate (4BS). Special emphasis is placed on the importance of selecting a paste mixer with the correct mixing/blending/shearing action, and both monitoring and controlling the mixing sequence, paste temperature, acid-to-oxide ratio, moisture content (density) and plasticity. Additionally, the capabilities of the Oxmaster paste-mixing equipment are detailed.

**Keywords:** Paste production; Lead/acid battery plates; Manufacturing systems

## 1. Introduction

The main objectives in paste mixing are to produce repeatedly an active material with the following characteristics:

- good plastic-flow properties (plasticity)
- sufficient moisture for effective curing
- uniform texture (crisp, crunchy consistency)
- controlled and defined paste density
- minimal monobasic lead sulfate
- homogeneous composition
- specified formulation (recipe and temperature)

In addition, paste mixes are formulated to take into account many parameters, such as

- type and nature of oxide
- free-lead content of oxide
- design and type of mixing equipment
- mix polarity (i.e., for positive or negative plates)
- intended use of battery plates e.g., automotive, motive-power and stationary applications
- optimization of various performance factors, e.g., active-material utilization at slow rates of discharge, high-rate discharge voltage, charge efficiency, and climatic zone of operation.

The demands of commercial competition, the demand for improved active-material utilization, and ever-in-

creasing levels of battery performance have highlighted the need for improved paste. In consequence, there is a corresponding requirement for the paste preparation process to be carried out under increasing control, by a highly developed production technique/mixing system that gives reproducible, high quality results.

## 2. Mixing sequence

During paste mixing, a significant proportion of the total leady oxide is converted to one of three possible basic lead sulfates, namely, monobasic,  $\text{PbO} \cdot \text{PbSO}_4$  (1BS), tribasic,  $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$  (3BS), or tetrabasic,  $4\text{PbO} \cdot \text{PbSO}_4$  (4BS). These compounds strengthen the plate material through the development of interlocking crystalline networks.

The presence of 1BS is detrimental to the durability of the active material, and, consequently, plate performance [1]. Monobasic lead sulfate is a fine, needle-like crystalline material that has poor cohesive strength and, as a result, promotes shedding and/or spalling of the active material during both plate formation and battery service. Accordingly, the level of 1BS should be kept below 10 wt.% [2]. This may be achieved by the selection of an appropriate acid-to-oxide ratio, the correct mix sequence, and by the introduction of the acid to the oxide in a well-regulated and uniform manner.

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Table 1  
Typical levels of monobasic lead sulfate in paste, as a function of mixer action

Mixer type	Monobasic lead sulfate (wt. %)
High shear (Oxmaster)	<2
Low shear	2–5
Muller	5–10

The effectiveness of the Oxmaster mixer in controlling the quantity of 1BS to a low level is demonstrated by the data given in Table 1.

### 3. Temperature

The temperature of the paste during the mixing process is critical for the development of the required active-material phase composition and morphology, appropriate to the specified plate/battery performance. The peak temperature and temperature profile of each paste mix must, therefore, be carefully controlled.

Peak temperatures below 65 °C result in the preferential formation of 3BS, at temperatures between 65

and 76 °C both 3BS and 4BS are formed; and above 76 °C, 4BS predominates (Fig. 1).

The 4BS 'seed' crystals begin to form and continue to grow while the paste temperature remains high. The longer the temperature remains above 65 °C, the larger the crystals grow. This has an adverse effect on the initial high-rate discharge capacity.

For certain plate/battery types, paste subjected to short processing times (in the mixer) at high temperatures may be beneficial by producing tetrabasic 'seed' crystals that can then grow during the hydroset process. For automotive batteries, these crystals can strengthen the battery plate and improve durability under cyclic charge/discharge conditions [3].

The acid-to-oxide ratio is also significant in controlling the level (Table 2) and size of the 3BS and 4BS crystals. The yields of 3BS and 4BS decrease, the size of 3BS increases, and the size of 4BS decreases, when using a low acid-to-oxide ratio [4]. Changes in the phase composition of paste (manufactured from the same starting leady oxide) that result from variations in the acid-to-oxide ratio are illustrated in Fig. 2 [2].

The key, however, in controlling the formation of 3BS and/or 4BS is accurate measurement of the temperature during the mixing process, and the capability to then control that temperature, precisely, to achieve

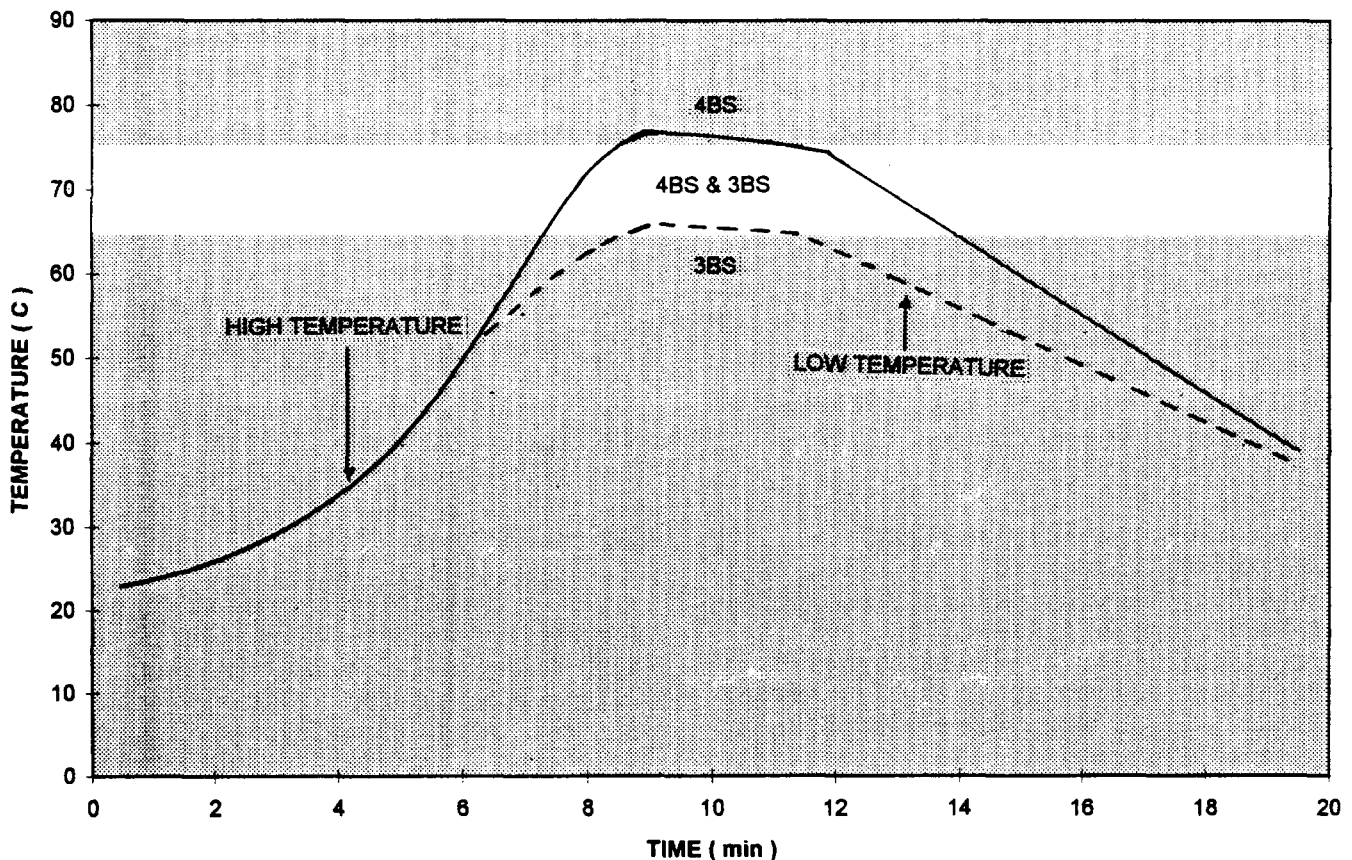


Fig. 1. Effects of paste temperature, during the mixing cycle, on the formation of 3BS and 4BS basic lead sulfates.

Table 2  
Phase analysis (wt.%) of pastes with varying acid-to-oxide ratios and densities [4]

Paste		Phase composition				
Acid:oxide (%)	Density (g cm <sup>-3</sup> )	Pb	$\alpha$ -PbO	$\beta$ -PbO	3BS	1BS
6.6	3.9	8	38	10	41	3
6.6	3.5	10	36	10	40	4
3.9	3.9	9	69		20	2
3.9	3.5	12	63		22	3

the desired result. The Oxmaster paste-temperature monitoring and control systems (Thermoprobe and Oxtempo) provide the required temperature/time profile for each specific paste formation, and reliable temperature information is given at any time during the mixing cycle. The Oxtempo software drives the cooling system so that the real temperature profile of the mix resembles very closely the target profile (Fig. 3). Under production conditions, the temperature of each paste mix deviates by only  $\pm 2$  °C from the programmed profile.

The service life of lead/acid batteries is often limited by disintegration of the positive active material (PAM)

from a cohesive, crystalline structure to an amorphous mass [5,6]. The structure of the PAM is influenced strongly by the phase composition, crystal morphology and density of the initial paste [1,7,8]. The conversion of either 3BS or 4BS to PbO<sub>2</sub> is metasomatic, that is, the PbO<sub>2</sub> is similar in size and shape to its precursor. It is also claimed that active masses produced from 4BS pastes have longer cycle lives than those obtained from a (conventional) 3BS precursor and that red lead can be used to reduce the size of 4BS crystals without reducing plate strength [3]. In addition, the morphology and structure of the 4BS active mass is influenced by the raw materials used for the paste and the production method [9]. This further illustrates the need for careful control of temperature during the paste mixing cycle, and requirement for a mixing system with the capability of handling and controlling the addition of many component materials.

#### 4. Paste density and moisture content

Battery paste is made up of several components. The density is dependent on the relative amounts of each component. Due to the great difference in the high mass density of the lead sulfates and the low mass

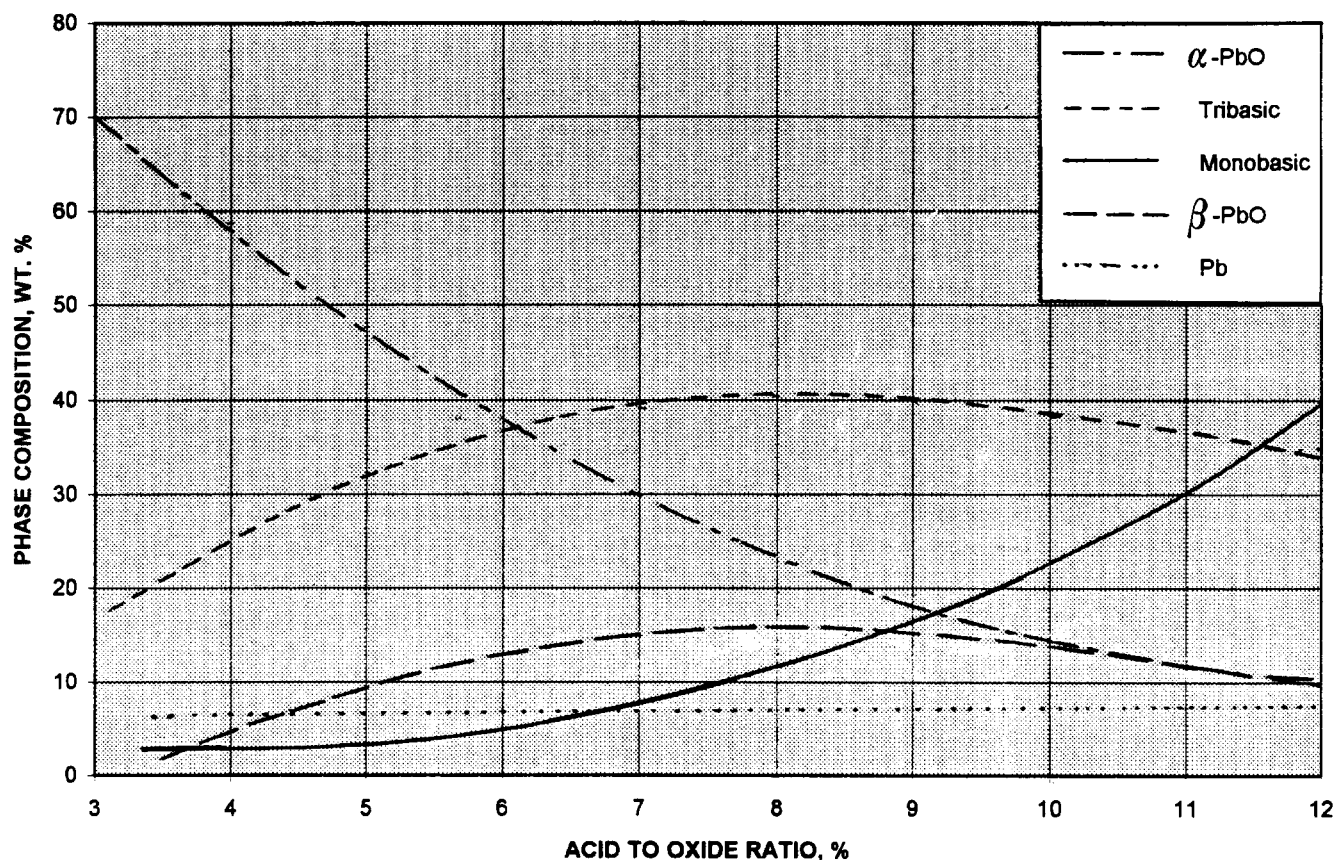


Fig. 2. Changes in paste composition with acid:oxide ratio for the same starting leady oxide [2].

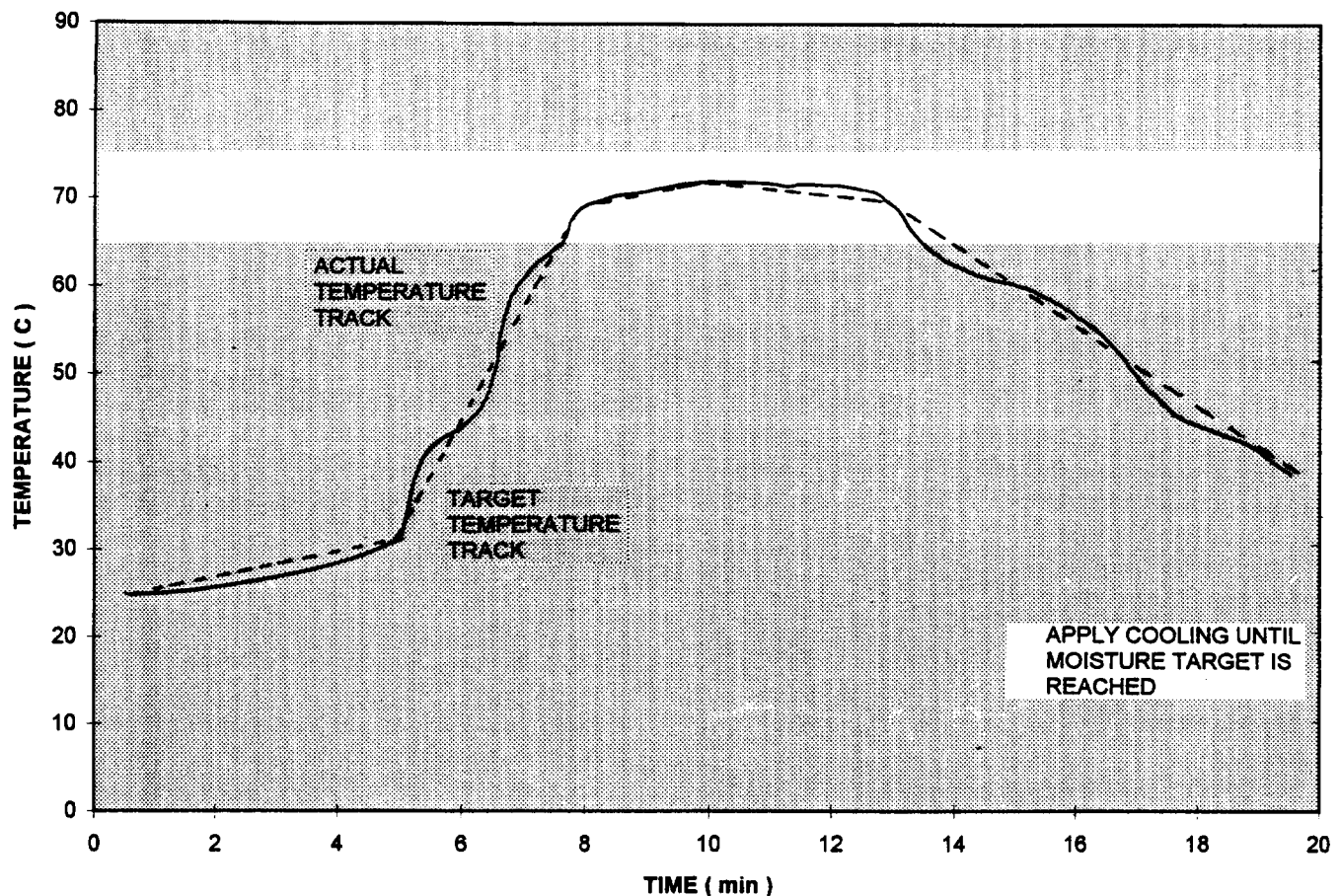


Fig. 3. Paste temperature profile under Oxtemplo control.

density of water, a small change in the moisture content will have a large effect on the density of the paste.

The torque required for kneading and mixing is a function of oxide characteristics (particle-size distribution, shape and surface roughness i.e., surface area), the mixing technique (stirring, shearing, pressing and kneading), the speed of blending and the rate of water addition. Provided that sufficient water is added to the lead oxide to attain a plastic mix, the differences in paste densities of various lead oxides (e.g., Barton and mill) depend strongly on water content [10].

The rheology of the subsequent paste is, therefore, specific to the oxide, mixer, and overall paste formulation. The required plasticity depends solely on the type of pasting machine to be used. Conventional techniques for correcting density errors (adding water and continuing mixing if density is too high, or continuing cooling air while mixing to drive off moisture if the density is too low) are indicative of a poor (unacceptable) level of process control, and are also time-consuming. The ability of the Oxmaster system to manage the temperature and time relationship is further enhanced by its ability to monitor the moisture and density relationship both during, and at the end of, the paste-mixing process. The Oxmode system includes both the

hardware and patented software to determine accurate moisture content of the paste mass as it is being mixed, and to automatically stop the mix when the desired moisture content is reached [11]. During the cooling process, the change of the weight in the mixer is continuously reported to the PLC; and when the preset weight (i.e., moisture content) of the mix is reached, the mix is terminated.

Conventional control of the paste-manufacturing process is usually carried out by measuring the paste density (cube density). This provides control of the prescribed water content of the paste, for a similar lead oxide and acid-to-oxide ratio. The typical measurement procedure requires opening the mixer, taking a hand-picked sample into a standard cup of specified volume, carefully packing the sample into the cup so as not to change the density, raking the top of the sample flush with the top of the cup, and weighing the cup and contents to derive the density (of a very small sample). The density of this sample must be within the specification or the paste is not accepted. Recent tests by one manufacturer have emphasized the inaccuracy of this test. After repeated density samples were taken on the same mix, by the same operator, a ( $3\sigma$ ) variation of  $\pm 0.2 \text{ g cm}^{-3}$  was recorded. By comparison, the

moisture content of paste prepared under manufacturing conditions using the Oxmode system (by taking three, random, density samples from each paste batch, over a series of production periods) had a ( $3\sigma$ ) variation of  $\pm 0.007 \text{ g cm}^{-3}$ . The correlation between density and moisture, in these tests using the Oxmode system, is much better than previous density measurements used in the industry. In addition, it was not necessary either to add water at the end of the mix, or to continue mixing to drive off moisture, in order to meet the criteria for batch acceptance.

### 5. Paste penetration (plasticity)

It is well known that the addition of sulfuric acid (typically 1.400 sp. gr.) will stiffen paste, while the addition of water will soften it. Nevertheless, excessively high acid-to-oxide ratios result in a paste texture that is unsatisfactory for use.

For the same mix ratios, the plasticity and texture are related to the mixing sequence; the masses with the best plastic properties result from the addition of dilute acid to the oxide [12]. More uniform and better plastic masses are produced if the mixing sequence begins with the addition of water and then sulfuric acid.

Penetration tests on paste are performed by most battery manufacturers in an effort to predict the performance of the paste during the grid-pasting process. Several additional factors affect the paste penetration (plasticity) and should also be considered. The moisture content of the paste is particularly important. A higher moisture content yields a higher penetration value. The crystal morphology of the paste also exerts an effect on the penetration value. The presence of 4BS crystals reduces the penetration (increases the stiffness) of pastes with equal moisture content. Tribasic lead sulfate (3BS) crystals offer less mechanical resistance, thereby increasing penetration values (softening the paste). Extended mixing times will cause the lead sulfate crystals, already formed, to fracture showing increased penetration values. Paste penetration and density may be well within specification but the paste can lose its 'crunch'. This causes plate-pasting difficulties and a loss in paste quality and battery performance.

The normal corrective action for low penetration (stiff paste) is the addition of water and the continuation at intervals of the mixing process to include the water in the paste mass. For the correction of high penetration readings, no water is added, but the cooling and the mixing process is continued for a short period, usually

at the discretion of the mixer operator. This reduces the paste moisture and, thereby, lowers the penetration reading. With the control of time, temperature and density (i.e., moisture content) by using the Oxmode system, penetration values are consistent from batch-to-batch.

### 6. Summary of Oxmaster features

The paste-quality control system of the Oxmaster system allows battery manufacturers to automatically manage paste temperature, paste density and paste penetration. The result is high-quality paste with predictable and repeatable characteristics. By determining the end of the mixing procedure in terms of moisture content, the penetration has been proven to be extremely reliable with a sigma value of 0.17 points (Globe #1 penetrometer).

The Oxmaster blade design, with high shearing action, provides superior wetting action of the oxide particles. This leads to increased material utilization and, most importantly, to a very low percentage of inactive materials.

The Thermoprobe provides an accurate measurement of paste temperature because it can take a sample of paste while the mixer is running and rapidly report the temperature of the sample. The sample is then automatically returned to the mixing chamber. Mixers equipped with the Oxtempo system can control peak temperature and the duration at peak temperature.

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