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Formation and Characterization of Lead Monoxide Prepared by the Alkoxy-Method

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Synopsis. Lead alkoxide was hydrolyzed at various temperatures from 28 to 85 °C. The products consisted of only massicot or litharge, or a mixture of the two for modifications of PbO, depending on the reaction temperature and pH of the suspension.

PbO has two polymorphic modifications, litharge (tetragonal) and massicot (orthorhombic). Although litharge transforms into massicot at about 500 °C,[1] the reverse transformation does not occur. On the other hand, massicot transforms readily into litharge by grinding[2-4] or wet ball-milling.[5,6] Commercial PbO, prepared by oxidation of the molten Pb, is usually a mixture of the two modifications.[6] The present paper is concerned with the conditions for the formation of the two modifications and the characterization for the alkoxy-derived PbO.

Experimental

An alcoholic solution containing 6.5 wt% lead alkoxide was prepared by the reaction of anhydrous lead acetate with sodium isopropoxide in the presence of an excess amount of isopropyl alcohol:

$$Na + C_3H_7OH \longrightarrow Na(OC_3H_7) + 1/2H_2, \quad (1)$$

$$Pb(CH_3COO)_2 + 2Na(OC_3H_7) \xrightarrow[C_3H_7OH]{83°C,\ 12\,h} Pb(OC_3H_7)_2 + 2CH_3COONa\downarrow. \quad (2)$$

The purities of anhydrous lead acetate and sodium metal used in the reaction were 99.5 and 99.9%, respectively. Isopropyl alcohol was purified by fractional distillation of the guaranteed reagent. The hydrolysis was carried out as follows. A five-necked flask was equipped with a reflux condenser, a dropping funnel, a stirring rod, a thermometer and a thermo-controller. A definite quantity of water in the range from 100 to 1000 ml was introduced into the flask, and then heated to the desired temperature. A solution of 100 ml of the alkoxide in the dropping funnel was added dropwise to the stirred water in the fiask. After completion of the addition, the suspensions were further stirred for 15 min. The products were separated from the suspensions by filtration, washed repeatedly with water, and dried at 60 °C under reduced pressure. The products were examined by means of X-ray diffraction using Ni filtered Cu$K\alpha$ radiation.

Results and Discussion

All products obtained at various temperatures in 400 ml of water were identified as PbO only as massicot or a mixture of massicot and litharge. The yield was about 67%. Table 1 shows the composition of the two modifications for each PbO powder. The composition was determined by measuring the relative intensities, I_M and I_L, of the strongest peaks in the massicot and litharge spectra. For the alkoxy-derived PbO, as described subsequently, these peaks correspond to $d(002)=2.95$ Å for massicot and $d(002)=2.51$ Å for litharge. The product consisting of only massicot was obtained at 28 °C. A small amount of litharge in addition massicot was formed at 40 °C and the litharge content of the products increased with an increase in temperature up to 85 °C, but no product consisting of only litharge was formed. On the other hand, the products consisted of only litharge when the alkoxide solution was added to water all at once at temperatures ranging from 70 to 85 °C. Judging from the yield described above, it can be assumed that the unreacted sodium alkoxide was involved in the lead alkoxide (see Reaction 2). In view of the fact that sodium alkoxide changes into sodium hydroxide upon hydrolysis, the difference between the results at 70 to 85 °C may be ascribed to a change in

Table 1. Composition of the two modifications for PbO obtained by hydrolyzing lead alkoxide

Run	Temp (°C)	Composition (%)	
		Massicot	Litharge
1	28	100	—
2	40	98.6	1.4
3	50	97.4	2.6
4	60	96.3	3.7
5	70	76.8	23.2
6	85	38.8	61.2
7[a]	70	—	100
8[a]	85	—	100

a) Obtained by rapid hydrolyzation.

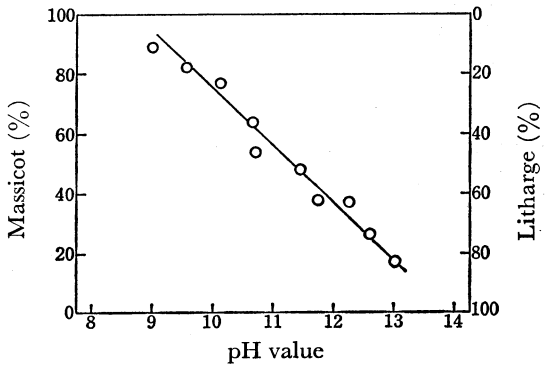
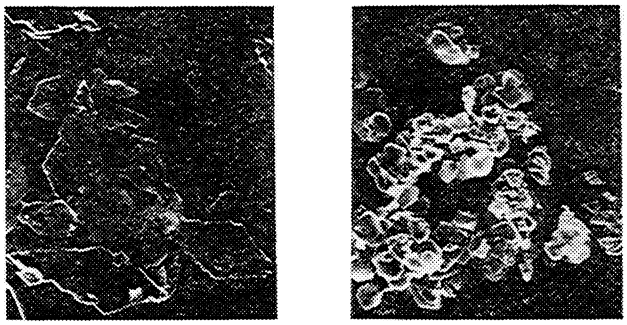
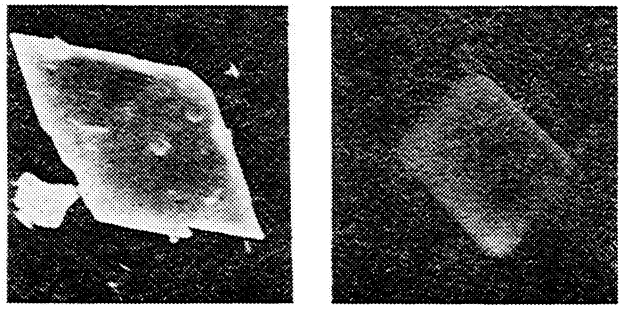


Fig. 1. Relationship between the composition of two modification for PbO and pH of suspensions obtained by hydrolyzing at 85 °C.
The lead alkoxide was in the pH range from 13.6 to 13.8.



(A) (B) (X800)

Fig. 2. Electron micrographs of the massicot (A) and litharge (B) powders.



(A) (B) (X1500)

Fig. 3. Electron micrographs of massicot (A) and litharge (B) showing rhombic and tetragonal morphology, respectively.

the pH of the suspensions during the course of hydrolysis. Accordingly, the 100 ml alkoxide solution was added dropwise to various quantities of water at 85 °C. As shown in Fig. 1, an approximately linear relationship exists between the composition of the two modifications in the products and the pH of the suspensions. When the pH value of the suspensions was below about 11.4, the massicot content of the products were greater than the litharge content. A further increase in the pH resulted in the formation of litharge. From the results, it was found that the compositon of the two modifications for PbO prepared by the alkoxy-method is due to the pH of the suspension, as well as the hydrolysis temperature.

Electron micrographs of the PbO powders are shown in Fig. 2. Massicot with an orthorhombic crystal structure consists of rhombic plate-like particles. On the other hand, litharge with a tetragonal crystal structure is composed of tetragonal plate-like particles. The morphology is shown more clearly in Fig. 3, in which well-defined rhombic and tetragonal plates are easily discernible.

X-Ray diffraction patterns of PbO prepared by the present method showed a preferred orientation in the direction of the c axis in comparison with those of massicot and litharge described in the X-ray powder data file (Fig. 4).[7,8] This phenomenon was observed particularly for massicot.

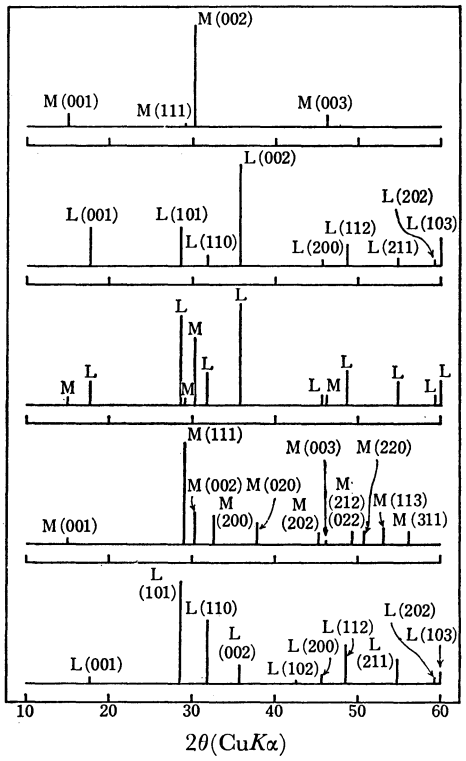


Fig. 4. X-Ray diffraction patterns of PbO prepared by alkoxy-method and described in X-ray powder data file.

M: massicot L: litharge

(A) massicot
(B) litharge } from alkoxide
(C) specimen of run 6 in Table 1
(D) massicot
(E) litharge } from X-ray powder data file

References

1) For example, R. Soderquist and B. Dickens, *J. Phys. Chem. Solids.*, **28**, 823 (1967).
2) G. L. Clark and R. Rowan, *J. Am. Chem. Soc.*, **63**, 1302 (1941).
3) F. Dachille and R. Roy, *Nature*, **186**, 34, 71 (1960).
4) W. B. White, F. Dachile, and R. Roy, *J. Am. Ceram. Soc.*, **44**, 170 (1961).
5) M. Senna and H. Kuno, *J. Am. Ceram. Soc.*, **54**, 259 (1971).
6) C. A. Sorrel, *J. Am. Ceram. Soc.*, **55**, 47 (1972).
7) X-Ray powder data file (ASTM card 5-0570).
8) X-Ray powder data file (ASTM card 5-0561).