

The influence of stand time on tribasic and tetrabasic lead sulfate containing lead/acid battery active masses

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Abstract

The influence of standing on positive lead/acid battery active mass was investigated by laboratory scale preparation of two different types of active masses – one containing tribasic lead sulfate (=3BS), another containing tetrabasic lead sulfate (=4BS) – and subsequent monitoring of the changes in phase composition and morphology as a function of stand time. The characterization methods used were powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). In order to ensure the applicability of the results from laboratory tests to real lead/acid battery processes the same phase composition and morphology monitoring was performed with a 3BS paste from a lead/acid battery factory. A continuous recrystallization process and a clear growth of crystal size were observed both in the laboratory and factory 3BS pastes during standing. In the 4BS paste the crystal growth due to rearrangement of the crystals finished after one hour of standing.

Introduction

In lead/acid battery production the active mass for the pasted positive plate is normally prepared in 400–1500 kg batches. Partially oxidized lead powder (leady oxide), water, diluted sulfuric acid solution, chemically resistant fibers and sometimes red lead are used in the preparation of positive active masses [1–4].

In the first step of positive paste preparation, leady oxide is mixed with water forming a mixture with an pH value of about 9. In the beginning of the second step, when a small portion of the total amount of sulfuric acid solution is added to the mixture, the sulfate ions are assimilated into the PbO lattice. This process takes place without pronounced lattice change and without the precipitation of any known stoichiometric lead compounds. With increasing quantities of sulfuric acid, the tribasic lead sulfate, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (=3BS), is eventually precipitated. At temperatures above approximately 70 °C, the initially formed 3BS undergoes a recrystallization to the tetrabasic lead sulfate, $4\text{PbO} \cdot \text{PbSO}_4$ (=4BS). The development of a third monobasic

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lead sulfate (= 1BS) takes place only when pH falls locally due to poor mixing or, when an excess of sulfuric acid is used in paste preparation. In practice, the amount of sulfuric acid added is not sufficient to convert all the PbO to basic lead sulfates during the mixing. The metallic lead remains largely unreacted during paste mixing. At the end of the mixing the paste will contain some or all of the following solid species: Pb, PbO, Pb₃O₄, PbO · nH₂O, 1BS, 3BS and 4BS [1, 3, 5–7].

The fact that 4BS is chemically inert to water has been utilized in 'long-life battery plate technology', where synthesized 4BS powder is first mixed with water in order to obtain a paste for mechanically strong battery plate. The paste is then spread onto the grids and cured and dried in a humid atmosphere containing CO₂. This is to overcome the shedding of the active mass from the plates when placed in H₂SO₄ solution. These pastes are known as 'non-reactive' because no chemical reactions — only rearrangement of the crystals — take place during the preparation and drying of the pastes [2–4, 8].

Despite the fact that the 4BS paste with large crystals results in long life and cyclable plates, its presence, in large amounts in the positive paste, is considered undesirable in starter batteries. This is due to the problems in formation and lower initial capacity of the 4BS paste. Pavlov and Kapkov [9, 10] have recently published paste preparation methods by which it is possible to overcome the formation problems existing in conventional 4BS plates. The basis of the method is the use of red lead (Pb₃O₄) to replace part of the leady oxide as a raw material of 4BS paste.

In the battery industry the routine characterization procedures of the paste are density and consistency measurements. Density determines the bonding between particles under static conditions and consistency does the same under dynamic conditions. Both parameters are functions of the water and sulfuric acid content in the paste. In paste mixing the aim is to reach a plastic state, characterized by a definite density and consistency, which not only allows the paste to be spread uniformly onto grids but also to be retained there [11].

Usually, the active mass is spread onto the grids by pasting machines as soon as possible after mixing. For large batches, however, there is considerable stand time during which chemical processes occur in the paste. In addition, pasting is often delayed due to interruptions or poor synchronizing in the production, and thus the paste has to wait for pasting, in most cases in a silo. During long stand times, the evaporation of water has significant influence on the processability of the mass; the dried paste is difficult to spread onto the grids, the mass amount in the plates will vary and the contact between the active mass and the grid may not be sufficiently strong. Although the process parameters can be adjusted to account for an aged paste this is undesirable in an industrial process.

In addition to the changes in the physical properties of the paste, e.g. density, consistency, as well as electrical and mechanical properties of the plates, it is also useful to see if there are any significant changes in the phase composition and morphology of the paste due to the standing, and the speed of these changes. This is important in order to understand the nature of the possible problems in the subsequent process steps caused by the long standing, as well as to minimize them by maintaining the properties of the 'fresh', constant quality paste. In this study the effect of standing on the phase composition and morphology of the positive plate paste was investigated by preparing 3BS and 4BS pastes and monitoring their phase composition and morphology during standing by XRD and SEM, respectively. A comparison between the results of 3BS pasted prepared in the laboratory and in a battery factory was also carried out.

Experimental

The syntheses of the pastes were carried out in a simple laboratory mixer system composed of an open beaker, mechanical stirrer, hotplate and water bath. Mill oxide from a battery plant, sulfuric acid (sp.gr. = 1.40) and deionized water were used as the raw materials in the syntheses. Each batch of the syntheses was composed of 200 g of mill oxide, 6 wt.% of H_2SO_4 with respect to mill oxide and water to adjust the density of the paste to 4.2 g/cm^3 . The final adjustment of the density of the paste was performed with water at the end of the mixing. The mixing temperatures and mixing times of 3BS and 4BS containing pastes were 55–60 °C, 30 min and 80 °C, 60 min, respectively. The mixing times and temperatures were selected so that the only basic lead sulfate present at the lower temperature was 3BS and at the higher temperature 4BS.

After mixing, the paste was left to stand and the paste temperature was allowed to decrease slowly, with a profile similar to the actual factory scale mixer. The reaction vessel was sealed with a cover during standing to reduce water evaporation. The changes in phase composition and morphology in the pastes were monitored by XRD and SEM. The X-ray diffraction analyses were performed with a Siemens Diffrac 500 diffractometer and the interpretation of the diffraction patterns with the help of JCPDS reference data. The electron micrographs were obtained on a JEOL 840A scanning electron microscope.

For the purposes of comparison, a 3BS paste sample from the factory process (700 kg batch) was taken and subjected to similar standing and sampling procedure as the laboratory pastes. The mixing temperature of the 3BS factory paste was the same as in the laboratory; the mixing time was 20 min. The paste sample was inserted in an isolated container with a cover immediately after mixing and transported to the laboratory for the analyses. Due to the distance between the factory and the laboratory the monitoring of the paste could only be started 40 min after the end of the paste mixing.

Results and discussion

The changes in phase composition as a function of stand time in 3BS and 4BS laboratory pastes are presented in Figs. 1 and 2. The phase composition of the pastes was monitored by following the change in relative intensity of the characteristic diffraction lines. Since it was not possible to use the strongest line of tetragonal lead monoxide (T-PbO) as the characteristic line due to the peak overlap, a weaker line ($48.59^\circ (2\theta)$) was chosen. Thus the interpretation of the quantitative amounts of phases present on the basis of relative intensities is even more difficult. However, the use of relative intensities of diffraction lines is adequate, if one wants to indicate changes in phase composition. Only the intensity measurement of the relevant diffraction lines of each monitored phase was used in order to shorten the scanning time and thus to minimize further reactions in the paste during diffraction runs. The stand time at zero minutes corresponds to the moment after 30 min mixing in the case of the 3BS paste (Fig. 1) and to the moment after 60 min mixing in the case of the 4BS paste (Fig. 2).

In the 3BS paste periodic changes of relative intensities of T-PbO and 3BS ($27.40^\circ (2\theta)$) diffraction peaks as a function of stand time were observed. These fairly small changes in relative peak intensities can be explained by inhomogeneities in the laboratory

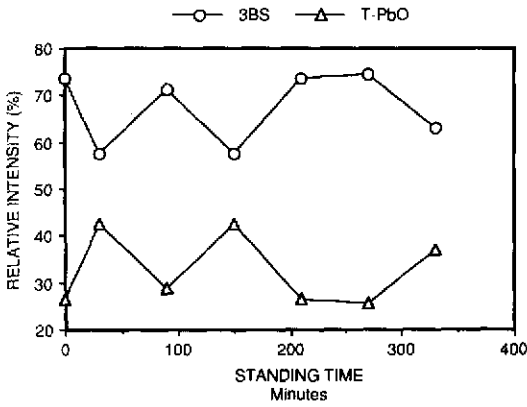


Fig. 1. Changes in phase composition of 3BS paste as a function of stand time. Mixing time 30 min; temperature 55–60 °C.

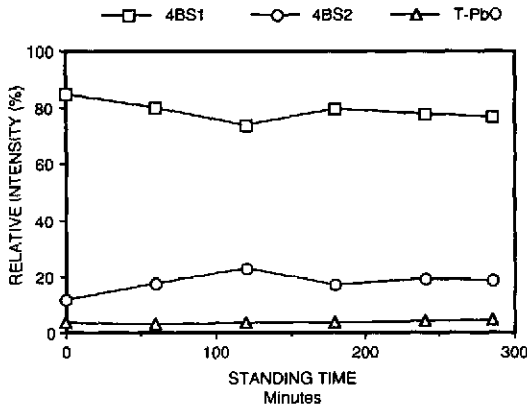


Fig. 2. Changes in phase composition of 4BS paste as a function of stand time. Mixing time 60 min; temperature 80 °C. 4BS1 and 4BS2 correspond to diffraction lines at 27.58 and 30.99° (2θ), respectively.

paste mix rather than any real changes in phase composition. This explanation is also supported by SEM micrographs, which show that the particle size of 3BS gradually increases during standing and no differences in the morphology of the paste at the two extreme stages of the 'phase oscillation' were observed. Some crystals even reached a size of 8 μm in length and 3 μm in width after 5 h (Fig. 3 (c)). This particle size is much larger than in a normally cured 3BS paste reported by Pavlov and Papazov [11]. They found 3BS crystals that were usually 1–3 μm long.

In the 4BS paste the changes in phase composition during standing were smaller than in the 3BS paste. The relative intensity of the 4BS diffraction line at 27.58° (2θ) decreased slightly while at same time the intensity of the other 4BS peak 30.99° (2θ) increased during the first hour of standing. This is probably due to orientation changes during particle growth. The particle growth can be seen when comparing the SEM micrographs taken from the paste immediately after mixing and from the paste which

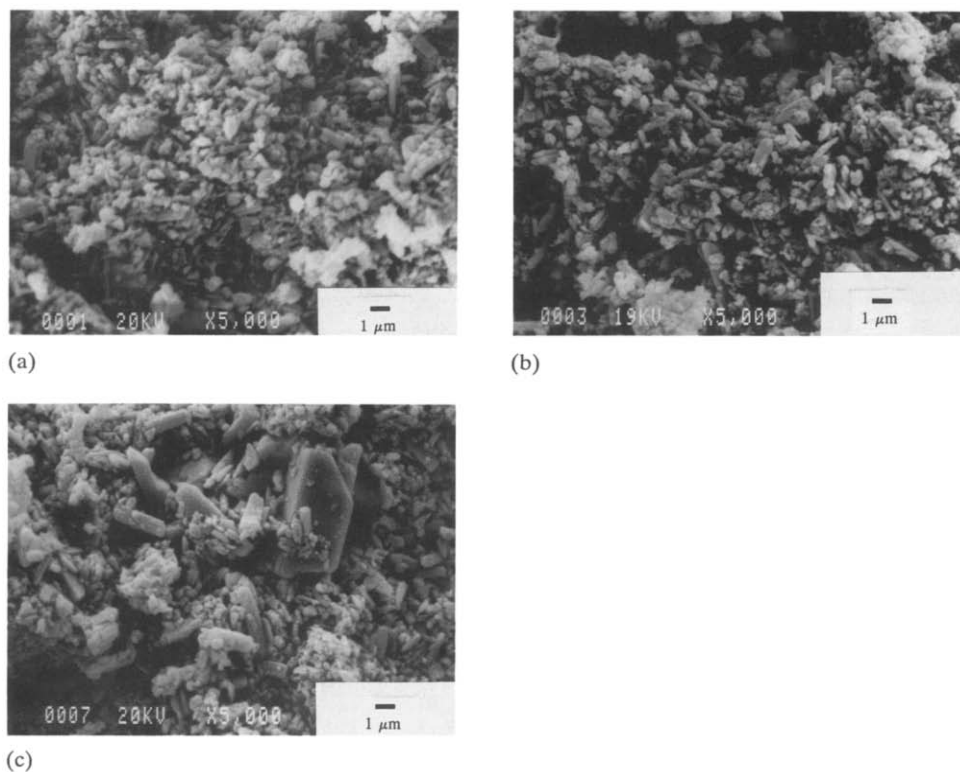
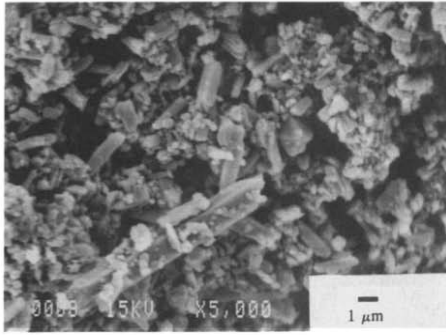


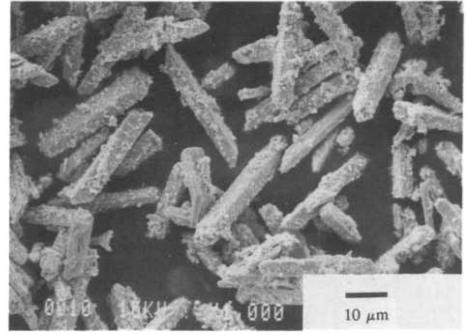
Fig. 3. Scanning electron micrographs of 3BS paste; stand times (a) 0 min, (b) 90 min, and (c) 330 min after mixing.

has been standing for 60 min after mixing (Fig. 4). The SEM micrographs show that the particle size of 4BS is much bigger after 60 min of standing (Fig. 4 (b)) than immediately after mixing (Fig. 4 (a)), but further prolongation of standing time, upto nearly 5 h (Fig. 4 (c)), did not have any significant influence on the particle size of the 4BS. In addition, the X-ray diffraction analyses of the paste show that the recrystallization process from initially formed 3BS to 4BS is completed during 60 min of mixing. This was noted in an earlier investigation with the same mixer system [12].

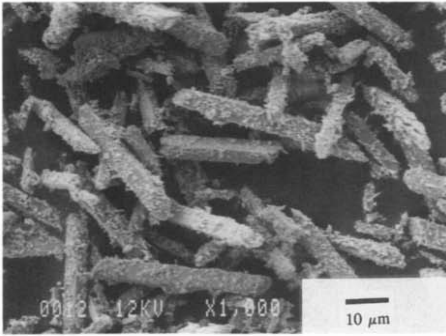
When monitoring the 3BS factory paste a similar recrystallization process was observed as seen earlier in the 3BS laboratory paste but it proceeded without the 'phase oscillation' observed in the 3BS laboratory paste due to poor homogeneity (Fig. 5). The growth of 3BS crystals and partial fading away of amorphous material as a function of stand time can be clearly seen in the SEM pictures taken after 40, 170 and 340 min stand time (Fig. 6). The SEM pictures show that the morphology of the factory paste and the laboratory 3BS paste is very similar at the end of the standing period, except for some very large crystals existing in the laboratory paste. The difference observed between the laboratory and factory pastes could be due to the difficulty in ensuring identical preparation conditions, e.g. mixing mode in the small laboratory mixer and large plant mixer.



(a)



(b)



(c)

Fig. 4. Scanning electron micrographs of 4BS paste; stand times (a) 0 min, (b) 60 min, and (c) 285 min after mixing.

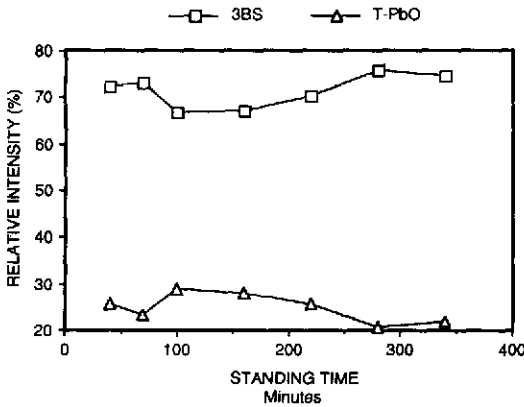
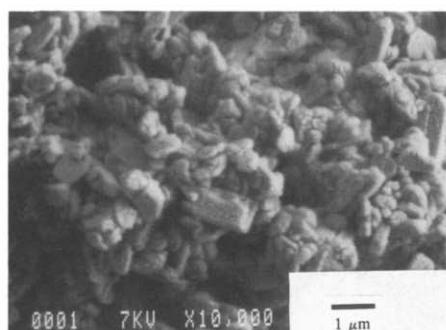
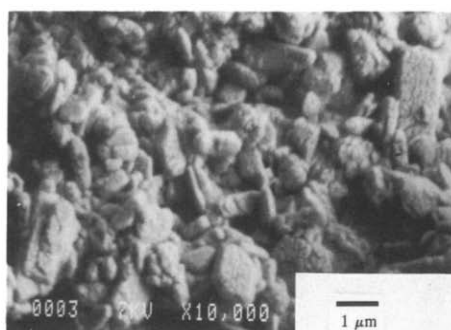


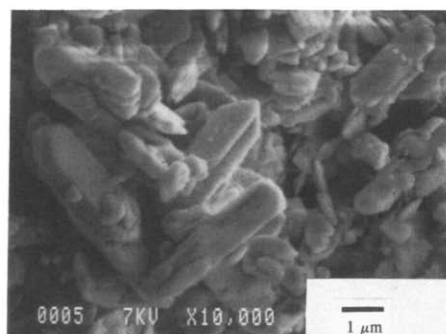
Fig. 5. Changes in phase composition of a factory paste as a function stand time. Mixing time 20 min.



(a)



(b)



(c)

Fig. 6. Scanning electron micrographs of a factory paste; stand times (a) 40 min, (b) 110 min, and (c) 280 min after mixing.

Conclusions

In the 4BS paste there was practically no change in phase composition due to the standing of the paste, although a clear increase in crystal size during the first hour of standing was evident. This rather fast crystal growth may change the processability of the paste and make the pasting more difficult immediately after mixing. After one hour of standing the particle size growth in the 4BS paste was practically finished. Therefore, it can be concluded that when using an appropriate quantity of additional water, the paste would be processable and could be used in plate production. The only remaining question is how to assure good mechanical and electrical properties of the plates without prolonged processing times and additional production costs.

Generally, there was no end point in crystal growth of either of the 3BS paste types investigated; the crystal growth continued for the whole stand time. It would be interesting to study the large 3BS crystals, seen especially clearly in the laboratory paste after 5.5 h of standing (Fig. 4(c)), to see if they result in some permanent changes to the 'genetic code' of the paste and thus to the performance of the final battery plates.

In the factory paste a crystal growth due to a recrystallization process was also noticed. On the basis of X-ray diffraction the factory paste was, however, more homogeneous than the laboratory paste. In addition, the large 3BS crystals observed

in the laboratory paste at the end of standing did not exist in the factory paste. This difference can be explained by the different conditions in the small laboratory mixer and in the battery plant mixer.

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