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# The thermal behaviour of copper diphosphates made by wet process

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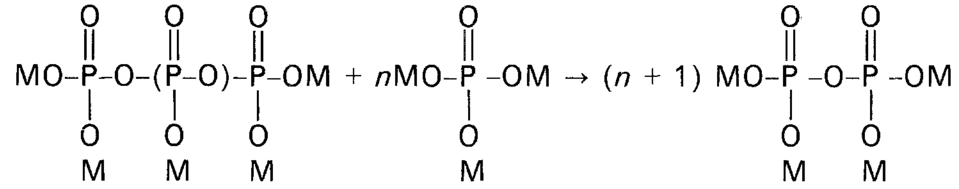
Copper diphosphates ($Cu_2P_2O_7 \cdot 5H_2O$, $Cu_{1.6}K_{0.8}P_2O_7 \cdot 1.7H_2O$, and $Cu_{1.5}K_{1.0}P_2O_7 \cdot 2.8H_2O$) were made by mixing aqueous solutions of tetrapotassium diphosphate and copper dichloride. When the diphosphates were heated, the decomposition of the diphosphates to orthophosphate was observed at a temperature lower than 150° C. The orthophosphate was polymerized by condensation to polyphosphates in the temperature range of about 150 to 450° C. The polyphosphates reorganized to diphosphate at 450 to 550° C according to the following reaction:



$$\mathrm{MO{-}\underset{\underset{M}{O}}{\overset{O}{P}}{-}O{-}(\underset{\underset{M}{O}}{\overset{O}{P}}{-}O){-}\underset{\underset{M}{O}}{\overset{O}{P}}{-}OM} + n\mathrm{MO{-}\underset{\underset{M}{O}}{\overset{O}{P}}{-}OM} \rightarrow (n+1)\ \mathrm{MO{-}\underset{\underset{M}{O}}{\overset{O}{P}}{-}O{-}\underset{\underset{M}{O}}{\overset{O}{P}}{-}OM}$$

where M stands for 1/2 copper and/or potassium.

## 1. Introduction

Polyphosphates have been used for agricultural treatment, detergents, food additives, chemical manufacture, ceramics and so on [1]. Although the usage of these compounds is extending to other industrial fields, for example, electrical manufacture and biomaterials, the physical and chemical properties of these compounds still have not been well studied. Diphosphates have been used for water treatment, additives of food, and so on. A solution of diphosphoric acid has been used for plating [2]. Copper diphosphate has been employed as a copper plating reagent. Copper diphosphate has usually been made by mixing solutions of tetrapotassium diphosphate and copper dichloride or copper sulphate, but the relation between the condition and the chemical composition in the synthesis of the diphosphate has not yet been well established. This paper describes the synthesis of copper diphosphates by the wet chemical process, and their thermal behaviour.

## 2. Experimental procedures

### 2.1. Materials and methods

Tetrapotassium diphosphate was prepared by heating dipotassium hydrogenorthophosphate at 600° C for 6 h. The diphosphate was dissolved in water to make 1.0- and 0.1-mol dm$^{-3}$ aqueous solutions. An aqueous solution of copper dichloride with the same concentration as that of the diphosphate was added dropwise to the diphosphate solution. The dropping rate of the copper dichloride solution was regulated. The pH of the solution was controlled with hydrochloric acid and an aqueous solution of potassium hydroxide. The temperature of the reaction mixture was kept at 22° C during the treatment.

### 2.2. Determination of metals

Copper in a sample was determined by the EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) titration method with a PAN indicator. The atomic absorption analysis was used for the quantative analysis of potassium by using a Shimadzu AA-646 spectrophotometer.

### 2.3. Separation and determination of phosphates

One-dimensional paper chromatographic separation and colorimetric determination of phosphates were used [3]. A modified stock solution of a molybdenum(V)-molybdenum(VI) reagent was employed for the determination [4].

### 2.4. TG and DTA analysis

A sample was heated at the heating rate of 10° C min$^{-1}$ in air by use of a Cho Balance TRDA-H apparatus.

### 2.5. X-ray diffractometry

An X-ray diffraction diagram of a powder sample was recorded on a Rigaku X-ray diffractometer, RAD-1B, with nickel filtered Cu$K_\alpha$ radiation.

### 2.6. Measurement of particle size

Particle size distribution was measured according to the centrifugal sedimentation technique with iso-butanol

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TABLE I Composition, particle size and yield of copper diphosphates

| Concentration* ($mol\,dm^{-3}$) | pH | Dropping† time (min) | Product | Composition | Modal diameter ($\mu m$) | Yield (%) |
|---|---|---|---|---|---|---|
| 1.0 | 2–3 | 30 | I | $Cu_2P_2O_7 \cdot 5H_2O$ | 12.3 | 74 |
|  | 4–5 | 30 | II | $Cu_{1.6}K_{0.8}P_2O_7 \cdot 1.7H_2O$ | 3.5 | 98 |
|  | 4–5 | 240 | III | $Cu_{1.5}K_{1.0}P_2O_7 \cdot 2.8H_2O$ | 26.5 | 97 |
| 0.1 | 2–3 | 30 | IV | $Cu_2P_2O_7 \cdot 5H_2O$ | 26.2 | 75 |
|  | 3–4 | 30 | V | $Cu_2P_2O_7 \cdot 5H_2O$ | 14.3 | 75 |
|  | 4–5 | 30 | VI | $Cu_2P_2O_7 \cdot 5H_2O$ | 10.4 | 80 |
|  | 5–6 | 30 | VII | $Cu_2P_2O_7 \cdot 5H_2O$ | 3.1 | 80 |

*Concentration of the solutions of tetrapotassium diphosphate and copper dichloride.

† Spending time to mix the two solutions drop wise; 40 $cm^3$ of 1.0-mol $dm^{-3}$ copper dichloride solution was added to 25 $cm^3$ of 1.0-mol $dm^{-3}$ tetrapotassium diphosphate solution, and 120 $cm^3$ of 0.1-mol $dm^{-3}$ copper dichloride solution was added to 75 $cm^3$ of 0.1-mol $dm^{-3}$ tetrapotassium diphosphate solution.

as a sedimentation medium by using a Shimadzu SA-CP3.

## 3. Results and discussion

### 3.1. Composition of the products

The compositions of the copper diphosphates are shown in Table I. In all cases, the precipitated products were aged for 1 h in the solutions. When the 1.0-mol $dm^{-3}$ solutions of tetrapotassium diphosphate and copper dichloride were used, dicopper diphosphate pentahydrate, $Cu_2P_2O_7 \cdot 5H_2O$, was obtained at pH 2 to 3, while the diphosphate which was produced at pH 4 to 5 contained potassium and copper and the particle diameter increased with increased mixing time. When 0.1-mol $dm^{-3}$ solutions were used, only dicopper diphosphate pentahydrate was obtained at pH 2 to 6. The particle size decreased and the yield increased with an increase in the pH value of the solution. The X-ray diffraction diagrams of the products are shown in Fig. 1. The data for $Cu_2P_2O_7 \cdot 5H_2O$ made in this experiment agree well with the JCPDS index.

### 3.2. Thermal analysis

TG and DTA curves of product I are shown in Fig. 2. The thermal products as numbered in Fig. 2 were removed from the furnace and subjected to further analysis. The analytical data are listed in Table II. Up to about 120° C, product I showed an endothermic peak accompanying a rapid weight loss. The reaction seemed to be due to an elimination of the water of crystallization along with the simultaneous decomposition of a small amount of the diphosphate to orthophosphate:

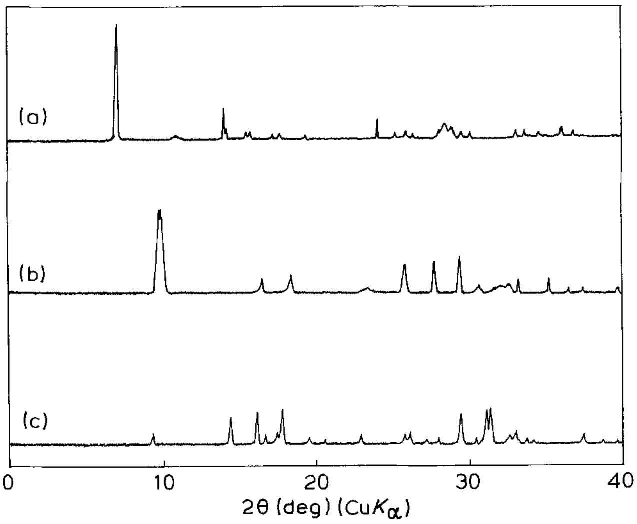


*Figure 1* X-ray diffraction diagrams of products (a) I, (b) II, and (c) III.

$$Cu_2P_2O_7 + H_2O \rightarrow 2CuHPO_4 \qquad (1)$$

The water in Equation 1 can come from the water of crystallization of the diphosphate. The next large endothermic reaction accompanied by a large weight loss can be caused by a removal of the rest of the water of crystallization. The data in Table II show that the diphosphate decomposed to orthophosphate and a small amount of the diphosphate and/or the orthophosphate converted to triphosphate. The orthophosphate produced according to Equation 1 can only make diphosphate by the following thermal condensation at the temperature range

$$2CuHPO_4 \rightarrow Cu_2P_2O_7 + H_2O \qquad (2)$$

It is impossible to make triphosphate at the temperature range by the condensation

$$Cu_2P_2O_7 + CuHPO_4 \rightarrow Cu_2HP_3O_{10} + CuO \qquad (3)$$

or

$$Cu_2P_2O_7 + CuHPO_4 \rightarrow Cu_{5/2}P_3O_{10} + Cu_{1/2}HO \qquad (4)$$

The formation of polyphosphates with longer chains than diphosphate can be explained by the following disproportionation or metathesis of the orthophos-

TABLE II Weight loss and composition of the thermal products of I

| Thermal product | Weight loss (%) | X-ray diffraction | Phosphates (%P) |  |  |  |
|---|---|---|---|---|---|---|
|  |  |  | Ortho | Pyro | Tri | Higher |
| 1 | 9.9 | UC* | 1.1 | 98.9 | – | – |
| 2 | 13.7 | UC | 2.9 | 97.1 | – | – |
| 3 | 19.4 | AM | 44.5 | 52.6 | 2.9 | – |
| 4 | 21.7 | α-$Cu_2P_2O_7$(vw)† | 24.8 | 60.1 | 8.8 | 6.3 |
| 5 | 22.2 | α-$Cu_2P_2O_7$(w) | 12.7 | 62.8 | 10.8 | 13.7 |
| 6 | 22.3 | α-$Cu_2P_2O_7$ | 4.3 | 84.9 | 5.3 | 5.5 |
| 7 | 22.3 | α-$Cu_2P_2O_7$ | – | 100 | – | – |

*UC and AM stand for the unknown crystalline and amorphous products, respectively.

†vw and w indicate X-ray diffraction diagrams with very weak and weak peaks, respectively.

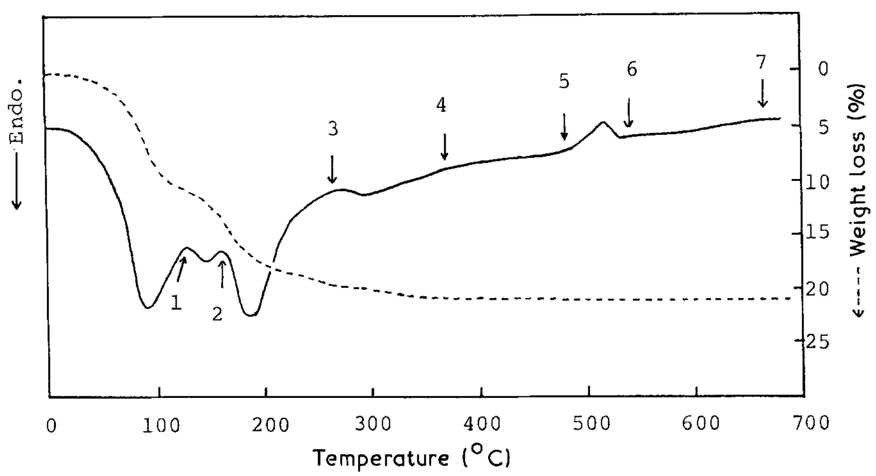


*Figure 2* DTA and TG curves of product I in air. (——) DTA, (- - -) TG.

phate:

$$2CuHPO_4 \rightarrow Cu_{3/2}PO_4 + Cu_{1/2}H_2PO_4 \quad (5)$$

The $Cu_{1/2}H_2PO_4$ can produce polyphosphates with longer chains than diphosphate as follows:

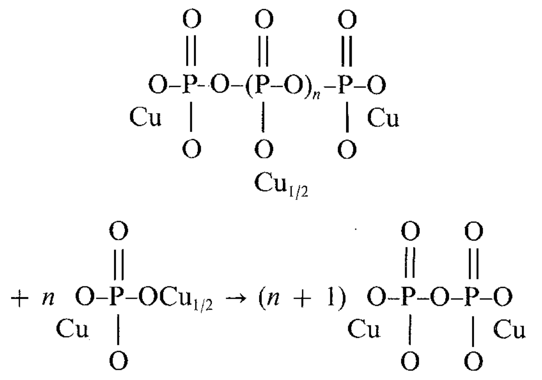
$$2CuHPO_4 + Cu_{1/2}H_2PO_4 \rightarrow Cu_{5/2}P_3O_{10} + 2H_2O \quad (6)$$

$$2CuHPO_4 + 2Cu_{1/2}H_2PO_4 \rightarrow Cu_3P_4O_{13} + 3H_2O \quad (7)$$

The condensation of the orthophosphate to diphosphate could be the main reaction for the fourth weak endothermic reaction accompanying a small amount of weight loss, and the diphosphate was crystallized to α-$Cu_2P_2O_7$ by heating. For successive heating up to about 500° C, no appreciable thermal change was observed, but the condensation of phosphates to phosphates with longer chains took place. After the exothermic reaction at about 530° C, the thermal product showed the X-ray diffraction diagram of α-$Cu_2P_2O_7$, and the content of diphosphate increased and that of the other phosphates decreased. Therefore, the reorganization of the phosphates to diphosphate seemed to occur through the thermal change. The degradation or reorganization of triphosphate to diphosphate can be written as follows:

$$Cu_{5/2}P_3O_{10} + Cu_{3/2}PO_4 \rightarrow 2Cu_2P_2O_7 \quad (8)$$

A general equation of the degradation or reorganization of polyphosphates to diphosphate can be described by the following equation:



$$\begin{array}{ccl} & \begin{array}{c} \mathrm{O} \quad\;\; \mathrm{O} \quad\;\; \mathrm{O} \\ \| \qquad\;\; \| \qquad\;\; \| \\ \mathrm{O{-}P{-}O{-}(P{-}O)_{\mathit{n}}{-}P{-}O} \\ \mathrm{Cu}\;| \qquad\;\; | \qquad\;\; |\;\mathrm{Cu} \\ \mathrm{O} \quad\;\; \mathrm{O} \quad\;\; \mathrm{O} \\ \mathrm{Cu_{1/2}} \end{array} & \\ + \; n & \begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{O{-}P{-}OCu_{1/2}} \\ \mathrm{Cu}\;| \\ \mathrm{O} \end{array} & \rightarrow (n+1) \begin{array}{c} \mathrm{O} \quad \mathrm{O} \\ \| \quad\;\; \| \\ \mathrm{O{-}P{-}O{-}P{-}O} \\ \mathrm{Cu}\;| \quad\;\; |\;\mathrm{Cu} \\ \mathrm{O} \quad \mathrm{O} \end{array} \end{array}$$

(9)

The thermal product did not melt up to 1000° C.

Product II gave different TG and DTA curves (Fig. 3) from those of product I. The first small endothermic reaction accompanying a slow weight loss was considered to be caused by an elimination of the water of crystallization of the product. The analytical data in Table III shows that a small amount of the diphosphate decomposes to orthophosphate:

$$M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4 \quad (10)$$

where M stands for 1/2 copper and/or potassium. The equation is similar to Equation 1. In the discussion below, the same exchange of copper to M in Equations

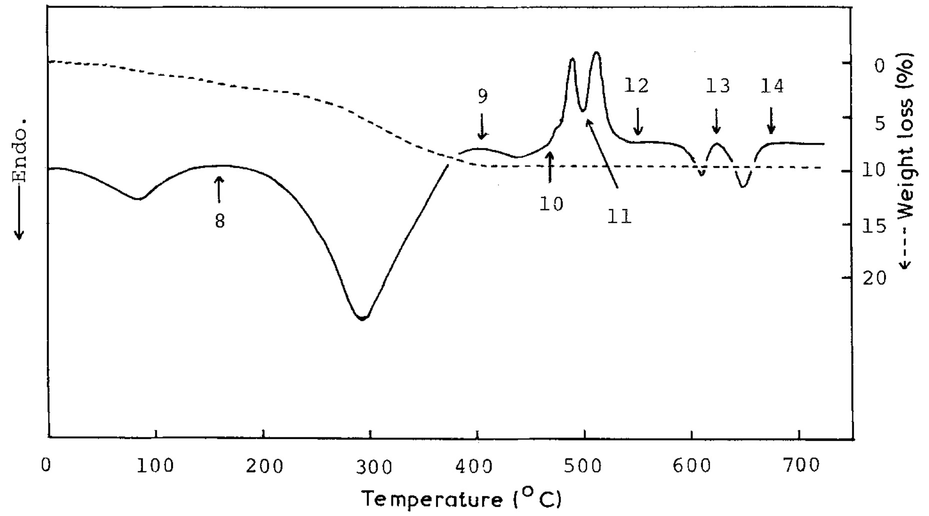


*Figure 3* DTA and TG curves of product II in air. (——) DTA, (- - -) TG.

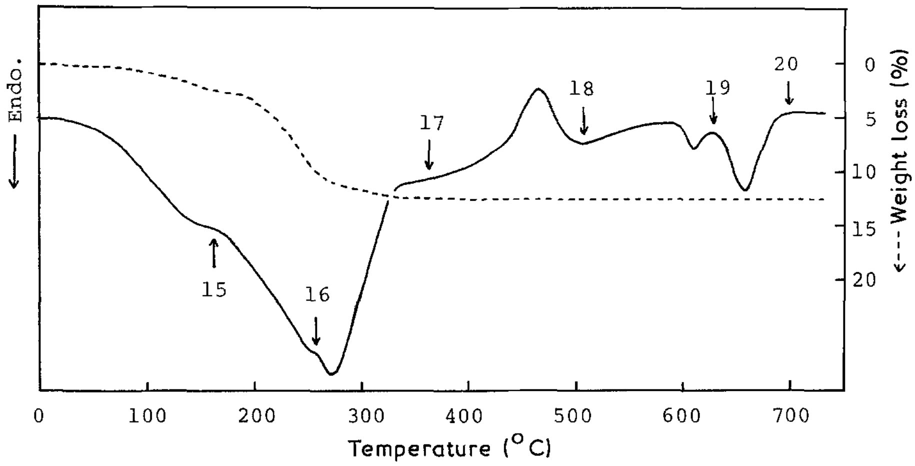


*Figure 4* DTA and TG curves of product III in air. (——) DTA, (- - -) TG.

2 to 9 is needed for an explanation of the thermal reactions. The next large endothermic peak associated with a large weight loss may be caused by an elimination of the water of crystallization, and the result in Table III shows that the degradation of diphosphate to orthophosphate by means of Equation 10, the disproportionation of the orthophosphate according to the process similar to Equation 5, and the condensation of the orthophosphate to polyphosphates through the processes similar to Equations 6 and 7, occur at the same time. The reorganization of polyphosphates to phosphates with longer chains was carried out up to about 450° C. The amorphous thermal product produced by the heating was crystallized to $\alpha$-$Cu_2P_2O_7$ through the next two exothermic processes, and the reorganization of the phosphates other than diphosphate to diphosphate was carried out according to reactions similar to Equations 8 and 9 at the same time, because the diphosphate content in the thermal product increased. The next two endothermic peaks were caused by a fusion of a part of the phosphates, and the sample melted completely at about 810° C.

DTA and TG curves of product III are shown in Fig. 4 along with the analytical results in Table IV. Product III gave a broad and large endothermic process up to about 320° C,. The weight loss of the process seemed to be due to an elimination of the water of crystallization and the condensation of the phosphates, which were made by the decomposition of product III through a thermal reaction similar to Equation 10. The amorphous phosphates made by the heating were crystallized and reorganized to diphosphate through the exothermic reaction at about 480° C. The reorganization proceeded up to about 620° C. The two endothermic peaks at about 600 to 700° C was caused by a fusion of a part of the phosphates. The complete melt of the sample was observed at about 810° C. The product which was made by rapid cooling of the melt showed the X-ray diffraction pattern of $\alpha$-$Cu_2P_2O_7$. This seemed to show that a metathesis occurred through the process as follows:

$$2Cu_{3/2}K_2O_7 \rightarrow Cu_2P_2O_7 + CuK_2P_2O_7 \quad (11)$$

TABLE III Weight loss and composition of the thermal products of II

| Thermal product | Weight loss (%) | X-ray diffraction | Phosphates (%P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 8 | 1.7 | SM* | 3.7 | 96.3 | – | – |
| 9 | 8.8 | SM(vw)† | 15.3 | 70.6 | 9.7 | 4.4 |
| 10 | 8.9 | AM | 16.2 | 60.7 | 16.7 | 6.4 |
| 11 | 9.0 | $\alpha$-$Cu_2P_2O_7$(w), UC(w) | 12.3 | 80.7 | 4.3 | 2.7 |
| 12 | 9.0 | $\alpha$-$Cu_2P_2O_7$, UC(w) | 5.5 | 94.5 | – | – |
| 13 | 9.0 | $\alpha$-$Cu_2P_2O_7$ | 9.5 | 80.0 | 10.5 | – |
| 14 | 9.0 | $\alpha$-$Cu_2P_2O_7$ | 9.6 | 77.6 | 9.4 | 3.4 |

*SM and AM stand for the starting material and the amorphous product, respectively.

† vw and w indicate the X-ray diffraction diagrams with very weak and weak peaks, respectively.

## 4. Conclusions

Dicopper diphosphate pentahydrate, $Cu_2P_2O_7 \cdot 5H_2O$, was made by mixing 0.1-mol dm$^{-3}$ solutions of tetrapotassium diphosphate and copper dichloride at pH 2 to 6. The particle size decreased with an increase in the pH of the solution. The yield of the diphosphate was 75 to 80%. When 1.0-mol dm$^{-3}$ solutions of tetrapotassium diphosphate and copper dichloride were used, $Cu_2P_2O_7 \cdot 5H_2O$ (at pH 2 to 3), $Cu_{1.6}K_{0.8}P_2O_7 \cdot 1.7H_2O$ (at pH 4 to 5 and with dropping time of 30 min), and $Cu_{1.5}K_{1.0}P_2O_7 \cdot 2.8H_2O$ (at pH 4 to 5 and with dropping time of 240 min) were produced.

The diphosphates showed thermal reactions as follows. Below 400–450° C,

1. Dehydration

$$M_4P_2O_7 \cdot nH_2O \rightarrow M_4P_2O_7 \cdot (n - x)H_2O + xH_2O$$
$$(0 < x \leqslant n)$$

TABLE IV Weight loss and composition of the thermal products of III

| Thermal product | Weight loss (%) | X-ray diffraction | Phosphates (%P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 15 | 3.4 | SM* | 13.3 | 86.7 | – | – |
| 16 | 8.8 | AM | 51.7 | 48.3 | – | – |
| 17 | 13.9 | AM | 8.4 | 62.1 | 18.8 | 10.7 |
| 18 | 14.3 | UC | 11.7 | 81.2 | 7.1 | – |
| 19 | 14.3 | UC | 6.6 | 89.2 | 2.5 | 1.7 |
| 20 | 14.4 | $\alpha$-$Cu_2P_2O_7$ | 5.7 | 80.5 | 10.0 | 3.8 |

*SA, AM, and UC stand for the starting material, the amorphous product, and the unknown crystalline product, respectively.

2. Decomposition

$$\mathrm{M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4}$$

3. Condensation

$$\mathrm{2M_2HPO_4 \rightarrow M_4P_2O_7 + H_2O}$$

4. Disproportionation or metathesis and condensation

$$\mathrm{2M_2HPO_4 \rightarrow M_3PO_4 + MH_2PO_4}$$

$$\mathrm{2M_2HPO_4 + MH_2PO_4 \rightarrow M_5P_3O_{10} + 2H_2O}$$

(a general equation of the condensation)

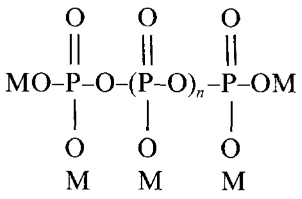
$$\mathrm{2M_2HPO_4 + nMH_2PO_4 \rightarrow M_{n+4}P_{n+2}O_{3n+7} + (n + 1)H_2O}$$

At 450–550° C

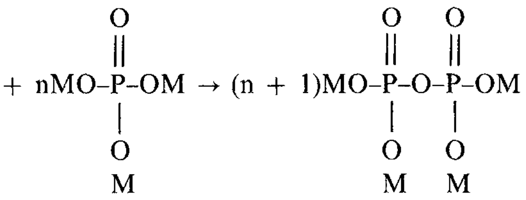
5. Degradation or reorganization

$$\mathrm{M_5P_3O_{10} + M_3PO_4 \rightarrow 2M_4P_2O_7}$$

(a general equation)



$$\mathrm{MO{-}\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}(\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}O)_{\mathit{n}}{-}\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}OM}$$



$$+\ \mathrm{nMO{-}\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}OM} \rightarrow \mathrm{(n + 1)MO{-}\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}O{-}\underset{\substack{|\\ O\\ M}}{\overset{\substack{O\\ \|}}{P}}{-}OM}$$

where M stands for 1/2 copper and/or potassium. Liquid copper potassium diphosphate was crystallized to $\alpha$-$\mathrm{Cu_2P_2O_7}$ by rapid quenching through the following disproportionation or metathesis:

$$\mathrm{2Cu_{3/2}KP_2O_7 \rightarrow Cu_2P_2O_7 + CuK_2P_2O_7}$$

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