Studies of the Preparation and Physical Properties of Multivalent Metal Condensed Phosphates. V.[1] The Grinding of Various Aluminum Phosphates

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Changes in the structures of various aluminum phosphates as a result of grinding were studied by a variety of physical methods—X-ray analysis, DTA, TGA, infrared absorption spectroscopy and electron microphotography, and their acidic properties were investigated in order to obtain information on the surface activity of the compounds. The X-ray diffraction patterns indicated that the A, B, and C types of $Al_4(P_4O_{12})_3$ and $AlPO_4$ (Berlinite) did not become completely amorphous even after grinding for 72 hr; this shows that the crystal structures of these compounds were relatively stable to grinding. Substance K was structurally more fragile than the other aluminum phosphates ($Al_4(P_4O_{12})_3$, $AlPO_4$), becoming completely amorphous on being ground for 72 hr. On DTA and TGA, the ground aluminum phosphates exhibited an endothermic peak, accompanied by a weight loss due to the loss of adsorbed water in the vicinity of 100 °C. A further weight loss at higher temperatures was presumably due to dehydration caused by the condensation of P–OH. The amounts of acids on the ground aluminum phosphates were almost independent of the acid strength, which was around $+1.5$ (pK_a). The amounts of acids of the A, B, and C types and of $AlPO_4$ tended to increase slightly with the grinding time. The amount of acid of the K substance reached a maximum after 6 hrs' grinding but decreased slowly when grinding was continued for longer than 15 hr.

Grinding is known to cause changes in the structure, composition, and properties of substances.[2-6] The present authors have previously reported the formation conditions and the acidic properties of various aluminum phosphates.[7,8] The present paper will describe an investigation of the change in the structure and acidic properties of various aluminum phosphates on grinding.

Experimental

Apparatus and Method. An Ishikawa grinder, model AGA (agate mortar), was used; grinding was carried out at room temperature and at a relative humidity of 20~25%. X-Ray analysis was carried out with a Rigaku Denki Geigerflex X-ray diffractometer, using Ni filtered Cu$K\alpha$ radiation. Hitachi EPI-S2 and EPI-G2 spectrophotometers were used for the infrared spectroscopy, spectra being taken by means of a KBr tablet or on Nujol mulls. A Rigaku Denki differential thermogravimetric analyzer, 8002 HD, was used for the DTA and TGA. The method reported by Tanabe and his co-workers[9,10] was used for measuring the acidic properties of various aluminum phosphates. The amount of water was determined by both the Karl-Fischer method and TGA.

Preparation of Various Aluminum Phosphates. *1) $AlPO_4$ (Berlinite)*: Aluminum hydroxide (hydrargillite type) or γ-alumina and phosphoric acid were mixed to give a Al_2O_3/P_2O_5 (R) molar ratio of 1.0/1.0. The mixture was then dehydrated over a small flame with vigorous agitation to complete the reaction; the product was heated at 500 °C for 20 hr in a thermostated electric furnace to prepare the sample. The heated product was proved to be $AlPO_4$, Berlinite, by the X-ray diffraction method.

2) A, B, and C types of $Al_4(P_4O_{12})_3$: α-Alumina and ammonium dihydrogen phosphate were mixed thoroughly to give a molar ratio of R=1/3~1/4. The A type product was obtained by heating the mixture at 750 °C for 20 hr in an electric furnace; the B type, by heating it at 500~550 °C for 20 hr, and the C type, by heating it at 650~700 °C for 20 hr. The products were thoroughly washed with water to remove the excess phosphoric acid and dried at 80 °C for 20 hr. The X-ray diffraction patterns of the A, B, and C types of $Al_4(P_4O_{12})_3$ were identical with those of the respective ASTM cards.

3) K Substance (the substance which we tentatively designated previously as the K substance has characteristic X-diffraction peaks at $2\theta=11.2$, 18.0, 26.8°): α-Alumina and phosphoric acid were mixed to give a molar ratio of R=1/3~1/4. The mixture was heated at 300 °C for 20 hr and then treated in a manner similar to that described above.

Results and Discussion

1) Changes Caused by Grinding of the A, B, and C Types of $Al_4(P_4O_{12})_3$. As an example, Fig. 1 shows the changes in the X-ray diffraction pattern of the A type caused by grinding. It can be seen that the X-ray diffraction peaks become weaker with the grinding time, as the destruction of the crystal structure to give an amorphous form progresses. However, as the X-ray diffraction pattern indicates that the A type does not become completely amorphous even after grinding for 72 hr, it can be seen that the crystal structure of the A type is relatively more stable when ground than sodium phosphates.[2,3] Changes in the X-ray diffraction patterns of the B and C types are similar

1) Part IV, M. Tsuhako, I. Motooka, and M. Kobayashi, *Nippon Kagaku Zasshi*, **92**, 1136 (1971).
2) I. Motooka, G. Hashizume, and M. Kobayashi, *ibid.*, **87**, 255, (1966).
3) I. Motooka, G. Hashizume, and M. Kobayashi, *ibid.*, **87**, 953 (1966).
4) I. Motooka, G. Hashizume, and M. Kobayashi, *Kogyo Kagaku Zasshi*, **71**, 1512 (1968).
5) I. Motooka, G. Hashizume, and M. Kobayashi, This Bulletin, **40**, 2095 (1967).
6) I. Motooka, G. Hashizume, and M. Kobayashi, *ibid*, **41**, 2040 (1968).
7) M. Tsuhako, I. Motooka, and M. Kobayashi, *Nippon Kagaku Zasshi*, **92**, 318 (1971).
8) M. Tsuhako, I. Motooka, and M. Kobayashi, *ibid.*, **92**, 1131 (1971).
9) K. Tanabe and T. Takeshita, "San Enki Shokubai," Sangyo Tosho, Tokyo (1966), p. 159.
10) G. Matsuzaki, Y. Fukuda, T. Kobayashi, K. Kubo, and K. Tanabe, *Shokubai*, **11**, 210 (1969).

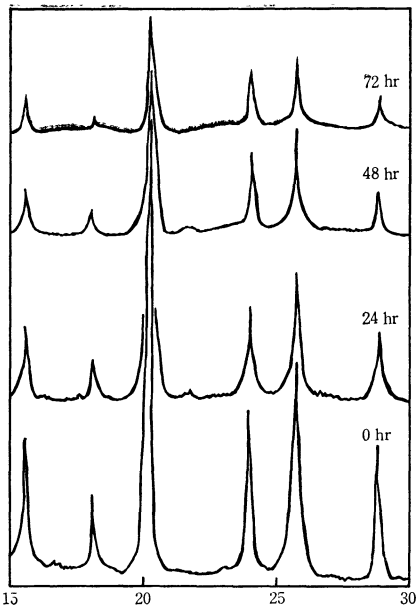

Fig. 1. The changes in X-ray diffraction pattern of type A of $Al_4(P_4O_{12})_3$ on grinding.

to that with the A type, though the results indicate that the crystal structure of the B type breaks down somewhat more easily than those of the A and C types. The changes in the infrared absorption spectrum of the A type caused by grinding are shown in Fig. 2. Although the changes are not appreciable, a new absorption (shoulder) due to grinding appears near 940 cm^{-1}, corresponding to a P–OH bending absorption.[11,12] Since absorptions due to the stretching and bending of P–OH groups appear at 2500~3000 and near 900 cm^{-1} respectively, it is assumed that P–OH is formed by the cleavage of the P–O–P or P–O–Al linkages on grinding. The absorptions at 3400~3600 and near 1600 cm^{-1} increase with the grinding time, presumably because of the adsorption of water onto active sites formed by grinding.

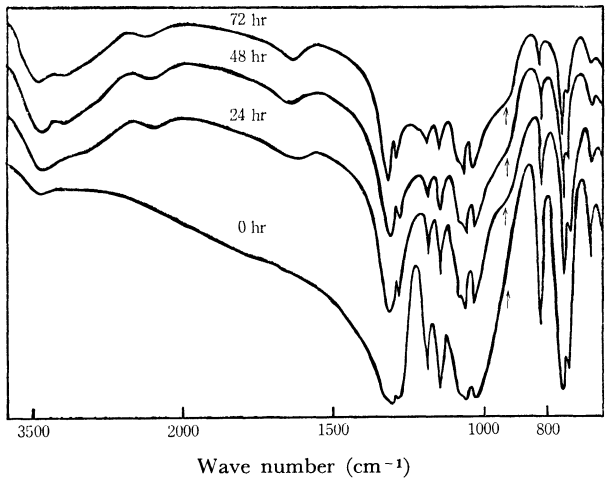

Fig. 2. The changes in infrared absorption spectra of type A of $Al_4(P_4O_{12})_3$ on grinding.

2) *Changes Caused by Grinding of $AlPO_4$ (Berlinite).* Changes in the X-ray diffraction pattern and IRS of $AlPO_4$ on grinding show the same tendencies as those for the A, B, and C types. The X-ray diffraction pattern of $AlPO_4$ does not indicate a completely amorphous state even after having been ground for 72 hr, showing that the crystal structure is somewhat stable to grinding. A shoulder appears near 940 cm^{-1} in the IRS when the sample is ground for 48~72 hr, presumably because of the formation of P–OH by the cleavage of the P–O–Al linkage.

3) *Changes Caused by Grinding of the K Substance.* Changes in the X-ray diffraction pattern of the K substance on grinding are shown in Fig. 3. The change in structure to an amorphous form is greater than those of the A, B, and C types of $Al_4(P_4O_{12})_3$ and $AlPO_4$

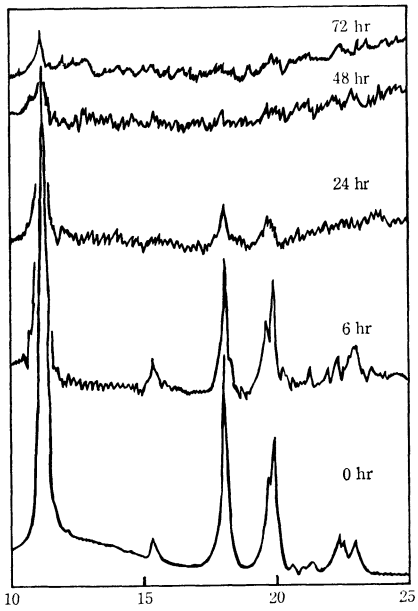

Fig. 3. The changes in X-ray diffraction pattern of substance K on grinding.

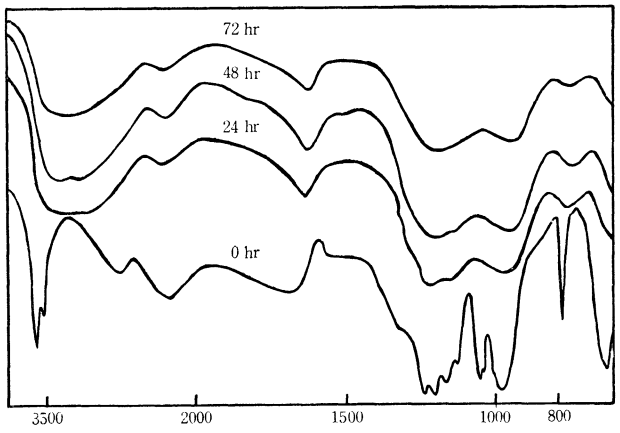

Fig. 4. The changes in infrared absorption spectra of substance K on grinding.

11) D. E. C. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956).
12) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, **1954**, 493, 4555.

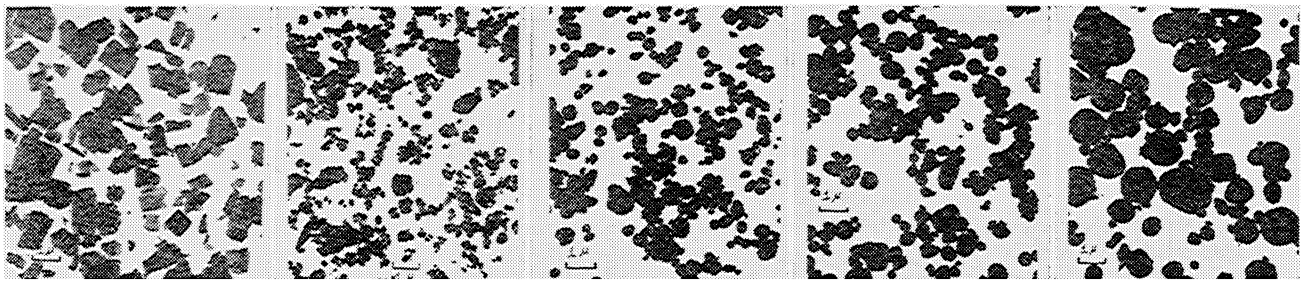

Fig. 5. Electron microphotographs of substance K; grinding time.
(a): Original, (b): 6 hr, (c): 15 hr, (d): 24 hr, (e): 72 hr.

(Berlinite), a completely amorphous form resulting after 72 hr's grinding. The crystal structure of the K substance is, therefore, more unstable than those of the A, B, and C types and $AlPO_4$. Fig. 4 shows the change in the IRS of the K substance on grinding. The K substance shows two sharp absorption peaks near 3600 cm^{-1} due to water of crystallization, and a broad absorption at 2600~2700 cm^{-1} due to P–OH. On grinding, the two sharp absorption peaks near 3600 cm^{-1} become smaller; the appearance of a broad absorption at a slightly lower wave number indicates that water of crystallization is released by the destruction of the crystal structure on grinding, and water molecules are adsorbed onto active sites of the surface of the ground K substance. Generally, water of crystallization is released when hydrated substances are ground, and their crystal structures break down easily.[4,13,14] The K substance contains water of crystallization and follows this general rule. It is, therefore, believed that the K substance is more unstable to grinding than the A, B, and C types and $AlPO_4$.

4) *Change in the Particle Size of the K Substance on Grinding.* The results of electron microphotography are shown in Fig. 5. It may be seen that particles of the K substance become very small after being ground for 6~15 hr. However, the particles gradually become larger again when grinding is continued for longer than 24 hr. This can be explained as resulting from the adsorption of moisture by the initially formed small-sized particles, leading to their subsequent agglomeration,[15] though this phenomenon is not seen with particles of the A, B, and C types or $AlPO_4$.

5) *Changes in the DTA and TGA of Various Aluminum Phosphates on Grinding.* Changes in the DTA and TGA of the K substance are shown in Fig. 6. The A, B, and C types and $AlPO_4$ show almost identical tendencies, an endothermic peak accompanied by weight loss due to the dehydration of adsorbed water around 100 °C. The endothermic peak and the weight loss increase with the grinding time, suggesting that the amount of water released increases with grinding.

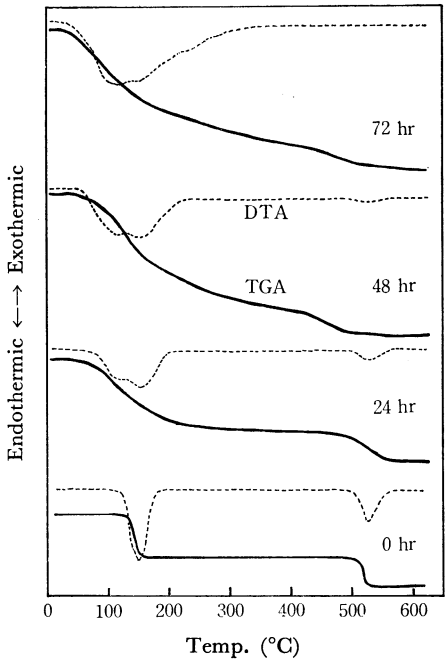

Fig. 6. The changes in DTA and TGA of substance K on grinding.

When the temperature is further increased, a further weight loss occurs, presumably because of dehydration caused by the condensation of the P–OH group. The unground K substance exhibits large endothermic peaks in the vicinity of 150~160 °C (the first endothermic peak, due to the dehydration of water of crystallization) and in the vicinity of 540 °C (the second endothermic peak, presumably due to the dehydration caused by the condensation of P–OH). However, the first endothermic peak becomes broader with an increase in the grinding time and overlaps with the endothermic peak due to the dehydration of adsorbed water, while the second endothermic peak gradually becomes smaller as the grinding time increases, and disappears almost completely after 48~72 hr's grinding. This again shows that the structure of the K substance is easily broken down by grinding. The changes in the water content on grinding are shown in Fig. 7, which shows the changes in the dehydration quantities of ground A, B, and C types, $AlPO_4$, and the K substance when they are heated to 650 °C. The K substance has a moisture content of about 16~17% in its original state, but the moisture content increases gradually with grinding.

13) I. B. Bleeker, *Chem. News*, **101**, 30 (1910).
14) Y. Arai, and T. Yasue, *Kogyo Kagaku, Zasshi*, **74**, 1343 (1971).
15) A similar tendency was observed when the surface area was measured by the BET method, though this point is being studied further because of problems in the measurement of the surface area of these aluminum phosphates.

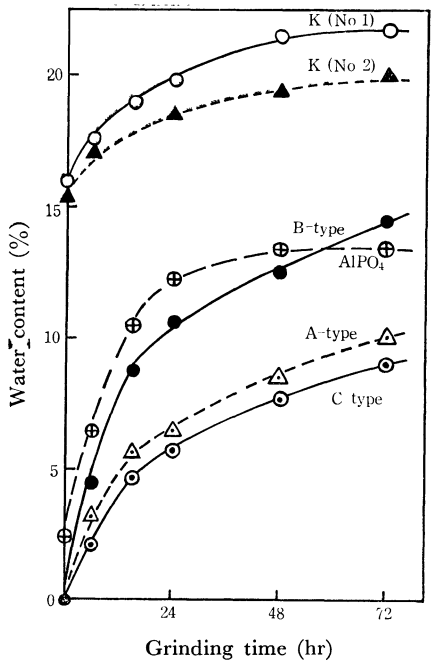

Fig. 7. The changes in water content of various aluminum phosphates on grinding.

The moisture contents of the A, B, and C types and $AlPO_4$ also increase gradually with grinding, and at a faster rate than for the K substance.

6) *Changes in the Acid Strength and Amounts of Acid of the A, B, and C Types of $Al_4(P_4O_{12})_3$ and $AlPO_4$ on Grinding.* The amounts of acid were not changed by the acid strength when the A, B, and C types and $AlPO_4$ were ground. The amounts of acid contained in unground samples of these aluminum phosphates are very small, but they increase slightly with the grinding time. It is considered that the increase in the amounts of acid is due to both the increase in surface area and the formation of P–OH by the cleavage of the P–O–P or P–O–Al linkages on grinding.

7) *Changes in the Acid Strength and Amount of Acid of the K Substance on Grinding.* As with the A, B, and C types and $AlPO_4$, almost no change in the amount of acid was observed upon a change in the acid strength when the K substance was ground. The amount of acid of the unground K substance is much larger than those of the A, B, and C types and $AlPO_4$. The changes in the amount of acid of the K substance on grinding are shown in Fig. 8. The amount of acid becomes very large when the sample is ground for 6 hr, but it gradually decreases with further grinding. This may be explained as follows. On grinding, the particles initially become smaller and the surface area of the sample increases, so there is an increase in the amount of acid per unit weight. However, upon more prolonged grinding the crystal structure breaks down and the agglomeration of the amorphous particles occurs, with a consequent decrease in the surface area and, hence, in the acidity of the K substance.

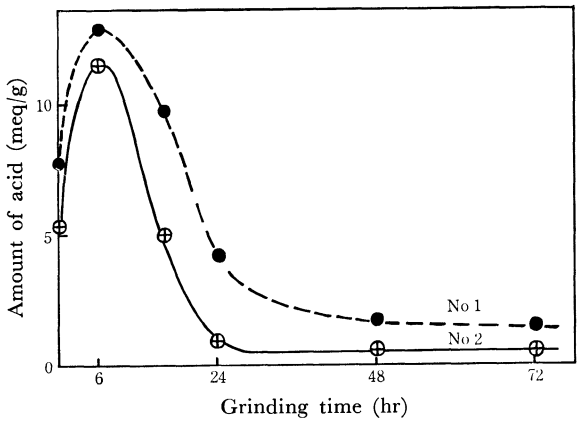

Fig. 8. The changes in amount of acid of substance K on grinding.
Amount of acid is the value at $pK_a = 1.5$

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