On the Basic Lead Sulphate in the PbO-H₂SO₄ Paste*

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It was already reported that the bound water decomposed at 170°C, should relate to the basic lead sulphate in the paste. (Part. 8). On the other hand, heretofore it was reported that perhaps there were the basic lead sulphate in the paste. As the basic lead sulphate by dry method, J.J. Lander reported 4 PbO·PbSO₄, 2 PbO·PbSO₄ and PbO·PbSO₄·(Fig. 1). G.L. Clark reported 4 PbO·PbSO₄, 3 PbO·PbSO₄ and 2 PbO·PbSO₄ as the basic lead sulphate by wet method, (Fig. 2), and then, J.J. Lander reported 4PbO·PbSO₄, 3 PbO·PbSO₄·x H₂O (x=1) and PbO·PbSO₄·(Fig. 3). As there were differences between the reports by G.L. Clark and J.J. Lander on the basic lead sulphate by wet method, so, the basic lead sulphates in the PbO-H₂SO₄ paste were not explained enough. Especially the relations to the preparation of the paste were not reported.

Fig. 2 Basic lead sulphate by wet method (G.L. Clark).

Fig. 1 Basic lead sulphate prepared by dry method (J.J. Lander).

Fig. 3 Basic lead sulphate by wet method (J.J. Lander).

Then, the composition of PbO-H₂SO₄ paste and the basic lead sulphate in the paste were studied, and the relations to the preparation were explained.

Experimental method. Because there are two crystal forms (yellow and red modification) in lead monoxide, the sample pastes, containing 0~79.7% of PbSO₄, were prepared in each case by the same method described in Part 6 and dried. After these were powdered, their X-ray diffraction patterns were obtained.

The composition of heated PbO(y)-H₂SO₄ paste. Samples were prepared with lead monoxide (yellow modification) and sulphuric acid (Table. 1).

Table 1 Samples, PbO(y)-H₂SO₄ paste heated at 75~85°C

	Sample	Mixing fluid to PbO 100 g		PbSO ₄ % in paste
		s.g. of H ₂ SO ₄	c.c. of H ₂ SO ₄	
1	PbO(y)	—	—	—
2	PbO(y)-H ₂ O paste	1.00	proper	0.0
3	PbO(y)-H ₂ SO ₄ paste	1.10	18	8.8
4	"	1.18	22	19.2
5	"	1.21	25	25.1
6	"	1.21	28.5	28.2
7	"	1.25	26	31.1
8	"	1.27	28	36.9
9	"	1.30	29	40.6
10	"	1.30	35	48.2
11	"	1.35	37	58.2
12	"	1.35	54	79.7
13	PbSO ₄	—	—	100

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The X-ray diffraction patterns were shown in Fig. 4. Sample No. 1 was $\text{PbO}(\gamma)$ and No. 13 was PbSO_4 prepared with lead-nitrate and sulphuric acid. From these X-ray diagram, it was clear that there were two steps in the paste containing 0-100% of PbSO_4 .

The first step appeared in the paste containing 8.8~31.1% of PbSO_4 , and the second in the paste containing 40.6~48.2% of PbSO_4 . These steps should indicate the basic lead sulphate. Then, the one appeared on the first step was called α -type and the other on the second step was called β -type provisionally.

The composition of heated $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste. Samples were prepared with PbO (red modification) and sulphuric acid (Table 2) and their X-ray patterns were shown in Fig. 5. From these X-ray diagram, it was also clear that there were two steps. The first step appeared in the paste containing 19.2~36.9% of PbSO_4 and the second appeared in the paste containing 48.2~58.2% of PbSO_4 .

Table 2 Samples, $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste heated at 75~85°C.

No.	Sample	Mixing fluid to PbO 100 g		$\text{PbSO}_4\%$ in paste
		s.g. of H_2SO_4	c.c. of H_2SO_4	
14	$\text{PbO}(\gamma)$	—	—	—
15	$\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste	1.18	22	19.2
16	"	1.21	25	25.1
17	"	1.21	28.5	28.2
18	"	1.25	26	31.1
19	"	1.27	28	36.9
20	"	1.30	29	40.6
21	"	1.30	35	48.2
22	"	1.35	37	58.2
23	"	1.35	54	79.7

X-ray patterns of the latter were identical with β -type named in the $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste, so the basic salt appeared on the second step was β -type. X-ray patterns of the former were not entirely the same as α -type named in the $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste, but this also should be called α -type, because their patterns were analogous.

Therefore, there were also two kinds of basic lead sulphate (α -type and β -type).

Table 3 Sample $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste steamed

No.	Sample	Mixing fluid to PbO 100 g		$\text{PbSO}_4\%$ in paste
		s.g. of H_2SO_4	c.c. of H_2SO_4	
30	$\text{PbO}(\gamma)$	—	—	—
31	$\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste	1.21	25	25.1
32	"	1.25	26	31.1
33	"	1.30	29	40.6
34	"	1.35	37	58.2

$\text{PbSO}_4\%$

Fig. 4 X-ray diffraction patterns of $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste heated.

$\text{PbSO}_4\%$

Fig. 5 X-ray diffraction patterns of $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste heated.

The composition of $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ steamed paste. Samples were prepared with lead monoxide (red modification) and sulphuric acid (Table 3), and dried after steaming. Their X-ray diffraction patterns were shown in Fig. 6. Sample No. 30 was $\text{PbO}(\gamma)$ steamed. From these X-ray diagram, it was clear that $\text{PbO}(\gamma)$ steamed was identical with $\text{PbO}(\gamma)$

and the results obtained were equal to that obtained in $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste heated. There were also α -type and β -type basic lead sulphate provisionally.

The composition of $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste steamed. Samples were prepared with lead monoxide (yellow modification) and sulphuric acid (Table 4) and dried after steaming. Their X-ray diffraction patterns were shown in Fig. 7.

Table 4 Samples $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste steamed

No.	Sample	Mixing fluid to PbO 100 g		$\text{PbSO}_4\%$ in paste
		s.g. of H_2SO_4	c.c. of H_2SO_4	
43	$\text{PbO}(\gamma)$	—	—	—
44	$\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste	1.10	18	8.8
45	"	1.18	18	15.5
46	"	1.21	25	25.1
47	"	1.21	28.5	28.2
48	"	1.25	26	31.1
49	"	1.27	28	36.9
50	"	1.30	29	40.6
51	"	1.35	27	44.6

Sample No. 43 was $\text{PbO}(\gamma)$ steamed and changed to $\text{PbO}(\gamma)$. From these X-ray diagrams, it was also observed that these results were not identical with that obtained in $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste heated and there were three steps in the paste containing 0~100% of PbSO_4 .

The first step appeared in the paste containing 15.5~25.1% of PbSO_4 , the second in the paste containing 28.2~31.1% of PbSO_4 and the third in the paste containing 40.6~44.6% of PbSO_4 respectively. These steps should indicate the basic lead sulphate and in comparison with the results already described, that which appeared in the second step was identical with α -type and that which appeared in the third step was identical with β -type. That which appeared on the first step was observed as new type basic salt and it was called γ -type provisionally. Therefore, it was observed that the drying of the paste by steaming was not the so-called drying, but affected the composition of the paste.

Then, how did the γ -type appeared in proportion to the duration of steaming, was studied. Samples were $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste containing 25.1% of PbSO_4 and steamed for 0~5 hrs. (Table 5), and their X-ray diffraction patterns were shown in Fig. 8. From these X-ray diagrams, it was observed that γ -type appeared in the paste by steaming for 1 hr.

The relations between the basic salts and the bound water. The distribution of the basic lead sulphate

Table 5 Sample $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste
(25.1%) steamed

No.	Sample	$\text{PbSO}_4\%$	During of Steaming
37	$\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ paste	25.1	—
52	"	25.1	0.5
53	"	25.1	1
54	"	25.1	2
55	"	25.1	5
56	"	25.1	3

PbSO_4 (%)

Fig. 6 X-ray diffraction patterns of
 $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ pastes steamed

PbSO_4 (%)

Fig. 7 X-ray diffraction patterns of
 $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ pastes steamed

steaming time (hr.)

Fig. 8 X-ray diffraction patterns of
 $\text{PbO}(\gamma)\text{-H}_2\text{SO}_4$ pastes (25.1%)
steamed in various hrs.

in the paste was compared with that of the bound water in the paste described in Part. 8 (Fig. 9 and 10) and it was observed that α -type basic lead sulphate should contain the bound water decomposed at 170°C, and β -type and γ -type contained nothing.

Fig. 9 Distribution of the basic salts in the paste heated.

Fig. 10 Distribution of the basic salts in the paste steamed.

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