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Studies of the Grinding of Condensed Phosphates. III. The Effect of the Relative Humidity on Grinding of Sodium Trimetaphosphate*1

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The effect of the atmosphere, particularly of the relative humidity, on the process of grinding of sodium trimetaphosphate was examined, and the following results were obtained: 1) In the case of grinding in air, as the relative humidity increased, the grinding effect—for example, the time required to reduce trimetaphosphate molecules to one half—decreased in the humidity range from 20 to 60%. 2) In the case of grinding in nitrogen or carbon dioxide gas, the grinding effect was the same as that in air. In view of these results, it may be said that humidity is one of most important factors in the process of grinding sodium trimetaphosphate.

It is well known that the process of grinding various substances is affected by the atmosphere. For example, the grinding of cementclinker, glass, and limestone in various kinds of vapor was studied by Götte and Ziegler,1) and the grinding of quartz in neon, nitrogen, hydrogen, or air was investigated by Batel.2)

In the previous paper,3) it was reported that

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*1 Presented at the 19 th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) A. Götte and E. Ziegler, *VDI-Z.*, **98**, 373 (1956).

2) W. Batel, *Chem. Ing. Tech.*, **30**, 651 (1958).

3) Part I: I. Motooka, G. Hashizume and M. Kobayashi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 255 (1966).

sodium trimetaphosphate was changed by grinding according to the following equations:

$$Na_3P_3O_9 + H_2O \rightarrow Na_3H_2P_3O_{10} \quad (1)$$

$$Na_3H_2P_3O_{10} + H_2O \rightarrow Na_2H_2P_2O_7 + NaH_2PO_4 \quad (2)$$

$$Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4 \quad (3)$$

As water molecules participate in these reactions, it can be anticipated that these processes will be affected by the relative humidity. In view of this, the effect of the relative humidity was first studied, and then the change due to grinding in nitrogen or carbon dioxide gas was investigated.

Experimental

The materials,[3] grinding method,[3] analytical procedure,[3,4] and apparatus[5] were essentially the same as those used in the previous paper, except for the following method. The X-ray diffraction patterns for determining the crystallite size and the lattice distortion were taken with a Rigaku Denki Geigerflex diffractometer using nickel-filtered Cu$K\alpha$ radiation. The crystallite size and the lattice distortion were determined in the usual manner.[6]

The relative humidity was measured with a hair hygrometer, which was calibrated by a dew point hygrometer, a wet and dry bulb hygrometer, and the vapor on the saturated solutions of calcium chloride and nitrate.

Results and Discussion

The Effect of the Relative Humidity. The changes in the X-ray diffraction patterns of sodium trimetaphosphate due to grinding are shown in Fig. 1. It can be seen that the higher the relative humidity, the longer the diffraction lines of $Na_3P_3O_9$. Sodium trimetaphosphate becomes amorphous when ground for 48 hr at a relative humidity of 20%, but some diffraction lines of $Na_3P_3O_9$ remain at 40%. At 60%, these lines remain even after 72 hrs' grinding.

The changes in the crystallite size and the lattice distortion due to grinding are given in Fig. 2. The crystallite size in all the relative humidities becomes smaller with the grinding time and has a tendency to reach a constant value after 24 hr. On the other hand, the lattice distortion increases with the grinding time, and the change in the lower relative humidity is faster.

Figure 3 shows the changes in the infrared spectra upon grinding of sodium trimetaphosphate at the relative humidities of 20 and 40%. It can be seen from a comparison of Fig. 3(1) with Fig. 3(2) that the change due to grinding at 20% was faster than that at 40%. That is, the absorptions at 686, 757, 773, 890, 1162, 1169, and 1262 cm^{-1} for the sample of 3 (or 48) hrs' grinding at 20% are similar to those for that of 6 (or 72) hrs' grinding at 40%.

As has been described in the preceding paper,[3]

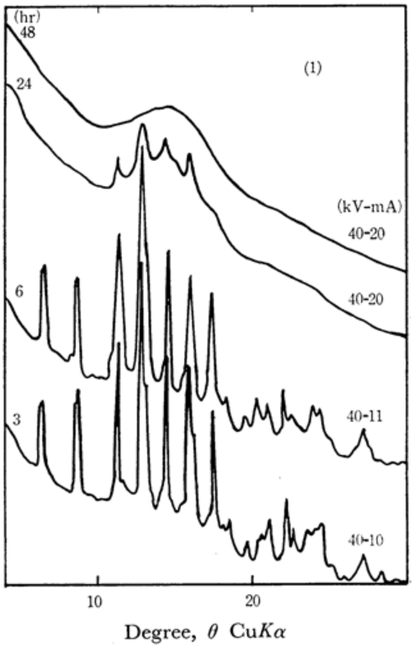

Fig. 1. (1)

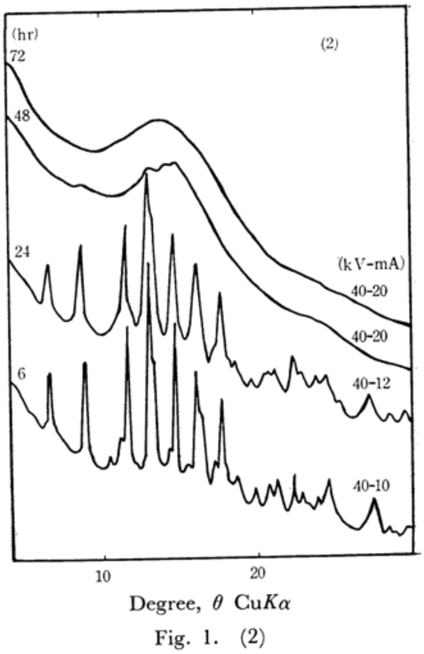

Fig. 1. (2)

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[4] I. Motooka, M. Ishizaki, H. Nozu and M. Kobayashi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2071 (1966).

[5] Part II : I. Motooka, G. Hashizume and M. Kobayashi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 953 (1966).

[6] For example, Chemical Society of Japan, "Jikken Kagaku Koza," Vol. 1, Maruzen Co., Ltd., Tokyo (1956), p. 238; H. Takahashi, *Hyomen (Surface)*, **4**, 288 (1966).

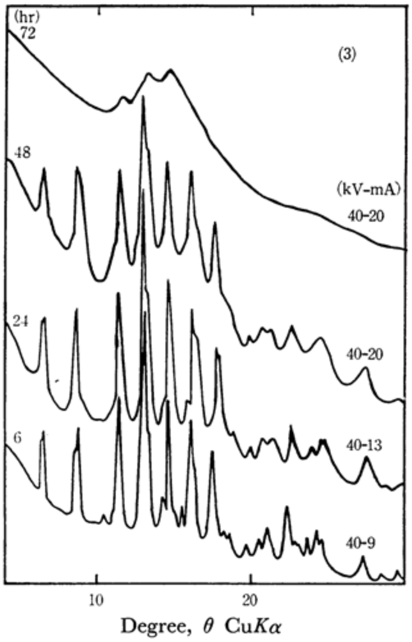

Fig. 1. (3)

Fig. 1. The change of the X-ray diffraction patterns of sodium trimetaphosphate due to grinding at various relative humidities.
(1) at the relative humidity of 20%.
(2) at that of 40%
(3) at that of 60%
The numbers represent the grinding time.

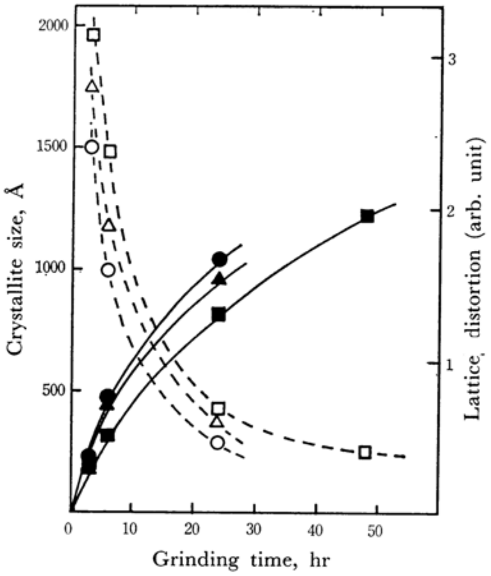

Fig. 2. The changes of crystallite size and lattice distortion due to grinding at various relative humidities.
Broken line: Crystallite size
Solid line: Lattice distortion
○: at the relative humidity of 20%
△: at that of 40%
□: at that of 60%

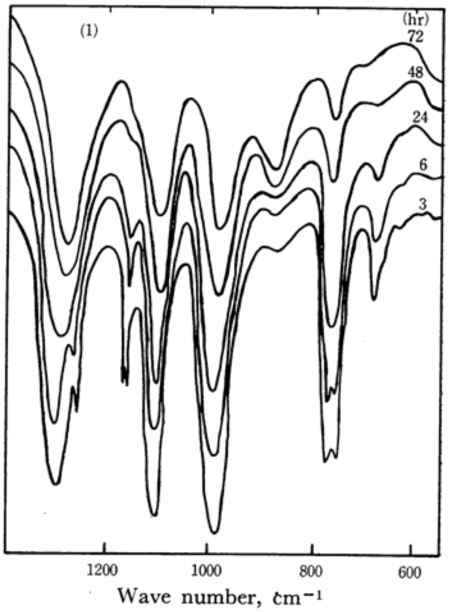

Fig. 3. (1)

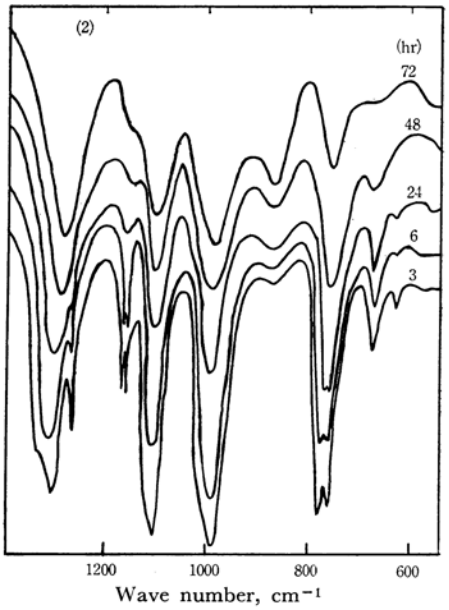

Fig. 3. (2)

Fig. 3. The change in infrared spectra of sodium trimetaphosphate due to grinding.
(1) at the relative humidity of 20%
(2) at that of 40%
The numbers represent the grinding time.

the percentage of trimetaphosphate decreased with the grinding time. Figure 4 shows the rate of the decrease of trimetaphosphate molecules by grinding at various relative humidities.*2 The

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*2 There were some ground samples which contained some polyphosphates higher than tetraphosphate.[7]

[7] I. Motooka *et al.*, unpublished work.

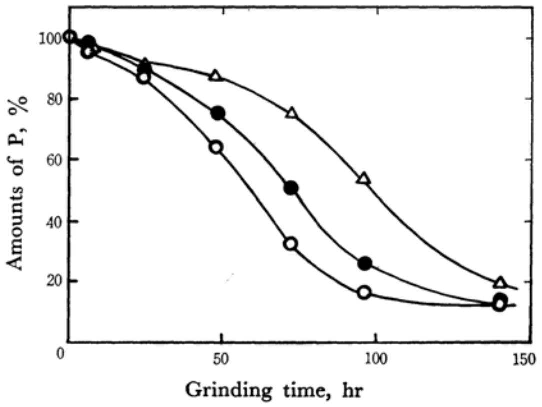

Fig. 4. The rate of decrease of trimetaphosphate molecules due to grinding at various relative humidities.
○ at the relative humidity of 20%
● at that of 40%
△ at that of 60%

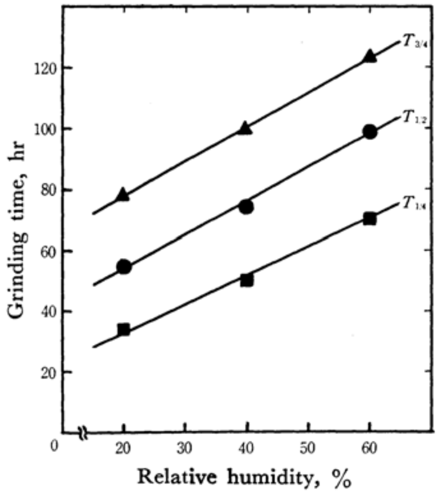

Fig. 5. $T_{1/2}$, $T_{1/4}$ and $T_{3/4}$ at various relative humidities.

fact that trimetaphosphate remains longer at the higher humidities agrees well with the results of X-ray diffraction and infrared absorption analyses.

As is shown in Fig. 5, the half life $T_{1/2}$, the time required for the degradation of one half of the trimetaphosphate molecules, increased linearly with the relative humidity. Similarly, the quarter life, $T_{1/4}$, and the three-quarter life, $T_{3/4}$, also increased.

As the amounts of the cleavage of the P–O–P linkages does not increase with the increase in the relative humidity or water molecules, in spite of the fact that the reactions shown in Eqs. (1), (2), and (3) were hydrolytic in form, the following can be assumed: the reactions shown by these equations differ from hydrolysis in an aqueous solution[8] and are reactions in which the P–O–P linkages are severed and in which water molecules act at the active points. As the cleavage of the P–O–P linkages seems to be the rate-determining step, the amounts of water molecules may be beside the question, because these can be sufficiently supplied even at a relative humidity of 20%.

The active molecules of sodium trimetaphosphate shown in Eq. (4) may be formed by grinding before the cleavage of the P–O–P linkages:

$$Na_3P_3O_9 \underset{H_2O}{\overset{\text{Grinding}}{\rightleftarrows}} Na_3P_3O_9^* \qquad (4)$$

The active molecules are considered to be formed when the crystallites become small, and the lattice

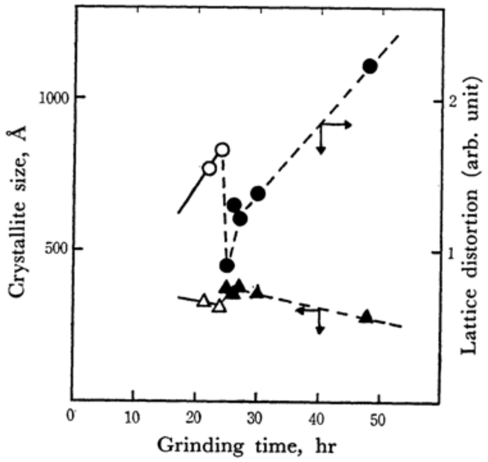

Fig. 6. The recovery of crystallite size and lattice distortion by increasing the relative humidity during grinding. The parts of solid lines were ground at the relative humidity of 20% and those of broken lines did at that of 50%.

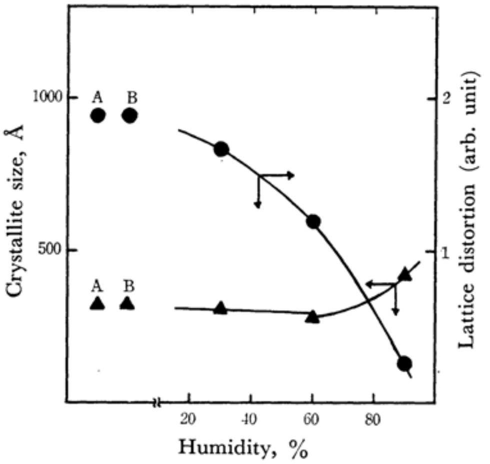

Fig. 7. The recovery of crystallite size and lattice distortion when the samples ground for 24 hr were left standing at various relative humidities for 24 hr.
A: Sample ground for 24 hr at the relative humidity of 20%.
B: The ground sample A left standing for 24 hr in the desiccator containing silica gel.

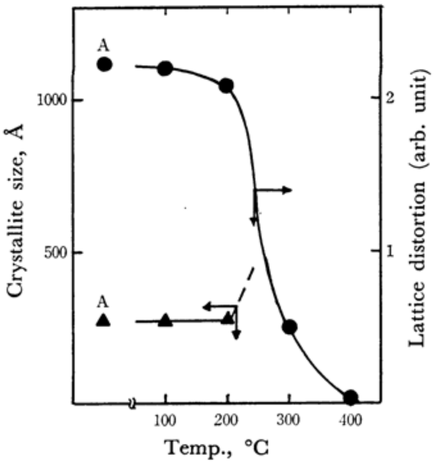

Fig. 8. The recovery of crystallite size and lattice distortion when the samples ground for 20 hr were heated at various temperatures for 3 hr. A: Sample ground for 20 hr at the relative humidity of 20%.

to be distorted largely by grinding.

In order to make clear the effect of water molecules, the recovery of the crystallite size and the lattice distortion was studied by increasing the relative humidity during grinding. As may be seen in Fig. 6, the increase in the relative humidity resulted in the recovery of the lattice distortion and in a slight increase in the crystallite size. Also, Figs. 7 and 8 show the changes in the crystallite size and the lattice distortion when the ground samples were left standing at various relative humidities for 24 hr and when they were heated at various temperatures for 3 hr respectively. The recovery of the lattice distortion was remarkable at higher humidities and the crystallite size was a nearly constant value, except for a slight increase at 90%, while the recovery by heating took place above 300°C, which is the formation temperature of sodium trimetaphosphate.[8]

From the above results, it seems reasonable to consider that water molecules play an important role in the recovery of the lattice distortion; the rate of back reaction in Eq. (4) increases with the increase in the relative humidity and, consequently, the amounts of the active molecules decrease and the rate of the decrease of trimetaphosphate molecules becomes smaller.

The Effect of Grinding in Nitrogen or Carbon Dioxide Gas. The grinding was carried out in nitrogen or carbon dioxide gas. The results of X-ray diffraction, infrared absorption, and ion exchange (or paper) chromatographic analysis were the same as those in air.

From these results, it is plain that this grinding process is much affected by water molecules.

Although the grinding at humidities lower than 20% is of interest, a special apparatus and a special technique will be required for this purpose. This problem will be examined in detail in the near future.

Conclusion

From the previous[3] and the present papers, the following can be concluded:

$$\mathrm{Na_3P_3O_9} \underset{\mathrm{H_2O}}{\overset{\text{Grinding}}{\rightleftarrows}} \mathrm{Na_3P_3O_9}^* \tag{4}$$

$$\mathrm{Na_3P_3O_9}^* \underset{?}{\overset{\text{Grinding}}{\rightleftarrows}} \mathrm{Na_3P_3O_9}\!: \tag{5}$$

$$\mathrm{Na_3P_3O_9}\!: + \mathrm{H_2O} \rightarrow \mathrm{Na_3H_2P_3O_{10}} \tag{6}$$

$Na_3P_3O_9$ was changed to such active molecules as $Na_3P_3O_9^*$ by grinding (Eq. (4)), while the reaction in the opposite direction takes place simultaneously in the presence of water molecules. The P–O–P linkages of $Na_3P_3O_9^*$ are severed and it becomes $Na_3P_3O_9$: which resembles the free radical*[3] (Eq. 5). Next, it becomes triphosphate, $Na_3H_2P_3O_{10}$ (Eq. (6)). Finally, the changes of Eqs. (2) and (3) take place.

The authers wish to express their gratitude to Miss Kayoko Amita for her measurement of the infrared spectra.

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[8] J. R. Van Wazer, "Phosphorous and its Compound," Vol. 1, Interscience Publishers, New York (1958), pp. 452, 607.

*[3] This material will be examined by the measurement of the ESR in the near future.