Preparation of Ammonium Polyphosphate Form II from the System of Ammonium Orthophosphate–Urea

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Ammonium polyphosphate (APP) form II was prepared by heating of a mixture of ammonium orthophosphates (triammonium, diammonium, and monoammonium orthophosphates) and urea at 280 to 300 °C under wet ammonia, which was made by passing air through 3 to 5% aqueous ammonia. The following reaction process is proposed:

Ammonium orthophosphate → APP form I → Amorphous APP → APP form II.

The addition of APP form II shortened the preparation time significantly. A wider range of concentrations (1 to 8%) of aqueous ammonia was available to prepare APP form II. The average particle size of the obtained APP form II was larger than 5 μm.

There are many kinds of ammonium ortho- and condensed phosphates. These phosphates are used as chemical fertilizers, food additives, flame retardants, and dye-leveling agents etc.[1—3] The ammonium phosphates have advantage in water-solubility and are useful as fertilizers, food additives, dye-levering agents, and flame retardants for wood and paper. Ammonium phosphates are used as flame retardants for wood and paper, which can absorb the phosphates in a solution of the phosphates. By the way, growing use of plastics and other flammable synthetic organic materials in construction, home furnishing, and various industrial applications is requiring polymer-compatible, thermally stable, environmentally friendly, and cost-efficient flame retardants. The water-soluble ammonium phosphates bleed easily when they are used as flame retardants for synthetic organic materials, and the materials are exposed to humid air at a moderately high temperature. Bleeding of flame retardants drops down a material power. Accordingly, water-insoluble ammonium phosphates are required for the organic materials to prevent bleeding. APP has six crystal forms of I to VI.[4,5] Among many ammonium phosphates, only ammonium polyphosphate (APP) forms II and V are hardly soluble in water; the solubility of the APPs is lower than 5 mg in 100 g of water at 25 °C after 60 min of stirring. APP form I can be prepared most easily by heating of an equimolar mixture of diammonium orthophosphate and urea at 250 to 270 °C. Crystals of APP form I are too small to determine the unit-cell dimension. It bleeds when used as a flame retardant for synthetic organic materials. APP form II has orthorhombic symmetry. The unit cell parameters are $a = 0.4256$, $b = 0.6475$, $c = 1.204$ nm. The most probable space group is $P2_12_12_1$. APP form II is made by heating of the APP form I at 300 °C for about 60 h in a well-covered container.[4] It seems to be difficult to apply the process to large-scale production in a factory. The present authors reported a preparation process of APP form II according to the phase transition of APP form I.[6] The process includes the preparation of APP form I and its transformation into form II. APP form II can also be prepared by heating a mixture of ammonium orthophosphate, diphosphorus pentaoxide, and urea at 270 to 290 °C. On the other hand, diphosphorus pentaoxide is very chemically active and harmful to the human body, and is commercially expensive and energetically disadvantageous due to its production from yellow phosphorus. Thus, it is very important to develop a new and simple process to prepare APP form II from an easy reaction system. This paper describes a new simple and direct preparation method of APP form II from ammonium orthophosphate–urea mixtures.

Experimental

Preparation of APP Form II. The reaction to prepare APP form II was carried out by heating a mixture of ammonium orthophosphate and urea at 250 to 300 °C under wet ammonia. Heating the mixture under air gave APP form I. In this work, a mixture of ammonium orthophosphate and urea was heated to prepare APP form II at 250 to 300 °C under wet ammonia, which was made by passing air at a flow rate of 40 $dm^3\ h^{-1}$ through 1 to 29% of aqueous ammonia. Aqueous ammonia was exchanged for a fresh supply every 20 min. to keep the concentration of ammonia constant. Various experimental conditions were examined by changing the mixing molar ratio of ammonium orthophosphate to urea, the heating temperature, the heating time, and the concentration of aqueous ammonia to prepare wet ammonia. Triammonium, diammonium, and monoammonium orthophosphates were used as starting ammonium orthophosphate. Among these ammonium orthophosphates, anhydrous diammonium hydrogenorthophosphate was mainly examined, because they gave favorable results. The reaction was run

in a glass tube placed in an electric furnace. The effect of an additive on the formation of APP form II was also examined. Powdered APP forms I and II were used as the additive.

Analytical Methods. An X-ray diffraction diagram (XRD) of a powdered sample was taken with nickel-filtered Cu $K\alpha$ radiation using a Rigaku RAD-1B diffractometer. The determination of APP form II in the product was made automatically using software installed in the XRD machine. Scanning electron microscopic (SEM) observations of the sample were made using an Akashi DS-180 instrument. The specific gravity was measured using an Auto True Denser MAT-500, made by Seishin. The particle-size distribution was measured by a centrifugal sedimentation technique, with isobutyl alcohol used as a sedimentation medium, on a Shimadzu SA-CP3 instrument. The determinations of phosphorus and nitrogen were made by the Molybdenum Blue method and the Kjeldahl technique, respectively.

Results and Discussion

A previous paper pointed out that the transformation of APP form I to form II was accelerated by the presence of amorphous APP. The formation of amorphous APP from APP form I could be made by introducing a small amount of moisture or by removing a small amount of ammonia.[4] From the results, we proposed the following transformation mechanism and established a simple and easy transformation reaction process of APP form I to form II:[6]

$$\text{APP form I} \xrightarrow[\text{Step1}]{} \text{Amorphous APP} \xrightarrow[\text{Step2}]{} \text{APP form II.}$$

XRD diagrams of the products prepared in the experiments are shown in Fig. 1. APP form I was formed at the initial stage (0.5 h) and converted to form II along with the progress of the reaction. This phenomenon was observed in every reaction of this experiment. The following mechanism can be given for the formation of APP form II:

$$\text{Ammonium orthophosphate} \xrightarrow[\text{Step1*}]{} \text{APP form I}$$

$$\xrightarrow[\text{Step2*}]{} \text{Amorphous APP}$$

$$\xrightarrow[\text{Step3*}]{} \text{APP form II.}$$

Based on the above consideration of the formation mechanism of APP form II, favorable reaction conditions for the direct preparation of APP form II from a system of $(NH_4)_{3-n}H_nPO_4$–$CO(NH_2)_2$ ($n = 0$, 1, or 2) were searched.

Diammonium hydrogenorthophosphate gave good results in preliminary experiments of the preparation of APP form II, and a favorable mixing molar ratio of diammonium hydrogenorthophosphate to urea was examined first under the following conditions: reaction temperature, 280 °C; heating time, 3 h; concentration of aqueous ammonia to prepare wet ammonia, 3%. The result are shown in Fig. 2. These reaction conditions, except for the molar ratio, gave a very good result

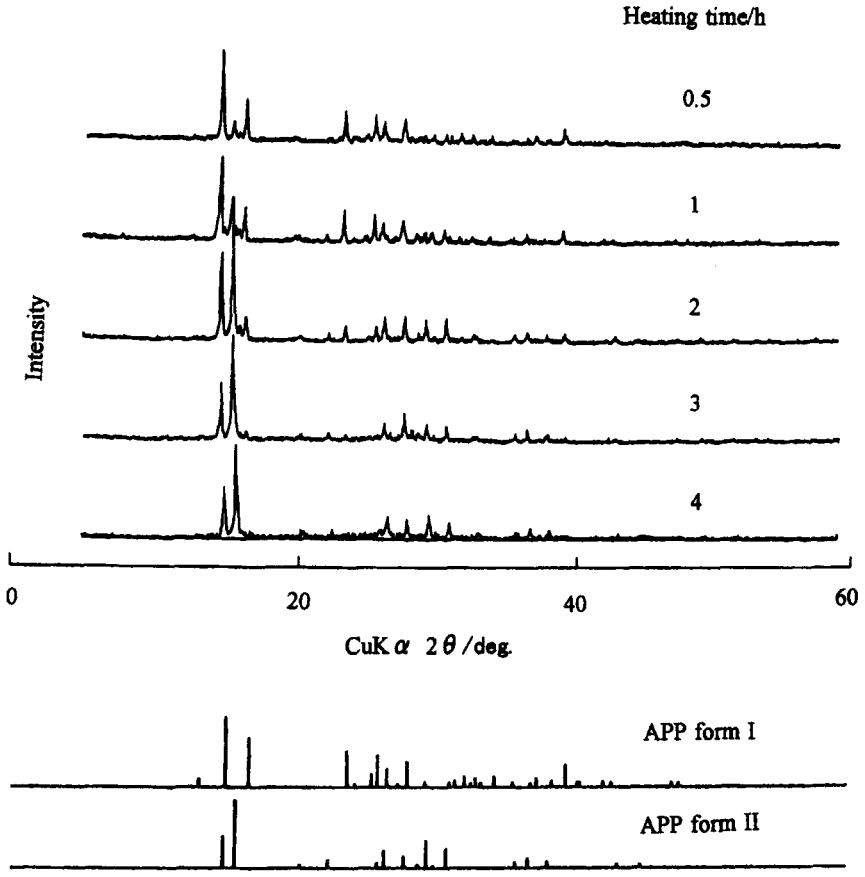

Fig. 1. XRD diagrams of APP forms I and II and the products of the $(NH_4)_2HPO_4$–$CO(NH_2)_2$ system with the molar ratio of 1/4 (heating temperature: 300 °C, concentration of aqueous ammonia: 3%).

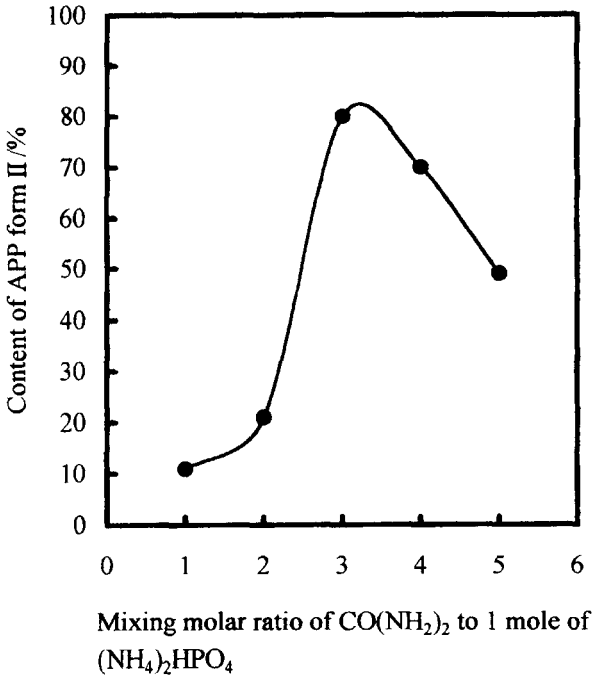

Fig. 2. Dependence of formation of APP form II on molar ratio (heating temperature: 280 °C, heating time: 3 h, concentration of aqueous ammonia: 3%).

for the conversion of APP form I to form II. As shown in Fig. 2, favorable mixing molar ratios of the orthophosphate to urea were 1/3 to 1/4.

The heating temperature necessary to give a good result for the preparation of APP form II was tested with molar ratios of 1/3 and 1/4. The results given in Fig. 3 show that reaction temperatures of 280 to 300 °C are favorable.

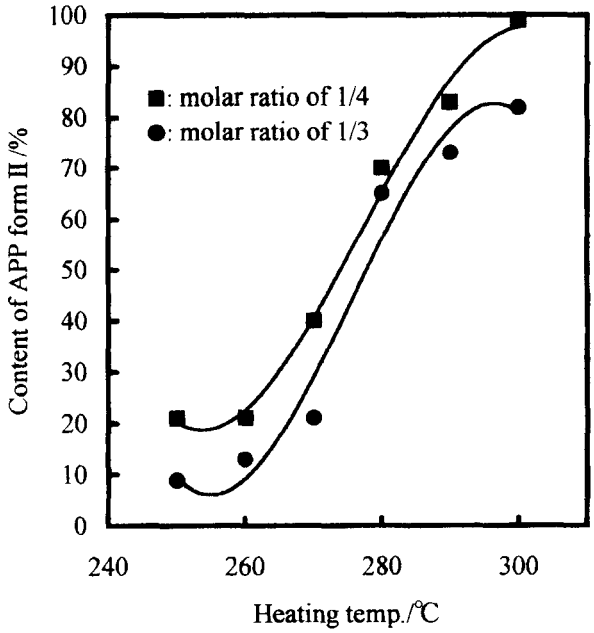

Fig. 3. Dependence of formation of APP form II on heating temperature (heating time 3 h, concentration of aqueous ammonia: 3%).

The effects of the heating time on the formation of form II APP are summarized in Fig. 4. A reaction time longer than 3 h was required to obtain a high APP form II content in the product.

The formation of APP form II from the system of $(NH_4)_2HPO_4$–$CO(NH_2)_2$ was very dependent on the concentration of aqueous ammonia, which was used to prepare wet ammonia. The dependence of the content of APP form II on the concentration of aqueous ammonia is shown in Fig. 5.

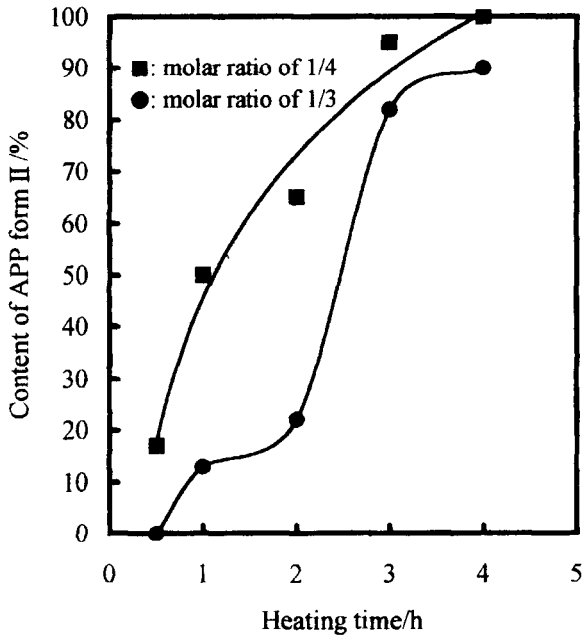

Fig. 4. Dependence of formation of APP form II on heating time (heating temperature: 300 °C, concentration of aqueous ammonia: 3%).

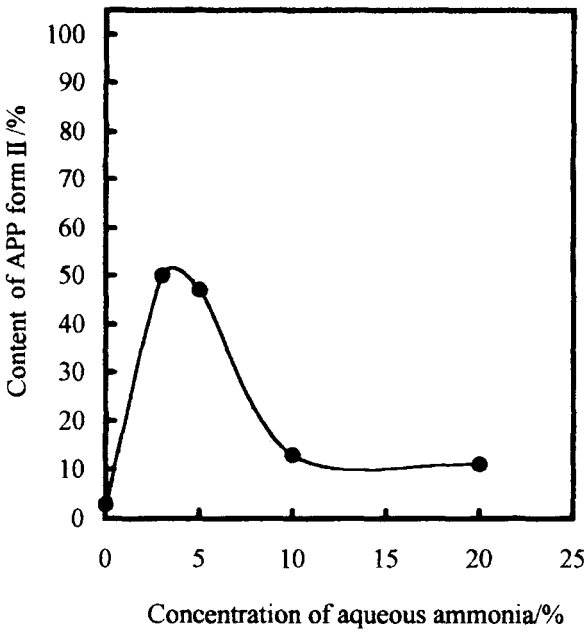

Fig. 5. Dependence of formation of APP form II on concentration of aqueous ammonia (heating temperature: 300 °C, heating time: 1 h).

Aqueous ammonia with concentrations of 3 to 5% gave favorable results. These results are similar to those obtained in the transformation of APP form I to form II, and seem to support the reaction mechanism proposed above. Moisture in wet ammonia is useful to form amorphous APP (Step 2*). As mentioned above, the amorphous APP seems to be ammonium-deficient. Ammonia in the atmosphere is effective to form well-crystallized APP form II from the amorphous APP (Step 3*).

Preparation of APP Form II from the System of Ammonium Orthophosphate–Urea Using APP Forms I and II as an Additive. As described above, it took a reaction time longer than 3 h to obtain a high content of APP form II. The reaction time should be shortened, because it is longer than that of practical APP preparation. Among the reaction steps shown above, the rate of the crystallization process of the amorphous phase to APP form II (Step 3*) is affected by the addition of APP crystals. The effect of added APP form II to the reaction system was examined under various reaction conditions. The same-mixing molar ratios of diammonium hydrogenorthophosphate to urea gave an excellent result. The mixing weight ratios of APP form II to the raw material larger than 1/15 gave a very good result. Reaction temperatures of 280 to 305 °C and reaction times longer than 0.5 h gave very good results. The effect of the concentration of aqueous ammonia on the preparation of APP form II was tested and concentrations of 1 to 8% indicated a favorable result. The effect of the crystal form of added APP was also examined by the addition of APP form I to the reaction system. The addition of APP form I to the reaction system gave APP form I mainly, even at 290 to 305 °C, which is favorable in the phase conversion of APP form I[6] and the above reaction system. Accordingly, it was found that a crystal form of the added APP had a very important effect on the crystal form of the produced APP.

Preparation of Form II APP with the $NH_4H_2PO_4$– and $(NH_4)_3PO_4$–$CO(NH_2)_2$ Systems. The preparation of APP form II from a system of $NH_4H_2PO_4$–$CO(NH_2)_2$ was examined. with a molar ratio of 1/3 (ammonium dihydrogenorthophosphate to urea), a weight ratio of 1/10 (APP form II to raw material), and a heating temperature of 290 °C, which gave favorable results in the preparation of APP form II from $(NH_4)_2HPO_4$–$CO(NH_2)_2$. The results are shown in Fig. 6. A higher content than 90% of APP form II was obtained after a reaction for 1 h with an aqueous ammonia concentration of 1 to 10%. Similar favorable experimental conditions to prepare APP form II were observed at the reaction of the $(NH_4)_2HPO_4$–$CO(NH_2)_2$ system. Accordingly, although one can use ammonium dihydrogenorthophosphate as the starting substance, diammonium hydrogenorthophosphate is better. Triammonium orthophosphate gave worse results than the $(NH_4)_2HPO_4$– and $NH_4H_2PO_4$–$CO(NH_2)_2$ systems.

Particle Size of the Product. Figure 7 shows SEM photographs of the products with APP form II contents of 35, 63, 85, and 100%. The particle size increased along with an increase in the APP form II content of the product.

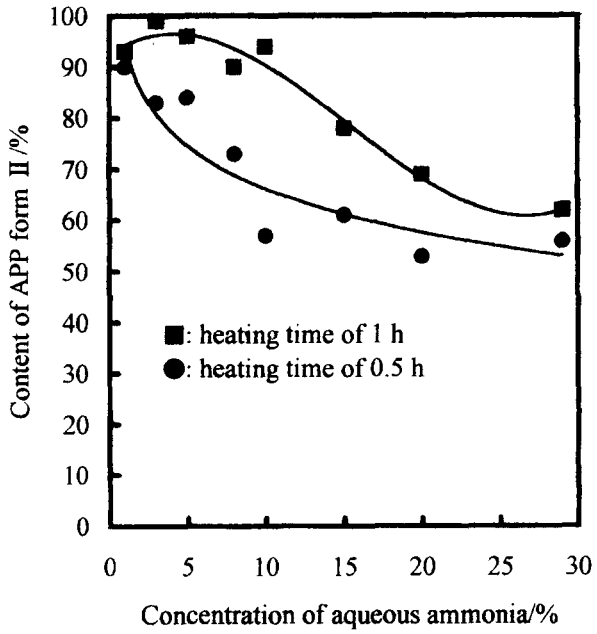

Fig. 6. Content of APP form II from the system of $NH_4H_2PO_4$–$CO(NH_2)_2$ (molar ratio of $NH_4H_2PO_4$ to $CO(NH_2)_2$: 1/3, weight ratio of APP form II to raw material: 1/10, heating temperature: 290 °C).

The average particle sizes of products with 100% content of APP form II were larger than 5 μm. The APP contained several percents of particles with sizes larger than 15 μm. The particle size of the product containing APP form II as an additive was similar to that of a product not containing an additive. Therefore, the added crystal seemed to accelerate the formation of crystal nuclei of APP form II, and the crystal growth of APP form II did not progress on the added crystal. When APP form II is used as a flame retardant for synthetic organic materials, a small particle size is preferable. The APP form II obtained in this experiment had a large particle size; it is useful as a flame retardant for many synthetic organic materials which do not require a small particle size. An APP form II crystal with a large crystal size is not available as a flame retardant for textile goods and thin films. A particle size smaller than 5 μm is required for organic materials. The P/N molar ratio of the APP form II prepared by the process agreed with the theoretical value. The measured specific gravity of the APP form II obtained in this experiment was 1.93, which is in satisfactory agreement with the calculated density of 1.94 g cm^{-3} for $4NH_4PO_3$ per unit cell.

Summary

The preparation of APP form II from the $(NH_4)_3PO_4$–, $(NH_4)_2HPO_4$–, and $NH_4H_2PO_4$–$CO(NH_2)_2$ systems was successfully achieved by heating a mixture of the starting materials at 280 to 305 °C under wet ammonia. The preferable reaction conditions are as follows:

(1) Preferable ammonium orthophosphate, diammonium hydrogenorthophosphate;

(2) Mixing molar ratio of diammonium hydrogenorthophosphate to urea, 1/3 to 1/4;

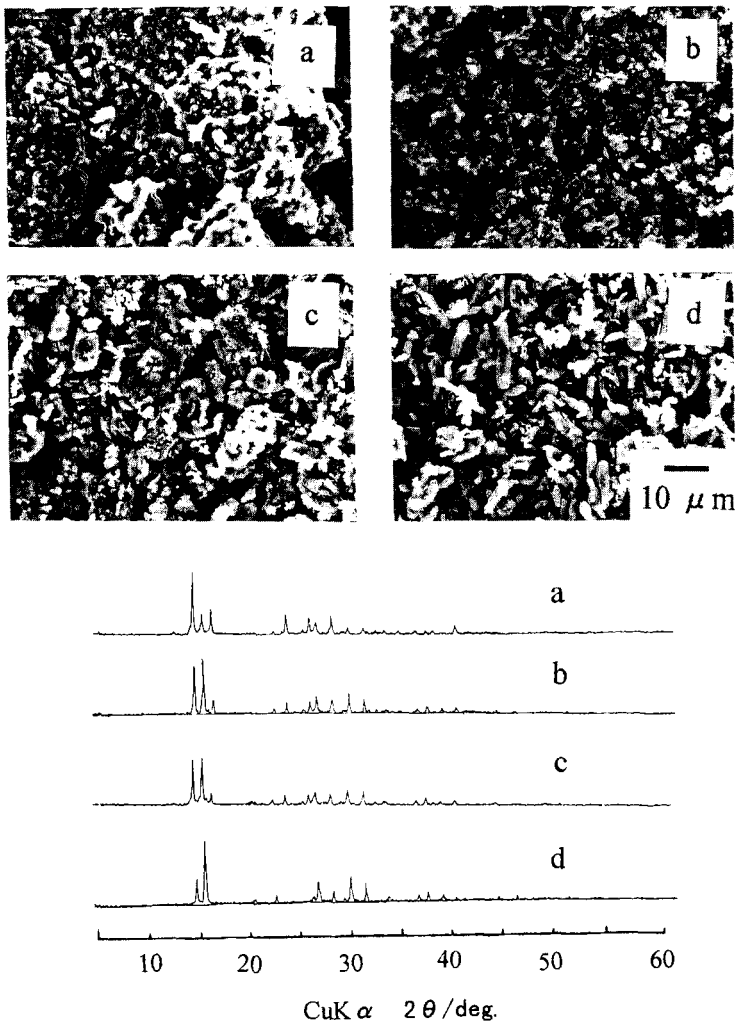

Fig. 7. SEM photographs and XRD diagrams of the products of the $(NH_4)_2HPO_4$–CO $(NH_2)_2$ system with the molar ratio of 1/4 and heating temperature of 300 °C, heating time of 1 h, and concentration of ammonia water of 5%:APP form-II content; (a) 35% (without addition of APP form II), (b) 63% (weight ratio of raw material to added APP form II: 50/1), (c) 85% (weight ratio of raw material to added APP form II:20/1), (d) 100% (weight ratio of raw material to added APP form II: 10/1).

(3) Mixing weight ratio of APP form II to the raw material as an additive, larger than 1/15;
(4) Heating temperature, 280 to 305 °C;
(5) Heating time, longer than 0.5 h;
(6) Concentration of aqueous ammonia, 1 to 8%.

The heating time is very dependent on the amount of raw material. A reaction time of 0.5 h is for about 1 g of raw material. The average particle size of APP form II prepared by the process was larger than 5 μm, and several percent of the APP form II product had particle sizes larger than 15 μm. This direct preparation process is a very profitable technique for the production of APP form II on a factory scale.

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