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STUDIES ON PREPARATIONS AND PHYSICAL PROPERTIES OF MULTIVALENT METAL CONDENSED PHOSPHATES. VII[1] THE EFFECT OF WATER CONTENT ON THE FORMATION OF THE TYPES A AND B OF $Al_4(P_4O_{12})_3$

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The effect of water content on the formation of the types A and B of $Al_4(P_4O_{12})_3$ from Al, Al_2O_3 or $Al(OH)_3$ and H_3PO_4 was studied. Upon heating at 500°C, a mixture of the types A and B of $Al_4(P_4O_{12})_3$ is generally obtained. However, type A is the main product of the secondary heat treatment when the water content of the primary product is below 10 % or over 25 %, whereas type B is readily formed when the water content is 12 ~ 18 %.

It is well known that the varieties of aluminum phosphates can be prepared by varying the conditions of formation, and d'Yvoire already reported $Al_4(P_4O_{12})_3$ (A), (B), (C), (D) and (E).[2,3] However, appropriate conditions for these phosphates are not yet fully revealed. We have already reported that the formation of the types A and B of $Al_4(P_4O_{12})_3$ is dependent on the molar ratio Al_2O_3/P_2O_5 (R) in the starting material, heating temperature, and heating time,[4,5] and that moisture largely influenced on the formation of $Al_4(P_4O_{12})_3$ (A), (B), though the relation between the water content of the starting material and the yield of these phosphates has not been clear. In the present experiment we have studied the relationship between the formation of $Al_4(P_4O_{12})_3$ (A), (B) and the amount of water taking part in the reaction of α-alumina, γ-alumina, aluminum

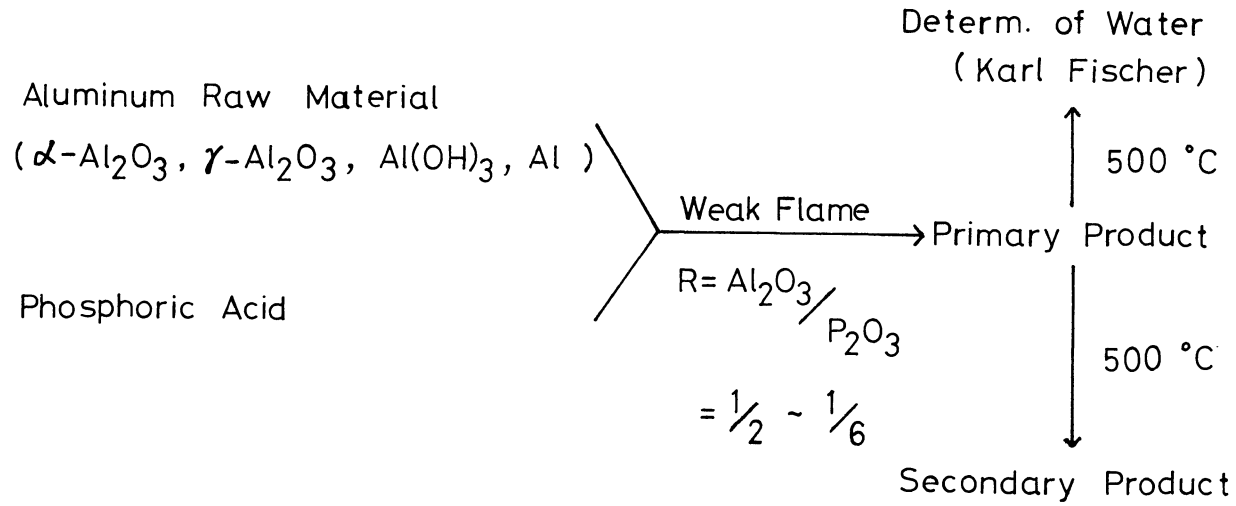

Fig. 1. The experimental method

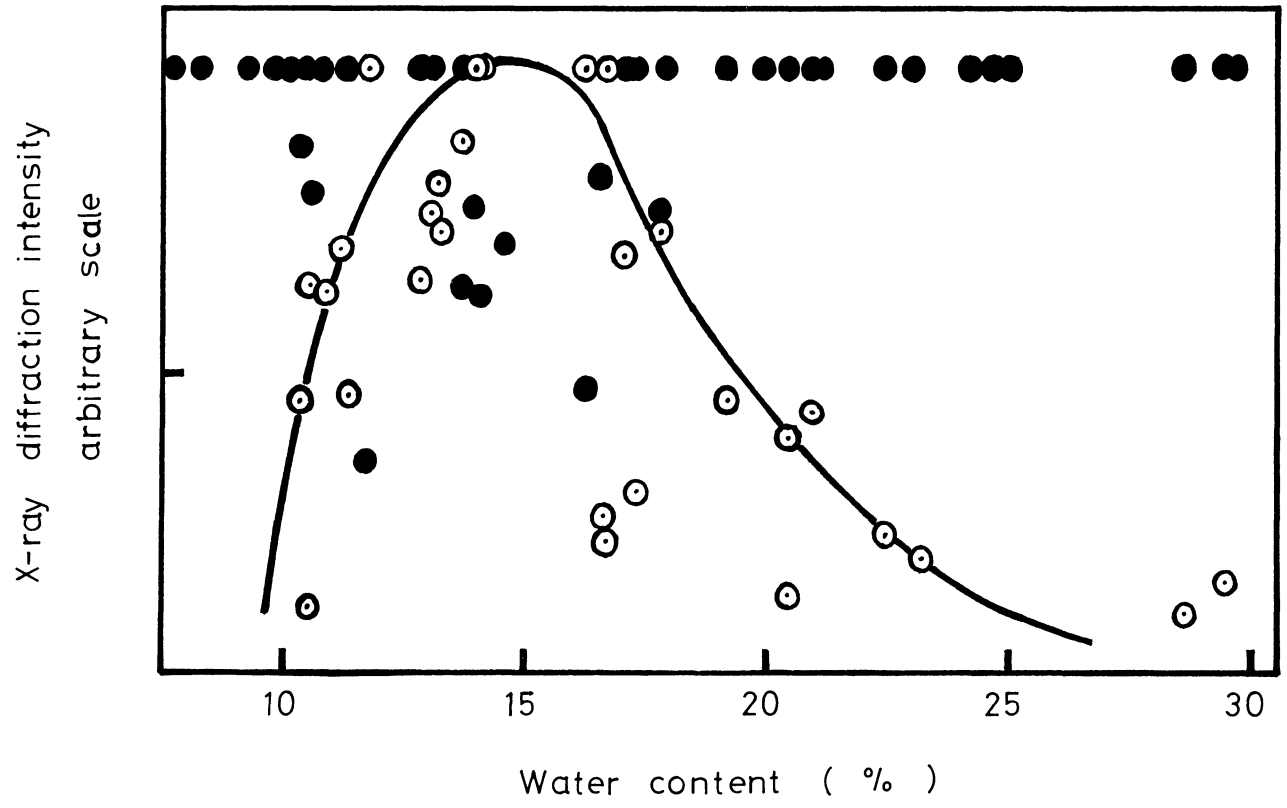

Fig. 2. Relationship between water content and the yield of various aluminum phosphates at 500 °C

● The type **A** of $Al_4(P_4O_{12})_3$

—⊙— The type **B** of $Al_4(P_4O_{12})_3$

hydroxide or aluminum metal with phosphoric acid. The experimental method is shown in Fig.1; the aluminum raw material and phosphoric acid were mixed in a porcelain crucible in molar ratios R of 1/2 ~ 1/6, and the mixture was dehydrated by heating over a weak flame with vigorous agitation to obtain a white, highly viscous product in each case (this is designated as the primary heat treatment, giving the primary products).

A small amount (0.5 ~ 0.6 g) of the product was accurately weighed, and its moisture content upon heating at 500°C was determined by the Karl Fischer method, while the main portion was heated in a thermostated electric furnace at 500°C for 20 hrs to obtain $Al_4(P_4O_{12})_3$ (A), (B) (this is designated as the secondary heat treatment, giving the secondary products).

The relative amounts of the types A and B of $Al_4(P_4O_{12})_3$ formed by the secondary heat treatment were determined from the integrated intensities of their characteristic X-ray diffraction peaks; i.e., the type A was determined by the peak at $2\theta = 20.4°$, and type B by that at 16.2°. Figure 2 shows the relationship between the water content of the primary product and the amounts of the types A and B of $Al_4(P_4O_{12})_3$ formed by the secondary heat treatment. The experimental results can be summarized as follows.

1) Upon heating at 500°C, a mixture of the types A and B of $Al_4(P_4O_{12})_3$ is generally obtained.

2) The type A is the main product of the secondary heat treatment when the water content of the primary product is below 10 %.

3) The type B is readily formed when the water content is 12 ~ 18 %.

4) The type A becomes again the main product when the water content is over 25 %.

5) The type A is most readily formed when the molar ratio R is less than 1/4; i.e., a high proportion of phosphoric acid.

6) The types C, D and E of $Al_4(P_4O_{12})_3$, the substance K, and the substance H are not formed at all on heating at 500°C.

7) Only the type B is difficultly formed under these reaction conditions.

The same tendencies were observed irrespective of the kind of the aluminum raw material.

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