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The influence of PbO modification on the kinetics of the $4PbO{\cdot}PbSO_4$ lead-acid battery paste formation

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The influence of PbO modification on the formation of $4PbO \cdot PbSO_4$ paste is determined by X-ray diffraction analysis and scanning electron microscopy. The paste was prepared from tetragonal PbO, orthorhombic PbO and several mixtures of both oxides at 80° C and a H_2SO_4/PbO ratio of 6 wt%.

The reaction scheme of $4PbO \cdot PbSO_4$ formation depends on the PbO modification. When tetragonal PbO is used, $3PbO \cdot PbSO_4 \cdot H_2O$ crystals are obtained first and then $4PbO \cdot PbSO_4$. If the initial oxide is orthorhombic PbO, $PbSO_4$, $PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4 \cdot H_2O$ are formed successively. When the correct ratio of $3PbO \cdot PbSO_4 \cdot H_2O$, orthorhombic PbO and tetragonal-PbO is achieved in the paste then $4PbO \cdot PbSO_4$ formation begins. This ratio is reached most quickly if tetragonal PbO is present at 30–60 wt% in the initial mixture of both modifications.

1. Introduction

The life of lead–acid battery positive plates depends on both grid corrosion and the softening and shedding of PbO_2 active material. It was established that the mechanical stability of the PbO_2 structure increases when big needle-shaped crystals of PbO_2 are present [1, 2]. Burbank [3] showed that it is the $4PbO \cdot PbSO_4$ paste that gives this PbO_2 needle-shaped crystals after formation.

For production of long-life lead–acid batteries a technology using synthetic $4PbO \cdot PbSO_4$ was developed [4]. $4PbO \cdot PbSO_4$ was synthesized in suspension by reaction between orthorhombic PbO and H_2SO_4 solution. This synthesis introduces some slow operations in the lead–acid battery production process. In addition the PbO_2 formation time from a $4PbO \cdot PbSO_4$ paste becomes rather long. Biagetti and Weeks [4] showed that positive plate life depends on the density of the $4PbO \cdot PbSO_4$ paste. Various wet paste densities were obtained by changing the amount of water added to the $4PbO \cdot PbSO_4$ powder and by varying the stirring time [5]. Fleischmann and Schlotter [6, 7] determined that the specific void volume of $4PbO \cdot PbSO_4$ paste was greater than that of pastes containing no $4PbO \cdot PbSO_4$.

We have set ourselves the aim of studying the possibility of $4PbO \cdot PbSO_4$ formation by the existing technology of paste preparation from oxidized lead powder and H_2SO_4 solution. Then the present production method can be preserved. Bode and Voss [8] established that $4PbO \cdot PbSO_4$ is formed in the paste at temperatures higher than 70° C. Pavlov and Papazov [9] determined the dependence of the $4PbO \cdot PbSO_4$ content in the paste on the H_2SO_4/PbO ratio. We established [10] that small quantities of organic substances in the paste stop $4PbO \cdot PbSO_4$ formation. This paper studies the influence of the PbO modification on the kinetics of $4PbO \cdot PbSO_4$ paste formation.

2. Experimental methods

The kinetics of the processes during paste preparation were followed by the changes in phase composition and crystal morphology over a period of 2 hours.

The pastes were prepared under the most favourable conditions for the $4PbO \cdot PbSO_4$ formation: temperature of stirring 80° C, absence of surface active organic substances and

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Table 1

d (nm)	*Compound*
0·300	$PbSO_4$
0·333	$PbO \cdot PbSO_4$
0·326	$3PbO \cdot PbSO_4 \cdot H_2O$
0·321	$4PbO \cdot PbSO_4$
0·281	tetragonal PbO
0·295	orthorhombic PbO

H_2SO_4/PbO ratio equal to 6 wt%. Chemically pure tetragonal- and orthorhombic-PbO were used.

2 kg of PbO and 1.2 sp.gr. H_2SO_4 solution were mixed in a Z-blade mixer. Samples were taken from the paste at various times after the beginning of mixing. To stop the reactions, the samples were cooled down quickly. A part of the sample was X-rayed. The crystal structure of the other part was observed by SEM.

The phase composition changes during the paste preparation were established by the relative intensity of the characteristic diffraction lines (see Table 1).

The basic lead sulphates and the lead oxides have similar diffraction patterns and many of the diffraction lines overlap or are very close. It was therefore necessary to use for characterization some lines with an intensity of less than 100. Hence the values of the relative intensities do not correspond to real percentages of the phases in the paste.

Another part of the sample was placed in a special container and dried in a vacuum. The paste crystals' morphology was observed by SEM.

3. Experimental results

3.1. *$4PbO \cdot PbSO_4$ paste formation from tetragonal PbO*

The relative intensity changes of the phases during paste preparation are presented on Fig. 1. $3PbO \cdot PbSO_4 \cdot H_2O$ and orthorhombic PbO are formed initially. After 10 min of stirring, $4PbO \cdot PbSO_4$ formation begins. Between 15 and 30 min the content of $3PbO \cdot PbSO_4 \cdot H_2O$, tetragonal PbO and orthorhombic PbO decreases and that of $4PbO \cdot PbSO_4$ increases. After that the paste contains mainly $4PbO \cdot PbSO_4$.

Fig. 2 presents SEM micrographs of the paste crystals after 1, 11, 21 and 61 minutes of stirring. During the initial 11 minutes only separate crystals (probably $3PbO \cdot PbSO_4 \cdot H_2O$) are well formed. After 21 min (Fig. 2c) the paste contains some $4PbO \cdot PbSO_4$ crystals, but they are small and hardly distinguishable from those of $3PbO \cdot PbSO_4 \cdot H_2O$. After 61 minutes (Fig. 2d) well-shaped big $4PbO \cdot PbSO_4$ crystals are observed. These changes of the crystals size and shape during paste preparation show that the process of $4PbO \cdot PbSO_4$ crystal growth occurs by transport of material through the solution.

3.2. *$4PbO \cdot PbSO_4$ paste formation from orthorhombic PbO*

The relative intensity changes of the phases during paste preparation are presented in Fig. 3. Initially, $PbSO_4$ is formed. After 10 min the paste contains $PbO \cdot PbSO_4$, $3PbO \cdot PbSO_4 \cdot H_2O$, tetragonal PbO and orthorhombic PbO. After 20 min

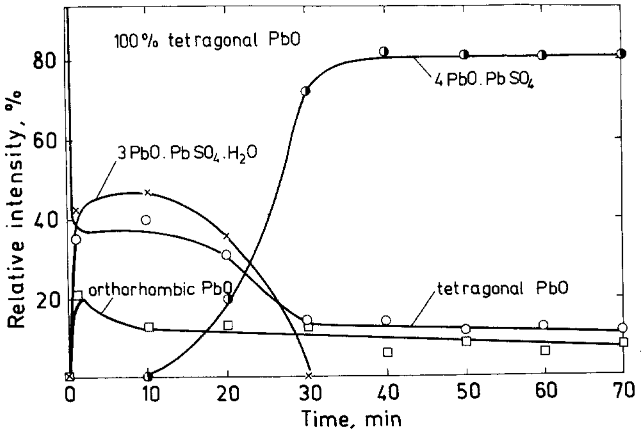

Fig. 1. Changes in phase composition during stirring of the paste. Initial oxide, 100% tetragonal PbO.

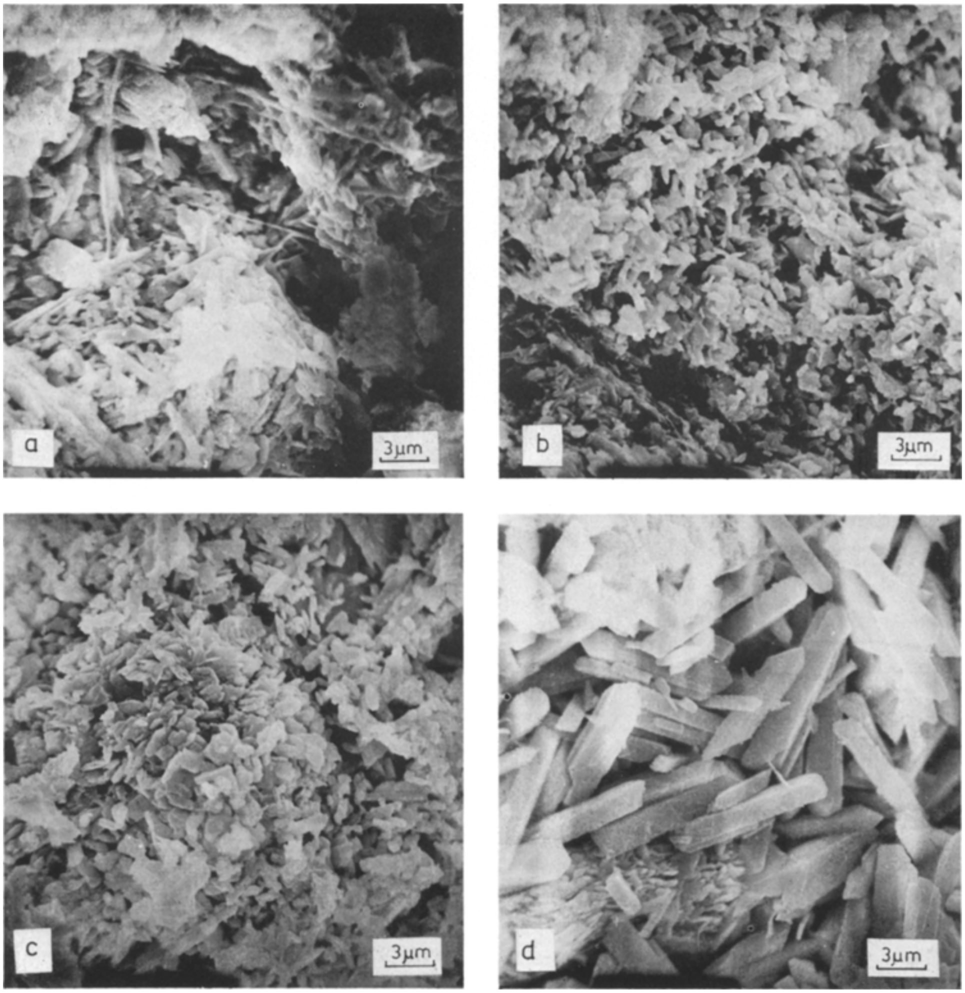

Fig. 2. Morphology of crystals during paste preparation. Initial oxide, 100% tetragonal PbO. The samples are taken after: (a) 1 min, (b) 11 min, (c) 21 min, (d) 61 min.

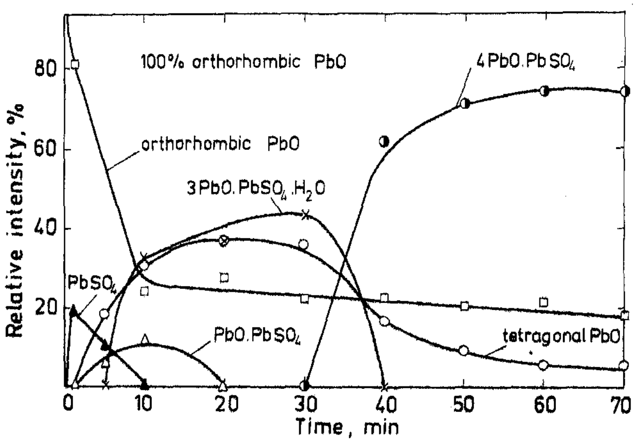

Fig. 3. Changes in phase composition during stirring of the paste. Initial oxide, 100% orthorhombic PbO.

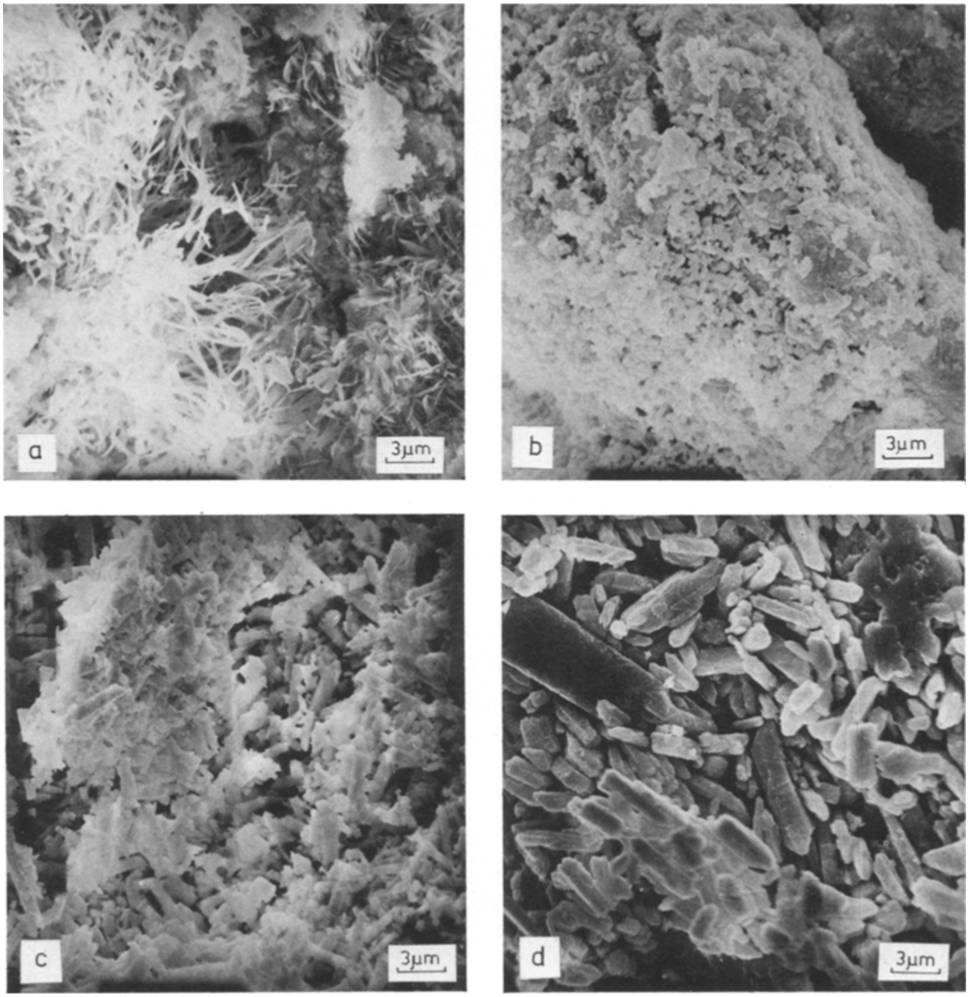

Fig. 4. Morphology of crystals during paste preparation. Initial oxide, 100% orthorhombic PbO. The samples are taken after: (a) 1 min, (b) 31 min, (c) 41 min, (d) 91 min.

$PbO \cdot PbSO_4$ transforms entirely into $3PbO \cdot PbSO_4 \cdot H_2O$. $4PbO \cdot PbSO_4$ formation begins after 30 min and up to 60 min its content in the paste grows.

Fig. 4 shows SEM micrographs of paste crystals after 1, 31, 41 and 91 min. $PbSO_4$ whiskers are observed on Fig. 4a. On Fig. 4c some $4PbO \cdot PbSO_4$ crystals can be distinguished. They are well shaped after 91 min (Fig. 4d). Figs. 1 and 3 show that $4PbO \cdot PbSO_4$ paste is formed from tetragonal PbO faster than from orthorhombic PbO.

3.3. *$4PbO \cdot PbSO_4$ paste formation from tetragonal and orthorhombic PbO mixtures*

A series of pastes were prepared by using tetragonal and orthorhombic PbO mixtures. The changes of phase composition during paste preparation from a 50% tetragonal PbO and 50% orthorhombic PbO mixture is given on Fig. 5. After 10 min $4PbO \cdot PbSO_4$ formation begins and after 20 min a steady-state paste composition is achieved. The rate of $4PbO \cdot PbSO_4$ formation

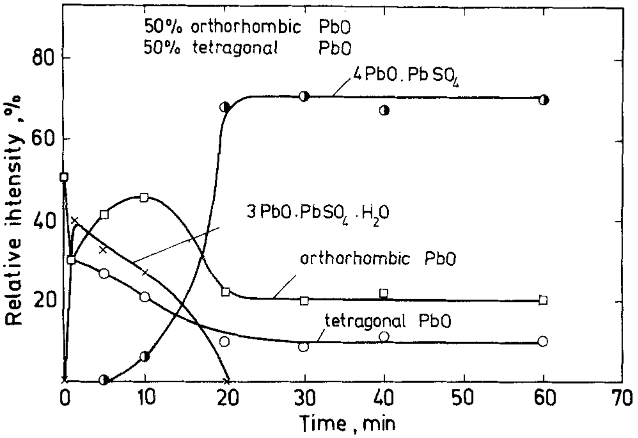

Fig. 5. Changes in phase composition during stirring of the paste. Initial oxide, 50% tetragonal and 50% orthorhombic PbO.

becomes high when the correct ratio of tetragonal PbO, orthorhombic PbO and 3PbO•PbSO$_4$•H$_2$O phases is achieved. We established that when the tetragonal PbO content in the initial mixture is between 30% and 60%, the rate of 4PbO•PbSO$_4$ formation is highest.

3.4. *Influence of the surface active organic additives on the paste processes*

Sodium lignosulphonate (SL) was chosen as a surface active additive in the paste.

Fig. 6 shows the phase content changes during paste preparation from tetragonal PbO, H$_2$SO$_4$ solution and 1 wt% SL. SL does not greatly influence 3PbO•PbSO$_4$•H$_2$O formation. The X-ray diffractometer patterns of these pastes contain both the lines of 5PbO•2H$_2$O (d = 0·305 nm) and PbO•PbSO$_4$ (d = 0·333 nm). The content of these compounds in the paste remains constant during the whole period of measurement.

Fig. 7 presents SEM micrographs of the crystals after 1 and 80 min of paste preparation from tetragonal PbO, H$_2$SO$_4$ solution and 1 wt% SL. The crystals on both micrographs are similar which shows that SL inhibits the processes of dissolution and growth of the crystal nuclei.

Fig. 8 gives the phase composition changes during the paste preparation from orthorhombic PbO, H$_2$SO$_4$ solution and 1 wt% SL. The rates of formation and dissolution of PbO•PbSO$_4$ are decreased by SL, as well as the rates of 3PbO•PbSO$_4$•H$_2$O and tetragonal PbO formation. 4PbO•PbSO$_4$ is not formed in the paste at all. This agrees with [10]. The orthorhombic PbO content in the paste decreases comparatively quickly up to 30 min. After that the tetragonal PbO and 3PbO•PbSO$_4$•H$_2$O contents in the paste increase, but PbO is necessary for this process. We suppose that amorphous hydroxides are formed at first in the paste. They supply the material for the above process. So, besides decreasing the

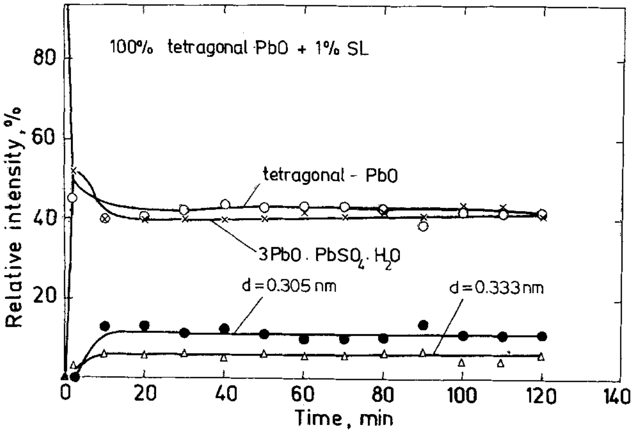

Fig. 6. Changes in the phase composition during stirring of the paste. Initial oxide, 100% tetragonal PbO; H$_2$SO$_4$ solution and 1 wt% sodium lignosulphonate (SL).

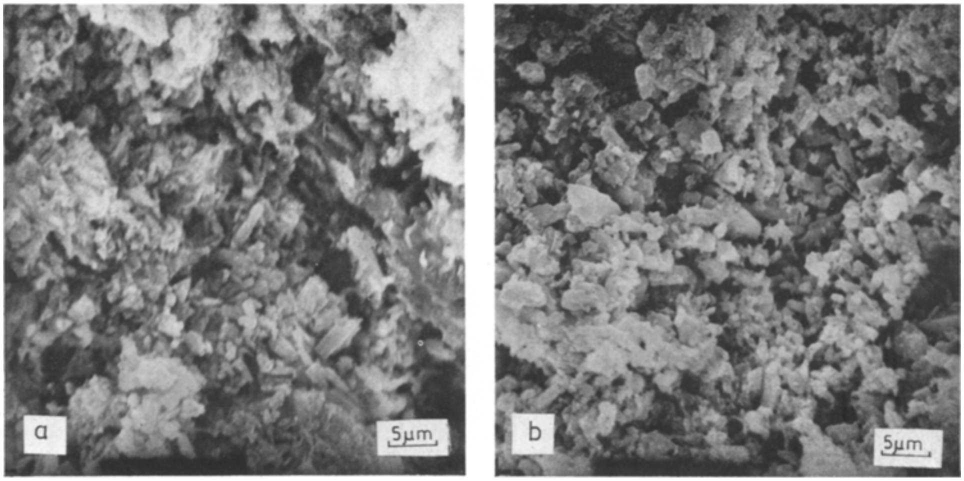

Fig. 7. Morphology of crystals during paste preparation. Initial oxide, 100% tetragonal PbO; H_2SO_4 solution and 1 wt% sodium lignosulphonate. The samples are taken after: (a) 1 min (b) 81 min.

rates of basic lead sulphate formation, SL favours the formation of the amorphous products.

SEM micrographs of the crystals after 1, 10, 30 and 120 min of paste preparation from orthorhombic PbO and 1 wt% SL are presented on Fig. 9. On Fig. 9b $PbO \cdot PbSO_4$ whiskers are observed. After 30 min (Fig. 9c) when orthorhombic PbO, tetragonal PbO, $PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4 \cdot H_2O$ are present in the paste, many tiny crystals are formed. Their shape is preserved even after 120 min (Fig. 9d) although the $3PbO \cdot PbSO_4 \cdot H_2O$ content is prevailing and $PbO \cdot PbSO_4$ has disappeared.

4. Discussion

The formation of one or another basic lead sulphate is determined by the pH of the paste solution. Bode and Voss [8] have presented a pH diagram of basic lead sulphates solubilities. The thermodynamically stable pH regions of $PbSO_4$, $PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4 \cdot H_2O$ can be determined from it. In Table 2 are given these pH regions calculated on the basis of Bode and Voss's data for two SO_4^{2-} ion activities.

In the reaction between PbO and H_2SO_4 solution, $PbSO_4$ should be formed initially, because the pH of H_2SO_4 is far below 6·8 (at $a_{SO_4^{2-}} = 10^{-3}$, Table 2). At the H_2SO_4/PbO ratio used, the whole H_2SO_4 reacts with only a part of the PbO. A considerable amount of unreacted PbO remains in the paste. This PbO hydrolizes, dissociates and the pH of the paste solution increases. As $PbSO_4$ is unstable at a pH above

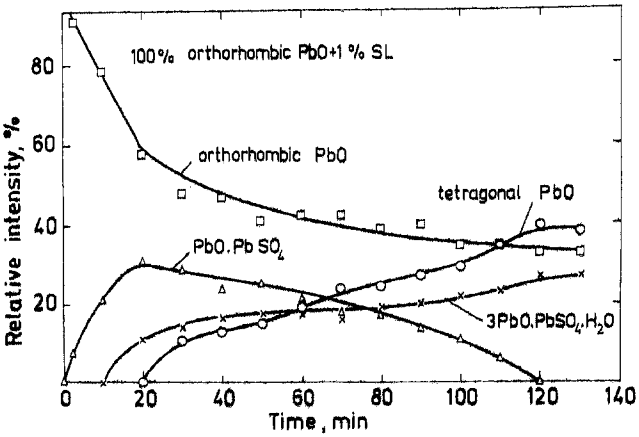

Fig. 8. Changes in phase composition during stirring of the paste. Initial oxide, 100% orthorhombic PbO; H_2SO_4 solution and 1 wt% sodium lignosulphonate.

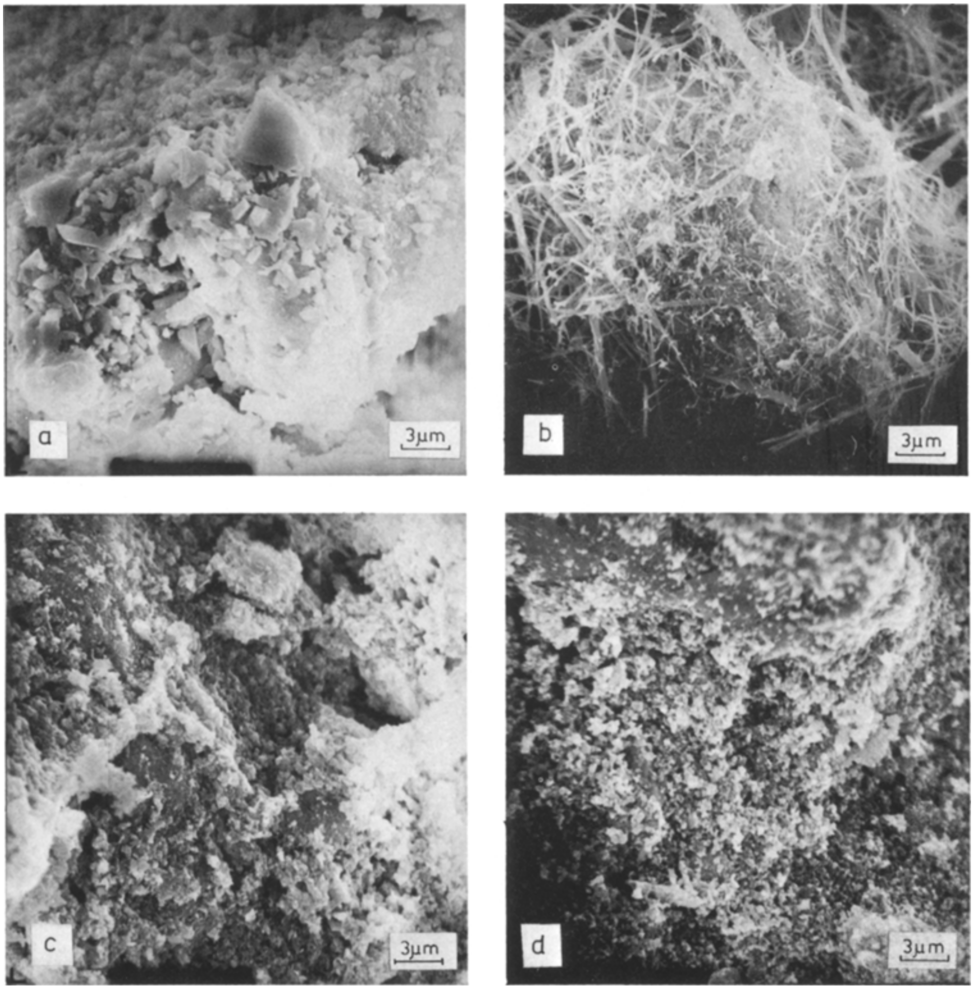

Fig. 9. Morphology of crystals during paste preparation. Initial oxide, 100% orthorhombic PbO; H_2SO_4 solution and 1 wt% sodium lignosulphonate. Samples are taken after: (a) 1 min, (b) 10 min, (c) 30 min, (d) 120 min.

6·8 (Table 2), it dissolves and basic lead sulphate is formed. This basic lead sulphate corresponds to the new pH value of the paste solution. Figs. 1, 3 and 5 show that the reaction scheme of 4PbO·$PbSO_4$ formation depends on the PbO modification. $PbSO_4$, PbO·$PbSO_4$ and 3PbO·$PbSO_4$·H_2O are formed successively. When a proper ratio of 3PbO·$PbSO_4$·H_2O, orthorhombic PbO and tetragonal PbO in the paste is achieved, 4PbO·$PbSO_4$ formation begins.

The PbO crystal lattice modification can influence the basic lead sulphate formation by the rate of nucleation. In the basic lead sulphate crystal nucleation several ions (Pb^{2+}, OH^-, SO_4^{2-}, HSO_4^- or their complexes) take part. Some oversaturation of every participating ion is necessary before the commencement of nucleation. The most favourable conditions for such oversaturations exist on the surface of the dissolving crystals because the concentrations of Pb^{2+} and OH^- ions are greatest there. The crystal

Table 2

	pH-stability region		
$a_{SO_4^{2-}}$ (M)	*$PbSO_4$*	*PbO·$PbSO_4$*	*3PbO·$PbSO_4$·H_2O*
10^{-1}	to 7·8	7·8–9·0	9·0–14·2
10^{-3}	to 6·8	6·8–8·1	8·1–13·2

lattice of basic lead sulphates are very close and its surface can participate, favouring one or another nucleation process.

The orthorhombic PbO is unstable at ambient temperature and has many crystal lattice defects. According to Figs. 3 and 4a, on mixing the H_2SO_4 solution with orthorhombic PbO powder, $PbSO_4$ whiskers are obtained first. This shows that $PbSO_4$ formation occurs at definite places of the PbO crystal lattice surface. During this process the H_2SO_4 concentration in the paste decreases very rapidly while the pH increases. Such a pH value is reached where $PbO \cdot PbSO_4$ or $3PbO \cdot PbSO_4 \cdot H_2O$ are stable. Fig. 3 shows that both basic lead sulphates are formed in the paste. This means that the rates of $PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4 \cdot H_2O$ nucleation are quite different and the rate of $PbO \cdot PbSO_4$ dissolution is small.

When the initial oxide has a tetragonal modification $3PbO \cdot PbSO_4 \cdot H_2O$ is formed first. Hence the rate of $PbSO_4$ and $PbO \cdot PbSO_4$ nucleation is many times lower than the rate of $3PbO \cdot PbSO_4 \cdot H_2O$ nucleation. The approximately equal and small dimensions of the $3PbO \cdot PbSO_4 \cdot H_2O$ crystals (Fig. 2b) leads us to suppose that the rate of $3PbO \cdot PbSO_4 \cdot H_2O$ crystal growth is rather slow. The presence of surface active organic substances accelerates the $3PbO \cdot PbSO_4 \cdot H_2O$ nucleation and hinders the $3PbO \cdot PbSO_4 \cdot H_2O$ crystal growth. That is why the paste with SL consists of tiny crystals (Fig. 7a and b).

The $4PbO \cdot PbSO_4$ crystals are big. This shows a rate of nucleation much lower than that of $4PbO \cdot PbSO_4$ crystal growth. The formation of $4PbO \cdot PbSO_4$ takes place when the correct ratio of orthorhombic PbO, tetragonal PbO and $3PbO \cdot PbSO_4 \cdot H_2O$ is achieved in the paste. We established that when the tetragonal PbO content in the initial mixture is between 30% and 60%, the ratio H_2SO_4/PbO is 6 wt% and the temperature 80° C then the $4PbO \cdot PbSO_4$ formation takes place at quite a good rate.

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