Studies on the Combined Water in Paste for Lead Storage Batteries*

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Works have been done by many workers to determine the chemical formulas for PbO-PbSO_4 compounds. In regard to the combined water of paste, J.J. Lander¹⁾ reported the formation of monohydrate of tribasic lead sulfate in samples formed by the wet method, and T. Takagaki²⁾ studied the formation of the same salt in the $\text{PbO-H}_2\text{SO}_4$ paste of storage batteries. But the temperature of decomposition of this salt was different from that of J.J., Lander.

Author and coworkers studied, by thermal and X-ray analysis, the composition of hydrous compound in the PbO (tetragonal)- H_2SO_4 paste, which was dried by steaming or air heating, and the nature of the combined water. This report is concerned with the result of thermoanalysis. The combined water was measured by the weight change of paste on heating by means of a silica spiral thermobalance in a vacuum of 10^{-2} to 10^{-3} mmHg.

The sample for analysis was prepared as follows :

- 1) by mixing PbO (tetragonal) with different activities³⁾ and dil. H_2SO_4 and drying the mixtures perfectly by heating at $70-80^\circ\text{C}$.
- 2) by mixing PbO and dil H_2SO_4 with the aid of the paste diagram of $\text{PbO-H}_2\text{SO}_4$ systems, and drying the mixtures by air heating at $70-80^\circ\text{C}$ or by steam heating at 100°C .
- 3) by standing the pasted plate containing 0-49% of PbSO_4 and the sample formed by the wet method in wet CO_2 , O_2 , and air at 1 atm.
- 4) by the wet method used by J.J. Lander., by boiling and standing at low temperature water suspensions of PbO and PbSO_4 (or H_2SO_4) in the proper ratio. These are represented by the formulas : $\text{PbSO}_4 \cdot \text{PbO}$, $\text{PbSO}_4 \cdot 3 \text{PbO}$, $\text{PbSO}_4 \cdot 4 \text{PbO}$ and $\text{PbSO}_4 \cdot 2 \text{PbCO}_3 \cdot \text{PbO}$.

The results obtained are summarized as follows :

- 1) There are two combined water in the paste dried by heating at $70-80^\circ\text{C}$, which are decomposed above about $90-120^\circ\text{C}$ and 170°C .
- 2) The combined water decomposed on heating at 170°C seems to relate to the monohydrate of tribasic lead sulfate ($\text{PbSO}_4 \cdot 3 \text{PbO} \cdot \text{H}_2\text{O}$), and the maximum water loss does not occur at 31% of PbSO_4 but at about 25%. It seems that this divergence from theoretical value is due to the particle size of PbO , but the water quantities are affected by the degree of catalytic activity of PbO .
- 3) When in air, there are the combined waters also which seem to depend on the basic lead carbonate decomposed at about 170°C . This basic lead carbonate releases CO_2 at about 225°C and this combined water does not exist in the paste containing about 30% of PbSO_4 , and it is considered that such combined water depends on the basic lead carbonate formed by reaction CO_2 and PbO which is remained in the paste as in (Fig. 1).
- 4) It is certain that the monohydrate of tribasic lead sulfate loses rather easily the combined water through action of the CO_2 in the air and anhydrous carbonate is formed.

The paste formed by steaming differs from that formed by heating the following points :

- 1) The combined water due to decomposition of the basic lead sulfate at 170°C does not exist in the paste containing 0-15% of PbSO_4 . But crystals which seem to be basic lead sulfate are observed by optical microscope. It seems that this salt may be an anhydrous compound as in (Fig. 2).
- 2) There is the combined water in the paste which is decomposed at about 210°C besides that

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Curve I; the paste was settled in CO_2 at room temp.
Curve II; the paste was settled in O_2 at room temp.
Curve III; the paste was dried in air at room temp.
Curve I', was recalculated from curve I under the case
as these pastes involved the same percent PbCO_3 .

Fig. 1 Combined water which was decomposed at about
 170°C in the paste dried by heating.

Curve I and II; the combined water decomposed at
about 17°C and 210°C respectively.
Curve III; the combined water decomposed at about
 210°C in the samples prepared by the wet method.

Fig. 2 Combined water in the pastes dried by steaming.

A; The sample was prepared by the wet method.
B; Sample A was settled in CO_2 .
C; The paste was dried by steaming.
D; Sample C was settled in CO_2 .

Fig. 3 Thermoanalysis curves.

which decomposes at about 170°C . Also this combined water seems to be related to the monohydrate of tribasic lead sulfate; and the maximum content is seen in the paste containing about 31% of PbSO_4 .
3) The combined water decomposed at 170°C is released by CO_2 in the same way as the paste dried by heating, but water decomposed at 210°C can not be observed in (Fig. 3).

It was supposed, that difference in decomposition temperature may be due to the degree of crystallization of the basic salt.

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