PREPARATION OF AMMONIUM POLYPHOSPHATE AND ITS USE AS A
FLAME RETARDANT

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Abstract Ammonium polyphosphate (APP) form II was prepared by heating a mixture of ammonium orthophosphate and urea at 280 to 300 °C under wet ammonia which was made by passing air through 3 to 5% ammonia water. Simple dry process of the preparation of APP form V was studied and APP form V was prepared by heating a mixture of ammonium orthophosphate and urea at 330 to 340 °C under wet ammonia which was made by passing air through 15 to 29% aqueous ammonia. These APPs showed an oxygen index higher than 26 when they were added to synthetic organic polymers.

INTRODUCTION

There are many kinds of ammonium ortho- and condensed phosphates. These phosphates are used as chemical fertilizers, food additives, flame retardants, dye-leveling agents etc.¹⁻³ The 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 organic materials to prevent bleeding. Among many ammonium phosphates, it is found that only ammonium polyphosphate (APP) forms II and V are hardly soluble in water. Therefore, the APPs are thought to be a good flame retardant containing phosphorus and nitrogen. The preparation of APP forms II and V is not easy and requires a very sophisticated process.⁴ It is very important to develop a new and simple process to prepare APP forms II and V from an easy reaction system. This paper describes a simple and direct preparation processes of APP forms II and V from the system of ammonium orthophosphate-urea.

EXPERIMENTAL PROCEDURE

Preparation of APP Forms II and V The reaction to prepare APP forms II and V was carried out by heating a mixture of ammonium orthophosphate and urea at 250 to 300 °C and 330 to 340 °C, respectively, under wet ammonia which was made by passing air with a flow rate of 40 dm³/h through ammonia water. Ammonia water was exchanged to new one every 20 min to prevent a lowering of the concentration of ammonia water. Dry ammonia was also used for the preparation of APP form V. Dry ammonia was prepared by passing the wet ammonia through a column filled with tablets of potassium hydroxide. Experimental conditions of a mixing molar ratio of ammonium orthophosphate to urea, heating temperature, heating time, and a concentration of ammonia water to prepare wet ammonia were examined. The reaction was run in a glass tube placed in an electric furnace.

Analytical Methods Determination of APP forms II and V in a product was made automatically using a software installed in an XRD machine, Rigaku RAD-1B diffractometer. Scanning electron microscopic (SEM) observation of a sample was made using an Akashi DS-180 instrument. Particle size distribution was measured by the centrifugal sedimentation technique, with isobutyl alcohol as a sedimentation medium, using a Shimadzu SA-CP3 instrument. The determination of phosphorus and nitrogen was made by the Molybdenum Blue method and the Kjeldahl technique, respectively. To examine flame-retardation effect of the APPs, oxygen index of polypropylene containing the APPs was measured.

RESULTS AND DISCUSSION

Preparation of APP Form II A previous paper pointed out that the transformation of APP form I to form II was accelerated by the presence of amorphous APP and the formation of amorphous APP from form I APP was able to be made by introducing a small amount of water vapor or by removing a small amount of ammonia.⁴ From the result, present authors proposed the following transformation mechanism and established a simple and easy transformation reaction process of form I APP to form II on the basis of the consideration,⁵

An XRD study on the products prepared in this experiment gave a result that APP form I was formed at the initial step and the APP converted to form II as progress of the reaction. This phenomenon was observed in every reaction in this experiment and the following formation mechanism of APP form II can be given to this reaction system,

On the above basic consideration of the formation mechanism of APP form II, favorable reaction conditions of direct preparation of APP form II from the system of $(\text{NH}_4)_{3-n}\text{H}_n\text{PO}_4\text{-CO}(\text{NH}_2)_2$ ($n=0, 1, \text{ or } 2$) were examined.

Mixing Molar Ratio 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 mainly examined under constant other reaction conditions (reaction temperature: 280 °C, heating time: 3 h, concentration of ammonia water to prepare wet ammonia: 3%) and the result is indicated in Table 1. These reaction conditions except for the molar ratio gave a very good result for the conversion of form I APP to form II. As shown in Table 1, favorable mixing molar ratios of the orthophosphate to urea were 1/3 to 1/4.

TABLE 1 Dependence of Formation of APP Form II on Molar Ratio
(heating temperature:280 °C, heating time:3 h, concentration of ammonia water:3%)

Molar ratio [(NH ₄) ₂ HPO ₄ :CO (NH ₂) ₂]	Content/% of form II APP
1:1	11
1:2	21
1:3	80
1:4	70
1:5	49

Heating Temperature and Time Heating temperature and time to give a good result for the preparation of APP form II were tested under constant other reaction conditions. Mixing molar ratios of 1/3 and 1/4 were adopted according to the result obtained above. It was found that a reaction temperature of 280 to 300 °C and a reaction time longer than 3 h were favorable.

Concentration of Ammonia Water The formation of APP form II from the system of (NH₄)₂HPO₄-CO(NH₂)₂ was very dependent on the concentration of ammonia water which was used to prepare wet ammonia. Ammonia water with a concentration of 3 to 5% gave a favorable result. This result is the same as that obtained in the transformation of form I APP to form II and this seems to support the reaction mechanism proposed above for this reaction system. Water vapor in wet ammonia is useful to form amorphous APP (Step 2*). As mentioned above, the amorphous APP seems to be ammonium-deficient APP. Ammonia in the atmosphere is effective to form well crystallized form II APP from the amorphous APP (Step 3*).

Preparation of APP Form V The preparation of form V APP did not progress well under dry ammonia and form I APP was formed mainly. A reaction under wet ammonia which was obtained by passing air through ammonia water with a concentration lower than 15% did not give a good result and a product containing a large amount of APP form I and/or amorphous

APP was prepared. Under any reaction condition, a reaction temperature lower than 330 °C did not give a favorable result and a product containing a large amount of APP form I was obtained, and a sample melted at a reaction temperature higher than 340 °C. Accordingly, reaction temperatures of 330 and 340 °C were adopted. When ammonium dihydrogen- and diammonium hydrogenorthophosphates were used as a starting material, a mixture of the ammonium orthophosphate and urea with a molar ratio (ammonium orthophosphate/urea) larger than 1/0.7 melted at 330 °C. In the case of triammonium orthophosphate, a mixture with a molar ratio larger than 1/0.8 melted at 330 °C. Therefore, mixtures with molar ratios smaller than these ratios were used for the preparation of APP form V. Under these reaction conditions, APP form V exhibiting two different XRD patterns was obtained. One of the XRD diagrams was an usual pattern of APP form V and the other one was found to be given by incomplete form V APP with N/P molar ratio smaller than unity. In any reaction condition, the product containing usual or

TABLE 2 Content of APP form V in the products of $(\text{NH}_4)_3\text{PO}_4\text{-CO}(\text{NH}_2)_2$ system

Heating temp./°C		330		340	
Heating time/min.		30	45	30	45
Mixing molar ratio [$(\text{NH}_4)_3\text{PO}_4\text{:CO}(\text{NH}_2)_2$]	Concentration of NH_3 water/%				
1:2.0	29	⊙	○	⊙	⊙
	15	○	⊙	⊙	⊙
1:1.5	29	○	○	⊙	⊙
	15	⊙	⊙	⊙	⊙
1:1.0	29	○	⊙	⊙	⊙
	15	⊙	⊙	⊙	⊙
1:0.9	29	⊙	⊙	⊙	⊙
	15	⊙	⊙	⊙	⊙

incomplete APP form V and/or form I was prepared. The result of the reaction system of $(\text{NH}_4)_3\text{PO}_4\text{-CO}(\text{NH}_2)_2$ is given in Table 2. In the table, a double circle stands for the product with an APP-form V content higher than 90%, a single circle indicates the product with a content of incomplete APP form V higher than 90%. When $\text{NH}_4\text{H}_2\text{PO}_4$ was used as a starting material, form V APP was prepared well at 340 °C for 45 min under any other reaction condition. Mixtures with the molar ratios of 1/1.0 to 1/0.8 gave a good result under any other reaction condition. In the case of a starting material of $(\text{NH}_4)_2\text{HPO}_4$, APP form V was prepared well under 15% of ammonia water and any other reaction condition. The molar ratios of 1/1.0 to 1/0.8 gave a good result even under 29% of ammonia water.

The preparation of APP form V under air was examined because the atmosphere of the above reaction system seemed to contain enough ammonia, but the reaction under air did not give a good result in any reaction condition.

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