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Dependence of the properties of the lead-acid battery positive plate paste on the processes occurring during its production

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The phase composition, microstructure, porosity, density and consistency of positive plate pastes prepared at 35 and 80° C were determined as functions of the amount of H_2SO_4. It was found that the phase composition of the paste is determined by the H_2SO_4 oxidized lead powder ratio and by the temperature at which the paste is mixed. The paste density is determined by the liquid powder ratio. The total pore volume is controlled by the paste density while the average pore radius and the consistency are determined by the phase composition. Stoichiometric calculations were made for the phase composition of the pastes. It is concluded that the paste represents a non-equilibrium system consisting of crystalline basic lead sulphates and oxides and amorphous sulphate-containing components.

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1. Introduction

The phase composition and the microstructure of the positive plate active material of the lead-acid battery depend to a large extent on the paste from which the active material has been produced. The paste is obtained by mixing partially oxidized lead powder with a sulphuric acid solution. It has been established that basic lead sulphates form in these conditions [1–9]. At room temperature $3PbO.PbSO_4.H_2O$ is generated [1, 3, 4] while at a mixing temperature of 70° C $4PbO.PbSO_4$ appears [2, 5]. During the last few years attention has been focused on $4PbO.PbSO_4$ because of its very interesting structure [5, 7]. The properties of plates obtained from previously synthesized pure $4PbO.PbSO_4$ have been studied [6, 7].

The present paper is the first of a series which aims to elucidate the dependence of the specific energy of the positive active material on the phase composition and the properties of the paste from which it has been produced. The relationship between the parameters of the paste (density, consistency, microstructure, porosity) and the phase composition of the paste are considered in the present paper.

2. Experimental

Industrial lead powder with an oxidation degree of 66% was used in the preparation of the pastes. The X-ray diffraction pattern of the powder showed the presence of tetragonal PbO and Pb. In the lead-acid battery industry the pastes are prepared with H_2SO_4 in a proportion of 4–5 wt % with respect to the lead powder. In order to express more clearly the dependence of the paste parameters on its phase composition pastes were prepared at temperatures of 35 and 80° C with a content of H_2SO_4 from 0–12 wt % with respect to the lead powder. The H_2SO_4 concentration was selected so that pastes of equal densities were obtained. Paste preparation was performed in a laboratory mixer. The components were introduced in the following sequences: lead powder, water, H_2SO_4 solution. The mixing was continued for 40 min. The temperature was maintained constant within ± 5°C. After completion of mixing the paste prepared at 80° C was cooled down to room temperature. After this, phase composition was determined by X-ray diffractometry and consistency be means of a consistometer. Metallic lead content and humidity were determined by

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wet chemical analysis. Grids for 14 AH starter battery plates were pasted manually. The plates were then stacked and left to cure at room temperature for 72 h. The phase composition was then determined as well as the remaining unoxidized lead content and the humidity of the plate. The pore size distribution and total porosity were determined by mercury porosimetry. The microstructure of the paste and the morphology of the crystals were observed by scanning electron microscopy.

3. Results

3.1. *Phase composition of the pastes*

The presence of a given phase in the paste was determined by the presence of all its reflections in the X-ray diffractometer trace. The following characteristic reflections were used: $d = 0{\cdot}280$ nm for tetragonal PbO, $d = 0{\cdot}295$ nm for orthorhombic PbO in the pastes containing up to 8% H_2SO_4 (when the H_2SO_4 content is higher than this percentage the 0·295 nm reflection must be assigned to $PbO.PbSO_4$), $d = 0{\cdot}321$ nm for $4PbO.PbSO_4$, $d = 0{\cdot}325$ nm for $3PbO.PbSO_4.H_2O$, $d = 0{\cdot}333$ nm for $PbO.PbSO_4$ and $d = 0{\cdot}284$ nm for Pb. The change in phase composition brought about by the H_2SO_4 content was expressed by the change in the relative intensity of the reflections belonging to this phase, $I_a/\Sigma I_n$, where I_a denotes the intensity of the reflection belonging to the given phase and ΣI_n is the sum of the intensities of the characteristics of reflections belonging to all phases.

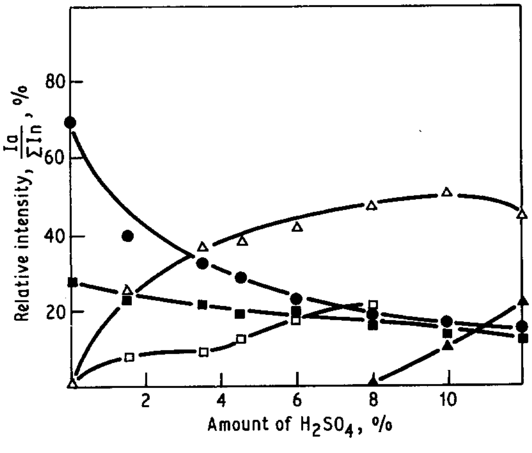

Fig. 1. Dependence of the phase compositions of uncured paste prepared at 35° C on the amount of H_2SO_4. (●) tetragonal PbO (□) orthorhombic PbO (△) $3PbO.PbSO_4.H_2O$ (▲) $PbO.PbSO_4$ (■) Pb.

Fig. 1 illustrates the change of the phase composition of the pastes prepared at 35° C. Up to 10% H_2SO_4 the major phase which forms is $3PbO.PbSO_4.H_2O$. The amount of this compound increases in proportion to the H_2SO_4 content. In addition, orthorhombic-PbO is formed in the paste, and above 8% H_2SO_4 $PbO.PbSO_4$ predominates. The values of the relative intensities do not reflect quantitative relationships among the phases since characteristic reflections which have widely differing intensities are used.

Fig. 2 shows the change in phase compositions of the pastes mixed at 80° C. Up to 6% H_2SO_4 the main compound is $4PbO.PbSO_4$. Orthorhombic PbO also forms in this range. Above 6% H_2SO_4, $3PbO.PbSO_4.H_2O$ and above 8% H_2SO_4, $PbO.PbSO_4$ are found.

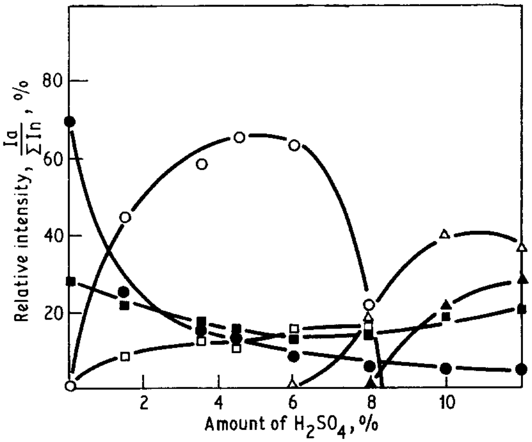

Fig. 2. Dependence of the phase composition of uncured paste prepared at 80° C on the amount of H_2SO_4. (●) tetragonal PbO (□) orthorhombic PbO (△) $3PbO.PbSO_4.H_2O$ (○) $4PbO.PbSO_4$ (▲) $PbO.PbSO_4$ (■) Pb.

3.2. *Density and consistency of the pastes*

Paste density and consistency are parameters which characterize the paste as a macroscopic system as a function of water and sulphuric acid content. Whereas paste density is a parameter which determines the relationships among the individual particles in the pastes under static conditions, consistency does this under dynamic conditions. Since the crystals of the individual phases

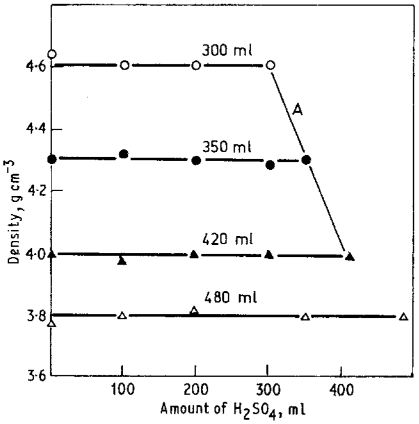

Fig. 3. Dependence of the paste density on the amount of H_2SO_4 at a constant liquid amount and 2 kg of oxidized lead powder.

differ, it should be expected that the phase composition of the paste should affect its consistency.

In order to check the extent to which the contents of the individual phases affect density, pastes were prepared in which the liquid volume was kept constant, the H_2SO_4 amount being varied up to 8%. Fig. 3 displays the dependence of the paste density on the H_2SO_4 content for a total volume of H_2SO_4 + H_2O of 300, 350, 420 and 480 ml. The figure indicates that density does not depend on the amounts of the individual phases (tetragonal PbO, $3PbO.PbSO_4.H_2O$ and orthorhombic PbO) present in the paste. Fig. 3 (curve A) shows that between 300 and 420 ml the density decreases linearly with the increase in the amount of liquid in the paste, irrespective of the phase composition.

Fig. 4 shows the results of the measurements of the paste consistences of pastes having identical densities as a function of the H_2SO_4 content. The measurements were performed on four series of pastes prepared at 35° C at four different densities, the H_2SO_4 content being varied between 0 and 6%. Consistency, k, increases linearly with the H_2SO_4 percentage in the paste

$$k = a + bC_{H_2SO_4}$$

where a denotes the consistency of the paste prepared only with H_2O and b is a constant which depends on the phase composition of the paste. A comparison of Figs. 1 and 4 shows that the linear increase in consistency is brought about by a linear increase in the $3PbO.PbSO_4.H_2O$ content.

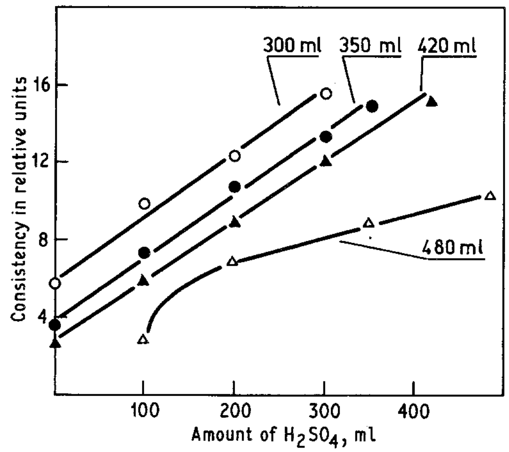

Fig. 4. Dependence of the paste consistency on the amount of H_2SO_4 at a constant amount of liquid and 2 kg of oxidized lead powder.

The relationship was established in two series of pastes prepared at 35 and 80° C. Fig. 5 illustrates the experimental data obtained from these measurements. In the case of pastes prepared at 80° C, with an increasing $4PbO.PbSO_4$ content the consistency of the paste increases linearly up to 6% H_2SO_4. At a H_2SO_4 content of 8% H_2SO_4, $3PbO.PbSO_4.H_2O$ predominates in the paste prepared at 80° C. This leads to a decrease in the amount of $4PbO.PbSO_4$ (Fig. 2). This, in turn, brings about an abrupt increase in the consistency of the paste. From the results of Figs. 4 and 5 it is easily seen that consistency is controlled by the nature and the amount of the basic lead sulphate. When the same quantity of H_2SO_4 is used in the preparation of the pastes the friction among the crystals of $3PbO.PbSO_4.H_2O$ is considerably

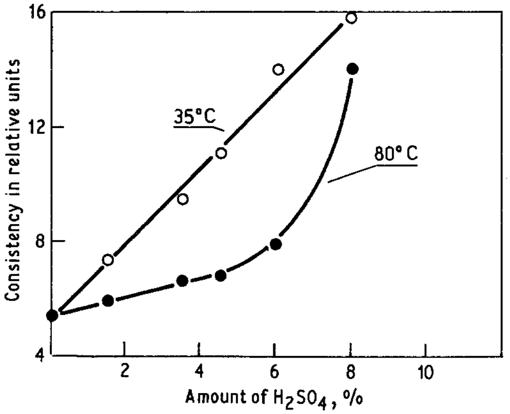

Fig. 5. Dependence of the paste consistency on the amount of H_2SO_4.

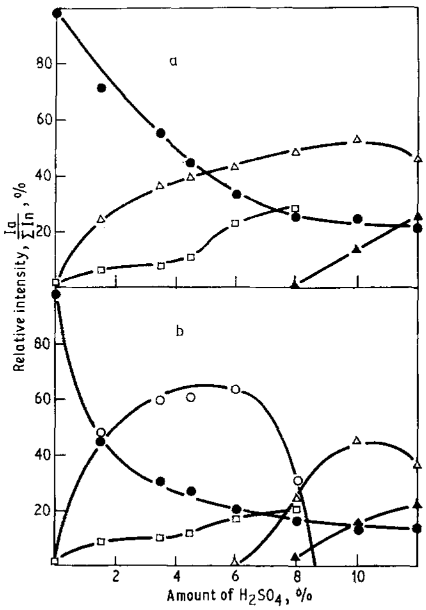

Fig. 6. Dependence of the phase composition of cured paste prepared at 35° C (a) and 80° C (b) on the amount of H_2SO_4. (●) tetragonal PbO, (□) orthorhombic PbO, (△) $3PbO.PbSO_4.H_2O$, (○) $4PbO.PbSO_4$, (▲) $PbO.PbSO_4$.

larger than that among those of $4PbO.PbSO_4$. This leads to a higher consistency of the pastes prepared at 35° C as compared with those mixed at 80° C.

3.3. *Phase composition of cured pastes*

After pasting on factory grids the plates were left to cure at room temperature for 72 h. At the end of the curing process the lead content in the paste was lower than 1% for pastes prepared with up to 8% H_2SO_4 and 10–11% unoxidized lead for pastes prepared with more than 10% H_2SO_4. Fig. 6a illustrates the phase composition of the cured pastes prepared at 35° C and Fig. 6b that of the pastes mixed at 80° C. A comparison among the curves reflecting the changes in the phase composition (Figs. 1, 2, 6a and b) clearly shows that during the curing lead oxidizes to tetragonal-PbO. Only in the pastes prepared at 80° C with 8 and 10% H_2SO_4 do small amounts of $PbO.PbSO_4$ transform into $3PbO.PbSO_4.H_2O$.

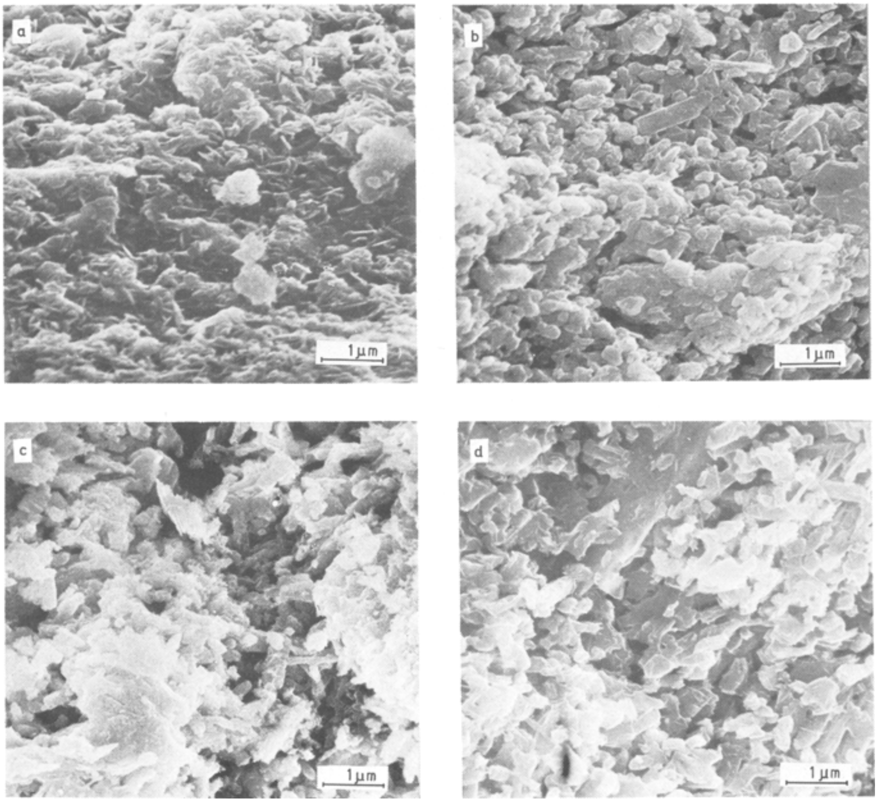

Fig. 7. Electron micrographs of cured paste prepared at 35° C with H_2SO_4: (a) 0%; (b) 4.5%; (c) 8%; and (d) 10%.

3.4. *Morphology of the crystals*

Fig. 7 represents electron micrographs of cured pastes prepared at 35° C with 0% (7a), 4.5% (7b), 8% (7c) and 10% H_2SO_4 (7d). The pastes consist of a finely crystalline mass which is built up from crystals up to 1 μm long. At some locations of the paste sample prepared with 4.5% H_2SO_4, thin needle-shaped crystals were observed with lengths of 2–3 μm. The micrographs show that the sizes of the PbO, $3PbO.PbSO_4.H_2O$ and $PbO.PbSO_4$ crystals under these mixing conditions are of the same order of magnitude.

Fig. 8 illustrates micrographs of cured pastes prepared at 80° C with 0% (8a), 6% (8b), 8% (8c) and 12% H_2SO_4 (8d). The paste with 6% H_2SO_4 consists of $4PbO.PbSO_4$ crystals 15–20 μm long and 1–3 μm wide. Well-expressed growth steps may be seen on their faces. At 8% H_2SO_4 the paste contains large $4PbO.PbSO_4$ crystals as well as small $3PbO.PbSO_4.H_2O$ crystals. At 12% H_2SO_4 well-formed needle-shaped crystals are observed.

3.5. *Porosity of cured pastes*

The total pore volume and the pore size distribution in the pastes were determined by mercury porosimetry. It was found that for the pastes with equal densities the total pore volume increases very slightly upon addition of H_2SO_4. It ranges between 0·06 and 0·07 $cm^3 g^{-1}$ for the pastes mixed at 35° C and between 0·065 and 0·08 $cm^3 g^{-1}$ for the pastes mixed at 80° C. Fig. 9 illustrates the integral curves of pore size distribution in pastes prepared with 6% H_2SO_4 at 35 and 80°C. It is seen that the pores have radii which vary within a very narrow interval. If the point of inflexion in these curves is taken as the average pore radius the dependence between this quantity and the phase composition of the paste can be followed. Fig. 10 illustrates the change in the average pore radius as a function of the H_2SO_4 percentage at 35 and 80° C. From Fig. 10 it is seen that the average pore radius is in fact independent of the phase composition of the paste mixed at 35° C. This is due to the nearly identical

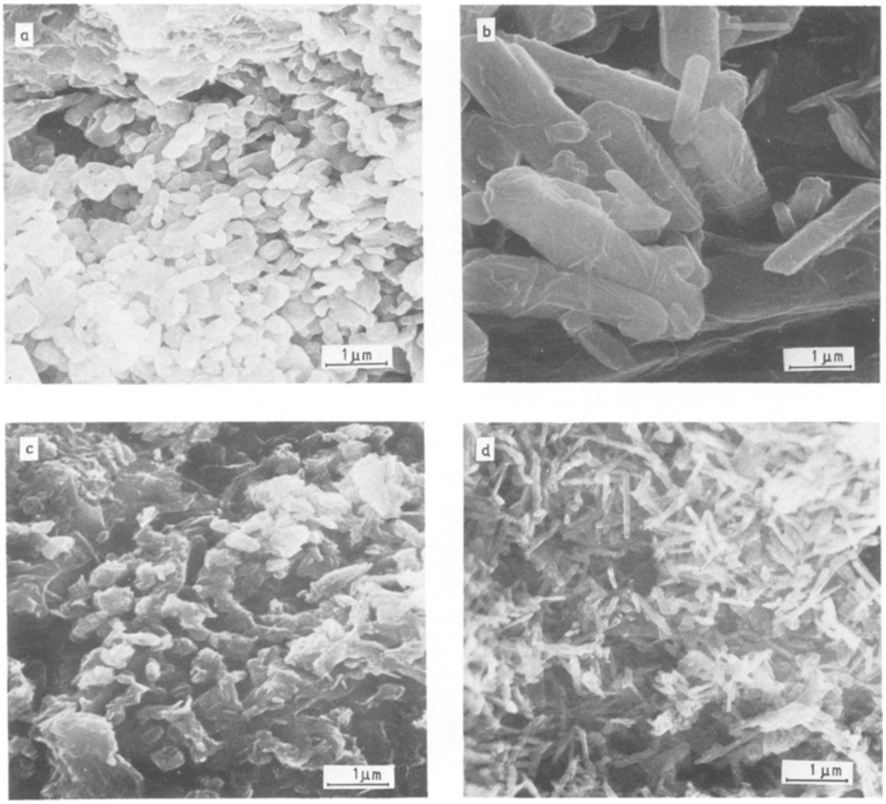

Fig. 8. Electron micrographs of cured pastes prepared at 80° C with H_2SO_4: (a) 0%; (b) 6%; (c) 8%; and (d) 12%.

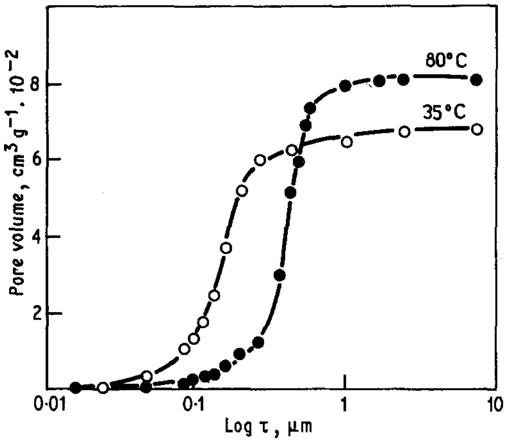

Fig. 9. Pore size distribution diagrams for cured pastes.

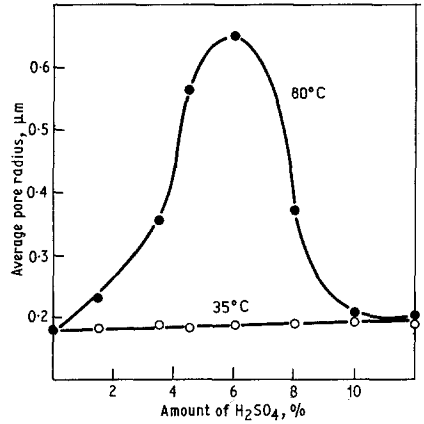

Fig. 10. Dependence of the average pore radius on the amount of H_2SO_4.

size of the $3PbO.PbSO_4.H_2O$, $PbO.PbSO_4$ and tetragonal-PbO crystals which build up the paste. The average pore radius in the pastes mixed at 80° C passes through a maximum which corresponds to 0·65 μm and coincides with the maximum in the amount of $4PbO.PbSO_4$ crystals present in the paste. At 10% H_2SO_4, when $4PbO.PbSO_4$ crystals disappear, the average pore radius coincides with that found in the pastes mixed at 35°C since they consist of the same phase. The large size of the $4PbO.PbSO_4$ crystals (Fig. 8) leads to an increase in the average pore radius in the paste but does not affect the total pore volume which depends to a large extent on the paste density.

4. Discussion

The mixing of a sulphuric acid solution with oxidized lead powder initiates heterogeneous reactions which lead to the formation of lead hydroxides, of crystalline basic lead sulphates, and of orthorhombic PbO. The nature of the basic lead sulphate obtained should depend on the molar ratio between the lead oxide and the sulphuric acid. The larger the amount of H_2SO_4 with respect to that of lead oxide, the larger will be the $PbSO_4$ content in the basic lead sulphate. The reactions which represent the formation of $4PbO.PbSO_4$, $3PbO.PbSO_4.H_2O$, $PbO.PbSO_4$ and orthorhombic PbO may be expressed in terms of the following chemical equations:

$$5PbO + H_2SO_4 = 4PbO.PbSO_4 + H_2O \quad (1)$$

$$4(4PbO.PbSO_4) + H_2SO_4 + 4H_2O = 5(3PbO.PbSO_4.H_2O) \quad (2)$$

$$2(3PbO.PbSO_4.H_2O) + 2H_2SO_4 = 4(PbO.PbSO_4) + 4H_2O \quad (3)$$

$$4PbO + H_2SO_4 = 3PbO.PbSO_4.H_2O \quad (4)$$

$$\text{tetragonal PbO} = \text{orthorhombic PbO}. \quad (5)$$

From the above equations one can calculate the quantity of sulphuric acid required for transforming the quantity of lead powder used in the present study to $4PbO.PbSO_4$ and $3PbO.PbSO_4.H_2O$. The calculations show that at 6·15% H_2SO_4 the paste should consist only of $4PbO.PbSO_4$ (according to Reaction 1) whereas at 7·75% H_2SO_4 only of $3PbO.PbSO_4.H_2O$ (according to reactions 2 or 4). The values obtained during preparation of the paste at 80° C show that the maximum amount of $4PbO.PbSO_4$ is formed at about 6% H_2SO_4 and that of $3PbO.PbSO_4.H_2O$ at about 10% H_2SO_4. At the same time tetragonal PbO is identified even in the paste prepared with 12% H_2SO_4. This means that the reactions between sulphuric acid and lead oxide take place with kinetic hindrances. This is why the paste is a non-equilibrium system consisting of various phases and components. The shift of the maximum amount of $3PbO.PbSO_4.H_2O$ from 7.73 to 10% H_2SO_4 is indicative of the formation of compounds rich in lead sulphate. The formation of these phases leads to the partial consumption of sulphuric acid.

As a result of this a certain amount of unreacted tetragonal PbO remains. These sulphate-containing hydroxides and oxides should be amorphous or colloidal and may be present in quantities lower than those detectable by X-ray diffraction analysis. In order to identify the reactions which take place in this system X-ray diffraction should be supplemented by other physico-chemical analytical techniques aimed at determining the nature of the non-crystalline components.

A comparison of Figs. 1, 2 and 6 shows that the non-equilibrium state of the paste is retained even after curing of the paste.

Figs. 1 and 2 indicate that orthorhombic PbO is formed in the paste exclusively upon mixing of lead powder with H_2SO_4. When the pastes are prepared with tetragonal PbO and water, orthorhombic PbO does not form. This shows that orthorhombic PbO forms at a pH value lower than that for the formation of tetragonal PbO.

A full description of the paste composition should also take account of the unoxidized lead particles. The mixing of the paste is performed in air. This means that lead is partially oxidized by oxygen dissolved in the paste. Up to 8% H_2SO_4 the lead particles in the paste are rapidly oxidized during the curing. At 10–12% H_2SO_4 the oxidation rate of lead strongly decreases. This is probably due to differences in the pH of the solution in the paste. At a high H_2SO_4 content the pH of the solution is low. This contributes to the formation of a passivating layer at the surface of the lead particles which strongly hinders their oxidation.

The electron micrographs of Figs 7 and 8 show that the $4PbO.PbSO_4$ crystals are well-formed, with clear-cut growth fronts, whereas those of $3PbO.PbSO_4.H_2O$ are small and are not bounded by well-developed faces and edges. These pictures show that the formation of $4PbO.PbSO_4$ proceeds via the formation of new crystals which strongly differ from the initial ones. This process can take place exclusively through a liquid phase.

It was established [10] that $3PbO.PbSO_4.H_2O$ and orthorhombic PbO are the first phases to form when the paste is mixed at 80° C. After a certain mixing time (which strongly depends on the temperature) a reaction begins between $3PbO.PbSO_4.H_2O$ and tetragonal PbO which leads to $4PbO.PbSO_4$. For this reaction to proceed, orthorhombic PbO must be present and the temperature of the paste should not be lower than 65–70° C.

The presence of basic sulphates with greatly varying crystal size affects the consistency of the paste. The friction among the thin, needle-shaped $PbO.PbSO_4$ crystals is larger than that among the small, rounded $3PbO.PbSO_4.H_2O$ grains. The smallest friction exists among the large and not very numerous $4PbO.PbSO_4$ crystals. This is why the pastes containing $PbO.PbSO_4$ have a small consistency. This is in accord with the results illustrated in Figs. 4 and 5. The change in the size of the solid phase individuals determines the size of the pores in the paste. Thus, the large $4PbO.PbSO_4$ crystals give rise to pores with a large average radius (Figs. 9 and 10) whereas the crystals of the other phases are small and form pores with a small average radius. Consequently, the microstructure of the paste is controlled by the chemical and crystallization processes which take place during preparation of the paste. These processes depend on the ratio between sulphuric acid and oxidized lead powder as well as on the temperature and duration of mixing of the paste.

References

[1] J. J. Lander, NRL Report No. C-3262, March 22 1948.

[2] H. Bode and E. Voss, *Electrochim. Acta* **1** (1959) 318.

[3] S. Satoshi, J. Hugeuki and Denki Kagaku, **36** (1968) 609.

[4] V. V. Kurochkina, A. I. Rusin, N. A. Mikhalkov and M. A. Dasoyan, *Sb. rabot khim ist. toka,* No. 8. 32. Energiya, Leningrad (1973).

[5] J. R. Pierson, 6th International Power Source Symp. Brighton, Sussex, 23–25 Sept. 1968.

[6] R. V. Biagetti and M. C. Weeks, *Bell Syst. Tech. J.* 49 (1970) 1305.

[7] C. F. Yarnell. *J. Electrochem. Soc.* **117** (1970) 246.

[8] J. Burbank, *Ibid* **113** (1966) 10.

[9] E. Skoluda, J. Kwasnik, K. Nowac and J. Kranska, *Electrochim. Acta* **17** (1972) 1353.

[10] D. Pavlov and V. Iliev, *Elektrokihimiya* **11** (1975) 1735.